ACADEMIC TASK FORCE

REVISION SERIES

CHEMISTRY

ATAR COURSE REVISED EDITION

YEAR 12 UNITS 3 & 4

AUSTRALIAN CURRICULUM

ANDREW DEAN
ROY SKINNER

ACADEMIC
TASK FORCE

CHEMISTRY

Year 12 ATAR COURSE

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Roy Skinner and Andrew Dean

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UNIT 3

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How to Use this Study Guide

This book should be used in conjunction with a class textbook to reinforce the most important principles and understandings. The essentials are presented so students can teach themselves the concepts. Students then work through the many example questions. Answers should be entered in this workbook to produce a progressive learning in a student friendly manner.

An active learning style is supported through the use of simple pictures and diagrams within the text.

Sets of example questions are supplied throughout on concepts which reflect those used for class tests and examinations (these are titled Set 1, Set 2, etc.).

Items shown in grey boxes are of interest but are not directly examinable.

Dr Roy Skinner and Andrew Dean

Chapter
1

Chemical Equilibrium

1.1 REACTIONS

Most of the chemical equations you have experienced have been those that go to completion.

$$HCl\ (g) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

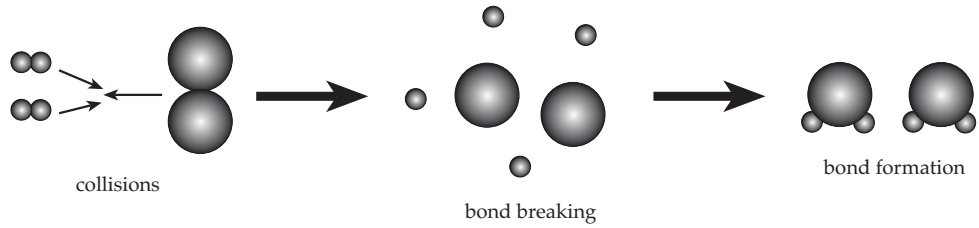
The arrow shows that all of the HCl has been converted into hydronium and chloride ions. However, chemical changes can be almost instantaneous like the one above, or may take many years to complete, depending upon many factors, such as closeness of particles and temperature.

Not all reactions convert all the reactants to products. Often products can also react to reform the reactants. Thus an intermediate equilibrium situation is obtained. The products are converted to reactants as quickly as they are formed.

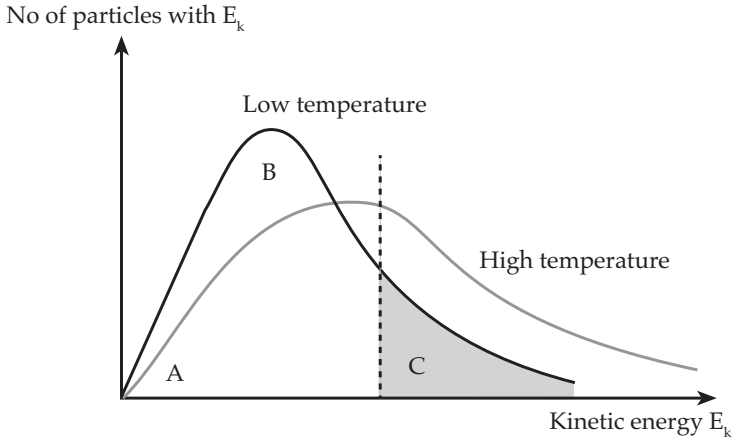
This Dynamic Equilibrium situation is the main focus of this chapter.

1.2 COLLISIONS ARE CRITICAL

Any reaction between two molecules requires the following to occur: a) collisions between molecules, b) breaking of bonds, c) re-joining of new bonds.



Collisions must occur with sufficient energy to cause bonds to break, but only a fraction of the total number of particles will have this critical energy, called Activation Energy (E_a). Sometimes reactions occur spontaneously (e.g. sodium in water) other times kinetic energy has to be added to particles (by heating) to cause critical collisions to occur (e.g. $2H_2 + O_2 \rightarrow 2H_2O$). Therefore reaction rates always rise with temperature because the colliding particles move faster and collide more frequently. The graph below shows the distribution of fast-moving and slow-moving particles in a gas or solution.



1.3 REACTION RATE

In the gaseous or liquid phases, particles are moving in random directions with a random distribution of speeds (kinetic energies).

The graph on page 1 shows the distribution of energy amongst the gas molecules, i.e. the number with a particular kinetic energy. It can be seen in the left-hand part of the graph that at point A where the molecular speed is very low, the number with this E_K is small and at point C, the number with a very high velocity is also very small. The most frequent E_K of the particles is shown at point B.

The Activation Energy (E_a) of a reaction is the amount of kinetic energy with which molecules must collide in order to break bonds and form an **activated complex**. This transfered state then reforms into the final products. There is always a wide range of molecular kinetic energies at any temperature and so only a fraction of molecules collide with the correct orientation (the right way round) and sufficient energy to produce this high energy (activated complex) Transition State. Others simply rebound without reacting. The activated complex then reforms into a more stable product and gives out or takes in a net amount of energy called Heat of Reaction (ΔH).

In order to collide and break bonds the particles must be moving with a velocity corresponding to the Activation Energy (E_a), which only a fraction of the total particles will possess. This fraction is shown as the shaded area in the diagram on page 1. If E_a is higher then the shaded area will be smaller and the rate of the reaction will therefore be low at a particular temperature.

If the temperature is raised then E_a stays the same but the whole graph moves to the right and hence there will always be a larger fraction of the total number that have energies past that point i.e. the rate of any reaction will always increase if the temperature increases.

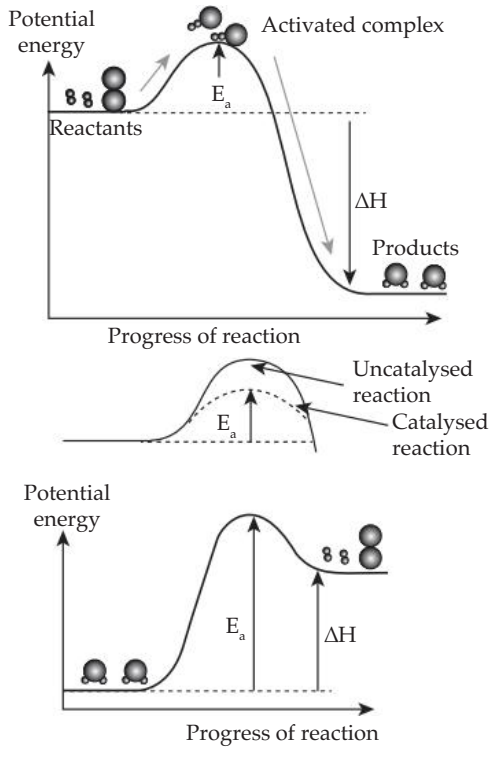
The diagram on the right illustrates an exothermic reaction where there is a net energy output from the system, i.e. ΔH has a negative value.

In exothermic reactions the surroundings (air, solution, etc.) will become warmer.

The activated complex is a temporary structure which will not be able to exist for any considerable time and breaks up almost immediately.

The effect of a catalyst is to provide a new pathway with a lower activation energy by combining with the reactants to form an intermediate product with lower energy content.

With an endothermic reaction, the activation energy is large and the final products have more potential energy than the reactants. There is a net energy gain by the reaction and so heat is taken in and the heat of reaction, ΔH, is positive. In endothermic reactions the surroundings will become cooler.

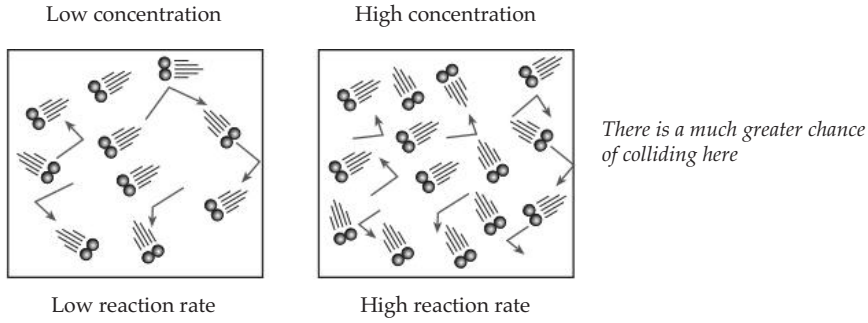


Other factors that affect reaction rate are:

Particle size: The same reactant divided into smaller particles will have a larger overall surface area exposed to the other reactant and there will be more collisions hence a higher reaction rate.

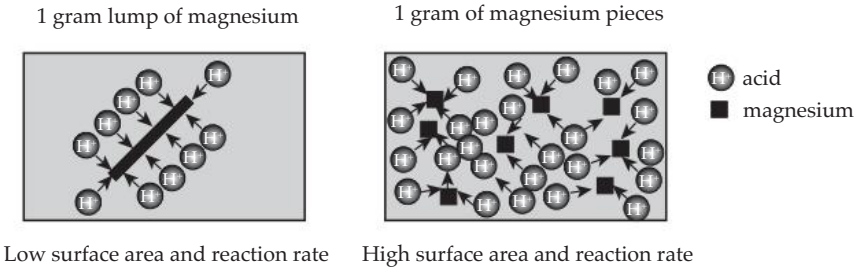
Concentration – the more concentrated an aqueous reactant is the closer the particles are and the shorter the distance to travel between collisions.

The **concentrations** of the reactants also affect reaction rates – see diagram below.



Molecules or ions in solutions can have a much higher reaction rate than in gases, as the particles are much closer.

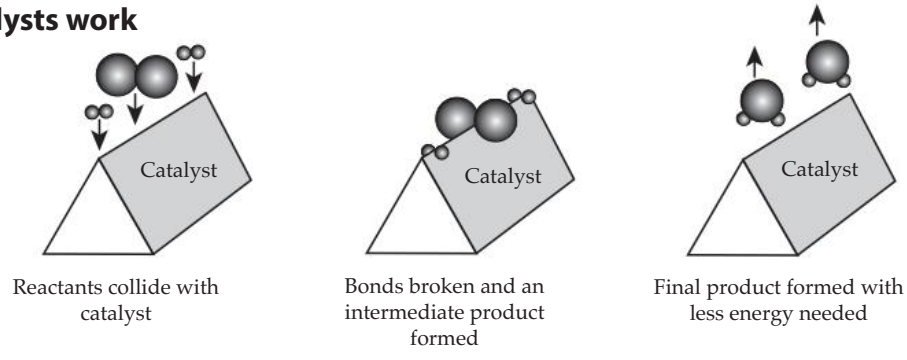
In reactions between solids and liquids (e.g. metal in acid) the reaction rate will also depend on the amount of surface area of the solid exposed.



1.4 CATALYSTS

Catalysts are substances that increase the chance of a reaction occurring without themselves being used up in the reaction. The reactants first collide with the catalyst surface, bonds are broken and an intermediate product is formed with the catalyst. This catalytic process requires less reaction energy to produce the final product than an uncatalysed reaction.

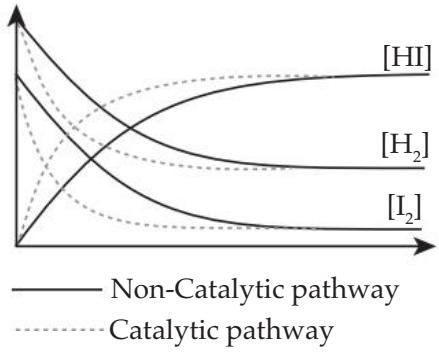
How catalysts work



Catalysts speed up the rate at which equilibrium is attained and are used in industry to make a reaction take place faster. Consider the reaction where HI is produced from reacting hydrogen and iodine: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

From the graph we can see that the catalysed reaction reaches equilibrium (horizontal line) quicker than the uncatalysed reaction.

Although the rate of a reaction is increased, it is important to note that catalysts will have no effect on the yield and are not consumed in any reaction. Enzymes are nature's version of catalysts for biological reactions, e.g. the yeast enzyme converts sugar to alcohol. Enzymes are important in biological systems because temperature is often low. The human body at 37°C uses extensive enzyme systems as particles have little kinetic energy and would have a low rate of reaction.

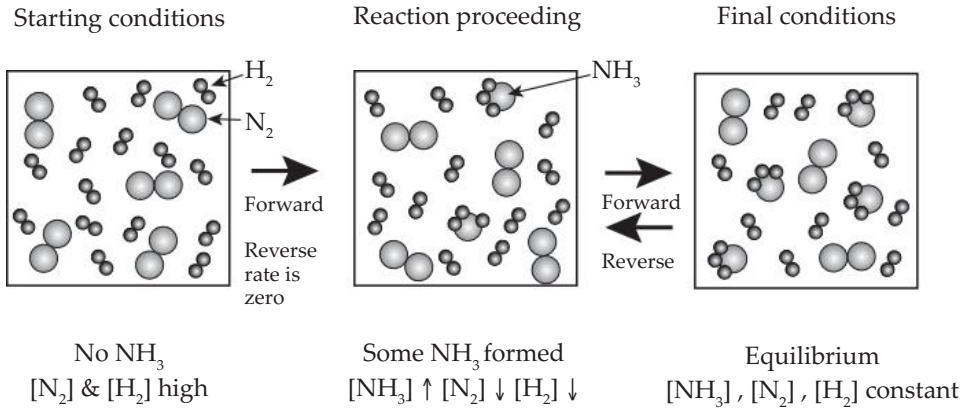


1.5 REVERSIBLE REACTIONS

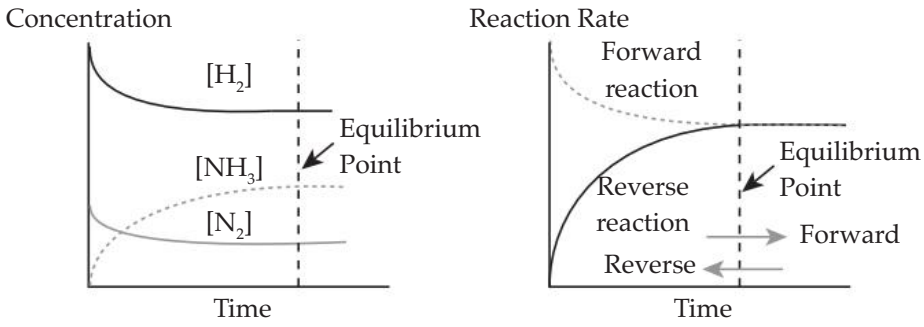
Most chemical reactions are reversible (symbol ⇌). When a reversible reaction is said to be in equilibrium it is in a stable, or balanced, state because the concentrations of the reactants and the products are constant.

Reactions can never be stationary because collisions are occurring all the time; it is just that when enough product molecules have been formed they can then collide to reform the reactants back again and then the forward rate = the reverse rate (a state of dynamic equilibrium).

e.g. Ammonia formation: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

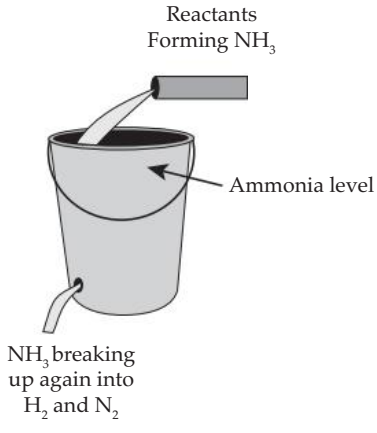


As the reaction proceeds the concentrations of the reactants drop as they start to be used up and the concentration of the products rises as they become formed. Now that there are products, these can also collide and break up and will re-form the reactants back again.



The rate at which the reactants are breaking up equals the rate at which the products are breaking up and returning to become reactants again – this stable situation is called a Dynamic Equilibrium.

Imagine a bucket with a hole in the side that was being filled with a hose. Water is lost through the hole at the bottom at the same time but starts to fill up as the rate the water coming in is greater than the rate it is being lost. However, as the water height gets greater the pressure at the bottom increases, so the rate it flows out increases (deeper water exerts more pressure). At a certain depth of water the bucket will be being filled at the same rate as it is emptying.



Here the water coming in represents the reactants (H_2 and N_2) producing the ammonia and the level of water in the bucket represents the amount of ammonia present.

The water running out through the hole represents the NH_3 breaking up to give H_2 and N_2 again.

1.6 EQUILIBRIUM CONSTANT

The equilibrium constant (K) for a particular reaction indicates the relative proportions of products and reactants, once equilibrium has been reached.

$$K = \frac{[\text{Product 1}] \times [\text{Product 2}]}{[\text{Reactant 1}] \times [\text{Reactant 2}]}$$

For the ammonia reaction above, this gives: $K = \frac{[NH_3] \times [NH_3]}{[N_2] \times [H_2] \times [H_2] \times [H_2]} = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$

Example

At a particular temperature the concentrations of the gases present in a closed vessel are: hydrogen 2.4 mol L^{-1}; nitrogen 0.25 mol L^{-1}: ammonia 0.10 mol L^{-1}. Calculate the value of the equilibrium constant for ammonia.

Solution

$$K = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{[0.1]^2}{[0.25]\,[2.4]^3} = 2.9 \times 10^{-3}\ \text{mol}^{-2}\ \text{L}^2$$

The K value for this reaction will always be the same, regardless of the starting concentration, which is about 3×10^{-3} at 300°C. This value will, however, change with temperature.

The low K value for ammonia formation shows that there is far less product than reactant once equilibrium has been reached. As a comparison, the K value for the ionisation of a strong acid is very large (about 1000), showing the acid exists almost totally as ionic products. As a rough rule if $K > 10^4$, the forward reaction is fully favoured and if $K < 10^{-4}$ the reverse reaction is fully favoured.

The K value for the reaction $2NO_{2(g)} \rightleftharpoons N_2O_{4\,(g)}$ is 0.48. This means that at equilibrium there will be a roughly equal amount of both gases.

However, in the reaction $SO_{3(g)} \rightleftharpoons SO_2 + \frac{1}{2}O_{2(g)}$ the K value is 10^{-12}, meaning that the mixture would almost entirely consist of SO_3 molecules at equilibrium.

1.7 LE CHÂTELIER'S PRINCIPLE (LCP)

Le Châtelier's Principle predicts the outcome when conditions (concentration,T, P, V, etc) at equilibrium are changed in a reversible reaction. This principle states that:

If conditions are changed from equilibrium then the system will always readjust to partially compensate for those changes.

The ammonia equation will illustrate this idea: $N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)} + 92\ \text{kJ}$

e.g. If we added more nitrogen, for instance, the reaction would move towards the right so that the amount of nitrogen would decrease.

Exam questions can be of 3 types – asking what effect there would be if 1) concentrations were changed, 2) vessel volume were changed and 3) temperature were changed. For each of these changes in conditions the question could ask about the change in reaction Yield (amount of products) or the new Rate of the reaction.

Question types

How Yield is affected	How Rate is affected
Change concentration of a reactant/product	
Change volume of the vessel	
Change temperature of the vessel	

Important note on heterogeneous equilibria: *A solid cannot have a concentration as it would need to be a solution – and a solid is not dissolved in anything!*

Concentration values are the number of moles of solute divided by number of moles of solvent. Similarly, a pure liquid, such as water cannot have a concentration value either and is discounted in equilibrium equations.

Example: NO_2 in equilibrium with N_2O_4 (NO_2 is brown and N_2O_4 is colourless, so an equilibrium mixture is pale brown.

Reaction: $2NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$ $\Delta H = -57\ kJ\ mol^{-1}$

Brown **Colourless**

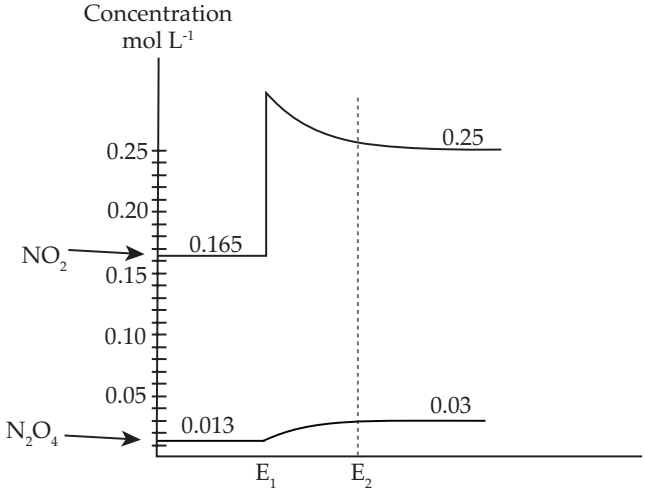
Change in conditions	Immediate effect	Change to equilibrium	Final observation	Prediction
NO_2 added	brown colour deepens	Moves to the right	Becomes paler	More N_2O_4 produced
N_2O_4 added	Becomes lighter	Moves to the left	Becomes darker	More NO_2 produced
Volume decreased	Becomes darker brown	Moves to the right	Slowly returns to paler brown	More N_2O_4 produced
Volume increased	Becomes paler	Moves to the left	Brown colour intensifies	More NO_2 produced
Temperature raised	Becomes darker	Moves to the left	Brown colour intensifies	More NO_2 is produced

1.8 THE EFFECT OF CONCENTRATION

In ammonia synthesis, if some more N_2 is added to an equilibrium mix then by LCP the system will produce more NH_3 (forward reaction) so as to use up the extra N_2 added. Why? Because with more N_2 molecules available more reactant collisions can occur than previously and so more NH_3 can be produced. The concentration values eventually settle back so that K has the same value as before.

This is predicted by Le Châtelier's Principle but it is better explained by talking about the change of Rate: At equilibrium the forward and reverse rates are equal. If we add more nitrogen the forward rate is now greater than the reverse rate and so the reaction must move to the right.

Consider the equilibrium: $2NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$



Initially there are equilibrium conditions (E_1) but when NO_2 is added the graph rises immediately. The forward rate now exceeds the reverse rate and so the equilibrium shifts to the right gradually, as shown by the upward slope of the graph, producing more N_2O_4 yield.

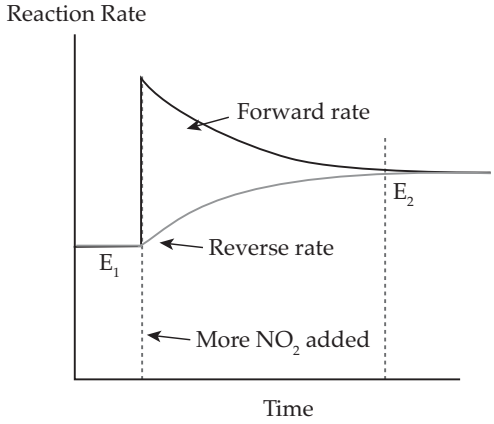
To produce more N_2O_4 the amount of NO_2 has to be gradually used up, and so its graph must gradually reduce but not to the original level as before. It will eventually level out when the new equilibrium (E_2) is reached. At E_1 the K value is given by:

$$K = \frac{[N_2O_4]}{[NO_2]^2} = \frac{[0.013]}{[0.165]^2} = 0.48$$

After the new equilibrium is established (E_2) the value of K is given by:

$$K = \frac{[0.03]}{[0.25]^2} = 0.48$$

Note that K attains the same value again and is unaffected by the addition of extra NO_2. The Rates graph looks like this:



We can see here that after the extra NO_2 has been added the forward rate increases instantly which gradually increases the amount of product, but uses up the reactant. Hence the probability of successful forward collisions will gradually reduce. As more product is produced the reverse rate will gradually increase until forward and reverse rates now become equal but at a higher value because there are now more particles present overall.

1.9 ENVIRONMENTAL ASPECTS

Due to Greenhouse Gas emission, the levels of CO_2 in our oceans is steadily rising but the carbonate ion content of the sea is important for the growth of coral reefs in Australian waters.

The formation of carbonate ions from carbon dioxide is shown by:

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + 2H^+_{(aq)}$$

Coral body is built from calcium carbonate when the carbonate ions combine with calcium ions in the water:

$$Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons CaCO_{3(s)}$$

Living coral polyps have a calcium carbonate skeleton and when they die these skeletons form part of the growing reef. Normally, sea water is slightly alkaline, with a pH of about 8.2 but as more CO_2 is absorbed its acidity rises, which affects the carbonate/hydrogen carbonate equilibrium:

$$HCO_3^-{}_{(aq)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + H^+_{(aq)}$$

Hence the effect of acidification is predicted to be to remove the carbonate ion from the water by favouring the reverse reaction in this equilibrium equation. This would cause a reduction in the ability of the coral polyp skeleton to form and thus stunt the growth of coral crops.

However, there is also a conflicting process attributable to rising sea temperatures. Higher temperatures cause the metabolism of these polyps to increase, thus increasing the growth of the coral reefs. It remains to be seen which of these two processes will become dominant.

Set 1. Concentration changes

For the reactions below use your knowledge of Le Châtelier's Principle to predict the effect on the final yield and rate when the indicated changes are made (after equilibrium has been re-established).

1. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6\,H_2O(l)$

   Change: More oxygen is added.

   Yield _____

   Rate _____

2. $SO_2(g) + ½\,O_2(g) \rightleftharpoons SO_3(g)$

   Change: Some SO_2 is removed.

   Yield _____

   Rate _____

3. $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

   Change: Some more water is added.

   Yield _____

   Rate _____

4. $Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$

   Change: Some solution is evaporated.

   Yield _____

   Rate _____

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

   (i) Change: Some hydrochloric acid is added.

   Yield _____

   Rate _____

   (ii) K for this reaction is 1.8×10^{-5}. What does this tell you about the strength of ethanoic acid and how would K be affected by the addition of H^+?

   _____

6. $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ $K = 4.3 \times 10^{-7}$

   (i) Change: Some sodium hydroxide is added.

   Yield _____

   Rate _____

   (ii) What does this tell you about the strength of carbonic acid and how would K be affected by the addition of H^+?

   _____

7. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

   (i) Change: Some more calcium carbonate lumps are added.

   Yield of CO_2 _____

   Rate _____

   (ii) Change: The partial pressure of CO_2 is increased.

   Yield of CO_2 _____

   Rate _____

8. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

   Change: Some HI is removed.

   Yield _____

   Rate _____

9. $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

   (Solution colour is orange/yellow mix)

   (i) Change: Some water is added.

   Yield _____

   Rate _____

   (ii) CrO_4^{2-} is yellow and $Cr_2O_7^{2-}$ is orange. What effect will the change make to the colour?

   _____

10. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

    (NB Ammonia is very soluble in water.)

    Change: Some water is added.

    Yield _____

    Rate _____

1.10 THE EFFECT OF VOLUME CHANGE

If the size of the vessel containing a gas is decreased then the pressure of the gases is increased by decreasing the space between particles. Le Châtelier's Principle predicts that the equilibrium will move in the direction which reduces the pressure. Pressure is produced by the bombardment of particles – the larger the number of particles colliding per second, the larger the partial pressure it exerts.

Consider this gaseous production reaction: $X_{2(g)} + 3Y_{2(g)} \rightleftharpoons 2XY_3$

There are 4 particles on the left and only 2 on the right, so Le Châtelier predicts that, with a decreased vessel volume, the equilibrium will shift to the right in order to reduce the number of particles bombarding per second.

Looking at this reaction mathematically: $K = \dfrac{[XY_3]^2}{[X_2][Y_2]^3}$

Suppose, at equilibrium, all the reactants are contained in a 1 litre vessel and have a concentration of 1 mol L^{-1}, then. For K:

$$K = \frac{[1]^2}{[1][1]^3} = 1.$$ The equilbrium constant for this reaction equals 1.

K must remain constant after any change (except for temperature) so suppose we reduce the volume of the vessel to 0.5 litre. All the concentrations are now doubled to 2 mol L^{-1} so, before equilibrium is reached, the equation fraction will have changed to a temporary value called Q:

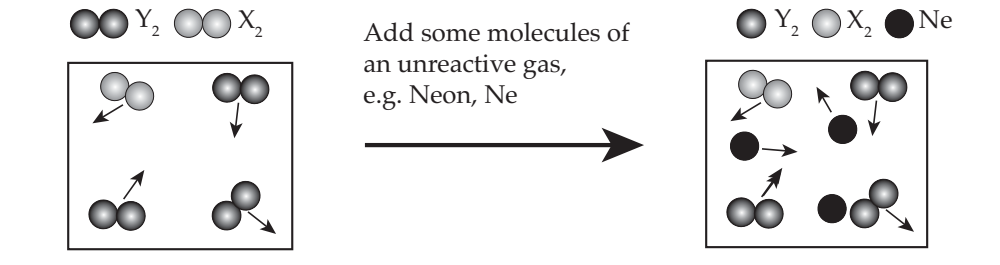
Q is now $\dfrac{[2]^2}{[2][2]^3} = 0.25$ which is smaller than the constant value that K must attain.

The equilibrium concentrations must now change in a direction which will increase K back up to 1 again, i.e. more products.

We can see here why Le Châtelier's Principle works - if the pressure is increased, to preserve K, the equilibrium must move to the side with least particles.

This logic only works if the pressure change is brought about by a change in volume. The total pressure could also be increased by adding another gas which does not take part in the reaction, e.g. a noble gas. Here, the pressure would increase because there are now more collisions, but the particles would actually stay at the same spacing, so this would have no effect at all!

Although the pressure is higher in the right-hand vessel, the yield and rate are unaffected.



Partial pressure of X_2 = 20 kPa
Partial pressure of Y_2 = 30 kPa
Total pressure = 50 kPa

Partial pressure of X_2 = 20 kPa
Partial pressure of Y_2 = 30 kPa
Partial pressure of Ne = 30 kPa
Total pressure = 80 kPa

Set 2. Changing Pressures

1. For the reactions below use your understanding of Le Châtelier's Principle to predict the effect on the pressure, yield and forward rate after the indicated changes are made (after equilibrium has been re-established).

   $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l)$

   Change: The volume of the vessel is reduced

   Pressure _____

   Yield _____

   Rate _____

2. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K = 3 \times 10^{-3}$

   Change: The size of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

   How would the value of K change?

3. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

   Change: The size of the vessel is decreased

   Pressure _____

   Yield _____

   Rate _____

   How would the mass of CaO change?

4. $COBr_2(g) \rightleftharpoons CO(g) + Br_2(g)$

   Change: The size of the vessel is decreased

   Pressure _____

   Yield _____

   Rate _____

5. $As_4O_6(s) + 6C(s) \rightleftharpoons As_4(g) + 6CO(g)$

   Change: The size of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

   How would the mass of As_4O_6 change?

6. $Cl_2(g) + H_2O(l) \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq)$

   Change: The size of the vessel is decreased

   Pressure _____

   Yield _____

   Rate _____

   Write the expression for K for this reaction _____

7. $Ba^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons BaCl_2(s)$

   Change: The size of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

8. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

   Change: The size of the vessel is decreased

   Pressure _____

   Yield _____

   Rate _____

9. $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

   (i) Change: Some nitrogen gas was introduced into the flask, with volume remaining constant.

   Pressure _____

   Yield _____

   Rate _____

   (ii) Change: Some nitrogen gas was introduced into the flask, with pressure remaining constant.

10. $Cr_2O_7^{2-}(aq) + 2H^+(aq) + 3SO_2(g) \rightleftharpoons 2Cr^{3+}(aq) + H_2O(l) + 3SO_4^{2-}(aq)$

    Change: The size of the vessel is increased

    Pressure _____

    Yield _____

    Rate _____

11. Draw fully labelled energy level diagrams for the following reactions paying attention to the activation energies of the forward and reverse reactions.

(a) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ ΔH = +ive (readily reversible)

(b) $CH_{4(g)} + 2O_{2(g)} \rightleftharpoons CO_{2(g)} + 2H_2O_{(g)}$ ΔH = -ive (difficult to reverse)

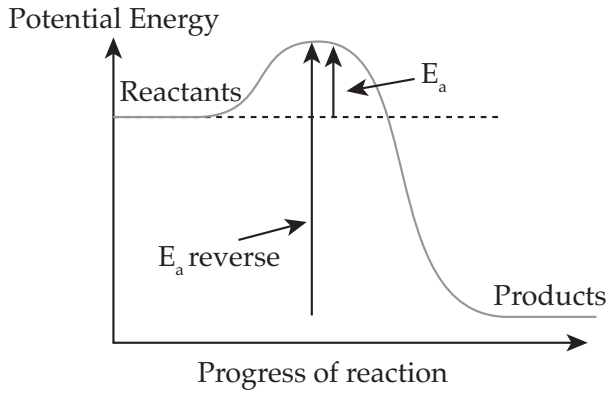
1.11 THE EFFECT OF TEMPERATURE CHANGE

According to Le Châtelier's Principle, an increase in temperature will favour the direction that removes heat from the system. In the example of ammonia synthesis, heat is given out when the stronger bonds in the hydrogen and nitrogen molecules form into weaker bonds holding the ammonia molecule together. So, when the reactants transform into products, this difference in bond energies emerges as heat energy given out to the surroundings i.e. an exothermic reaction.

$$N_{2\,(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3\,(g)} + 92 \text{ kJ mol}^{-1}$$

This reaction is exothermic and the forward reaction will produce more heat so if the temperature is raised, the reverse reaction will be favoured (more reactants) by the LCP.

To understand this fully we must look at the energy profile for this reaction.



Interpreting this graph, we can see that, in an exothermic reaction, the activation energy forwards is much smaller than the activation energy for the reverse reaction i.e. it takes less energy for the H_2 and N_2 to jump the forward barrier than for NH_3 to jump the reverse barrier.

If more energy is supplied to the reaction the forward and the reverse rates of reaction will both increase but it will affect the reverse rate more. Imagine that it is like high jump, where the forward height to jump is 1.0 m but the reverse height is 2.5 m. Consequently 92% of people might be able to jump over the forward barrier but only 2% can jump from right to left. If we give everyone extra energy (e.g. by putting strong springs in their shoes) both the forward and reverse jumpers would be more successful, so the figures might now become 98% successful forward and 35% successful in reverse jumping.

We can see that it would benefit the reverse reaction rate proportionately more than the forward rate. Hence if heat is supplied to an exothermic reaction the equilibrium would favour the endothermic (reverse) direction. Likewise, heating will favour the forward direction in the case of an endothermic reaction.

Changes in K

Consider the ammonia production equation again: $N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3(g)} + 92 \text{ kJ mol}^{-1}$

We can see that if we were to cool the reaction vessel down the forward reaction would be favoured to produce more ammonia and heat. However, if more ammonia is to be produced this will affect the value of K, as the reactants must go down and products increased.

Example

Originally hydrogen = 2.4 mol, nitrogen = 0.25 mol, ammonia = 0.10 mol so K =2.98×10^{-3}.

Now at a lower temperature: $H_2 = 2.0$, $N_2 = 0.06$, $NH_3 = 0.15$ so K = 0.094.

This is larger than before – so, for a rise in temperature, K reduces for an exothermic reaction and increases for an endothermic reaction.

Set 3. Changing Temperatures

For the reactions below use your understanding of Le Châtelier's Principle to predict the effect on the pressure, yield and rate when the indicated changes are made (after equilibrium has been re-established).

1. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l)$ $\Delta H = -907$ kJ mol^{-1}

   Change: The temperature of the vessel is reduced

   Pressure _____

   Yield _____

   Rate _____

2. $SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$ $\Delta H = -99$ kJ mol^{-1}

   Change: The temperature of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

3. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\Delta H = +179$ kJ mol^{-1}

   (i) Change: The temperature of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

   (ii) How would the mass of $CaCO_3$ change?

   (iii) Write an equation for the equilibrium constant _____

4. $2HI(g) \rightleftharpoons H_2(g) + I_2(s)$ ΔH is > 0

   (HI is colourless and I_2 is purple)

   (i) Change: The temperature of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

   (ii) How would the temperature change affect the colour of the mixture?

   _____

5. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +180$ kJ

   Change: The temperature of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

For the reactions below predict the effect on the pressure, yield and rate when the indicated changes are made and explain your answers with reference to the rates of the forward and the reverse reactions.

6. $Ag^{+}(aq) + Cl^{-}(aq) \rightleftharpoons AgCl(s)$ ΔH is < 0

   (i) Change: The temperature of the vessel is increased

   Yield _____

   Rate _____

   (ii) How would this change affect the mass of AgCl? _____

7. $Br_2(l) + 3F_2(g) \rightleftharpoons 2BrF_3(g)$ ΔH = -255 kJ

   (i) Change: The temperature of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

   (ii) How would this change affect the volume of liquid bromine?

   _____

8. $2ZnO(s) + 2SO_2(g) \rightleftharpoons ZnS(s) + 3O_2(g)$ ΔH = +897 kJ

   (i) Change: The temperature of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

   (ii) How would this change affect the mass of ZnO? _____

9. $Cl_2(g) + H_2O(l) \rightleftharpoons HOCl(aq) + H^{+}(aq) + Cl^{-}(aq)$ ΔH is +ve

   Change: The temperature of the vessel is increased

   Pressure _____

   Yield _____

   Rate _____

10 (a) $Fe(s) + Cl_2(g) \rightleftharpoons FeCl_2(s)$ ΔH = -342 kJ

   (b) $FeCl_2(s) + \frac{1}{2}Cl_2(g) \rightleftharpoons FeCl_3(s)$ ΔH = -57 kJ

   The two reactions a) and b) above occur one after the other. If the vessel containing the mixture is cooled, what happens to:

   (i) The concentration of chlorine? _____

   (ii) The concentration and mass of $FeCl_2$? _____

   (iii) The mass of iron? _____

   (iv) The pressure in the vessel? _____

   (v) What would be the total enthalpy change going from iron to iron (III) chloride? _____

1.12 COMPROMISE CONDITIONS

Le Châtelier's Principle suggests several ways of achieving more yield. These are:

- Add more of the reactants
- Remove the products as they form
- Set and maintain pressure as necessary to produce a greater yield
- Set and maintain temperature as necessary to produce the optimum yield
- Use a suitable catalyst.

Industrial processes need to produce the highest yield for the lowest cost in the shortest time.

The Haber process

In this process ammonia is made industrially according to the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ kJ$$

In the Haber Process N_2 and H_2 react at high pressure as this favours the forward reaction (producing more NH_3) – about 200 atmospheres is used. Being exothermic, the forward reaction would be favoured by lowering the temperature, but this would in turn reduce the reaction rate and would take too long to obtain product because ammonia decomposes more at higher temperatures.

Hence a compromise temperature of about 400-450°C is used (less yield but produced at a higher rate), using a catalyst of iron/iron oxide to further increase reaction rate.

Getting less product, but in a shorter time will give more product overall in a day!

Ammonia is extracted from the mix by liquefying – thus removing the product. If NH_3 is removed in the equation above then the equilibrium must continually move to the right and produce more yield.

The Contact Process

In the Contact Process sulfuric acid is produced according to these steps:

Sulfur is burnt in air:

$$S(l) + O_2(g) \rightleftharpoons SO_2(g)$$

Molten sulphur is sprayed into the gaseous O_2 increasing surface area and collisions.

SO_2 is then oxidised to SO_3 at high temperatures:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The forward reaction is favoured by high pressure and low temperature but again, compromise conditions are used in practise.

As the rate of the reaction is important economically, high temperatures (600°C) and pressures are used, with a catalyst (V_2O_5).

198 kJ of heat is released per mole.

If SO_3 is added directly to water it produces lots of heat and so these reactions are used to control the rate.

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$$

Finally, $SO_3(g)$ is absorbed in concentrated $H_2SO_4(l)$ to produce oleum, $H_2S_2O_7(l)$ and the oleum is added to water to produce H_2SO_4.

Set 4. Equilibrium

Multiple Choice Questions

1. The reason for an increase in the rate of reaction at higher temperatures is due to:
   1) an increase in the number of collisions between the particles.
   2) lowering of the activation energy for the particles.
   3) an increase in the average kinetic energy of the reactant particles.

   (a) All are correct
   (b) 2 and 3 are correct
   (c) 1 and 3 are correct
   (d) 2 is correct
   (e) 1 is correct

2. Which of the following is **false**?
   (a) Activation energy is required for both exothermic and endothermic reactions.
   (b) Catalysts shift reaction equilibrium toward the side of the products.
   (c) Reaction rates depend on temperature, state of subdivision, concentration of the reactants and the presence of catalysts.
   (d) Enzymes are catalysts in living organisms.

3. A catalyst
   (a) increases the kinetic energy of the reaction.
   (b) provides a path of lower activation energy.
   (c) undergoes changes to speed up the rate of a reaction.
   (d) lowers the potential energy of the products compared to reactants.
   (e) increases the number of collisions of reactant molecules.

4. Use LCP to predict in which of the following the reaction will proceed more to the right by increasing the pressure.
   1) $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$
   2) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$
   3) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
   4) $Ni_{(s)} + 4CO_{(g)} \rightleftharpoons Ni(CO)_{4(g)}$
   5) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

   (a) 1, 4, 5
   (b) 2, 3, 4
   (c) 1, 3
   (d) 2, 3
   (e) 1, 2, 3

5. Using Le Châtelier's Principle state which of the following reactions is the product formation favoured by decreased pressure.

   1) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ $\Delta H = +172$ kJ
   2) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -91.8$ kJ
   3) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H = -21.7$ kJ
   4) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +181$ kJ
   5) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $\Delta H = +484.6$ kJ

   (a) 2, 3
   (b) 3, 4
   (c) 2, 4
   (d) 1, 5
   (e) 3

6. Using Le Châtelier's Principle state which of the following reactions is the product formation favoured by an increase in temperature.

   1) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ $\Delta H = -206.2$ kJ
   2) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ $\Delta H = +172.5$ kJ
   3) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = -9.4$ kJ
   4) $3O_2(g) \rightleftharpoons 2O_3(g)$ $\Delta H = +285$ kJ
   5) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $\Delta H = +484.6$ kJ

   (a) 2, 4, 5
   (b) 3, 5
   (c) 1, 2, 5
   (d) 1, 3
   (e) 1, 3

7. Using Le Châtelier's Principle state which of the following reactions is the product formation favoured by a decrease in temperature.

   1) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ $\Delta H = +172.5$ kJ
   2) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -91.8$ kJ
   3) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH$ $\Delta H = -21.7$ kJ
   4) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +181$ kJ
   5) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $\Delta H = +484.6$ kJ

   (a) 3
   (b) 3 ,4
   (c) 2, 3
   (d) 1, 4, 5
   (e) 2, 4

8. Using Le Châtelier's Principle state which of the following reactions is the product formation favoured by low pressure and high temperature.

    1) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -91.8$ kJ
    2) $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$ $\Delta H = +566$ kJ
    3) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ $\Delta H = +9.4$ kJ
    4) $3O_{2(g)} \rightleftharpoons 2O_{3(g)}$ $\Delta H = +285$ kJ
    5) $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H = +66$kJ

    (a) 5
    (b) 4
    (c) 1
    (d) 2
    (e) 3

9. Using Le Châtelier's Principle state which of the following reactions is product formation favoured by high pressure and low temperature.

    1) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -91.8$ kJ
    2) $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$ $\Delta H = +566$ kJ
    3) $3O_{2(g)} \rightleftharpoons 2O_{3(g)}$ $\Delta H = +285$ kJ
    4) $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$ $\Delta H = -542$ kJ
    5) $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H = +66.4$ kJ

    (a) 4
    (b) 5
    (c) 2
    (d) 1
    (e) 3

10. Using Le Châtelier's Principle state which of the indicated changes will cause the reaction to proceed to the right.

    1) $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$ - add CH_4
    2) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ - remove NH_3
    3) $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$ - add F_2
    4) $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ - remove O_2
    5) $BaO_{(s)} + SO_{3(g)} \rightleftharpoons BaSO_{4(s)}$ - add BaO

    (a) 3.5
    (b) 2,3,5
    (c) 1,4,5
    (d) 1,4
    (e) 2,3

11. Using Le Châtelier's Principle state which of the indicated changes will cause the reaction to proceed to the right.

    1) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ - remove water
    2) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ - add iodine
    3) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ - add $CaCO_3$
    4) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ - remove O_2
    5) $BaO(s) + SO_3(g) \rightleftharpoons BaSO_4(s)$ - add SO_3

    (a) 1,3
    (b) 1,4
    (c) 3,4
    (d) 2,3,5
    (e) 2,5

12. Using Le Châtelier's Principle state what change will occur for the following reaction if a few drops of HCl are added.

    $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

    (a) A decrease in the number of acetate ions.
    (b) A decrease in the number of hydronium ions
    (c) An increase in the number of acid molecules ionised.
    (d) An increase in the number of water molecules dissociated.

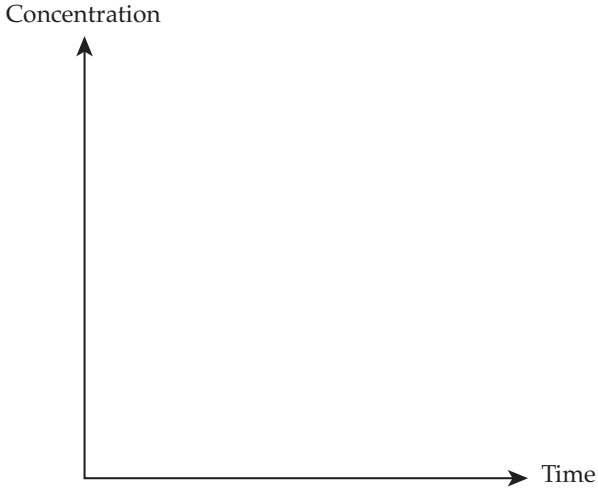
Longer Questions

1. If $Pb(NO_3)_2$ solution and KI solution are mixed in the correct stoichiometric ratio, a precipitate is formed.

    (a) Write an equation for this reaction.

    _____

    (b) Sketch a graph showing what happens to the concentration of Pb^{2+} ions, I^- ions and the precipitate during the course of this reaction.



    (c) How do you know that the reaction has reached equilibrium?

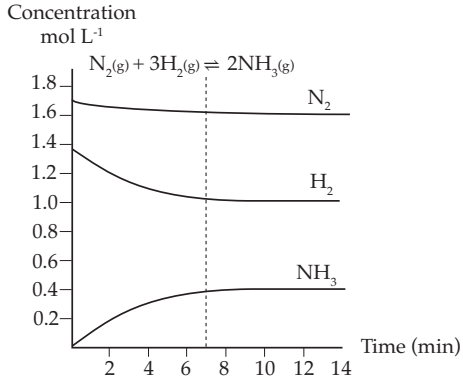
    _____

(d) How could you show that the reaction has not stopped at equilibrium?

_____

_____

2. Study the equilibrium graph shown here.



(a) What substances are present at equilibrium?

_____

(b) What is the final concentration of each of these substances?

_____

(c) What is the concentration of each of these substances at time = 3 minutes?

_____

(d) When did the concentration of H_2 reach 1.2 mol L^{-1}?

_____

(e) When did the reaction reach equilibrium?

_____

(f) What is the concentration of each substance at equilibrium?

_____

3.

(a) List ways in which a chemical reaction rate can be increased.

_____

_____

_____

(b) In an aqueous solution of a mixture of $K_2Cr_2O_7$ and K_2CrO_4 in equilibrium, what would be the effect of adding the following:

$$Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + H_2O(l)$$

(i) Sodium hydroxide solution? _____

(ii) Hydrochloric acid solution? _____

(iii) Water? _____

(c) When a bottle of soft drink is opened bubbles come out profusely, according to the equation:

$CO_{2\,(aq)} \rightleftharpoons CO_{2\,(g)}$

Why does this happen? Explain using Le Châtelier's Principle.

_____

_____

(d) When copper carbonate is heated, it decomposes into copper oxide and carbon dioxide. Explain what happens to the equilibrium position in this reaction if performed in:

(i) an open container

_____

_____

(ii) a sealed container

_____

_____

4. What effect would decreasing the pressure have on each of the following systems in equilibrium:

(a) $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$?

_____

_____

(b) $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$?

_____

_____

(c) $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + O_{2(g)}$?

_____

_____

(d) $2H_2O_{(g)} + 2I_{2(g)} \rightleftharpoons 4HI_{(g)} + O_{2(g)}$?

_____

_____

5. What effect would raising the reaction temperature have on the equilibrium position of each of the following equilibrium systems:

(a) $SO_{3(g)} + CO_{(g)} \rightleftharpoons SO_{2(g)} + CO_{2(g)}$? $\Delta H = -120\ kJ\ mol^{-1}$

_____

_____

_____

(b) $S(s) + O_2(g) \rightleftharpoons SO_2(g)$? $\Delta H = -297 \text{ kJ mol}^{-1}$

(c) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$? $\Delta H = +108 \text{ kJ mol}^{-1}$

6. What would be the effect of lowering the temperature in the above systems?
   (a) _____
   (b) _____
   (c) _____

7. Write the equilibrium expressions for the following reactions:
   (a) $Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$ _____
   (b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ _____
   (c) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ _____
   (d) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightleftharpoons Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$
   _____
   (e) $2MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H^+(aq) \rightleftharpoons 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$
   _____

8. A filter paper dipped in cobalt chloride solution (blue) can be used as an indicator of humidity in air (turns pink). The paper soaked in the solution and dried will absorb moisture from the air as follows:

   $[CoCl_4]^{2-}(aq) + 6H_2O(l) \rightleftharpoons [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$

   Blue Pink

   (a) Write an equilibrium expression for the reaction.

   (b) If you add some sodium chloride solution what will you observe? Explain your observation.

(c) If you put these papers into a microwave oven and turned it on, what change will you observe to a blue cobalt chloride paper and to a pink cobalt chloride paper? Explain your observation.

_____

_____

_____

9. A copper chloride ionic equilibrium is set up for the following ions in 1 litre of solution:

$CuCl_2^-$ (aq) + Cl^- (aq) ⇌ $CuCl_3^{2-}$ (aq) $\Delta H = -21$ kJ mol^{-1}

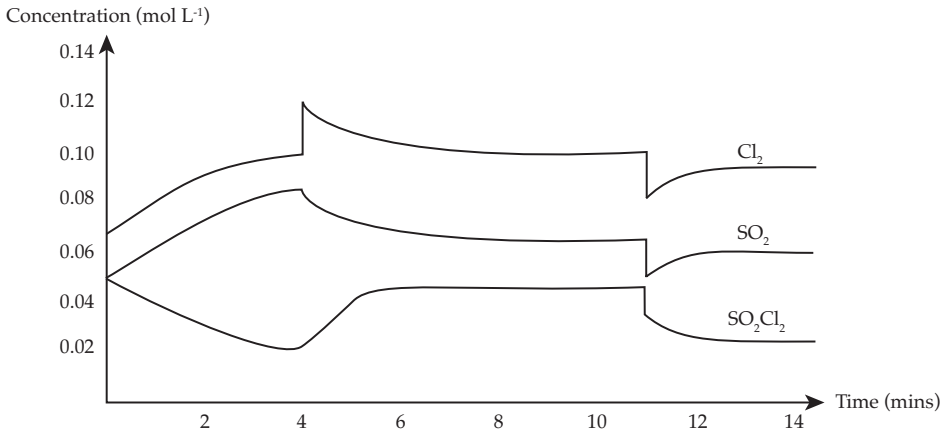
The pressure of the day was 100 kPa and the temperature was 25°C.

Write into the boxes below "increase", "decrease" or "no change" for the changes made.

Change made	Change in rate	Change in yield
Increase in pressure		
Increase in temperature		
Add some NaCl solid		
Divide the solution into 100 mL portions to increase the state of subdivision		

10. The graph below shows the results of the effects of changes to equilibrium in the reaction:

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ $\Delta H = +67$ kJ mol^{-1}



(a) What substances are present at the beginning of the reaction and what are their concentrations?

_____

(b) Write the equilibrium expression for this reaction.

_____

(c) Describe the change introduced and the effects that followed at time, t = 4 min.

_____

(d) When did the system next reach equilibrium?

_____

(e) What changes and effects occurred after time, t = 11 minutes?

_____

11. Using Le Châtelier's Principle state the observation, direction of shift in equilibrium and an explanation for what happens in the following reactions, after each change is introduced:

(a) $Ba(OH)_{2(s)} \rightleftharpoons Ba^{2+}_{(aq)} + 2OH^{-}_{(aq)}$

White Colourless

(i) $BaCl_2$ solution is added to the mixture.

_____

_____

(ii) More $Ba(OH)_2$ solid is added to the mixture.

_____

_____

(b) $CaCO_{3(s)} + \text{heat} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

(i) A few drops of NaOH solution are added to the mixture.

_____

_____

(ii) Temperature of the system is decreased.

_____

_____

(iii) Water is added to the system.

_____

_____

(iv) Volume of the system is decreased.

_____

_____

(c) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + 99\ kJ$

(i) The volume of the system is increased.

_____

_____

(ii) An inert gas introduced in the system.

_____

_____

12. For the following reaction at equilibrium, changes are made to the reaction mixture as listed one after the other. Describe the effects that occur as a result of each of these changes. Show these on an equilibrium graph.

(a) A solution of hydrochloric acid is added to the reaction mixture.

_____

_____

(b) A solution of $Ba(NO_3)_2$ is added to the mixture.

_____

_____

(c) The pressure on the system was increased.

_____

_____

(d) A solution of potassium hydroxide is added to the system.

_____

_____

(e) More SO_2 is pumped into the system.

_____

_____

13. Yellow bismuth oxybromide reacts with acid and makes the following equilibrium:

$BiOBr_{(s)} + 2H^+_{(aq)} \rightleftharpoons Bi^{3+}_{(aq)} + Br^-_{(aq)} + 2H_2O_{(l)}$

Different test tubes a, b and c containing BiOBr and HCl were prepared and subjected to 3 different experiments shown below as changes.

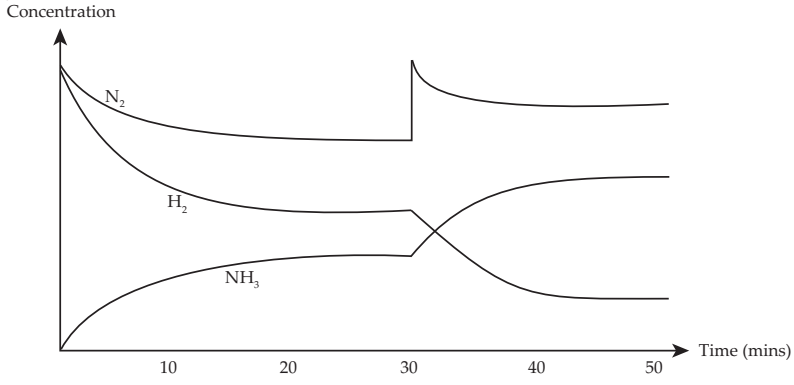
Using collision theory and, using Le Châtelier's Principle, complete the table below to show how the equilibrium will shift with these changes and explain the reason.

Tube No.	Change imposed	Shift in equilibrium Left, Right or None	Explanation
a	5 mL of water added		
b	A few drops of HBr added		
c	A few drops of $AgNO_{3\,(aq)}$ added		

14. Consider the ammonia production equation below:

$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H = -92\ kJ\ mol^{-1}$

The graph below shows the concentrations of the three gases involved in the reaction:



Explain:

(i) Why do the pressures of all gases stabilise around the 20 minute mark?

_____

(ii) Why the partial pressure of the H_2 decreases more rapidly than that of the N_2?

_____

(iii) What has occurred at the 30-minute mark to cause the changes shown in the graph?

_____

(iv) What will the change made at the 30-minute mark have made by the time it has reached 50 minutes to the rate of:

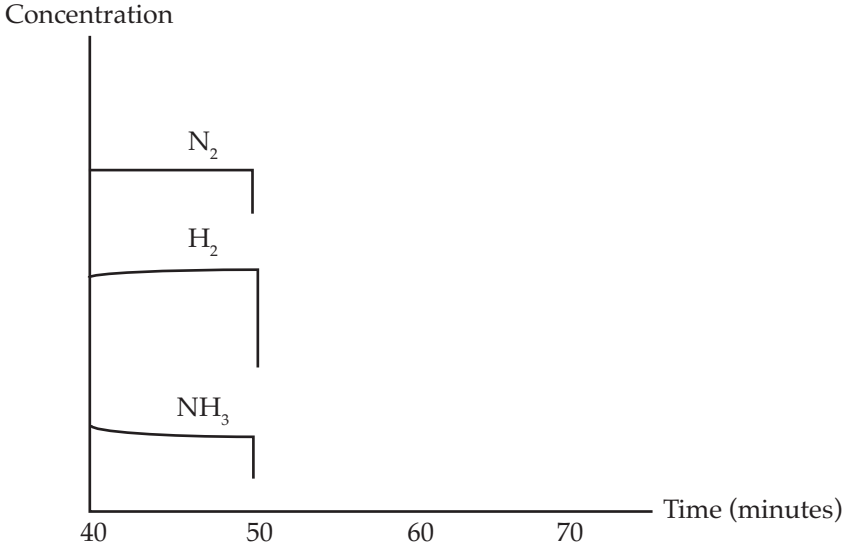
The forward reaction? _____

The reverse reaction? _____

(v) Use the Collision Theory to explain your answers to part (iv).

_____

At 50 minutes, the contents of the reaction vessel are rapidly expanded by increasing the volume. The changes in the concentrations of the gases are shown on the following graph.



(vi) Complete the graph above by drawing over it to show how the concentration of each gas will change as it moves to reach equilibrium at a time of 70 minutes.

15. The amount of gaseous atmospheric CO_2 is increasing as a direct result of human activities such as deforestation, cement manufacture and the burning of fossil fuels. Atmospheric CO_2 absorbs heat which otherwise would have radiated out from the planet through the atmosphere, resulting in global warming. Increased atmospheric CO_2 has also increased the levels of aqueous CO_2 dissolving into the oceans and ocean acidity.

(a) Write an equation showing the equilibrium that occurs between gaseous atmospheric CO_2 and aqueous oceanic CO_2 concentrations.

_____

(b) Given that CO_2 dissolving into the oceans is an exothermic process, what effect could increasing oceanic temperatures have on the equilibrium equation in (a) above?

_____

(c) Write an equilibrium equation showing how the increased dissolution of CO_2 into the ocean increases the acidity.

_____

(d) Explain, using collision theory and with reference to the relative rates of the forward and reverse reactions from your answer to (c) above, how the increase of aqueous oceanic CO_2 contributes to ocean acidification.

_____

_____

_____

_____

_____

_____

Increased acidity removes CO_3^{2-} from the water, reducing the ability of sea organisms to build their calcium carbonate shells and body structures. In addition the increased acidity can cause their shells to dissolve.

(e) Using your equation from (c) above, and Le Châtelier's Principle, explain how the concentration of CO_3^{2-} in sea water is reduced.

_____

_____

_____

_____

_____

_____

(f) Give an ionic equation for the dissolution of calcium carbonate caused by increased ocean acidity.

_____

Chapter

2

Acids and Bases

2.1 INTRODUCTION

Today acids and bases are part of our everyday life. Our food could not be digested without the aid of the hydrochloric acid in our stomachs and window-cleaner would not work without having a base (ammonia) as its main component. We can also find acids in lemons and oranges and use acids to dissolve metals in mining or to clean paving stones.

Toothpaste is slightly basic to counteract the acid formed by bacteria in our mouth. Acids have a sharp taste and bases have a soapy feel to them, but there have been different methods of defining what acids and bases are.

2.2 DIFFERENT DEFINITIONS

In 1815 Davy identified acids as substances that contained replaceable hydrogen - hydrogen that could be partly or totally replaced by metals. He saw that when acids reacted with metals they formed salts and he also defined bases as substances that reacted with acids to form salts and water. His definitions were accepted as standard during most of the 1800s.

Arrhenius

Svante Arrhenius was a Swedish Chemist who, besides developing the theory of dissociation of ions, the Greenhouse Effect and winning a Nobel Prize, also developed a theory of acids and bases in 1884. With the Arrhenius model of what an acid is, an acid was viewed as a substance which simply provided H^+ ions in solution, e.g. hydrochloric acid is an acid:

$$HCl \rightarrow H^+ + Cl^-$$

A base is a substance, which provides OH^- ions in solution, e.g potassium hydroxide is a base:

$$KOH \rightarrow K^+ + OH^-$$

The Arrhenius model helps us to classify many of the common chemicals as acids or bases:

Some common acids are: HCl, H_2CO_3, HNO_3, H_2SO_4, CH_3COOH, H_3PO_4 - all of which produce hydrogen ions in solution.

Common bases are: KOH, NaOH, $Ca(OH)_2$, NH_3, $Mg(OH)_2$- all of which produce hydroxide ions in solution.

However, the Arrhenius theory does not help to explain how some salts which do not contain H^+ ions can show acidic properties and have a low pH. These reactions are classified as hydrolysis reactions and are dealt with by a different notion of an acid, called the Brønsted-Lowry model.

Brønsted-Lowry

In 1923 the Brønsted–Lowry definition was proposed quite independently by Brønsted in Denmark and Lowry in England.

The Brønsted-Lowry (Brønsted-Lowry) model views acids as H^+ or proton donors and bases as proton acceptors. With this model, we say that a species is **acting** as an acid or base, rather than the species is an acid or base. Using that Brønsted-Lowry approach all the Arrhenius and Lewis acids would still be classified as acids but it now allows for the species that can act as an acid or a base.

The Brønsted-Lowry model will be the main approach used in this book, as it provides the most flexible system.

2.3 ACID/ BASE REACTIONS

Acids and bases react with each other to produce a salt and water.

Example: $H_2SO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$

Acids react with reactive metals (Ca, Mg, Zn, Al etc.) to produce hydrogen gas.

Example: $Ca_{(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(aq)} + H_{2(g)}$

Acids react with carbonates to produce $CO_{2(g)}$ and $H_2O_{(l)}$.

Example: $CuCO_{3(s)} + 2HCl_{(aq)} \rightarrow CuCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$

Acids react with hydrogen carbonates to produce $CO_{2(g)}$ and $H_2O_{(l)}$.

Example: $KHCO_{3(s)} + HCl \rightarrow KCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

Acids react with metal oxides to produce salt and water.

Example: $MgO_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_2O_{(l)}$

Al, Cr, Pb and Zn are called amphoteric metals as they can react with both acids and bases to produce hydrogen gas. The metals also produce complex compounds with bases.

Example: $2Al_{(s)} + 3H_2SO_{4(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + 3H_{2(g)}$

but: $2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)} + 3H_{2(g)}$

Certain metal hydroxides are also known as amphoteric because they can react with both acids and bases to produce a complex ion, e.g. aluminium, zinc and chromium hydroxides.

Chromium hydroxide, for example, reacts with acid:

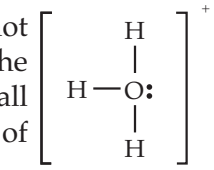
$$Cr(OH)_{3(s)} + 3HCl_{(aq)} \rightarrow CrCl_{3(aq)} + 3H_2O_{(l)}.$$

It can also react with a base:

$$Cr(OH)_{3(s)} + NaOH_{(aq)} \rightarrow NaCr(OH)_{4(aq)}$$

2.4 THE BRØNSTED–LOWRY APPROACH

One main discovery that this model incorporates is that a single proton cannot exist on its own, but it will combine with a water molecule to form H_3O^+ (the electron-dot diagram of the hydronium ion is shown on the right). So all Brønsted-Lowry equations involve a reaction with water, e.g. the ionisation of hydrochloric acid now becomes:



$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

According to the Brønsted-Lowry model, an acid is defined as a proton donor and a base as a proton acceptor. In an acid-base reaction, a proton (H^+) is transferred from the acid to the base. As a result, what the acid changed into can now act as base, called conjugate base, and the base has changed into a new acid called conjugate acid.

In the reaction $HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$ the HCl molecule donates a proton to the water molecule and H_2O accepts this proton. Hence HCl is acting as an acid and H_2O is acting as a base. After giving up a proton, the HCl has now changed into the Cl^- ion and becomes the conjugate base of HCl. The water molecule, which acted as the original base, now becomes its conjugate acid, H_3O^+.

HCl and Cl^- are termed "Conjugate acid/base pairs"and H_2O and H_3O^+ are also termed "Conjugate acid/base pairs"

Consider the reaction: $NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)}$

NH_4^+ is acting as an acid, and NH_3 would be its conjugate base. H_2O is now acting as a base and H_3O^+ would be its conjugate acid.

Example

In the reaction $HSO_4^- + CH_3COO^- \rightleftharpoons SO_4^{2-} + CH_3COOH$, experimental evidence indicates that the forward reaction is dominant which makes HSO_4^- the Brønsted-Lowry acid and CH_3COO^-, a Brønsted-Lowry base. SO_4^{2-} is the conjugate base of HSO_4^- and CH_3COOH the conjugate acid of CH_3COO^-.

Conjugate acid-base pairs

Following the Brønsted-Lowry concept, that an "acid minus a proton is a conjugate base", and "base plus a proton is a conjugate acid", we can identify the conjugate acid-base pairs for many species.

Species	Conjugate base	Conjugate acid
H_2O	OH^-	H_3O^+
HCO_3^-	CO_3^{2-}	H_2CO_3
NH_3	NH_2^-	NH_4^+
HSO_4^-	SO_4^{2-}	H_2SO_4
$H_2PO_4^-$	HPO_4^{2-}	H_3PO_4
HSO_3^-	SO_3^{2-}	H_2SO_3

2.5 POLYPROTIC ACIDS

Acids that donate only one proton in aqueous solutions are called **Monoprotic** acids. For example, HCl and HNO_3 are examples of monoprotic acids. Acids such as H_2SO_4 and H_3PO_4 can donate more than one proton in aqueous solutions – these two acids are termed **Diprotic** and **Triprotic** acids respectively. Polyprotic acids such as these donate their protons in stages. The first stage donation always has a higher ionisation constant than the following stages.

With sulfuric acid:

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq) \text{ then}$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

With the 1st, strong, ionisation this goes to completion, i.e. 100% ionisation but the 2nd stage ionisation is fairly weak as 1 mole of HSO_4^- only gives about 0.3 moles of H_3O^+ ions. Overall then, 1 mole of H_2SO_4 would give about 1.3 moles of hydrogen ions.

Phosphoric acid has 3 stages of ionisation, each with different K values:

$$H_3PO_4(aq) + H_2O(aq) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq) \qquad K_1 = 7.25 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq) \qquad K_2 = 6.31 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(aq) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq) \qquad K_2 = 4.80 \times 10^{-13}$$

Phosphoric acid is triprotic and all the ionisations are weak, as shown by the low K values.

Set 1. Brønsted-Lowry acids and bases

1. (a) Write balanced equations for the following:

   (i) hydrochloric acid is added to magnesium metal.

   (ii) sulfuric acid is added to sodium hydroxide solution.

   (iii) nitric acid is added to solid calcium oxide.

   (iv) hydrobromic acid is added to potassium carbonate solution.

   (b) Explain using the equations that you have written for parts (i) and (iii) why Davy would have classified hydrochloric acid and nitric acid as acids.

   _____

   _____

   _____

   (c) Can magnesium metal be considered a 'Davy' base? Explain.

   _____

   _____

2. Classify each of the following as strong or weak Arrhenius acids or bases and write equations to support your answers.

   (a) H_3PO_4 _____

   (b) NH_3 _____

   (c) HF _____

   (d) LiOH _____

   (e) H_2SO_4 _____

3. Identify which reactant is acting as an acid and which is reacting as a base in each of the following:

   (i) $H_2O_{(l)} + CN^-_{(aq)} \rightleftharpoons HCN + OH^-_{(aq)}$

   The Brønsted-Lowry acid is_____

   The Brønsted-Lowry base is_____

(ii) $CH_3COOH_{(aq)} + S^{2-}_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + HS^-_{(aq)}$

The Brønsted-Lowry acid is_____

The Brønsted-Lowry base is_____

(iii) $HS^-_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons S^{2-}_{(aq)} + HCO_3^-{}_{(aq)}$

The Brønsted-Lowry acid is_____

The Brønsted-Lowry base is_____

4. Using the examples in question 3 write down the Brønsted-Lowry conjugate acid/base pairs in each case.

(i) Conjugate acid/base pair #1 _____

Conjugate acid/base pair #2 _____

(ii) Conjugate acid/base pair #1 _____

Conjugate acid/base pair #2 _____

(iii) Conjugate acid/base pair #1 _____

Conjugate acid/base pair #2 _____

5. A student was given a 0.200 mol L^{-1} hydrochloric acid solution and a 0.100 mol L^{-1} sulfuric acid solution. She tested the acidity of each solution using a pH meter and found that the sulfuric acid solution was less acidic (higher pH) than that of the hydrochloric acid solution. Explain this observation. Include equations in your answer.

_____

_____

_____

6. In which of the reactions below is water acting as a base? (Circle answer)

A. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

B. $NaCl + H_2O \rightleftharpoons Na^+ + Cl^-$

C. $O^{2-} + H_2O \rightleftharpoons 2OH^-$

D. $HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

7. Which of the following compounds would be acidic in solution? (Circle answer)

CO_2, MgO, CuO, SO_3, $Ba(OH)_2$, OCl_2, NO_2

8. Which one of the following would have the highest electrical conductivity in a 1 mol L^{-1} solution? (Circle answer)

CO_2, MgO, CuO, SO_3, $Ba(OH)_2$, OCl_2

9. Which of the following can act as both a Brønsted-Lowry acid and base? (Circle answer)

   CH_3COOH OH^- HCO_3^- NH_3 H_3O^+

10. (i) Distilled water which has been exposed to air for a long time is slightly acidic (pH 5) but when it is boiled its pH increases to 7 again.

    Explain how the other gases in air, apart from oxygen, contribute to this change in acidity.

    _____

    _____

    At 95ºC pure water has a K_a of 5×10^{-13}, which corresponds to a pH of 6.8.

    (ii) Explain why, at this temperature, the pH is not exactly 7.

    _____

    _____

    (iii) Would water at 95ºC be acidic, basic or neutral? Explain.

    _____

    _____

11. Which of the following equations is **not** a Brønsted-Lowry acid/base reaction? (Circle answer)

    (i) $NH_3 + OH^- \rightleftharpoons NH_2^- + H_2O$

    (ii) $Cu + 2H^+ \rightleftharpoons Cu^{2+} + H_2$

    (iii) $HOCl + C_2H_5COO^- \rightleftharpoons OCl^- + C_2H_5COOH$

    (iv) $Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$

    (v) $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

12. (i) 25 mL of NH_3solution is added to 25 mL of HCl with a concentration of 0.050 mol L^{-1} and the solution becomes neutral.

    Explain what the possible quantitative characteristics of the ammonia solution are.

    _____

    _____

    (ii) In a solution of ammonia with a concentration of 0.10 mol L^{-1}, which species would be the most plentiful? (Circle answer)

    Choose from: NH_3 OH^- H_3O^+ NH_4^+

13. Define a Brønsted-Lowry acid. Why are all soluble acids considered to be Brønsted-Lowry acids?

_____

_____

_____

14. Write the chemical equation for the addition of a proton to each of the following.

NH_3, H_2O, HCO_3^-, CO_3^{2-}, CN^-, OH^-.

_____

_____

_____

_____

_____

_____

15. The hydrogen carbonate ion, HCO_3^-, is amphoteric. Illustrate this property by using appropriate equations.

_____

_____

_____

16. List all the Brønsted-Lowry acids and Brønsted-Lowry bases from among the following:

SO_3^{2-} $AlCl_3$ Cl^- NH_4^+ H_2O HBr.

_____

_____

_____

17. (i) Write the conjugate acids of: Cl^- CN^- S^{2-} NH_3.

_____

(ii) Write the conjugate bases of: OH^- H_2Se NH_3 HCO_3^-

_____

2.6 ACIDIC AND BASIC SALTS

Ions that react with water to form acidic solutions are called acidic ions. Ions such as:

HSO_4^-, $H_2PO_4^-$, HCO_3^-, NH_4^+, H_3O^+, Al^{3+} complexes, Fe^{3+} complexes can all donate protons.

e.g. $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

Ions which react with water to form basic solutions are called Basic Ions. For example:

O^{2-}, OH^-, F^-, PO_4^{3-}, CO_3^{2-}, S^{2-} can gain protons.

e.g. 1. Sodium carbonate solution is basic because the carbonate ion can accept a proton:

$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

Sodium carbonate is the salt made from a strong base (NaOH) and a weak acid (H_2CO_3)

e.g. 2. Ammonium nitrate solution is acidic because the ammonium ion can donate a proton:

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$.

Ammonium nitrate is a salt made from a strong acid and a weak base.

From the examples above we could derive a principle that if the acid the salt is prepared from is strong, then the solution of the salt will be acidic, or if that acid is weak, then the salt solution will be basic.

The exception to this would be the salts made from sulfuric acid, which most people would classify as strong. Actually, only the first ionisation of H_2SO_4 is strong (100% ionised) – but the second ionisation is fairly weak:

1st: $H_2SO_4(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$ – 100% ionised $K = 2 \times 10^6$

2nd: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$ – feebly ionised $K = 10^{-2}$.

This means that the HSO_4^- ion can only act as an acid to produce SO_4^{2-} but some of the SO_4^{2-} ions will move to the left of the equilibrium mixture, accepting a proton to produce a basic solution.

e.g. Na_2SO_4 will be basic in solution and $NaHSO_4$ will be acidic.

A salt made from a strong acid and a strong base (e.g. NaCl) will be neutral because neither the Na^+ nor the Cl^- ion will react with water in a Brønsted-Lowry reaction.

Nitrates, chlorides, bromides and iodides all produce neutral salt solutions.

Carbonates, sulfides and cyanides all give basic solutions.

Nitrates, chlorides, bromides and iodides of the ammonium ion and some metals produce acidic solutions.

NB: weak acid/weak base salts are neutral (e.g. CH_3COONH_4).

Amphiprotic Species

Some species can donate or accept protons – these are called amphoteric or amphiprotic. Hence these substances can act both as acids or bases.

Water is a good example of such an amphiprotic substance:

$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$ (water acting as an acid)

$H_2O + H_2SO_4 \rightleftharpoons HSO_4^- + H_3O^+$ (water acting as a base)

HSO_4^-, $H_2PO_4^-$, HCO_3^- are other examples of amphoteric or amphiprotic substances which can both accept or donate protons.

2.7 STRENGTHS OF ACIDS AND BASES

Acids and bases are classified as either strong or weak, depending on the extent to which they become ionised.

Examples of strong acids are: HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4 (1^{st} ionisation) which all have a very high equilibrium constant.

Examples of strong bases are: hydroxides and oxides of Groups 1 metals and hydroxides and oxides of Group 2 metals, except beryllium.

Examples of common weak acids are: HF, HCN, CH_3COOH, HNO_2, H_3PO_4, H_2CO_3.

Examples of common weak bases are solutions of: NH_3, Na_2CO_3, CH_3NH_2.

Concentrated acids and bases are not the same as strong acids and bases.

A concentrated solution is one which has a large number of particles per litre.

For example, 10 mol L^{-1} solution of an acid or base is a concentrated solution. However, this may be a solution of a strong acid such as HCl or a weak acid such as CH_3COOH, or a strong base such as NaOH, or a weak base such as Na_2CO_3.

A dilute solution is one which has a low concentration of particles in it.

For example, it can be a 10^{-4} mol L^{-1} solution of HCl, or CH_3COOH, or NaOH or Na_2CO_3.

Thus you can have a dilute solution of a strong acid or base in which all particles are ions, or a concentrated solution of a weak acid or base in which most of the particles are molecules and very few ions.

You can also have a concentrated solution of a weak acid in which most of the particles are molecules with very few ions, or a strong acid or base in which most of the particles are ions.

2.8 ACID DISSOCIATION CONSTANTS

Water contains a very small proportion of H^+ and OH^- ions.

The equilibrium expression for the water dissociation reaction is: $2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$.

The product $[H_3O^+] \times [OH^-]$ is called the ionic product constant K_w.

For water, K_w is 1×10^{-14} $mol^2 L^{-2}$ at $25^{\circ}C$ as one molecule of water produces one H_3O^+ and one OH^- ion in solution, pure water is said to be neutral.

A solution which has a greater H^+ ion concentration than its OH^- ion concentration is said to be acidic, whereas a solution which has a greater OH^- ion concentration than H^+ ion concentration is said to be basic.

As there is a fixed relationship between the hydrogen and hydroxide ion concentrations, a basic solution is one in which hydroxide ion concentration varies from 10^{-7} to 10 mol L^{-1}, and an acid solution is one in which the hydrogen ion concentration varies from 10^{-7} to 10 mol L^{-1}.

2.9 THE pH SCALE

Because the concentration of ions in solution varies so greatly (from about 10 to 10^{-7} mol L^{-1}), it would be very difficult to display the change in concentration graphically. Hence a logarithmic variation is used which displays all concentrations as powers of 10. A logarithm of a number is the power to which 10 must be raised to produce that number.

e.g. 1000 is 10^3, hence log (1000) = 3. Log (0.01) = -2 because $0.01 = 10^{-2}$.

To find the log of number which is not a simple power of 10 we must use a calculator:

e.g log (3000) = 3.48

A conventional way to indicate the extent of acidity is to take the power to which 10 is raised to give the H^+ ion concentration and discard the negative sign.

pH is therefore defined as the negative log of the hydrogen ion concentration.

For example, if the H^+ ion concentration is 10^{-5} mol L^{-1}, then the pH is 5.

$$pH = - \log [H^+]$$

As the $[H^+]$ increases, the pH will decrease.

A change in pH of 1 corresponds to a 10-fold change in the concentration of the H^+ ions e.g. If pH changes from 2 to 3 the $[H^+]$ changes from 10^{-2} to 10^{-3}.

Acid solutions can have pH values from below 0 up to 7, and basic solutions can have a pH from 7 to 14+.

Distilled water has a pH of 7 at 25°C and is neutral. The pH of human blood is normally between 7.3 and 7.5.

Hydroxide ions

K_w for water is given by $[H^+] \times [OH^-]$ and stays constant if temperature remains constant. From the previous chapter on equilibrium, we learnt that if $[H^+]$ increases then the $[OH^-]$ must decrease so the product always remains at a value of 10^{-14}.

If a base is added to pure neutral water with a hydrogen ion concentration of 10^{-7} mol $L^{-1,}$ the concentration of H^+ ions decreases because the OH^- ions from the base react with the H^+ ions in the water hence the pH value increases.

For example, a 0.1 M NaOH solution has $[OH^-] = 0.1$ mol L^{-1}, the corresponding hydrogen ion concentration becomes 10^{-13} mol L^{-1} and hence the pH becomes 13. The calculation is based on the fact that H^+ ion concentration and OH^- ion concentration bear a constant relationship:

$[H^+] \times [OH]^- = 1.0 \times 10^{-14.}$

This calculation could also be done using the concept of pOH which is the negative log of the hydroxide ion concentration and the equation: pH + pOH = 14.

For the 0.1 molar NaOH, the pOH = -log (10^{-1}) $\rightarrow$ pOH= 1

Hence pH = 14 – 1 = 13.

This method is often quicker than using the equation $[H^+] \times [OH^-] = 1 \times 10^{-14}$

pH Calculation Examples

a) If the $[H]^+ = 1 \times 10^{-3}$ mol L^{-1}, the pH is 3.

b) If the $[OH]^-$ concentration is 1×10^{-4} mol L^{-1}, then the pOH = 4.

This gives a value for pH of 14 – 4 = 10. So the concentration of $H^+ = 1.0 \times 10^{-10}$ mol L^{-1}

c) To find the pH of NaOH solution with concentration 0.05 mol L^{-1}, first we find the pOH

pOH = -log (0.05) = 1.30

$\therefore$ pH = 14 – 1.3 = 12.7

When equal volumes of a strong acid and a strong base of equal concentrations are added, the pH of the resulting solution will be 7.

Mixing acid and base

If we mix an acid and a base, the resulting solution can be acidic or basic, depending on the final concentration of hydrogen ions. If the number of hydrogen ions is in excess, then the final solution will be acidic. Acid/base mixing calculations will always require you to find the limiting reagent from the number of moles of each.

2.10 ACID/BASE INDICATORS

Commercial pH papers are able to give colours for every main pH unit. Universal Indicator, which is a solution of a mixture of indicators is able to also provide a full range of colours for the pH scale.

There is a variety of indicators that change colour at various pH levels. A properly selected acid-base indicator can be used to visually "indicate" the approximate pH of a solution sample by changing its colour. Indicators are usually weak organic acids or base dye obtained from plants that change colours at particular pH values.

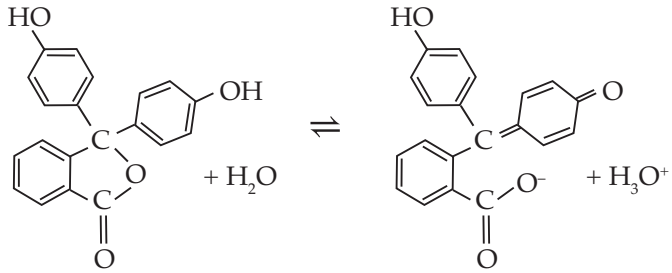
The weak acid form of the indicator (HIn) will have one colour and its conjugate base (In^-) will have a different colour.

The weak acid equilibrium in water is:

$$\underset{\text{(ACID FORM)}}{\mathbf{HIn}} + \mathbf{H_2O} \rightarrow \underset{\text{(CONJUGATE BASE FORM)}}{\mathbf{H_3O^+}} + \mathbf{In^-}$$

Colour A Colour B

Phenolphthalein is an example of a colourless, weak acid which dissociates in water forming pink anions. Under acidic conditions, the equilibrium is forced to the left (colourless) and in basic conditions the H_3O^+ are removed which causes the equilibrium to move to the right to produce more of the pink conjugate base species.



colourless (Acid) pink (Base)

Some common indicators used in acid/base titrations are: Litmus, Phenolphthalein, Methyl Orange, Bromothymol Blue, etc. Each of these would be appropriate for different titration endpoints

Litmus colour changes are: pH 4.5 = red; pH 8.2 = blue

Phenolphthalein: pH 8.2 = colourless; pH 10 = pink.

Bromophenol blue: pH 6.5 = yellow; pH 7.2 = blue.

Methyl orange: pH 3.5 = red; pH 4.5 = yellow.

2.11 THE ACIDITY OF NATURAL SYSTEMS

Example

50 mL of 0.015 mol L^{-1} solution of KOH is mixed with 30 mL of 0.021 mol L^{-1} HNO_3.

Calculate the final pH of the mixture.

Answer

$n(OH^-) = 0.015 \times 0.05 = 7.5 \times 10^{-4}$ mol

$n(H^+) = 0.021 \times 0.03 = 6.3 \times 10^{-4}$ mol

H^+ is the limiting reagent and the excess $n(OH^-) = 7.5 \times 10^{-4} - 6.3 \times 10^{-4} = 1.2 \times 10^{-4}$ mol.

Total volume of solution is now 50 + 30 = 80 mL = 0.08 L

Concentration of $OH^- = \frac{1.2 \times 10^{-4}}{0.08} = 1.5 \times 10^{-3}$ mol L^{-1}

$pOH = -\log(1.5 \times 10^{-3}) = 2.82$

So pH = 14 – 2.82 = 11.2.

The internal, physiological functions of many organisms are pH-dependent. Body enzymes, protein digestion, blood and body cells all require different pH environments to function. If these are not controlled then enzymes can often cease to work and the organic system might fail.

The gastric juice in the stomach has a pH of 1.0 to 2.0. Blood has a pH of 7.3 to 7.5 and the pancreas can only function in a slightly alkaline environment.

Soil pH determines the kind of plants that will grow in that environment. For example, strawberries need a soil pH of about 7.5, and ferns need to grow in a soil pH of around 5.

Normal rain has a pH of about 6 because it dissolves atmospheric carbon dioxide and nitrogen oxides produced during lightning strikes.

However, acid rain has a pH of about 3 which is often produced in heavy industrial areas where SO_2 and NO_2 dissolve in rain water.

The reactions are as follows:

$$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$$

$$2NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{2(aq)} + HNO_{3(aq)}$$

Acids like citric acid and ethanoic acid are used in food preservation. Food is pickled in vinegar (5% ethanoic acid) to prevent bacterial and fungal growth and has been used like this for thousands of years.

Many cleaning agents are slightly basic, so household ammonia can easily remove oil stains from clothes and skin as most oils tend to be acidic. Most soaps and detergents are slightly basic as they are actually salts of long-chain weak organic acids.

The approximate pH values of some well-known substances are shown below:

0.1 M HCl (1); gastric juice (1.4); lemon juice (2.3); vinegar (2.9); orange juice (3.5); tomatoes (4.2); coffee (5.0); rain water (6.2); pure water (7); blood (7.4); seawater (8.2); soap (11.0); household ammonia (11.5); 0.1 M NaOH oven-cleaner (13.0).

Set 2. Acidity

Multiple Choice Questions

1. Calcium hydroxide is a strong base. Calculate the $[Ca^{2+}]$ and $[OH^-]$ for a solution prepared by dissolving 0.60 g of $Ca(OH)_2$ in enough water to make 1.50 L of solution.

   (a) 5.4×10^{-3}; 1.1×10^{-2} (b) 5.4×10^{-3}; 5.4×10^{-3}

   (c) 5.4×10^{-3}; 9.1×10^{-13} (d) 8.1×10^{-3}; 8.1×10^{-3}

   (e) 8.1×10^{-3}; 1.6×10^{-2}

2. What is the conjugate acid of CH_3NH_2?

   (a) CH_3NH^- (b) CH_3NH^+ (c) $CH_3NH_3^+$ (d) $CH_3NH_2^-$

   (e) CH_3NH^{2+}

3. What is the conjugate acid of H_2SO_4?

   (a) SO_4^{2-} (b) $H_2SO_4^-$ (c) $H_3SO_4^+$ (d) HSO_4

   (e) HSO_4^+

4. What is the pH of human muscle fluid with a hydronium ion concentration of 1.6×10^{-7} mol L^{-1}?

   (a) 7.20 (b) 7.16 (c) 7.80 (d) 6.80

   (e) 6.20

5. The hydrogen ion concentration of the oceans is about 7.1×10^{-9} mol L^{-1}. What is the pH of ocean water?

   (a) 5.85 (b) 7.15 (c) 8.15 (d) 8.85

   (e) 9.71

6. A brand of vinegar has a hydroxide ion concentration of 1.3×10^{-12} mol L^{-1}. What is the pH of the vinegar?

   (a) 3.11 (b) 2.89 (c) 3.88 (d) 2.11

   (e) 11

7. What is the pH of a 0.012 mol L^{-1} solution of calcium hydroxide?

   (a) 12.00 (b) 1.62 (c) 11.10 (d) 12.38

   (e) 12.20

8. The pH of a 0.10 mol L^{-1} solution containing 0.10 mol L^{-1} NH_4Cl is 9.20. What is the concentration of the H_3O^+ ions in it?

   (a) 2.0×10^{-9} (b) 6.3×10^{-10} (c) 1.7×10^{-10} (d) 1.0×10^{-1}

   (e) 1.6×10^{-5}

9. The pH of milk of magnesia, ($Mg(OH)_2$) is 10.50. What is the concentration of OH^- ions in it?

(a) 3.2×10^{-3} (b) 5.0×10^{-10} (c) 3.2×10^{-11} (d) 5.0×10^{-11}
(e) 3.2×10^{-4}

10. In the reaction, $HCO_3^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2CO_3(aq)$, the conjugate base is

(a) HCO_3^- (b) H_2O (c) OH^- (d) H_2CO_3
(e) none of these

11. The K_a values for HF and HNO_2 are 6.8×10^{-4} and 4.5×10^{-4} respectively. Therefore, it follows that HF is a _____ acid than HNO_2 and F^- is a_____ base than NO_2^-.

(a) weaker, stronger (b) weaker, weaker
(c) stronger, weaker (d) stronger, stronger

12. Which of the following metals can react with a base and produce hydrogen?

1. Magnesium 2. Chromium 3. Lead 4. Sodium 5. Tin

(a) 1,2,3 (b) 2,3 (c) 4,5 (d) 3,4 (e) 1,3,5

13. What is the concentration of OH^- ions in a neutral solution of water at 37°C where K_w is 2.5×10^{-14}?

(a) 1.5×10^{-8} (b) 2.6×10^{-8} (c) 2.6×10^{-7}
(d) 1.6×10^{-7} (e) 1.0×10^{-7}

14. What is the concentration of a $Ba(OH)_2$ solution that has a pH 9.30?

(a) 1.00×10^{-5} mol L^{-1} (b) 2.00×10^{-5} mol L^{-1}
(c) 2.50×10^{-10} mol L^{-1} (d) 5.01×10^{-10} mol L^{-1}

15. How much water must be added to 200 mL of a 0.010 M solution of HCl to raise the pH to 2.5?

(a) 232 mL (b) 332 mL (c) 432 mL
(d) 532 mL (e) 632 mL

Longer Questions

1. What is the relationship between the strength of an acid and its numerical value of K_a?

2. How will the following ions react with water? Give the equation, where applicable:

   I^-, NO_2^-, K^+, HSO_4^-, CO_3^{2-}?

3. Predict whether aqueous solutions of the following salts would be acidic, alkaline, or close to neutral: KCl, NH_4NO_2, Na(HCOO).

4. Predict whether aqueous solutions of the following salts would be acidic, alkaline or close to neutral: NH_4CN, KI, $LiCH_3COO$.

5. Identify the acids and bases according to the Brønsted-Lowry theory of acids and bases in the following

   (a) $HNO_{3(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$

   (b) $HCl_{(g)} + NH_{3(g)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-_{(aq)}$

   (c) $H_2SO_{4(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HSO_4^-{}_{(aq)}$

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

6. Write equations to show how a solution of CO_2 becomes acidic and Na_2O in water becomes basic.

_____

_____

_____

7. (a) What is meant by hydrolysis?

_____

_____

_____

List three ions that hydrolyse to give

(b) an acidic solution

_____

_____

_____

(c) a basic solution.

_____

_____

_____

8. If 32.0 mL of a 0.1M H_2SO_4 is required to precipitate all the barium ions from a solution of $BaCl_2$, what mass of $BaCl_2$ was present in the solution?

_____

_____

_____

9. Calculate the pH of the following solutions

(a) 0.10 M HBr _____

(b) 0.00001 M HNO_3 _____

(c) 0.010 M KOH _____

(d) 0.01 M $Ba(OH)_2$ _____

(e) 0.0172 M HCl _____

10. Calculate the final pH when the following are added to 1.00 L of 0.100 M HCl solution. (Assume there is no change in volume).

(a) 0.010 mol of KOH

_____

_____

(b) 0.050 mol of $Ba(OH)_2$

_____

(c) 0.100 mol of HCl

_____

11. Determine the pH of the solution formed by mixing equal volumes of the two solutions in each case.

(a) 0.10 M HCl and 0.10 M NaOH

_____

(b) 0.20 M HCl and 0.10 M NaOH

_____

(c) 0.40 M HCl and 0.20 M NaOH

_____

(d) 0.10 M HCl and 0.10 M $Ba(OH)_2$

_____

12. A 1.50 litre water solution contains 1.7 micrograms of pure HCl (1 microgram = 10^{-6} grams).

(i) Calculate the concentration of HCl in ppm.

_____

_____

(ii) Calculate the concentration of hydrogen ions in the solution.

_____

_____

(iii) The calculated pH of this solution appears to be 7.50 which indicates a basic solution of an acid - but this cannot be correct. What is wrong with the assumption here?

_____

_____

13. If 4.90 g of sulfuric acid is added to water so that the final volume is 100 mL, what will be the pH of the solution, if 1 mole of H_2SO_4 gives 1.3 moles of H_3O^+?

_____

_____

_____

14. If 25.0 mL of 0.200 M sodium hydroxide solution is added to 30.0 mL of 0.175 mol L^{-1} sulfuric acid, what is the pH of the mixture?

_____

_____

_____

15. 200 mL of 0.0500 mol L^{-1} barium hydroxide solution is mixed with 400 mL of 0.200 M nitric acid. The mixture is then diluted with water so that the final volume is 6.00 L.

    What is the pH of the final solution?

16. A 10.0 mL sample of 0.005 mol L^{-1} calcium hydroxide is diluted with water to make 1.0 L.

    (a) What is the pH of the original solution?

    (b) How does the pH change due to the dilution?

    (c) What mass of calcium hydroxide is present in the undiluted and the diluted solution?

    (d) What volume of CO_2 at 25ºC and 110 kPa pressure must be bubbled through the solution above in order to precipitate all the Ca^{2+} ions?

17. Explain using equations, why aqueous solutions of sodium carbonate, sodium sulfide and sodium ethanoate all have a pH value greater than 7.

18. A solution has a pH of 6. If you dilute it to 100 times its original volume its pH only changes to 8. Explain this.

_____

_____

19. Ammonium carbonate dissolves in water as follows:

$(NH_4)_2CO_{3(s)} \rightarrow 2NH_4^+(aq) + CO_3^{2-}(aq)$ (1)

Following dissolution, two further reactions occur as follows:

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ (2)

$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$ (3)

(a) In what way do reactions 2 and 3 differ from 1? (What kind of reactions?)

_____

_____

_____

(b) Indicators show that an aqueous solution $(NH_4)_2CO_3$ is basic, and pH tests confirm this. NH_4^+ ions are acidic and CO_3^{2-} ions are basic in solution.

Explain how a salt can produce a solution that is basic.

_____

_____

_____

20. Suggest a reason why $H_2PO_4^-$ is a weaker acid than H_3PO_4.

_____

_____

_____

2.12 VOLUMETRIC ANALYSIS

Volumetric analysis is the process of calculating the concentration of an unknown solution using another solution whose exact concentration is known. This latter solution is known as a Primary Standard and must be prepared carefully.

With liquid acids, the concentrations, when purchased, are not accurately known and cannot be used as primary standards. Their concentration must be standardised against a standard solution with a known concentration as a reference.

The criteria for selecting a primary standard substance for use are that

It must:

a) be a very pure soluble solid,

b) be stable in air,

c) have a fairly high relative formula mass.

Two compounds commonly used are sodium carbonate (Na_2CO_3) for acid/base titrations and oxalic acid ($H_2C_2O_4.2H_2O$) for redox titrations.

To produce a primary standard solution, an accurately weighed mass of the compound is made up to an accurately known volume in a volumetric flask. The concentration of the solution to be standardised can then be found by titration against this standard.

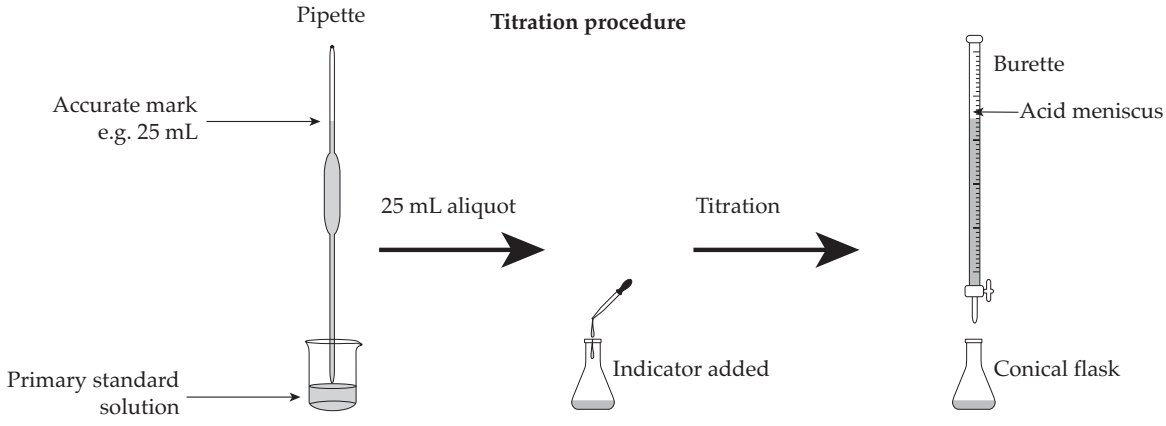
Example: To make up a standard solution of sodium carbonate solution

1.254 g of Na_2CO_3 powder was dissolved in water and then made up to exactly 250 mL of primary standard in a volumetric flask. To find the exact concentration of the solution, the following calculation is made:

Relative formula mass of $Na_2CO_3 = 105.99$

so $n(Na_2CO_3) = 1.254/105.99 = 0.01183$ moles.

$[Na_2CO_3] = 0.01183/0.25 = 0.0473$ mol L^{-1}.



Procedure: An **Aliquot** (accurate volume – typically 25 mL) of primary standard solution is drawn up into the pipette using a pipette filler bulb and is then transferred to a clean, conical flask. A few drops of a suitable indicator are added. The burette is initially rinsed with the acid of unknown concentration before finally filling. It is then zeroed by running some into a beaker until the meniscus reaches the zero mark. Acid is then run carefully into the conical flask containing the standard aliquot until the endpoint is reached (indicator colour change) and the volume of acid used is noted. This volume is called the **Titre**.

This procedure should be repeated three times for precision, with the first (rough) reading discarded and all other readings averaged. The three titre values should be concordant, which means they are within 0.1 mL of each other.

Example

A hydrochloric acid solution is required to be standardised. 25.00 mL of standard sodium carbonate solution was pipetted into a conical flask and the hydrochloric acid run into it from a burette until an endpoint was reached for three concordant readings, shown by an indicator.

The burette readings were: 17.0 mL, 16.75 mL, 16.77 mL and 16.73 mL.

Answer

(1) Equation: $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

(2) Mole ratio: 2HCl: 1 Na_2CO_3

Average titre = 16.75 mL (excluding the 1st rough reading)

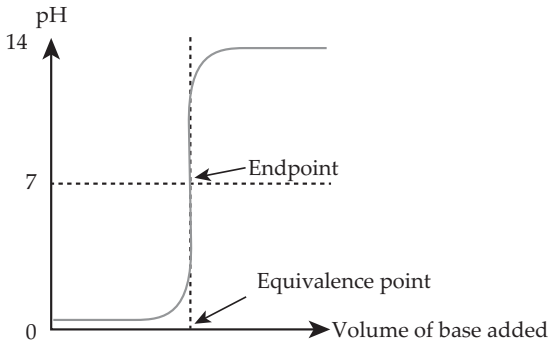
(3) Moles taken: $n(Na_2CO_3) = cV = 0.0473 \times 0.025 = 1.183 \times 10^{-3}$ mol.

(4) Moles used: $n(HCl) = 2 \times n(Na_2CO_3) = 2.366 \times 10^{-3}$ mol.

(5) Concentration of HCl: $c = n/V = 2.366 \times 10^{-3} / 0.01675 = 0.141$ mol L^{-1}.

2.13 TITRATIONS

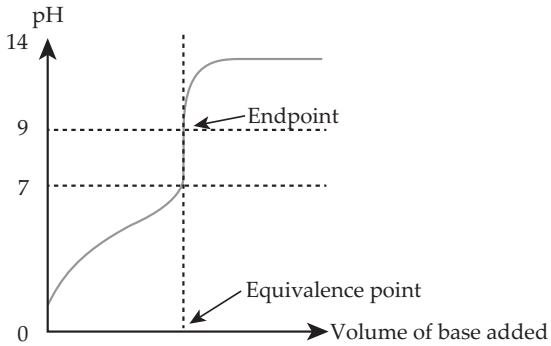
Strong acid versus strong base



With a strong acid/strong base titration the equivalence point occurs at a pH of 7. The equivalence point is when the stoichimetrically equivalent number of moles of acid and base have been added. 1 mole of strong acid will exactly neutralise 1 mole of strong base.

The titration curve is shown here which will be vertical at the equivalence point (25 mL of base). Because of this almost any indicator can be used that changes colour between pH 5 and pH 9. The titre value at which the colour changes is called the Endpoint.

Weak acid versus strong base



When a strong base is titrated against a weak acid at the equivalence point, the pH will be above 7 as the acid is providing less than one mole of H^+ ions per mole of base.

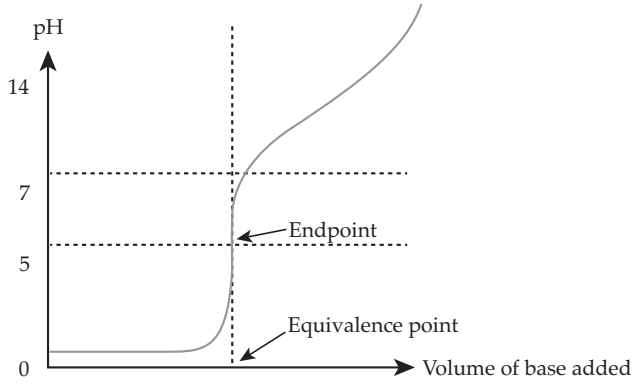
It is the equivalence point, determined by stoichiometry, which is important in calculating the concentration and so the Endpoint colour change must occur at the Equivalence Point. This can be arranged by a suitable choice of indicator.

For example, suppose we titrated 0.10 mole L^{-1} NaOH solution in the burette against a 25.00 mL aliquot of 0.1 mol L^{-1} acetic acid solution in the conical flask. Because the stoichiometric ratio for acid to base is 1:1, the correct reading on the burette at equivalence point should be 25.00 mL (number of moles of acid = number of moles of base).

However, at this point the solution will not be neutral at pH 7. It will be basic because the CH_3COO^- ion reacts with water to produce OH^- ions. Therefore, to obtain the correct reading of 25 mL, the indicator colour needs to change at a pH of around 9. A suitable indicator that changes at pH 9 is called phenolphthalein, which changes from colourless to pink at a pH of around 9.

Weak base versus strong acid

When a weak base is titrated against a strong acid however, at the equivalence point, the pH will be below 7 as the base is providing less than one mole of OH^- ions per mole of acid.



To arrange for the Endpoint to be the same as the Equivalence Point an indicator must be chosen which changes colour at pH 5.

A suitable indicator for strong acid / weak base titrations is methyl orange. This changes from orange to yellow as base is added at around pH 5.

Weak acid versus weak base

There will be no sharp endpoint for this type of titration so the only way the equivalence point can be assessed is by using a pH meter to monitor the solution.

2.14 BACK TITRATIONS

Back titrations are used if the unknown acid or base is insoluble or cannot be titrated for some reason, e.g. to find the mass of a particular metal in an alloy or % purity of an insoluble metallic compound.

Method:

Weigh the compound X

Add a large, measured amount of reagent (call this n_1) that will totally dissolve compound X (e.g. acid)

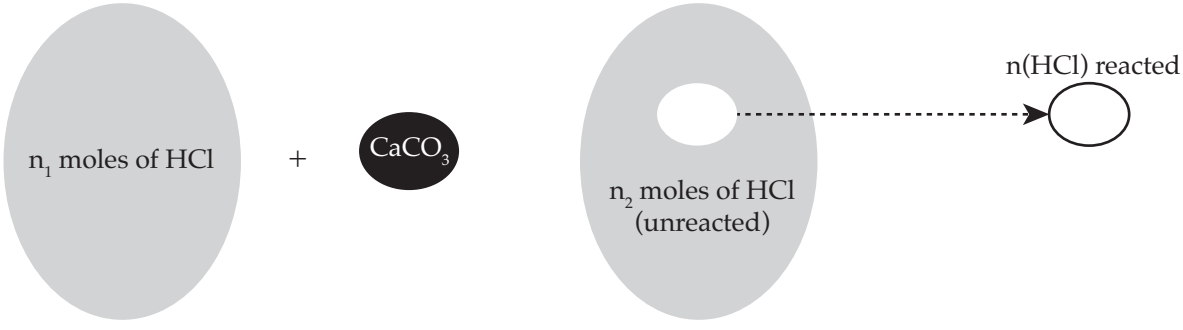
Titrate the excess reagent to find how much of it is left after reacting (call this n_2)

Calculate the number of moles n_R of reagent that reacted by subtracting, i.e. $n_R = n_1 - n_2$

Use the reaction equation to find the stoichiometric ratio and hence the number of moles of X present.

Graphic representation

e.g. To find the mass of $CaCO_3$ in limestone



n_1 moles of acid were added and n_2 left over, so the number of moles reacted must equal $n_1 - n_2$ from which $n(CaCO_3)$ can be found.

Example

A 4.432 g sample of a limestone containing $CaCO_3$ was reacted with 25.0 mL of 1.020 M HCl and it all dissolved, leaving a sandy residue. The excess acid was reacted with 0.275 M NaOH and the average titre value for the volume of NaOH (aq) was found to be 27.93 mL.

Determine the % of $CaCO_3$ in the limestone.

Answer

A flow-chart is often useful to hold all the information here:

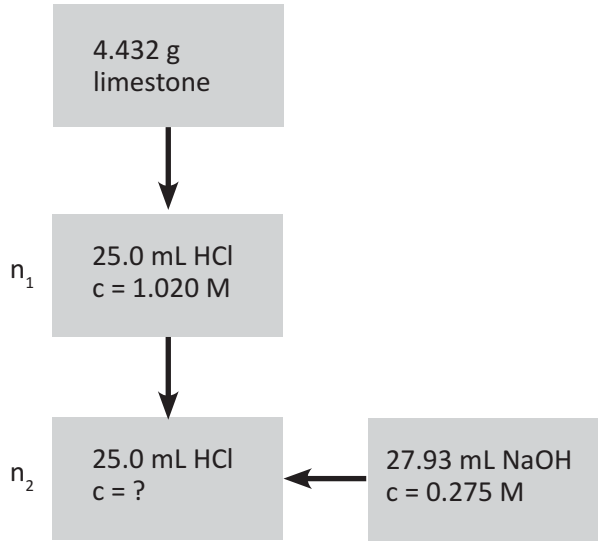
Rules for flowchart are:

Substances are shown in boxes

Processes are shown by arrows ("is added to")

n_1 is the original moles of HCl

n_2 is the remaining moles of HCl



Calculation

Number of moles of HCl added (n_1) = cv = 1.020 × 0.025 = 0.0255 mol

n(NaOH) titre = cv = 0.275 × 0.02793 = 7.680×10^{-3} mol

1: 1 ratio of NaOH with HCl, so n(HCl) remaining (n_2) = 7.680×10^{-3} mol

n(HCl) used in reaction with $CaCO_3$ = $n_1 - n_2 = 0.0255 - 7.680 \times 10^{-3} = 0.01782$ mol.

Reaction: $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

So $n(CaCO_3) = ½ \times n(HCl) = 0.5 \times 0.01782 = 0.00891$ mol

$m(CaCO_3) = nM_r = 0.\ 0.00891 \times 100.09 = 0.892$ g.

$$\% \ CaCO_3 = \frac{0.892}{4.432} \times 100 = 20.1\%$$

2.15 THE CHEMISTRY OF BUFFER SOLUTIONS

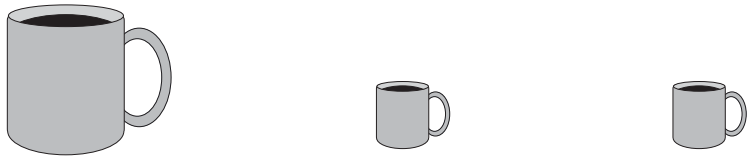
Many aqueous solutions can resist a change in pH when small amounts of acid or base are added. Such solutions are called Buffer Solutions – but they are limited in the extent to which they can resist change by their **Buffering Capacity**. Human blood, for example, is a complex aqueous solution with a pH buffered at about 7.4. Any large deviation from the pH can be serious and even be fatal, as vital enzymes cannot survive the large pH changes which would occur if too much H^+ or OH^- ions were present, i.e. the Buffering Capacity is exceeded.

Buffers generally require two species: an acidic one (to react with the added OH^-) and a basic one (to react with the added H^+). This requirement is fulfilled by having a weak acid-base conjugate pair such as CH_3COOH / CH_3COO^-, or, NH_4^+ / NH_3. The former (acidic buffer) can be prepared by adding CH_3COONa to a solution of acetic acid (CH_3COOH). The latter (basic buffer) can be prepared by adding ammonium chloride (NH_4Cl) to a solution of ammonia, NH_3. In general, a buffer mixture consists of an aqueous solution of an acid-base conjugate pair prepared by mixing a weak acid or base with a salt of that acid or base.

How do buffers work?

Consider the ionisation of ethanoic acid, which has a small value of K_a so that, for a 1 mol L^{-1} solution, there will only be about 10^{-3} of each product in 1 litre of solution:

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$



1 mole cup 10^{-3} mole cup 10^{-3} mole cup

Imagine that a base is now added to the solution so that OH^- ions are present to interact. The H^+ ions will be reduced by their reaction with the OH^- ions to form water and therefore their concentration will be reduced. The pH will momentarily go up, but by Le Châtelier's Principle, more CH_3COOH must ionise and replace them – to a large extent. By the analogy above, the large cup can pour more H^+ and CH_3COO^- ions back into the smaller cups. Hence the excess of OH^- ions has been successfully **buffered**.

Now consider the situation where an acid is added to the equilibrium solution above. By Le Châtelier's Principle, the equilibrium will move to the left so as to reduce the amount of H^+ ions. However, the capacity of the small cups is very low – 10^{-3} moles, so if the amount of acid added exceeds the 10^{-3} buffering capacity of the right side of the equation then the pH must drop down and successful buffering cannot be achieved. The CH_3COO^- ions will have all been used up! Buffering capacity is the number of moles of acid/base that can be absorbed before the pH changes significantly.

How can this problem be overcome? Simply by replacing the small cups on the right with large, 1 mole cups, i.e. add some more of the conjugate base to equal the number of moles of acid – there will now be a reservoir 1 mole of CH_3COO^- ions.

An acidic buffer solution is an equal mix of acid and conjugate base (CH_3COOH/CH_3COO^-) and a basic buffer solution would be an equal mix of base and its conjugate acid (NH_3/NH_4^+).

The Buffering Capacity is the maximum amount of acid/base that can be absorbed without a significant change in the pH of the solution. In this case, it is now 1 mole, rather than 10^{-3} moles.

2.16 BUFFER ACTION IN BLOOD

The pH of the human blood varies from 7.38 to 7.42. There are two buffer systems that help the pH levels to be maintained at a near constant value. One is the carbonic acid/hydrogen carbonate ion equilibrium. The other is the hydrogenated and dehydrogenated forms of haemoglobin, the component of blood that transports oxygen.

Carbonic acid forms in blood due to the reaction between water and the carbon dioxide gas from the inhaled air and that which is produced from respiration in the cells:

$$H_2O_{(l)} + CO_{2(g)} \rightleftharpoons H_2CO_{3(aq)}$$

The aqueous carbonic acid, then, gives away a proton to form hydrogen carbonate ion:

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

The HCO_3^- ion is amphiprotic and so can absorb or donate a proton on its own. This means that it can act as a buffer for the blood without the need for the addition of another species:

$$CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \leftarrow OH^-_{(aq)} + \mathbf{HCO_3^-{}_{(aq)}} + H^+_{(aq)} \rightarrow H_2CO_{3(aq)}$$

Homeostasis is the term used for the ability of an organism to counteract environmental changes with physiological responses.

For example, the concentration of carbonic acid is controlled by respiration. When we exhale air CO_2 is released from the system and the concentration of H_2CO_3 decreases. This raises the

pH of the blood. When we inhale air, CO_2 and H_2CO_3 in the system increase and this lowers the pH of the blood.

The function of the kidneys also helps maintain the pH balance. The ammonia formed by the release of nitrogen from some amino acids combines with excess H^+ ions to form ammonium ions which are removed by urination.

When the pH of the blood rises above 7.45 a condition known as *alkalosis* occurs which may produce a stroke in a patient. When a person hyperventilates or has excessive respiration, the result is an increase in the pH. To rectify this, people are asked to breathe into a paper bag. This shifts the equilibrium backward to increase the levels of CO_2 and H_2CO_3 in the blood which lowers the blood pH again. So the chemical buffering system in humans is a crucial part of our bodily make-up.

Set 3. Acid/Base reactions

1. A diprotic acid H_2X is fully ionised in water. The concentrations of the X^{2-} ions and the hydronium ions in an aqueous solution containing 1.0×10^{-5} moles of H_2X in 0.100 L of water are, respectively:

   (a) 1.0×10^{-4}; 2.0×10^{-4} (b) 1.0×10^{-4}; 1.0×10^{-4}

   (c) 2.0×10^{-9}; 1.0×10^{-4} (d) 1.0×10^{-4}; 2.0×10^{-10}

   (e) 2.0×10^{-4}; 1.0×10^{-4}

2. Given the following K_a values, determine which one is the strongest base.

   $HSO_4^- = 1.2 \times 10^{-2}$; $H_2PO_4^- = 6.3 \times 10^{-8}$; $HCO_3^- = 4.7 \times 10^{-11}$; $H_2CO_3 = 2.50 \times 10^{-4}$

   (a) H_2CO_3 (b) HPO_4^{2-} (c) H_2SO_4 (d) SO_4^{2-}

   (e) CO_3^{2-}

3. Which one(s) of the following salts, when dissolved in water, will produce a neutral solution?

   1) Calcium chloride 2) Strontium nitrate 3) Potassium carbonate

   (a) only 1 (b) only 2 (c) 2 and 3 (d) only 3 (e) 1 and 2

4. Which of the following salts when dissolved in water produce a basic solution?

   1) Sodium nitrate 2) Potassium sulfide 3) Sodium carbonate

   (a) only 2 (b) 1 and 2 (c) only 3 (d) only 1 (e) 2 and 3

5. A 0.600 g sample of succinic acid is dissolved in water and titrated with 0.500 mol L^{-1} sodium hydroxide to equivalence point. The volume of base used is 20.4 mL. What is the molecular weight of succinic acid which contains two dissociable protons?

   (a) 83 (b) 118 (c) 156 (d) 230 (e) 59

6. A concentrated solution of K_2CrO_4 is 15.0% by mass and the density is 1.129 g cm^{-3}. What volume of this solution is required to prepare 200.0 mL of a 0.150 mol L^{-1} solution?

   (a) 33.4 mL (b) 36.0 mL (c) 34.4 mL (d) 36.9 mL (e) 35.2 mL

7. A concentrated solution of HI is 47% by mass and has a density of 1.50 g mL^{-1}. What volume of this solution is required to prepare 250.0 mL of a 1.50 mol L^{-1} HI solution?

   (a) 102 (b) 48.0 (c) 68.0 (d) 62.3 (e) 66.4

8. A solution containing Mn^{2+} ions is prepared by dissolving 1.485 g of pure manganese in nitric acid and diluting it to 1.00 L. A 100.0 mL aliquot is then diluted to 500.0 mL.

   What is the concentration of the final solution of Mn^{2+} ion in mol L^{-1}?

   (a) 5.06×10^{-3} (b) 0.0253 (c) 0.0506

   (d) 2.53×10^{-4} (e) 5.41×10^{-3}

9. Which one of the following substances is the most suitable as a primary standard for acid–base titrations?

   (a) sodium hydroxide (b) nitric acid (c) oxalic acid

   (d) sodium carbonate

10. A 10.0 mL sample of concentrated HF (16.5 mol L^{-1}) is diluted to a final volume of 250.0 mL. What is the concentration of the final solution in mol L^{-1}?

    (a) 0.570 (b) 0.690 (c) 0.630 (d) 0.600

    (e) 0.660

11. In a HCl/Na_2CO_3 titration, where the Na_2CO_3 solution is placed in the conical flask, the correct rinsing procedure for the pipette is:

    (a) detergent, distilled water, acid (b) detergent, distilled water, base

    (c) detergent, distilled water (d) detergent, base

    (e) distilled water, acid

12. To 100 mL of a 0.200 mol L^{-1} HCl, 100 mL of a 0.40 mol L^{-1} of sodium hydroxide is added. After equilibrium is established, the $[H^+]$ and $[OH^-]$ in mol L^{-1} respectively are

    (a) 2.0×10^{-1}, 5.0×10^{-13} (b) 5.0×10^{-13}, 2.0×10^{-2}

    (c) 1.0×10^{-7}, 1.0×10^{-7} (d) 1.0×10^{-1}, 1.0×10^{-13}

    (e) 1.0×10^{-13}, 1.0×10^{-1}

Questions 13 and 14 are based on the following information. The equations shown below represent reactions which occur to an extent greater than 90% in the direction indicated.

$$HNO_{3(aq)} + H_2O_{(l)} \rightarrow H_3O^+ + NO_3^-$$

$$H_3O^+ + CN^-_{(aq)} \rightarrow HCN_{(aq)} + H_2O_{(l)}$$

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

$$H_2O_{(l)} + CH_3O^-_{(aq)} \rightarrow CH_3OH_{(aq)} + OH^-_{(aq)}$$

13. The strongest base among all the above substances is

    (a) CH_3O^- (b) H_2O (c) CN^- (d) NO_3^-

    (e) CH_3OH

14. An acid stronger than H_2O but weaker than H_3O^+ is

    (a) HNO_3 (b) CH_3OH (c) HCN (d) NO_3^- (e) CN^-

15. A buffer solution is made by adding 0.1 mol of CH_3COOH (aq) to 0.1 mole of potassium ethanoate solution. As small amount of a strong base is now added to the solution.

    $CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$

    Once the equilibrium has been established, the final effect would be:

    (a) The equilibrium shifts to the left

    (b) An overall increase in CH_3COO^- ions

    (c) A substantial increase in OH^- ions

    (d) An increase in the K_a value for the acid

16. Which one of the following correctly identifies the acidity, basicity or neutrality of each of the given solutions?

	Potassium phosphate	**Sodium hydrogensulfate**	**Ammonium chloride**	**Magnesium nitrate**
(a)	Acidic	Acidic	Acidic	Basic
(b)	Basic	Neutral	Neutral	Acidic
(c)	Basic	Acidic	Acidic	Neutral
(d)	Neutral	Basic	Basic	Neutral

17. A student obtained the following results when titrating ethanoic acid solution with 20.00 mL of sodium hydroxide solution.

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
Vol of HCC (mL)	21.6	22.4	20.3	21.8

    Which one of the following could lead to such a set of results?

    (a) Using only a few drops of phenolphthalein indicator

    (b) Washing the conical flasks with distilled water and then leaving some water inside.

    (c) Washing the burette with water and then leaving some water inside

    (d) Always reading to the bottom of the meniscus in the burette

18. Consider the following acid-base reaction

$HS^-(aq) + HSO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2S(g)$

Which of the following cells correctly identifies the acid/base conjugate pairs in this equilibrium?

	Base	Conjugate acid	Acid	Conjugate base
a)	SO_4^{2-}	H_2S	HSO_4^-	HS^-
b)	HS^-	H_2S	HSO_4^-	SO_4^{2-}
c)	HS^-	SO_4^{2-}	HSO_4^-	H_2S
d)	H_2S	SO_4^{2-}	HS^-	HSO_4^-

19. Which one of the following solutions would have a pH of 10?

(a) 1×10^{-10} mol L^{-1} sodium hydroxide

(b) 5×10^{-5} mol L^{-1} barium hydroxide

(c) 1×10^{-4} mol L^{-1} calcium hydroxide

(d) 1×10^{-10} mol L^{-1} nitric acid

20. Which one of the following lists the oxides in order of increasing acidity?

(a) MgO, CaO, SrO, BaO

(b) SO_2, Al_2O_3, MgO, Na_2O

(c) Na_2O, MgO, Al_2O_3, SO_2

(d) CuO, Fe_2O_3, CaO

Acid Base Calculations

1. 20.0 mL of a 0.015 mol L^{-1} solution of $Ca(OH)_2$ is mixed with 80.0 mL of a 0.010 mol L^{-1} solution of HNO_3. What would the final pH be?

_____

_____

_____

2. If 25.0 mL of 0.200 M sodium hydroxide solution is added to 30.0 mL of 0.175 M nitric acid, what is the pH of the mixture?

_____

_____

_____

3. 200 mL of 0.0500 mol L^{-1} barium hydroxide solution is mixed with 400 mL of a 0.200 M nitric acid. The mixture is then diluted with water so that the final volume is 6.00 L. What is the pH of the final solution?

_____

_____

_____

4. (a) What mass of HCl must be dissolved in 300 mL of solution to give a solution of pH = 2?

_____

(b) What will be the pH of the solution containing 0.0730 g of HCl made up to 2.00 L of solution?

_____

5. (a) What mass of sodium hydroxide must be dissolved in 600 mL of solution to give a pH of 13?

_____

(b) If 0.600 g of sodium hydroxide is dissolved in 1500 mL of solution, what will be the pH of the final solution?

_____

6. What volume of water must be added to 20.0 mL of a 0.100 M hydrochloric acid to give a solution of pH 3?

_____

_____

7. What volume of HCl gas at STP must be added to 1.00 L of water to produce a solution which has a pH of 4?

_____

_____

_____

8. Explain, using equations, why aqueous solutions of sodium carbonate, sodium sulfide and sodium ethanoate all have pH values greater than 7.

_____

_____

_____

9. A 10.0 mL sample of 0.00500 M $Ca(OH)_2$ is diluted with water to 1.0 L.

(a) What is the pH of the undiluted solution?

_____

_____

(b) What change occurs in the pH of the solution due to the dilution?

_____

_____

(c) What mass of $Ca(OH)_2$ is present in the diluted solution?

_____

_____

(d) What volume of CO_2 at 25°C and 110 kPa pressure must be bubbled through the dilute solution in order to convert the OH^- ions into CO_3^{2-} ions?

_____

_____

_____

10. Exactly 23.6 mL of a 0.131 M HCl solution was required to completely react with 25.0 mL of NaOH solution. What was the concentration of the NaOH solution?

_____

_____

_____

11. An approximately 0.1 M HCl solution was standardised (its exact concentration found) by titrating it into a solution containing 0.1223 g of 99.95% pure Na_2CO_3.

The equation for the reaction is:

$Na_2CO_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$.

The equivalence point was reached when 22.65 mL of the HCl solution had been used.

What was the exact concentration of the acid?

_____

_____

_____

12. Calculate the concentration of ethanoic acid in a titration with sodium hydroxide after 30.0 mL of 0.100 M NaOH solution has been added to 50.0 mL of 0.100 M ethanoic acid solution.

_____

_____

_____

13. In the titration of 50.0 mL of a 0.020 M solution of $NaHCO_3$ with a 0.020 M HCl solution, what is the concentration of the excess species after 25.0 mL of the acid solution has been added?

_____

_____

_____

14. A hydrated form of sodium carbonate, called washing soda, has the formula $Na_2CO_3 . \times H_2O$.

    A crushed 0.561 g sample of washing soda required 30.50 mL of a 0.131 mol L^{-1} HNO_3 solution for complete neutralisation.

    Calculate the value of x, the number of molecules of water of crystallisation in the molecule.

    _____

    _____

    _____

15. Four 20.0 mL samples of different HBr solutions were titrated with 0.100 M NaOH solution. The volumes of base required to reach the equivalence point in each were

    (a) 27.5 mL (b) 21.8 mL (c) 48.9 mL (d) 25.5 mL

    Calculate the concentrations of the four HBr solutions.

    _____

    _____

    _____

    _____

    _____

16. A 20.0 mL sample of a 0.200 M HCl solution is titrated with 0.200 M NaOH solution. Calculate the pH of the solution after the following volumes of base have been added.

    (a) 5.00 mL (b) 15.0 mL (c) 19.9 mL

    _____

    _____

    _____

17. Three medicine tablets, which were claimed by the pharmaceutical company to contain 300 mg of aspirin each [$C_6H_4(OCOCH_3)COOH$], were heated in 50.00 mL of a 0.5090 M NaOH. The tablets reacted according to the following equation:

$$C_6H_4(OCOCH_3)COOH + 2NaOH_{(aq)} \rightarrow C_6H_4(OH)COONa_{(aq)} + CH_3COONa_{(aq)} + H_2O_{(l)}$$

    After cooling, the solution was transferred to a 100 mL standard flask and the volume was made up to exactly the 100.0 mL mark. Aliquots of 20.0 mL of this solution were then titrated against 0.1232 M HCl. The mean titre was 25.10 mL. (Note: this is a back-titration!)

    (a) What was the average mass of aspirin in each tablets?

    _____

    _____

    _____

    _____

    _____

(b) From your answer to a) comment on the pharmaceutical company's claim.

_____

_____

18. To analyse some household ammonia, the following procedure was followed:

A 15.14 g sample of cloudy ammonia mixture was weighed and transferred into a 250.0 mL flask. Then 100.0 mL of 0.6342 M HCl was added to the flask and the mixture was thoroughly agitated. The volume was then made up to 250.0 mL using distilled water. 20.0 mL aliquots of this final mixture were titrated against 0.1098 M NaOH. The mean titre was 18.75 mL.

(a) State the sequence of this procedure in the correct order.

_____

_____

(b) Write equations for each of the reaction steps.

_____

_____

(c) Calculate the % mass of ammonia in the original commercial cloudy ammonia.

_____

_____

_____

(d) If the student's final calculated % was less than that claimed by the company, does it conclusively mean that the company made a false statement?

_____

19. 20.0 mL of dilute sulfuric acid were placed in a flask and 3.00 g of barium hydroxide added. The solution was stirred until reaction was complete.

(a) Write a balanced equation for the reaction.

_____

_____

(b) The excess $Ba(OH)_2$ was back titrated with 0.100 mol L^{-1} HCl and 34.5 mL of the acid were required for neutralisation. Write a balanced equation for this reaction.

_____

_____

(c) Choose a suitable indicator for this reaction from the following:

Name of Indicator	pH Range	Color (low pH – high pH)
Methyl orange	3.1 – 4.4	Red – yellow
Bromothymol blue	6.0 – 7.6	Yellow – blue
Phenolphthalein	8.3 – 10.0	Colorless – red
Litmus	5.0 – 8.0	Red – blue

(d) Calculate the concentration of the original sulfuric acid solution.

_____

_____

20. In an experiment to determine the concentration of an HCl solution, 20.0 mL of 0.100 M Na_2CO_3 solution are placed in a conical flask and titrated to a methyl orange end point. The actual concentration of the HCl solution is 0.140 M, but several mistakes were observed during the experimental procedure. Four of these are listed below. For each mistake, state the correct procedure and, if the calculated concentration of the HCl would be more, less or unaffected by these mistakes.

(a) Before filling up the burette, it was rinsed with distilled water.

_____

(b) The conical flask is rinsed with distilled water before adding the Na_2CO_3 solution.

_____

(c) The pipette used to deliver the Na_2CO_3 is rinsed with water.

_____

(d) Phenolphthalein is used as the indicator, instead of methyl orange (phenolphthalein changes colour at pH 9 and methyl orange changes colour at pH 5).

_____

21. Outline a step-by-step procedure for the following:

(a) Prepare 250.0 mL of approximately 0.1 M Na_2CO_3 solution.

_____

_____

(b) Dilute 25.0 mL of 5.0 M sulfuric acid to a concentration of 0.50 M.

_____

_____

_____

(c) Make up 100 mL of approximately 0.1 M solution of HCl from a stock 10 M solution.

_____

_____

22. Select the right indicator from the list in Q. 19 for the following titrations:

(a) Ammonia solution with hydrochloric acid.

_____

(b) Ethanoic acid with sodium hydroxide.

_____

(c) Barium hydroxide with nitric acid.

_____

(d) Ethanoic acid with potassium hydroxide.

_____

23. Rain water is slightly acidic due to the dissolution of CO_2 from the atmosphere.

(a) Write an equation for this reaction.

_____

(b) Explain how you can determine the pH of rainwater in the laboratory.

_____

_____

_____

24. A solid organic, diprotic acid is hydrated in its crystalline form.

When a 0.808 g sample of the acid was heated at 110ºC to constant mass, the mass of anhydrous solid remaining was 0.576 g.

(i) What is the percentage by mass of water of crystallisation in the hydrated organic acid and what percentage is actual acid?

_____

Another 2.050 g sample of the hydrated acid was dissolved in water and made up to 250.0 mL in a volumetric flask. A 20.00 mL aliquot of this solution was titrated against a 0.110 mol L^{-1} sodium hydroxide solution and an end-point was reached at a volume of 23.70 mL.

(ii) Calculate the number of moles of acid (minus the water of crystallisation) in the 2.050 g sample and hence the molar mass of the acid.

_____

_____

_____

_____

(iii) Empirical analysis of the anhydrous acid gave an empirical formula of CHO_2. What is the molecular formula of the anhydrous acid?

_____

(iv) From part (i) determine the molecular formula of the hydrated acid.

_____

25. Solution X is a mixture of hydrochloric and sulfuric acids of unknown concentration. 20.0 mL of X required 10.7 mL of a 0.698 mol L^{-1} sodium hydroxide for complete neutralisation. An excess of barium chloride solution was then added to a separate 25.0 mL sample of X, and this resulted in a precipitate of 0.541 g of barium sulfate.

    Calculate the concentration of hydrochloric acid in solution X in moles per litre.

    _____

    _____

    _____

    _____

26. A bottle of Swab-It sewer cleaner has sodium hydroxide as its active ingredient. Some Swab-It is accidentally tipped into a farmer's water tank which will corrode the tank due to the OH^- ion present. In order to remove the ion the ex-chemist farmer realises that he can use copper sulfate to precipitate it as $Cu(OH)_2$.

    If either the OH^- ion or Cu^{2+} ion is left in excess this would be dangerous.

    The tank holds 10000 L of water and 4.00 kg of Swab-It was tipped into the tank. Swab-It solution contains 20.0% by mass NaOH solution and the concentration of the 45 kg mass of copper sulfate solution the farmer added was 5.00% by weight of $CuSO_4.5H_2O$.

    (i) Calculate which ion OH^- or Cu^{2+} was in excess in the tank after addition, and by how much. What is the final concentration of the excession in the tank?

    _____

    _____

    _____

    _____

    _____

    (ii) Suggest a substance that could be added to the water to remove the excess component and what mass would be needed.

    _____

27. Washing soda, sodium carbonate decahydrate ($Na_2CO_3.10H_2O$), is used to soften water. In a short period of time, the washing soda loses some of its water of crystallisation whilst in a cupboard. The amount of sodium carbonate in washing soda may be determined by adding excess hydrochloric acid to the washing soda and then determining the amount of unreacted acid by titration with a standard solution of sodium hydroxide.

    A sample of washing soda weighing 1.682 g was added to 20.00 mL of 1.00 mol L^{-1} hydrochloric acid. When the reaction was complete, the unreacted acid was titrated with a standardised solution of sodium hydroxide. Using bromothymol blue, which changes colour at a pH of 7 as the indicator to detect the endpoint, the titration of the acid required an average volume of 19.66 mL of 0.150 mol L^{-1} sodium hydroxide.

(a) Write an equation for the reaction of hydrochloric acid with sodium carbonate.

(b) Write an equation for the reaction of hydrochloric acid with sodium hydroxide.

(c) Calculate the number of moles of hydrochloric acid which reacted with sodium hydroxide.

(d) Calculate the number of moles of hydrochloric acid that was added to the washing soda.

(e) Calculate the number of moles and the mass of sodium carbonate in the sample of washing soda.

(f) Calculate the percentage mass of sodium carbonate in the sample of washing soda.

(g) Why should you use sodium hydroxide solution that has been standardised most recently?

(h) If phenolphthalein is used as an indicator for the hydrochloric acid – sodium hydroxide titration – instead of methyl orange, what effect would this have on the calculated percentage of sodium carbonate in washing soda? (Phenolphthalein changes colour at pH 9 and methyl orange at pH5). Explain your answer.

_____

_____

_____

_____

_____

28. An aspirin tablet of mass 0.4376 g was heated in a flask containing 50.0 mL of 0.196 mol L^{-1} sodium hydroxide solution. The active ingredient in aspirin reacts according to the equation

$C_6H_4(OCOCH_3)COOH + 2NaOH \rightarrow C_6H_4(OH)COO\ Na + CH_3COONa + H_2O$

After cooling, the resulting solution was titrated with 0.298 mol L^{-1} hydrochloric acid in order to determine the amount of excess sodium hydroxide. A titre of 18.64 mL of the acid was obtained. Calculate:

(a) The number of moles of sodium hydroxide that reacted with the hydrochloric acid.

_____

_____

(b) The number of moles of sodium hydroxide initially in the flask.

_____

_____

(c) The percentage by mass of aspirin in the sample.

_____

_____

29. In a back-titration experiment to find the percentage of MgO in antacid tablets a 4.47 g tablet was crushed and dissolved in 200 mL of 0.56 mol L^{-1} HCl. Of the remaining acid 25 mL was titrated with 0.050 mol L^{-1} NaOH solution and an endpoint was reached when 9.86 mL had been added.

Draw up a flow-chart of the titration process. Calculate the percentage of MgO in the antacid tablet.

_____

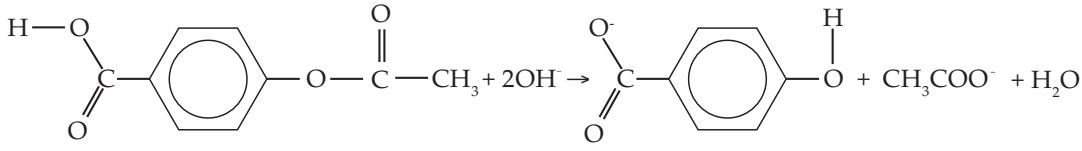
_____

_____

_____

_____

30. An analysis of Aspirin involves a back-titration where NaOH is used to react with the COOH group and the CO group in the molecule shown below.



2.00 g of powdered Aspirin was boiled with 150 mL of 0.45 M sodium hydroxide solution until dissolved. A 20 mL aliquot of the solution was then titrated with a standard 0.344 M HCl solution until an endpoint was reached at a volume of 17.65 mL.

(i) Draw up a flow-chart of the titration process and using it calculate the percentage of acetyl salicylic acid in the Aspirin tablet (molar mass of aspirin = 168.144 g mol^{-1}).

(ii) By law, the amount of actual acetyl salicylic acid in the table must exceed 90% of the total mass. Does the sample conform to this law? Explain.

Notes

Chapter

3

Redox Reactions

Older ideas of oxidation and reduction usually involved a notion of gaining or losing oxygen or hydrogen, e.g. iron oxidising to iron oxide. Oxidation and reduction reactions are involved in the rusting of metals, in cellular respiration, photosynthesis, in batteries, in the combustion of fuels, in the extraction of metals, in photography and in explosions.

In the definition of oxidation and reduction we think of electrons being transferred from one species to another. The following is not a redox reaction as there is no interchange of electrons:

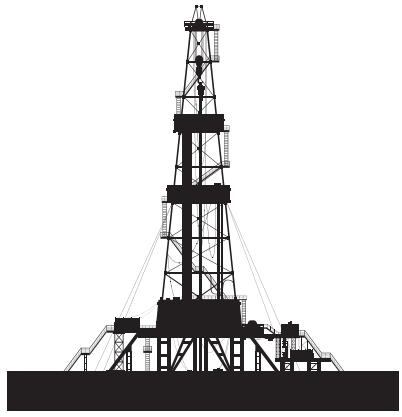
$$BaCl_{2(aq)} + K_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + 2KCl_{(aq)}$$

However, the majority of chemical reactions take place because of this transfer of electrons from one species to another. This chapter concentrates on these so-called Redox reactions.

3.1 KEY IDEAS IN REDOX REACTIONS

Electron Transfer

- Oxidation is a chemical process which involves the loss of electrons by a species.
- Reduction is a chemical process which involves the gain of electrons by a species.
- A way of remembering this is to use the word OIL RIG – Oxidation is Loss and Reduction is Gain.
- Oxidation is caused by oxidising agents, or oxidants, and reduction is caused by reducing agents, or reductants.
- Oxidants will always be reduced and reductants will always be oxidised.



OIL RIG

Oxidation is Loss and Reduction is Gain

Oxidation Numbers

Oxidation numbers can be assigned to reacting species before and after the reaction to identify those species that are oxidised and those that are reduced. Oxidation numbers (ON) indicate how many electrons the species appears to have lost. A positive value of ON means electrons have been lost and a negative value shows how many electrons have been gained, e.g. Fe^{3+} has an ON of +3 and N^{3-} has an ON of -3. The rules for assigning oxidation numbers are shown below.

- The oxidation number of any free element is zero, whether they are monatomic, diatomic or polyatomic, e.g. Ag, O_2, P_4.
- The oxidation number of monatomic ions is equal to the charge on the ion, e.g. K^+, Na^+, Cl^-, Br^- etc.
- Oxygen generally has an oxidation number of –2. OF_2 is an exception where it has an oxidation number of +2 and in peroxides the ON of oxygen is –1, as in H_2O_2.
- Hydrogen, when bonded to non-metals, has an oxidation number of +1. When bonded to the active metals (alkali and alkaline earth metals) as a hydride, like NaH or CaH_2, it is –1.

The sum total of all the oxidation numbers in a molecule or a formula unit is zero, e.g. H_2SO_4

The sum total of all the oxidation numbers in a polyatomic ion is equal to the charge of that ion, e.g. $Cr_2O_7^{2-} = -2$.

In compounds, the group 1 elements e.g. Li, Na, K, Rb, Cs and Fr always have an oxidation number of +1, and the group 2 elements, e.g. Be, Mg, Ca, Sr and Ba always have an oxidation number of +2.

Examples of Oxidation Numbers in Compounds

FeO	Fe = +2,	O = -2	
N_2O_3	N = +3	O = -2	
NO_3^-	N = +5	O = -2	
NH_4^+	N = -3	H = +1	
SO_4^{2-}	S = +6	O = -2	
H_2S	S = -2	H = +1	
$S_2O_3^{2-}$	S = +2	O = -2	
MnO_4^-	Mn = +7	O = -2	
CH_4	C = -4	H = +1	
CrO_4^{2-}	Cr = +6	O = -2	
NH_4NO_3	N = -3, and	N = +5	O = -2

Set 1. Oxidation and Reduction

Fill in the spaces for the following five reactions:

1. $4Na + O_2 \rightarrow 2Na_2O$

   Species Oxidised _____ Species reduced _____

   Oxidant _____ Reductant _____

2. $2Cr^{3+}(aq) + 3Zn(s) \rightarrow 6Cr(s) + 3Zn^{2+}(aq)$

   Species Oxidised _____ Species reduced _____

   Oxidant _____ Reductant _____

3. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

   Species Oxidised _____ Species reduced _____

   Oxidant _____ Reductant _____

4. $Cr_2O_7^{2-}(aq) + 3H_2S(g) + 8\ H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3S(s) + 7\ H_2O(l)$

   Species Oxidised _____ Species reduced _____

   Oxidant _____ Reductant _____

5. $H_2O_2(l) + H^+(aq) + Cl^-(aq) \rightarrow HClO(aq) + H_2O(l)$

   Species Oxidised _____ Species reduced _____

   Oxidant _____ Reductant _____

Write the oxidation numbers for each of the elements underlined here.

6. $\underline{Sn}Cl_4$ $H_3\underline{P}O_4$ $\underline{C}O_3^{2-}$ $H\underline{C}OOH$ $\underline{Mn}O_4^-$

For the following reactions, state the elements that have been oxidised and reduced by, observing any change in oxidation numbers.

7. $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

   Species Oxidised _____ Species reduced _____

8. $2SnCl_2 + 4HCl + O_2 \rightarrow 2SnCl_4 + 2H_2O$

   Species Oxidised _____ Species reduced _____

9. $Cr_2O_7^{2-} + 6Fe^{2+} + 14\ H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O.$

   Species Oxidised _____ Species reduced _____

10. $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$

    Species Oxidised _____ Species reduced _____

11. $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$

    Species Oxidised _____ Species reduced _____

Half Equations

In the reaction $Mg_{(s)} + H_2O_{(l)} \rightarrow MgO_{(s)} + H_{2(g)}$, magnesium is oxidised to MgO, but water is reduced to H_2.

There are two half-reactions occurring here:

Oxidation ½ equation	$Mg \rightarrow Mg^{2+} + 2e^-$	(electrons lost)
Reduction ½ equation	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	(electrons gained)

Here, magnesium is the reductant and hydrogen is the oxidant. Removal of electrons from the magnesium releases energy and this energy is used to push electrons onto the hydrogen ion in water. We can find the relative energies needed for redox reactions to occur in the Standard Reduction Potentials table (see later in this chapter).

Two metals can compete for the role of pushing electrons onto the other metal in Metal Displacement Reactions. The competition winner is the metal which is the most reactive – which, again, is shown in the Standard Reduction Potentials table.

Consider a piece of iron placed into a copper sulfate solution. The redox reaction is:

$$3Cu^{2+}_{(aq)} + 2Fe_{(s)} \rightarrow 2Fe^{3+}_{(aq)} + 3Cu_{(s)}$$

Here, the iron wins the competition, as it pushes its electrons off onto the copper ion, thus reducing it to copper metal. The iron, itself, becomes oxidised in the process to Fe^{3+}.

Copper is said to be *displaced* from the solution and will be precipitated as a salmon pink solid.

Fe is the reductant and Cu^{2+} is the oxidant.

Oxidation ½ equation	$Fe \rightarrow Fe^{3+} + 3e^-$	(electrons lost)
Reduction ½ equation	$Cu^{2+} + 2e^- \rightarrow Cu$	(electrons gained)

The number of electrons the Fe supplies must equal the number that the Cu^{2+} receives and so the two half equations must be balanced for electrons. Reaction (i) is multiplied by 2 and equation (ii) multiplied by 3. This will give the overall balanced redox equation:

$$3Cu^{2+}_{(aq)} + 2Fe_{(s)} \rightarrow 2Fe^{3+}_{(aq)} + 3Cu_{(s)}$$

Balancing Half Equations

The rules and order of balancing for an equation that does not appear in the Standard Reduction Tables are summarised in the phrase. An aid to memory is: **Breakfast We Have Eggs: B W H E.**

B – Add coefficients to **b**alance all species except for H and O.

W – Add **w**ater to the side of the equation with less oxygen.

H – Add $\mathbf{H^+}$ ions to the side of the equation with least hydrogen.

E – Add **e**lectrons to the side of the equation which is most positive overall.

Example: Balance this ½ equation: $SO_2 \rightarrow H_2S_2O_3$

B	Balance the sulfur atoms:	$\mathbf{2}SO_2 \rightarrow H_2S_2O_3$
W	Add water to the right:	$2SO_2 \rightarrow H_2S_2O_3 + \mathbf{H_2O}$
		(4 O on both sides now)
H	Add H^+ to the left:	$2SO_2 + \mathbf{4}H^+ \rightarrow H_2S_2O_3 + H_2O$
		(4 H on both sides now)
E	Add electrons to the left:	$2SO_2 + 4H^+ + \mathbf{4}e^- \rightarrow H_2S_2O_3 + H_2O$
		(zero charge on both sides now)

Final balanced reduction ½ equation:

$$2SO_2(g) + 4H^+(aq) + 4e^- \rightarrow H_2S_2O_3(aq) + H_2O(l) \quad \text{- (i)}$$

Suppose the reductant in this case was aluminium, then the oxidation ½ equation would be:

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \quad \text{- (ii)}$$

The overall redox equation is formed by amalgamating these two equations which makes the number of electrons given out by the aluminium the same as those taken in by the SO_2.

Equation (i) must be multiplied by 3 and equation (ii) multiplied by 4 to make the number of electrons the same (12).

(i) becomes: $6SO_2(g) + 12H^+(aq) + 12e^- \rightarrow 3H_2S_2O_3(aq) + 3H_2O(l)$

(ii) becomes: $4Al(s) \rightarrow 4Al^{3+}(aq) + 12e^-$

The final redox equation is: $6SO_2(g) + 12H^+(aq) + 4Al(s) \rightarrow 4Al^{3+}(aq) + 3H_2S_2O_3(aq) + 3H_2O(l)$

(NB: the equation will not proceed without the H^+ ions on the left, so this reaction must occur in acidic conditions. If no H^+ is present then it will not occur).

Splitting Equations

There may be a reaction where the simple balancing process seems very hard to do, such as this one:

$$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$$

This clearly is made up from two separate ½ equations and so separating them would make the balancing much easier:

Oxidation ½ equation is: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ - (i)

Reduction ½ equation is: $2NO_3^-(aq) \rightarrow 2NO_2(g)$ - (ii)

Applying BWHE to (ii): $2NO_3^-(aq) + 4H^+(aq) + 2e^- \rightarrow 2NO_2(g) + 2H_2O(l)$

Multiply (i) by 2 and add to (ii) to obtain the fully balanced equation:

$$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow 2NO_2(g) + Cu^{2+} + 2H_2O(l)$$

3.2 REDUCTANT STRENGTHS

If a substance gives up electrons readily it is said to be a strong reducing agent. Its oxidised form will be a poor oxidising agent, e.g. Zn is a good reductant but Zn^{2+} is a very poor oxidant.

If a substance gains electrons readily it is said to be a strong oxidising agent. Its reduced form is a poor reducing agent, e.g. Cl_2 is a good oxidant but Cl^- is a very poor reductant.

Though the strength of oxidising agents and reducing agents are relative, certain common substances in industry are known to be strong oxidising agents or strong reducing agents.

Carbon, carbon monoxide and hydrogen are used as strong reducing agents in industry, whereas nitric acid and sulfuric acid are used as strong oxidising agents. Acidified potassium permanganate and potassium dichromate are strong oxidising agents, used in redox volumetric analysis.

Other examples of strong oxidising agents are H_2O_2, ozone, halogens and active non-metals. Most reactive metals are strong reducing agents.

The table supplied on the Chemistry Data Sheet shows the relative strengths of species – all compared with hydrogen which is a standard and is defined as being zero on the scale.

Part of this table is shown below as Table 1.

3.3 SPONTANEOUS REACTIONS

The table below shows the energy that is given out by a particular reaction. If energy needs to be absorbed to make the reaction work, this is shown as a negative value.

For instance: Fluorine has seven electrons in its outer shell, so if it can gain an electron it will attain a full shell and reach a more stable state of F^- (full shell). Hence, the reaction $F + e^- \rightarrow F^-$ will give out energy (similar to exothermic reactions). The reduction of fluorine to F^- is a very energetic reaction, giving out 2.89 units of energy (measured in volts). It is therefore the best oxidant in the table.

The lithium ion Li^+ is the worst oxidant, requiring an **input** of 3.04 units of energy to reduce it to lithium metal. This makes it the best reductant because, if we look at the reverse reaction $Li \rightarrow Li^+$ we see that 3.04 units of energy would be released (going from right to left of the table, reverse the voltage sign).

In the reaction where fluorine is mixed with lithium, the two half equations would be

Reduction: $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ - exothermic 2.89 V

Oxidation: $Li(s) \rightarrow Li^+(aq) + e^-$ - exothermic 3.04 V

The total energy evolved would be found by adding the energy values = 5.93 V (very large!)

From table 1 below we can also find out whether a proposed reaction would be spontaneous or not, i.e. occur without an input of energy.

Table 1

Reduction Half-Reaction	Standard Reduction Potential (E^o) at 25°C
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.89
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.08
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(g)$	-0.14
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.18
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

E^o is the relative energy ouput, in volts, compared to hydrogen. An example of a reaction that could not occur from energy considerations is copper metal reacting with an acid.

Looking at the redox reactions required from the table above:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (i) - copper is oxidised by the acid

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ (ii) – hydrogen ions are reduced by the copper

However, if we add the E^o values for the two equations, we get -0.34 + 0.00 = -0.34 V

The negative value of overall E^o shows this reaction is **not** spontaneous and will not occur – so copper will not react with acids.

Of the two half reactions, the reduction reaction must always go from left to right and the oxidation reaction must be reversed (from right to left). If the energy given out by one reaction is less that the energy needed to make the other reaction proceed then the overall reaction will not occur spontaneously, i.e. energy must be supplied to make it work.

Example

Will silver metal react when placed into copper sulfate solution?

Answer

The half reactions that need to occur are:

$Ag_{(s)} \rightarrow Ag^+_{(aq)} + e^-$ $\quad E^0 = -0.80$ V

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $\quad E^0 = +0.34$ V

However, adding the E^o values, we see the total energy value here is -0.46 – a negative value. Hence, this reaction cannot occur spontaneously. The answer then is no, they will not react.

As a rule, if the reduction equation in the table is on the left and above the oxidation equation going from right to left, then the reaction will proceed – because the E^o values beneath are always lower than the ones above.

So zinc will be able to dissolve in acid because the reactions are:

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ $\quad E^o = +0.76$ V

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ $\quad E^o = 0.00$ V

} Total $E^o = +0.76$ V – a positive value

Strong oxidants usually contain an element in its highest oxidation state. For example, in MnO_4^- manganese is in an oxidation state of +7. In $Cr_2O_7^{2-}$, chromium is in an oxidation state of +6.

Strong reductants usually contain an element in its lower oxidation state. For example, the reactive metals such as potassium and sodium always have an oxidation state of zero.

3.4 DISPLACEMENT REACTIONS

A special type of redox reaction is where precipitation takes place of one ionic species A (usually a metal ion) by an elemental reductant B. The reductant metal then replaces species A in solution, e.g. $A^{2+}_{(aq)} + B_{(s)} \rightarrow A_{(s)} + B^{2+}_{(aq)}$

This type of reaction is called a **Displacement Reaction**. Metal B would have to be a stronger reductant than metal A for this to be energetically viable.

For instance:

Iron is placed in copper sulfate solution $\quad Fe_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Fe^{2+}_{(aq)}$

Cu^{2+} is above iron in the table and on the left.

Fe is to the right in the table and below so the total E^o values will be positive and allow a spontaneous reaction. Total $E^o = +0.34 + 0.44 = 0.78$ V

Any acid is shown as the H^+ reaction on the E^o table and so any metal that is below H^+ and on the right will be dissolved.

e.g. $\quad 2Al_{(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_{2(g)}$ $\quad E^o_{tot} = +1.68$ V

Displacement reactions can also occur with non-metals. Bromine water will displace iodine from sodium iodide solution:

Reduction: $\quad Br_{2(aq)} + 2e^- \rightarrow 2Br^-_{(aq)}$ $\quad$ Oxidation: $2I^-_{(aq)} \rightarrow I_{2(aq)} + 2e^-$

Redox overall: $Br_{2(aq)} + 2I^-_{(aq)}\ 2Br^- + I_{2(aq)}$ $\quad E^o_{tot} = +1.63$ V

3.5 DISPROPORTIONATION REACTIONS

In a disproportionation reaction an element in a certain oxidation state is both oxidised and reduced at the same time. For this to occur, a reactant must contain an element that is capable of having at least three oxidation states. The halogens and transition metals, with their many common oxidation states, undergo disproportionation in many ways:

e.g. $Cl_2 + H_2O \rightarrow HCl + HOCl$

Chlorine has gone from an oxidation number of zero up to +1 (oxidation to HOCl) and down to -1 (reduction to Cl^-)

A common reaction often asked about is the disproportionation of hydrogen peroxide as it is used to prepare oxygen in the lab, using a catalyst:

$2H_2O_2 \rightarrow O_2 + 2H_2O$

Other examples of disproportionation are:

$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4$

$Cu_2SO_4 \rightarrow Cu + CuSO_4$

$3MnO_4^{2-} + 4H^+ \rightarrow MnO_2 + 2MnO_4^- + 2H_2O$

Set 2. Oxidation

Multiple Choice Questions

1. What are the oxidation numbers of hydrogen in the compounds LiH, MgH_2 and NH_3 respectively?

   (a) +1, +1, +1 (b) +1, +2, +3

   (c) +1, +1, -1 (d) -1, -1, +1

   (e) -1, -1, -1

2. What is the oxidation number of oxygen in hydrogen peroxide?

   (a) -2 (b) -1 (c) 0 (d) +1 (e) +2

3. What are the oxidation numbers of nitrogen in the compounds NO_2, N_2O, N_2O_4 respectively?

   (a) +2, +1, +4 (b) +2, +1, +2

   (c) +1, +2, +2 (d) +4, +1, +4

   (e) +4, +2, +4

4. Among the following reactions, the one involving oxidation as well as reduction is

   (a) $H^+ + OH^- \rightarrow H_2O$ (b) $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

   (c) $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$ (d) $CuO + 2H^+ \rightarrow Cu^{2+} + H_2O$

   (e) $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$

5. Given that the oxidation state of cyanide ion, CN^- is -1, in the compound $K_4Ni(CN)_4$ the oxidation state of Ni is

   (a) +4 (b) +2 (c) 0 (d) -2 (e) -4

6. Sulfur dioxide was passed through aqueous bromine solution. The solution changed from orange to colourless. During the reaction, the oxidation number of bromine has changed from

   (a) +4 to +6 (b) +4 to 0 (c) 0 to -1 (d) +6 to+4 (e) +6 to 0

7. During the reaction referred to in question 6 above, the oxidation number of sulfur has changed from

   (a) +4 to +6 (b) +4 to 0 (c) 0 to -1 (d) +6 to +4 (e) +6 to 0

8. Which of the following is not a redox reaction?

   (a) $2H^+ + Zn \rightleftharpoons Zn^{2+} + H_2$ (b) $H^+ + OH^- \rightleftharpoons H_2O$

   (c) $Cu^{2+} + Zn \rightleftharpoons Cu + Zn^{2+}$ (d) $2Fe^{3+} + S^{2-} \rightleftharpoons S + 2Fe^{2+}$

   (e) $Fe + S \rightleftharpoons FeS$

9. Iron (III) chloride is formed when chlorine is passed over heated iron because

(a) chlorine is an oxidising agent (b) iron (III) chloride can sublime

(c). chlorine is very reactive (d) iron is a transition element

(e) iron (II) chloride is unstable at high temperature

10. Which substance involved in the following reaction has been oxidised?

$2FeCl_2 + 2HCl + H_2O_2 \rightleftharpoons 2FeCl_3 + 2H_2O$

(a) $FeCl_2$ (b) HCl (c) H_2O_2 (d) HCl and H_2O_2

(e) $FeCl_2$ and HCl

11. The oxidation number of iron in Fe_3O_4 is:

(a) +2 (b) +3 (c) 0 (d) +4 (e) +2 and +3

12. The oxidation number of carbon in carbon monoxide CO is

(a) +4 (b) +2 (c) 0 (d) -2 (e) -4

Written Questions

1. State the oxidation number of the species indicated in each:

(a) S in Na_2SO_4 _____

(b) Mn in $KMnO_4$ _____

(c) N in $Ca(NO_3)_2$ _____

(d) C in Na_2CO_3 _____

(e) N in NO_2 _____

(f) S in HSO_4^- _____

(g) S in $H_2S_2O_7$ _____

(h) S in Al_2S_3 _____

2. State the oxidation number of each of the elements in each species:

(a) H_2S (b) P_4O_{10} (c) Na_3P

(d) $Cr(OH)_4^-$ (e) SO_4^{2-} (f) $Ba(MnO_4)_2$

(g) SO_2 (h) H_3O^+ (i) $AlCl_3$

(j) KNO_3

3. (a) Which of these reactions will be spontaneous? (Yes/ No)

(i) $Ni + I_2$ _____

(ii) $Ag + Au^{3+}$ _____

(iii) $Al + Cd^{2+}$ _____

(iv) $Cl_2 + Br^-$ _____

(b) These are three metals and their ions used in an experiment:

A/A^+, B^{2+}/B^{3+} and C^{2+}/C^-.

Ion B^{3+} reacts with metal C. Ion B^{2+} does not react with ion C^{2+} but does react with metal ion A^+. Ion C^- does not react with any other metal or ion.

Place these metals and ions in order of reactivity: C^{2+}, A, B^{3+} from lowest to highest E^o values.

_____

4. In the following equations, state whether the substances underlined have been oxidised or reduced:

(a) $\underline{S}O_2 + 2H_2S \rightarrow 3S + 2H_2O$ _____

(b) $PbO_2 + 4H\underline{Cl} \rightarrow PbCl_2 + 2H_2O + Cl_2$ _____

(c) $H_2 + \underline{Cl}_2 \rightarrow 2HCl$ _____

(d) $3\underline{Cu}O + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2$ _____

5. State which of the following are redox reactions. For these reactions, identify the oxidising and the reducing agents. Balance the equations where necessary:

(a) $2H_2O_2 + MnO_4^- \rightarrow 3O_2 + Mn^{2+} + 2H_2O$

_____

_____

(b) $BaCl_2 + Na_2SO_4 \rightarrow 2NaCl + BaSO_4$

_____

_____

(c) $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

_____

_____

(d) $3H_2 + N_2 \rightarrow 2NH_3$

_____

_____

(e) $C + H_2O \rightarrow CO + H_2$

_____

_____

(f) $H^+ + NO_3^- + Fe^{2+} \rightarrow H_2O + NO_2 + Fe^{3+}$

_____

_____

(g) $3AgNO_3 + FeCl_3 \rightarrow AgCl + Fe(NO_3)_3$

_____

_____

(h) $Na_2S + AgNO_3 \rightarrow Ag_2S + NaNO_3$

(i) $2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$

(j) $NaClO + Na_2SO_3 \rightarrow NaCl + Na_2SO_4$

(k) $2CH_3OH + 2Na \rightarrow 2NaCH_3O + H_2$

(l) $SO_3 + H_2O \rightarrow H_2SO_4$

(m) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

(n) $NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl$

(o) $2NaCl + MnO_2 + H_2SO_4 \rightarrow MnSO_4 + Na_2SO_4 + H_2O + Cl_2$

(p) $2HBr + H_2SO_4 \rightarrow SO_2 + Br_2 + 2H_2O$

(q) $2HNO_3 + 2HCl \rightarrow 2NO_2 + Cl_2 + 2H_2O$

(r) $CuS + 2HNO_3 \rightarrow CuSO_4 + N_2O + H_2O$

6. Write partial ionic equations for the following reactions in acidic solution:

(a) $I_2 \rightarrow 2IO_3^-$

(b) $HClO \rightarrow Cl^-$

(c) $NO_3^- \rightarrow NO$

(d) $NO_3^- \rightarrow NO_2$

(e) $H_3PO_3 \rightarrow H_3PO_4$

(f) $MnO_4^- \rightarrow Mn^{2+}$

(g) $SO_2 \rightarrow SO_4^{2-}$

(h) $C_2O_4^{2-} \rightarrow 2CO_3^{2-}$

(i) $SO_3^{2-} \rightarrow SO_4^{2-}$

(j) $H_2O_2 \rightarrow O_2$

7. Balance the following equations and identify the elements that disproportionate in each reaction :

(a) $2H_2O_2 \rightarrow 2H_2O + O_2$ _____

(b) $3HNO_2 \rightarrow 2NO + NO_3^- + H_3O^+$ _____

(c) $3AuCl \rightarrow 2Au + AuCl$ _____

(d) $4KClO_3 \rightarrow KCl + 3KClO_4$ _____

(e) $Br_2 + H_2O \rightarrow HBr + HBrO$ _____

8. Write balanced equations for the following redox reactions:

(a) Producing chlorine by heating HCl gas and oxygen in the presence of a catalyst.

_____

_____

(b) The preparation of iron by passing hydrogen over hot solid iron (III) oxide.

_____

_____

9. Predict the products of the reactions between Zn and O_2, Zn and H_2, Zn and I_2.

_____

_____

_____

10. Gaseous chlorine is a good oxidant. Predict the products of the redox reactions between chlorine and:

(a) P (b) PCl_3 (c) CuCl (d) I^-

(a) _____ (b) _____

(c) _____ (d) _____

11. Identify the products of disproportionation reaction for the following species:

(a) Cu_2SO_4 (b) Hg_2Cl_2 (c) $NO_2 + H_2O$ (d) $Cl_2 + H_2O$

(a) _____

(b) _____

(c) _____

(d) _____

3.6 REDOX VOLUMETRIC ANALYSIS

Redox titrations serve the same purpose as acid/base titrations in that they are used to determine the concentration of an unknown solution. The species here would be of an oxidizing or reducing ion, where a redox reaction causes a colour change in itself, rather than having to use an indicator.

A Primary Standard would need to be made up, as with acid/base titrations, and the criteria for selection of this would be as before.

The Primary Standard substance must:

- Be a very pure soluble solid,
- Be stable in air,
- Have a fairly high relative formula mass and in addition be a good oxidizing or reducing agent.

Two compounds commonly used in redox titrations are oxalic acid and ferrous ammonium sulfate hexahydrate which has a formula $Fe(NH_4)_2(SO_4)_2.6H_2O$ and a large molar mass (392.17 g mol^{-1}). This latter substance is a transition metal complex but merely supplies the Fe^{2+} ion to be oxidised to Fe^{3+}. Oxalic acid is more useful as it is very low down on the right of the Reduction Potentials Table and hence can reduce many more species above it on the left.

To produce a primary standard solution of oxalic acid, an accurately-weighed mass of the compound is made up to an accurately-known volume in a volumetric flask. $H_2C_2O_4.2H_2O$ has a molar mass of 126.068 g mol^{-1}.

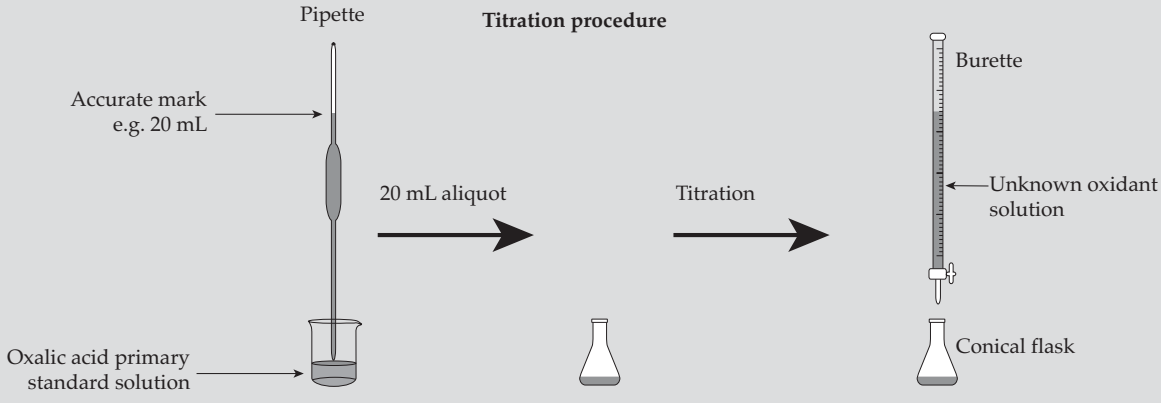
Example: To make up a standard solution of oxalic acid.

2.254 g of oxalic acid dihydrate powder was dissolved in water and then made up to exactly 500 mL of primary standard in a volumetric flask. To find the exact concentration of the solution, the following calculation is made:

Relative formula mass of $H_2C_2O_4.2H_2O$ = 126.068.

So n(Ox Acid) = 2.254/126.068 = 0.01788 moles.

[Ox Acid] = 0.01788/0.50 = 0.03576 mol L^{-1}.



Suppose we wanted to find the concentration of an iron (III) sulfate solution using oxalic acid as the reductant.

The half equations from the Table are:

(Red) $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^o = +0.77$

(Ox) $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$ $E^o = +0.43$

} Total E^0 = +1.20 V (spontaneous)

Overall: $2Fe^{3+}(aq) + C_2O_4^{2-}(aq) \rightarrow 2Fe^{2+}(aq) + 2CO_2(g)$

Procedure: An aliquot (accurate volume – typically 20 mL) of oxalic acid primary standard solution is drawn up into the pipette using a pipette filler bulb which is then transferred to a clean, conical flask. The burette is initially rinsed with the iron (III) sulfate solution being used before finally filling with the same solution and then zeroed by running some solution into a beaker until the burette meniscus reaches the zero mark.

Iron (III) sulfate solution is then run carefully into the conical flask containing the standard aliquot until the endpoint is reached. The colour change here would be from brown (Fe^{3+}) to green (Fe^{2+}) and the volume used is noted from the burette. This volume is called the Titre.

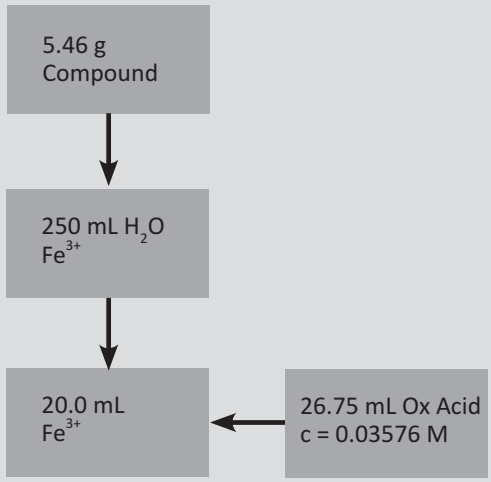
This procedure should be repeated 3 times for accuracy, with the first (rough) reading discarded and all other readings averaged. The three titre values should be concurrent, which means they are within 0.1 mL of each other.

Example calculation

5.46 g of a compound containing iron (III) sulfate was dissolved in 250 mL of water and a 20 mL aliquot of this solution was titrated with the Primary Standard oxalic acid prepared as above in the burette. An endpoint was reached for 3 concurrent readings, shown by a colour change from brown to green. The burette readings were: 27.0 mL, 26.75 mL, 26.77 mL and 26.73 mL.

Find the % of iron present in the compound.

Flow Chart



Calculation

(1) Equation: $2Fe^{3+}(aq) + H_2C_2O_4(aq) \rightarrow 2Fe^{2+}(aq) + 2CO_2(g) + 2H^+(aq)$

(2) Mole ratio: $2Fe^{3+}$: 1 $H_2C_2O_4$

Average titre = 26.75 mL (excluding the 1st rough reading)

(3) Moles taken: $n(\text{Ox Acid}) = cV = 0.03576 \times 0.02675 = 9.565 \times 10^{-4}$ mol.

(4) Moles used: $n(Fe^{3+}) = 2 \times n(\text{Ox Acid}) = 1.913 \times 10^{-3}$ mol in 20 mL

(5) In 250 mL: $n(Fe^{3+}) = 1.913 \times 10^{-3} \times \frac{250}{20} = 0.02391$ mol

(6) m(Fe^{3+}) $0.02391 \times 55.85 = 1.34$ g

(7) % $\frac{1.34}{5.46} \times 100 = 24.5\%$

Potassium permanganate, and potassium dichromate are two of the most common oxidising agents used in this process. Indicators are not needed because these oxidising agents act as their own indicators changing colour with changing oxidation states.

Note that these oxidising agents can only act in the presence of hydrogen ions. Sulfuric acid is the best acid to use here for acidification because, while others supply the necessary hydrogen ions in the reaction, sulfate ions cannot be oxidised and hence will not affect the reaction. Hydrochloric acid would be unsuitable as the chloride ion itself would be oxidised to chlorine.

The related half-equations for these two common oxidants are:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

In acid solutions, the purple potassium permanganate solution is reduced to colourless Mn^{2+} ions. Orange $Cr_2O_7^{2-}$ ions are reduced to green Cr^{3+} ions. These oxidants both need to be freshly prepared and cannot be used as primary standards as they deteriorate quickly.

Iodine (I_2) can also be used as an oxidising agent but, as it cannot maintain a stable concentration so it too needs to be freshly prepared before titration.

Iodine can be used, for instance, to determine the sulfur dioxide content in wines.

First iodine is added to absorb the SO_2:

$$SO_2 + I_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2I^-$$

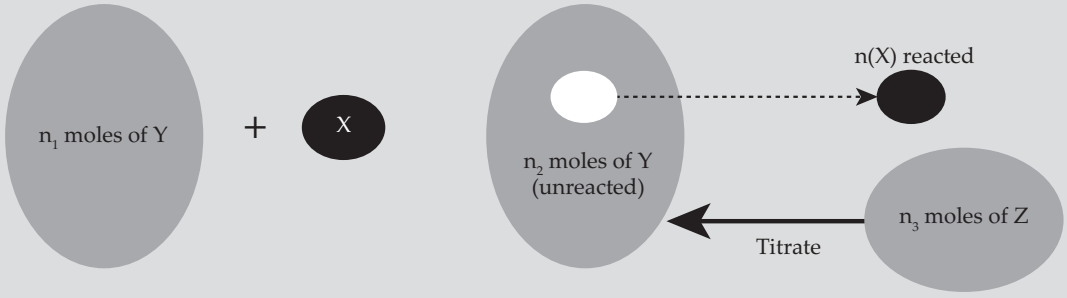
Then the H^+ ion concentration can be found by titrating with a standard base. $n(SO_2) = ½\ n(H^+)$

3.7 BACK TITRATIONS

The method for analysis using back-titrations has been dealt with before in the chapter on acids and bases, but recapping:

Excess reagent is added to an unknown, insoluble component which is, say, an oxidant (let this be X). The reagent needed to be added in excess would therefore be a reductant (let this be Y). The amount of reductant left over is then established by titrating this excess with a standard oxidant which the average titre values obtained would indicate (let this be Z).

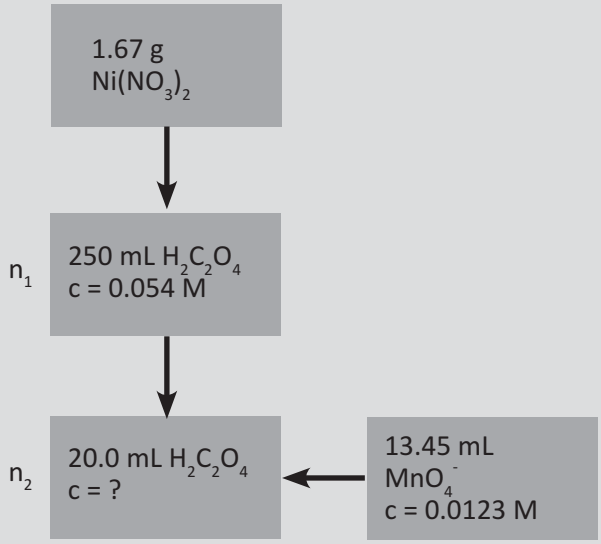
This diagram sums up the procedure:



Example Question

A 1.67 g sample of impure nickel nitrate was dissolved in 250 mL of oxalic acid with a concentration of 0.054 mol L^{-1}. A 20 mL aliquot of the remaining solution was then titrated with a 0.0123 mol L^{-1} solution of potassium permanganate solution oxalic acid solution and an endpoint was reached with an average titre of 13.45 mL.

Calculate the purity of the nickel nitrate powder.



Flowchart and calculation

$n(MnO_4^-) = 0.0123 \times 0.01345 = 1.654 \times 10^{-4}$ mol

Equation for reaction 2:

$2MnO_4^- + 5(COOH)_2 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

$n(\text{Ox Acid}) = \frac{5}{2} \times 1.654 \times 10^{-4} = 4.136 \times 10^{-4}$ mol

In 250 mL n(Ox Acid)

$= \frac{250}{50} \times 4.136 \times 10^{-4} = 5.170 \times 10^{-3}$ mol

$n_2 = 5.170 \times 10^{-3}$ mol

n_1 (Ox Acid) = 0.054 x 0.25 = 0.0134 mol

Moles of oxalic acid used = $n_1 - n_2 = 0.0134 - 5.170 \times 10^{-3} = 8.33 \times 10^{-3}$ mol.

Equation for reaction 1: $Ni^{2+} + H_2C_2O_4 \rightarrow Ni\ (s) + 2CO_2 + 2H^+$ (1: 1 ratio)

$m\{Ni(NO_3)_2\} = 8.33 \times 10^{-3} \times 182.71 = 1.52$ g. (91.1% pure).

Set 3. Redox Reactions

Multiple Choice Questions

1. Which of the following statements about the rusting of iron is **not** true?
   (a) Rusting is accelerated by the presence of carbon dioxide.
   (b) Rusting is accelerated by the presence of an electrolyte.
   (c) Rusting slows down if an alkali is present.
   (d) Rusting is accelerated if iron is connected to another metal which is more reactive than iron.
   (e) Rusting is accelerated by the presence of sodium chloride solution.

2. Acidified potassium dichromate solution is a strong oxidising agent because:
   (a) There are seven oxygen atoms in the compound.
   (b) Oxygen atoms in the compound combine with hydrogen easily.
   (c) Chromium in the compound has a high oxidation number which can easily be reduced to a lower oxidation number.
   (d) Chromium metal is a good oxidising agent.
   (e) K^+ ions in the solution can easily be reduced.

3. Which of the following reactions show that hydrogen peroxide is a reducing agent?
   (a) $PbO_2 + H_2O_2 \rightarrow PbO + H_2O + O_2$
   (b) $H_2O_2 + \text{dye} \rightarrow H_2O + (\text{dye} + O)$
   (c) $H_2S + H_2O_2 \rightarrow S + 2H_2O$
   (d) $H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$
   (e) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

4. The following reagents can be used to oxidise iron (II) ions to iron (III) ions except:
   (a) chlorine water.
   (b) hydrogen peroxide.
   (c) hydrogen sulfide H_2S.
   (d) hypochlorous acid HClO.
   (e) acidified potassium dichromate.

5. Which of is a good way of preventing the rusting of steel?
   (a) Connect it to the positive terminal of a cell.
   (b) Keep it free from oil.
   (c) Keep it in a humid atmosphere.
   (d) Plate it with a coating of copper.
   (e) Remove oxygen from around the iron.

6. Acidified potassium permanganate solution is a strong oxidising agent because:
   (a) There are 7 oxygen atoms in the compound.
   (b) Oxygen atoms in the compound combine with hydrogen easily.
   (c) Manganese in the compound multiple oxidation states that can be formed.
   (d) Manganese metal is a good oxidant.
   (e) K^+ ions in the solution can easily be reduced.

7. Which of the following cannot be used to reduce iron (III) ions to iron (II) ions?
   (a) Fresh hydrogen.
   (b) Hydrogen sulfide.
   (c) Potassium iodide solution.
   (d) Oxalic acid ($H_2C_2O_4$) solution.
   (e) Manganese dioxide.

8. A metal X is dissolved in dilute nitric acid. The excess acid is neutralised by sodium hydroxide. On further addition of sodium hydroxide, a white precipitate is formed which soon redissolves in the excess sodium hydroxide. X is:

   (a) Mn (b) Mg (c) Al (d) Fe (e) Cu

9. Which of the following statements about the uses of aluminium is **not** true?

   (a) Used for galvanising iron.
   (b) Used as domestic cooking utensils.
   (c) Used for the thermite process.
   (d) Used for making alloys for aircraft bodies.
   (e) Used as sinker weights in fishing.

10. Metal C can displace the ion of metal B but metal A cannot displace metal C ion from solution. Metal C can displace metal B ion from solution.

    What is the order of these metals going from the best to the worst oxidant?

    (a) ABC (b) BCA (c) CAB (d) BAC (e) ACB

Calculations

1. In a titration experiment, a student was required to standardise an iron(II) sulfate solution. She found that 20.0 mL of the solution, when acidified, required 25.0 mL of a 0.10 mol L^{-1} potassium permanganate solution for complete reaction.

   (i) Write the reaction equation.

   _____

   _____

   (ii) Calculate the molar concentration of the iron (II) sulfate solution.

   _____

   _____

   _____

2. A student was determining the concentration of a commercial H_2O_2 solution. She prepared a dilute solution by adding 100.0 mL of distilled water to 10.0 mL of the solution. 20.0 mL of this dilute H_2O_2 solution, when acidified, reacted with 30.0 mL of 0.10 mol L^{-1} potassium dichromate solution. Determine the concentration of the H_2O_2 in the commercial solution.

   _____

   _____

   _____

   _____

   _____

   _____

3. A solution of oxalic acid was prepared by boiling some rhubarb leaves. A number of 20.0 mL portions of this solution were titrated against a standard 0.11 mol L^{-1} $KMnO_4$ solution. The average titre was 10.0 mL. Calculate the concentration of the oxalic acid solution using the normal half equations.

4. A 1.70 g of mineral sample containing chromium was analysed as follows. The chromium was first converted to sodium dichromate. 50.0 mL of a 0.20 mol L^{-1} standard iron (II) sulfate solution were required to titrate the dichromate solution to an end point. Determine the percentage of chromium in the mineral sample.

5. 12.6 g of crystalline oxalic acid was dissolved in distilled water and the solution made up to one litre. 20.0 mL of this solution, when acidified, reduced 25.0 mL of a potassium permanganate solution. Calculate the concentration of the permanganate solution.

6. 2.00 mL of a H_2O_2 solution when acidified required 40.0 mL of a 0.020 mol L^{-1} $KMnO_4$ solution for complete oxidation. Determine the concentration of the H_2O_2 solution and the volume of oxygen liberated at 35°C and 100.6 kPa pressure.

7. In standardising a solution of $KMnO_4$, 20.0 mL portions of a 0.110 mol L^{-1} oxalic acid solution, when acidified, were required to completely react with 9.00 mL of the $KMnO_4$ solution.

   Calculate the molar concentration of the $KMnO_4$ solution.

8. In standardising a $K_2Cr_2O_7$ solution, 20.0 mL portions of a 0.05 mol L^{-1} iron (II) sulfate solution, when acidified, reacted with 7.50 mL of the $K_2Cr_2O_7$ solution.

   Calculate the molarity of the dichromate solution.

9. In determining the iron (II) ion concentration of water, it was found that 50.0 mL samples of the water, when acidified, required 1.50 mL of a 0.0010 mol L^{-1} $KMnO_4$ solution for complete oxidation. Calculate the concentration of Fe^{2+} ions in water.

10. Acidified potassium dichromate will oxidise hydrogen peroxide according to the following unbalanced equation:

    $$Cr_2O_7^{2-}(aq) + H_2O_2(aq) \rightarrow Cr^{3+}(aq) + O_2(g)$$

    (a) Balance the equation and determine the mass of potassium dichromate that is required for the complete oxidation of 1.0 g of hydrogen peroxide.

    (b) Calculate the volume of oxygen, measured at $0^{\circ}C$ and 100 kPa pressure that will be produced in this reaction.

11. Three 25.0 mL samples of a potassium oxalate solution ($K_2C_2O_4$), when acidified with sulfuric acid, required the following titres: 24.48 mL, 24.54 mL and 24.47 mL of potassium permanganate solution of concentration 0.020 mol L^{-1} for complete reaction.

The relevant unbalanced equation is: $C_2O_4^{2-}(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + CO_2(g)$.

Determine:

(a) The average titre value of $KMnO_4$.

(b) The concentration of the potassium oxalate solution.

(c) The volume of carbon dioxide that could be collected at S.T.P by the reaction of potassium permanganate with 25.0 mL $K_2C_2O_4$.

12. A 4.00 g sample of iron ore was crushed and dissolved to produces only iron (II) ions. The resulting solution was acidified with dilute sulfuric acid and the volume made up to 500 mL in a volumetric flask, using distilled water. 25.0 mL portions of this dilute solution required an average titre of 20.0 mL of potassium permanganate of concentration 0.020 mol L^{-1} for complete reaction.

The relevant unbalanced equation is: $Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

Calculate the percentage of iron in the iron ore.

13. A 40.0 mL sample of a commercial hydrogen peroxide solution was transferred to a volumetric flask and the volume made up to 1000.0 mL with distilled water. Separate 20.00 mL samples of the solution acidified with sulfuric acid, required an average volume of 20.20 mL of 0.016 M potassium permanganate solution for a complete reaction. The unbalanced equation is:

$H_2O_{2(l)} + MnO_4^-{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + O_{2(g)}$

Determine:

(a) The concentration of the commercial hydrogen peroxide in mol L^{-1}

(b) The percentage by mass of hydrogen peroxide in the commercial solution. (Assume the density of the solution to be 1 g cm^{-3}.)

(c) The volume strength of the commercial solution (how many moles of oxygen 1 mole of solution produces).

Redox Back-Titration Questions

14. The percentage of ethanol in a certain spirit can be determined by adding a known excess volume of potassium dichromate to the wine and then titrating the left-over $K_2Cr_2O_7$ with oxalic acid.

120.0 mL of 0.243 mol L^{-1} $K_2Cr_2O_7$ solution was added to 7.00 mL of white wine and made up to 250.0 mL with distilled water. 25.0 mL samples of the treated wine were then titrated with a 0.0504 mol L^{-1} solution of oxalic acid dihydrate ($C_2H_2O_4.2H_2O$) to react with the excess dichromate.

The following results were obtained.

Titration results	Trials			
	1	2	3	4
Final volume	29.4	26.45	27.30	24.80
Initial volume	2.5	3.31	4.27	1.70
Titre				

The relevant equations are given below:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

$C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$

$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(l) + 16\ H^+(aq) \rightarrow 3CH_3COOH(aq) + 4\ Cr^{3+}(aq) + 11\ H_2O(l)$

(a) Write a balanced equation for the reaction between potassium dichromate and oxalic acid.

_____

_____

_____

(b) Calculate the average titre to be used in the calculation.

_____

(c) Using the equations provided:

Determine the concentration of ethanol in the original wine in mol L^{-1}

_____

_____

_____

_____

_____

_____

15. The vitamin C content in vitamin C tablets can be determined by adding a known excess volume of iodine solution to a solution of the vitamin C tablet which contains ascorbic acid ($C_6H_8O_6$) as the active ingredient. The remaining excess iodine can then be titrated with sodium thiosulfate ($Na_2S_2O_3$).

A chemist analysing the vitamin C in a particular brand of tablets carried out the following two steps:

(i) A tablet with a mass of 250 milligrams was dissolved in 20 mL of water, and 100.0 mL of 0.0521 mol L^{-1} solution of iodine was added. This mixture was then made up to 250 mL with water in a volumetric flask.

(ii) 20.0 mL aliquots of the resulting solution were titrated with 0.0493 mol L^{-1} sodium thiosulfate solution ($Na_2S_2O_3$).

The results obtained are shown in the table below:

Titration Results	Trials (mL)			
	1	2	3	4
Final volume	15.27	16.12	14.48	15.87
Initial volume	0.22	2.16	0.70	1.95
Titre				

The relevant half-equations are:

$C_6H_8O_{6(aq)} \rightarrow C_6H_6O_{6(aq)} + 2H^+ + 2e^-$

$I_{2(aq)} + 2e^- \rightarrow 2\ I^-_{(aq)}$

$2S_2O_3^{2-}{}_{(aq)} \rightarrow S_4O_6^{2-} + 2e^-$

a) Write and balance the equation for the reaction between iodine and thiosulfate ions.

_____

b) Write a balanced equation for the reaction between ascorbic acid and iodine.

_____

c) Calculate the percentage by mass of vitamin C in the tablet.

_____

_____

_____

_____

_____

_____

16. In hospital it is required to find the amount of calcium in a patient's blood who has osteoporosis (weak bones). For this, the calcium in a sample of blood is mixed with oxalic acid to precipitate the calcium ions as calcium oxalate and then this solid is converted to oxalic acid by reaction with sulfuric acid. The amount of oxalic acid present is then found by titration of the oxalic acid with a permanganate solution.

Procedure:

- 100 mL of blood diluted to 200 ml with water and excess oxalic acid added.
- The CaC_2O_4 solid is washed, dissolved in 100 mL of H_2SO_4 and excess MnO_4^- added (50 mL of 0.0052 mol L^{-1} MnO_4^- solution).
- 20 mL of the excess permanganate solution is titrated with a 0.0087 M solution of iron (II) sulfate and an average titre value of 12.67 mL was obtained.

Using these results

(a) Write the equation for the reaction of the oxalate ion ($C_2O_4^{2-}$) with MnO_4^- solution.

_____

(b) Write the equation for the reaction of the MnO_4^- solution with the Fe^{2+} solution.

_____

(c) Find the mass of calcium present in the 100 mL sample of patient's blood.

_____

_____

_____

_____

_____

_____

(d) Find the concentration of calcium ions present in the blood.

_____

_____

_____

_____

_____

_____

3.7 CORROSION

Corrosion of metals is a redox reaction. Many metals such as copper, iron, aluminium and silver corrode by reaction with air to form their oxides or sulfides.

Aluminium does not appear to corrode although aluminium is a more reactive metal than iron. This is because the aluminium oxide layer prevents any exposure of the underlying metal to water and oxygen and prevents further corrosion:

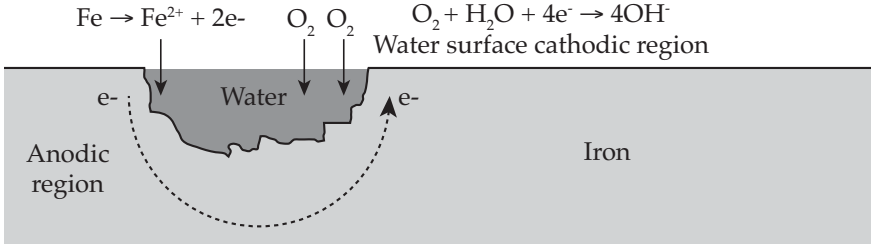
$Al \rightarrow Al^{3+} + 3e^-$ (Ox); $O_2 + 4e^- \rightarrow 2O^{2-}$ (Red); $4Al + 3O_2 \rightarrow 2Al_2O_3$ (Redox)

Hence aluminium can be used for window frames, boats and wheels without any apparent corrosion.

Silver reacts with the sulfur in the air or the hydrogen sulfide gas in the environment to become black silver sulfide. This is called *Tarnishing* and happens with silver spoons and trophies.

$$2Ag + S \rightarrow Ag_2S$$

The rusting of iron is an oxidation – reduction process. Where the iron surface is cracked or has a weakness in structure exposed to water, oxidation will take place:



Iron oxidises and donates the electrons:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

Oxygen dissolves in the water and absorbs these electrons, producing a basic solution:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Iron reacts with oxygen: $4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}$

Iron III reacts with water: $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

Iron hydroxide decomposes: $Fe(OH)_3 \rightarrow Fe_2O_3 . \times H_2O$ (Rust)

3.8 CORROSION PREVENTION

Corrosion can be minimised by protecting the surface from the environment. Painting, varnishing, greasing, plating with less reactive metals tin and coating with a thick oxidised layer of the metal which is non-porous are some of the usual measures taken to minimize corrosion.

Metals like chromium, when used as plating, will provide a non-porous, shiny layer that increases the value of the article and makes it last longer.

Galvanising

Covering iron in a thin layer of a more reactive metal produces a cell with a reverse voltage which pushes the electrons back onto the iron when it starts to oxidise. Suppose an iron sheet is coated with zinc. In wet conditions the following aqueous reactions can take place:

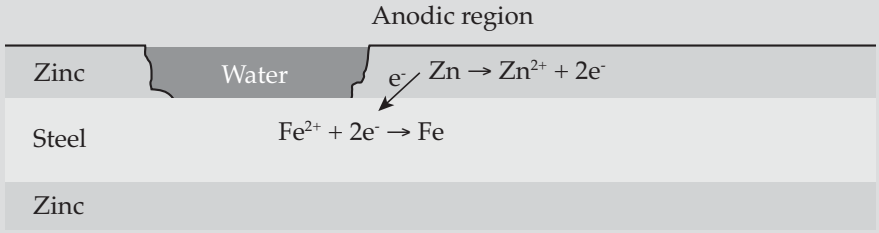
$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ $E^o = +0.76$ V

$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$ $E^o = +0.44$ V

For these two metals to work as a cell, the iron reaction must be reversed to give a positive overall voltage (0.76 V – 0.44 V). Hence to overall reaction would be:

$Zn_{(s)} + Fe^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Fe_{(s)}$

In other words, the zinc, being more reactive, would push the electrons back on to the iron should it begin to lose electrons and become ions. Instead of the iron dissolving, the zinc will dissolve, leaving the iron un-corroded. This method of cathodic protection is called Galvanising after the famous Italian scientist Galvani. Steel poles, sheets, etc. are dipped into molten zinc to coat them which protects the steel even where there are gaps in the coating.



Sacrificial anodes

With large structures, such as ships, steel piles, water tanks or floating oil rigs, blocks of zinc or aluminium are actually bolted onto the outside steel area, ensuring a good electrical contact. The principle is the same, with the zinc forming a cell with the steel and feeding electrons back to sites of potential oxidation of the iron. The zinc is sacrificed for the sake of the steel and will gradually dissolve. After some months or years the zinc block would be unbolted and replaced with a new one and the protective process would continue.

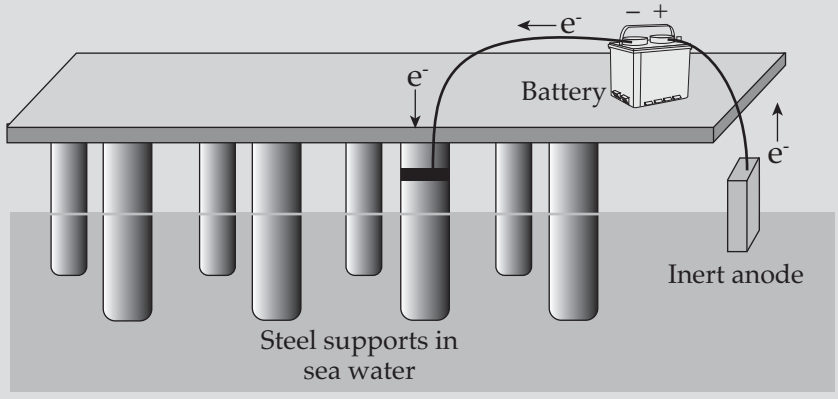
Cathodic Protection

Electrons can actually be "pushed back" onto rusting iron directly by using a cell, instead of making use of a more reactive metal to do this. This method connects an electron source, such as a battery or a transformer, directly to the exposed piece of iron or steel using a connecting wire.

The battery supplies the energy to reverse the reaction: $2e^- + Fe^{2+} \rightarrow Fe_{(s)}$ at the pipe support (cathode) and at the anode negative charge returns through the seawater from the reduction reaction carried by the OH^- ion.

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$

For the circuit to be complete a large piece of scrap iron is used as an inert anode, just hanging in the water and returning the electrons to the battery.



3.9 GALVANIC CELLS

We can make use of the different reactivities of metals in solution to drive electrons from one metal to another around an external circuit. In this way the chemical energy differences shown in the Standard Reduction Table can provide energy to an external source, e.g. light a lamp.

When this happens, the metal losing electrons is oxidised and the metal gaining electrons is reduced.

Solutions do not conduct by means of electron flow, as with metals, but use ions. To allow ions to flow in a cell and complete the circuit, the metals must be linked with a conducting liquid — an ionic salt solution — contained in a tube. This ion-filled tube is called a *salt bridge.*

Example Question

a) Show an galvanic cell using lead and iron as electrodes.

b) What is the output voltage of the cell?

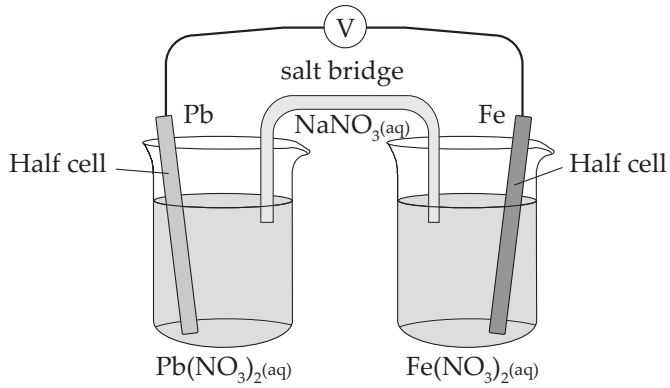
c) Identify which metal is the anode and which is the cathode.

d) Which way do the electrons flow?

e) Which way do the ions flow in the salt bridge?

Answers

This cell is represented by the symbols: $Fe/Fe^{2+}//Pb^{2+}/Pb$ (Convention is Oxidation//Reduction)



Here we have two competing reactions for reduction:

$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)} \quad E^0 = -0.13\ V$

$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)} \quad E^0 = -0.44\ V$

The lead reaction shows that it is a better reductant that iron and so the iron reaction must be reversed in order to gain a positive value of energy (E^o) overall. Hence the ½ equations must be:

$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)} \quad E^0 = -0.13\ V$

$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad E^0 = +0.44\ V$

$\Big\}\ E_{Tot}{}^0 = +0.31\ V$

Output voltage of the cell is 0.31 volts which will be the voltmeter reading in this case.

Note: The anode is where oxidation takes place and the cathode is where reduction takes place (Remember by: ANOX and REDCAT). Hence the **anode** is the iron, as it is oxidised to Fe^{2+} and lead will be the **cathode** as Pb^{2+} ions are reduced to Pb solid.

d) From the equations above we can see that electrons are coming out from the iron reaction:
$Fe \rightarrow Fe^{2+} + 2e^-$

Hence the electrons will flow from the iron electrode through the voltmeter and back to the lead where they are used to reduce the Pb^{2+} ions to Pb solid.

e) Negative charge flows out from the iron and must flow back to the right hand half-cell to complete the circuit through the salt bridge. So it must be the negative SO_4^{2-} ions that move from left to right through the salt bridge tubing.

The voltage of a cell and the electrode names can be found using the Standard Reduction Table. We just use the principle that, with two dissimilar metals and their ions, the species which is top left in the table will be the one reduced and therefore the cathode (REDCAT). The species on the bottom right in the table will be where the equation is reversed and will be the anode as it will be oxidised (ANOX).

e.g. Suppose a cell is made up from the metals silver and manganese.

Top left in the Table is the Ag^+ ion and bottom right will be Mn metal. So the half equations will be:

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^0 = +0.80$ V Cathode

$Mn(s) \rightarrow Mn^{2+} + 2e^-(aq)$ $E^0 = +2.36$V Anode

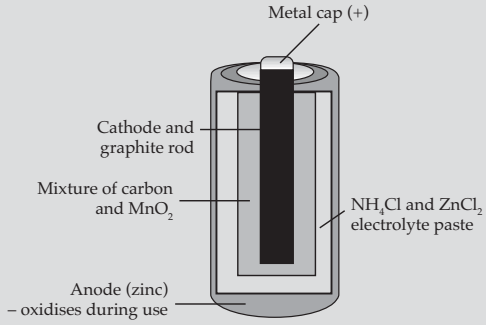
Total output cell voltage will be 0.80 + 2.36 = 3.16 V.

3.10 USEFUL GALVANIC CELLS

Voltaic cells provide portable energy sources and are very important in today's technological world. There are basically three types of voltaic cells: The common Dry Cell, Alkaline battery cells and the Lithium iodide cell. These cells, called Primary Cells, as they are non-rechargeable – so once used, they must be disposed of in a safe manner. The car battery and the nickel-cadmium cell are examples of Secondary Cells, i.e. they are rechargeable for repeated discharge and recharging. Cells which do not store the chemicals, such as the fuel cells, form the third type of cell.

PRIMARY CELLS

The Common Dry Cell



The electrolyte used is NH_4Cl and $ZnCl_2$ paste - so there is no liquid to spill.

The zinc container is the anode and a carbon rod and MnO_2 powder are the cathodes.

The anode reaction is: $Zn \rightarrow Zn^{2+} + 2e^-$

The cathode reaction is:

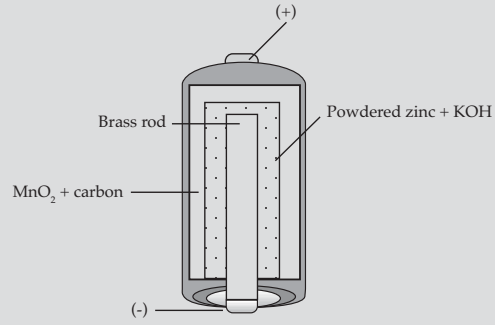
$2MnO_2(s) + 2H^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + H_2O(l)$

The H^+ ions needed for this reaction are provided by the ammonium ion in NH_4Cl: $NH_4^+ \rightarrow NH_3 + H^+$

Dry cells are mainly used for torches, children's electrical toys and TV remote controls. They give an output of 1.50 volts.

Advantages: cheap.

The Alkaline Cell



The electrolyte used is KOH solution with a zinc container is the anode. Carbon and MnO_2 are the cathodes.

The anode reaction is: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

The cathode reaction is:

$MnO_2 + 2H_2O + e^- \rightarrow Mn(OH)_3 + OH^-$

Mainly used for portable radios and CD players. They give an output of between 1.50 and 1.65 volts.

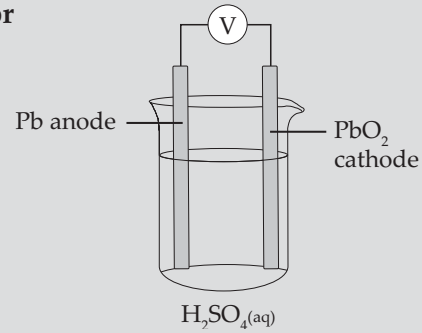
Advantages: they have a higher energy density and shelf-life than the dry cell.

Rechargeable Cells

All the Galvanic cells referred to so far have been what are termed Primary Cells. This means that, once the chemicals or metals have reacted then the cell is discarded; they cannot be charged up again. Secondary Cells, however, have the advantage of being able to be recharged and hence can save money on components.

One very common rechargeable battery in use is the one under the bonnet of most cars – used to start the car. This particular Secondary Cell is called the Lead-Acid Accumulator.

Lead-Acid Accumulator



Discharging

The anode reaction is: $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightleftharpoons PbSO_{4(s)} + 2e^-$ $(E^0 = +0.36V)$

The cathode reaction is:
$PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)} + 2e^- \rightleftharpoons PbSO_{4(s)} + 2H_2O_{(l)}$ $(E^0 = +1.69V)$

So the overall reaction for discharging the cell is:

$Pb_{(s)} + PbO_{2(s)} + 2SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)} \rightleftharpoons 2PbSO_{4(s)} + 2H_2O_{(l)}$ (Total $E^0 = +2.05$ V)

Normally, for car batteries, six of these cells are placed in series to give a voltage of 12.3 V overall.

The lead-acid battery is able to supply the very large current required to start the car. As the battery discharges both plates become "sulfated" so, when the battery is completely flat the anode and cathode have both become lead sulfate and the sulfuric acid pH has risen considerably. One way of telling that the battery is flat is by looking at the density of the electrolyte. Normally the density of the acid in the battery is around 1.2 g cm^{-3} but, as it loses its acid concentration, the density would become closer to 1.0 g cm^{-3}.

Charging

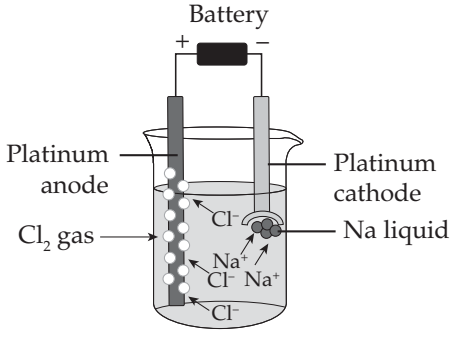
The Lead-acid battery can be recharged by connection to a 12 volts electrical supply so that the reactions above are reversed when the anode and cathode revert to their original components of lead and lead oxide.

$2PbSO_{4(s)} + 2H_2O_{(l)} \rightleftharpoons Pb_{(s)} + PbO_{2(s)} + 2SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)}$

Galvanic Cells

Galvanic cells generate a voltage by utilising the different reactivities of species to produce a spontaneous reaction. However, by supplying energy in the form of an applied external voltage reactions can be forced to reverse and produce a metallic or non-metallic product.

Cells where a voltage is applied to produce a redox reaction are called Electrolytic Cells, e.g. sodium and chlorine can be produced by the electrolysis of molten (fused) sodium chloride crystals using inert electrodes.



The anode reaction is $2Cl^-_{(l)} \rightleftharpoons Cl_{2(g)} + 2e^-$ (chlorine gas is evolved) E^o here is -1.36 V

The cathode reaction is $Na^+_{(l)} + e^- \rightleftharpoons Na_{(s)}$ (sodium metal is produced) E^o here is -2.71 V

The required voltage to reduce the Cl^- and oxidise the Na^+ would be 1.36 + 2.71 = 4.07 V.

Note: This redox reaction would not occur in an aqueous solution because the water would be electrolysed in preference to the NaCl. Reducing water at the cathode to hydrogen would only require a voltage of only 0.83 volts and oxidising water to oxygen at the anode would only require 1.23 volts. Hence a total applied voltage of only 0.83 + 1.23 = 2.06 volts would be needed. Compounds composed of highly reactive elements like sodium and chlorine can only be oxidised or reduced when they are in the fused, liquid form – not a solution.

An example of another vital element that has to be produced by the electrolysis of the fused compound is Aluminium.

Electrolysis of alumina

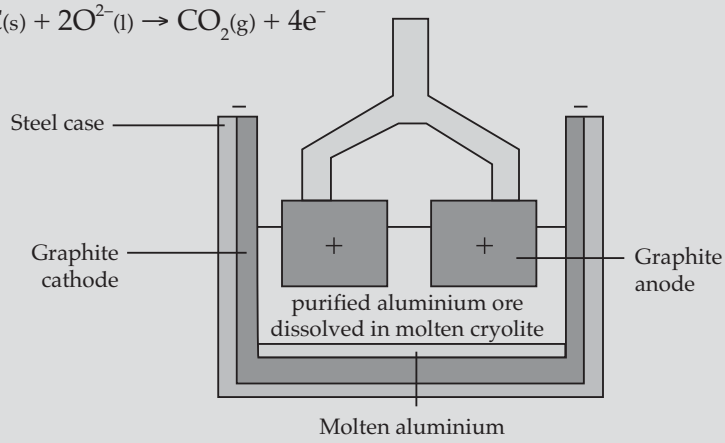
Alumina (Al_2O_3) is plentiful in Australia, but it has an extremely high melting point (over 2040ºC) which makes the reduction process energy intensive. By adding Cryolite (Na_3AlF_6) to the mix the melting point can be brought down to about 900ºC which makes the process more economically viable.

A steel container lined with graphite serves as the cathode and the anodes are a set of carbon rods. The temperature is kept over 900ºC throughout and aluminium is collected as a liquid while the liberated oxygen oxidises the carbon anode to CO and CO_2.

The reactions are:

Cathode: $Al^{3+} + 3e^- \rightarrow Al$

Anode: $C_{(s)} + 2O^{2-}_{(l)} \rightarrow CO_{2(g)} + 4e^-$



Molten aluminium is run off from the outlet at the bottom of the cell and CO_2 is evolved at the anode.

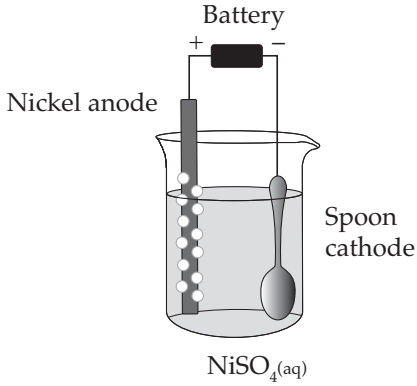
Electroplating

The electrolysis of some solutions of cations can be used to deposit a layer of metal onto another metal providing the reduction E^0 value is energetically lower that of water. Zinc, cadmium, nickel, copper and tin, for instance, can all be deposited onto a steel substrate by electrolysing a solution of the cation.

An example of how electroplating works is shown below, where a brass spoon is to be plated with nickel.

For the reaction $Ni^{2+}_{(aq)} + 2e- \rightleftharpoons Ni_{(s)}$ the E^o value is -0.24 V which means the reaction is endothermic. Hence if energy is supplied by connecting to a battery supplying at least +0.24 V the nickel ions will be precipitated as nickel metal. This is the basis of electroplating.

Nickel plating a spoon



A solution of nickel sulfate form the electrolyte and nickel metal acts as the anode.

Cathode reaction: $Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$ ($E^0 = -0.24$ V) (Nickel is deposited)

Anode reaction: $2H_2O_{(l)} \rightleftharpoons O_{2(g)} + 4H^+_{(aq)} + 4e^-$ ($E^0 = -1.23$) (Oxygen is released)

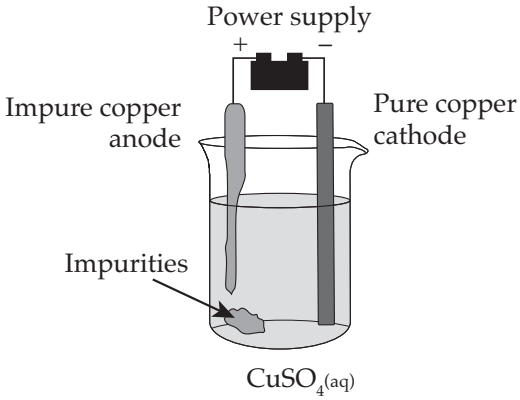
Total voltage that must be applied is 0.24 + 1.23 = 1.47 V.

(Note that the sulphate ion is non-reactive so it is water that becomes oxidised)

Electrowinning

Electrowinning or electro refining is a process by which a pure metal can be produced from an impure sample. This electrowinning is used to produce pure samples of metals such as copper, lead and cadmium as well as being used to recycle uranium metal from spent fuel rods. An example of the electrowinning process is shown below for the refining of copper from a metal sample which may have impurities of carbon, silver, etc. mixed with it.

Copper purification process



The impure copper sample is used as the anode and a purified (or pure copper plated) rod of copper is used as the cathode, with an electrolyte of copper sulfate solution. The copper ions dissolve from the anode into solution, leaving the impurities behind.

Anode reaction: $Cu_{(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2e^-$ ($E^0 = -0.34$ V)

Cathode reaction $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ ($E^0 = +0.34$ V)

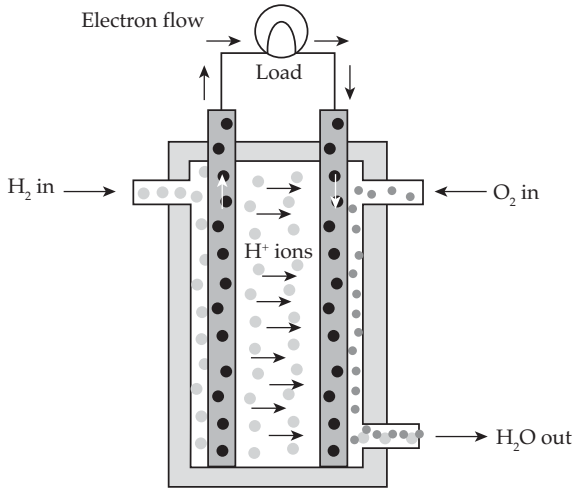
It seems that the total voltage required for this reaction would be zero (+0.34 + (-0.34 V) = 0.00 V) but some small voltage would actually be required to overcome the activation energy of the reactions.

Fuel cells

Many substances such as H_2 or CH_4 can also be used as fuels even though there are no ions present. The source of the electrical voltage is the energy released in the breaking of the bonds in the gases and forming new the ones in water molecules – the same as in combustion. Because combustion reactions are redox reactions, with fuel cells we can obtain a flow of current directly from the fuels being fed in.

Direct production of electricity from fuels via a galvanic cell yields a rate of energy conversion higher than 40%. Galvanic cells that utilise conventional fuels are known as fuel cells.

O_2/H_2 Fuel cells (e.g. Proton exchange membrane fuel cell)



Fuel cells tend to operate at high temperatures, using hydrogen which has to be stored and oxygen drawn in from the air. Some cars have now been designed to work using fuel cells and a battery such as the one shown above was used on the Apollo moon flights for electrical power. The electrodes are composed of hollow tubes of porous, compressed carbon, impregnated with a catalyst and an electrolyte of KOH solution. Because the reactants are supplied continuously, the fuel cell cannot go "dead" or "flat".

The reactions in the fuel cell are:

Anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Overall reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

The key advantage of this type of cell is that there are no metallic waste products and emit no toxic gases – just water. However, gases do need to be fed continuously to the cell and there are concerns about the storage of hydrogen for use in the fuel cell as it is very inflammable, or even explosive. NB: It currently takes 40% of the energy available from hydrogen gas to compress it for storage.

Cars running on fuel cells would offer a good alternative to petrol-engined cars.

The Energy Future – The International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE)

With the universal concern about the growth of CO_2 emissions and its link to Global Warming, governments around the world have set targets for the reduction of Greenhouse Gases (mainly CH_4, CO_2 and N_2O). Hence, the aim is to reduce a reliance on the burning of fossil fuels and to increase the use of Renewable Energies, such as wind, solar, geothermal and biomass which release no gases harmful to the environment. The use of fuel cells is a very promising new direction for generating electricity directly from gas oxidation in galvanic cells.

The IPHE was established in 2003 and is a forum for member governments to share information and policy experiences with the priority of accelerating the integration of hydrogen and fuel cell technologies into their economy. Many governments are now signed up to IPHE, including Australia, USA and UK, allocating research funding of more than $1 billion per year.

Hydrogen fuel cells can now be purchased off-the-shelf for houses and businesses requiring power outputs of up to 5 kW but are not in commercial use in vehicles due to concerns over safety and production costs of hydrogen. A tank of compressed hydrogen is highly explosive and to produce hydrogen it has been traditional to electrolyse water, which requires a large energy input. However, hydrogen is a by-product in some industries.

The NG fuel cell is a promising innovation in this field because, apart from hydrogen, it can also run on the methanol and methane contained in compressed natural gas (CNG). The advantage of this kind of cell is that it can generate electricity directly from the gas connections existing in most houses so as to charge an inboard battery.

The NG Fuel Cell works on a 2-stage process where the CNG is first broken down into hydrogen and then uses the hydrogen and oxygen to generate a voltage. The reaction occurs at quite high temperatures and uses steam mixed with CNG in stage 1:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

CO is poisonous and so a second stage reaction converts this into CO_2 thus:

$$CO + H_2O \rightarrow H_2 + CO_2$$

Hence the NG fuel cell does produce some CO_2, but the amount is about 30% lower than that emitted by power stations that generate the electricity needed to charge up battery-powered vehicles. An NG fuel cell powered car has efficiencies that are double that of similar cars charged from mains electricity and requires a much smaller battery. Using hydrogen in fuel cells at the moment is prohibitive in terms of safety and size of tank required, but an innovative storage technique has evolved recently where the low pressure CNG is adsorbed onto "Carbon sponges" inside the tank. These "sponges" can be manufactured simply and easily from charred common corn cobs which contain a kind of network of carbon nanotubes. 1 gram of the carbon substrate has an adsorption area equal to a football field! This would allow the storage tanks for the current 5 million vehicles around the world that run directly on CNG to be reduced to one third of their previous size.

Most CNG supplies presently come from non-renewable sources in the ground but methane can also be generated from waste organic material in bio-digesters and then compressed for use in a vehicle.

Using existing electric vehicle recharging technology, in order to travel a 600 km round trip the battery cost would be around $50,000 whereas, if the same vehicle were powered by an NG fuel cell, the battery cost would be very small in comparison.

Hence there are many problems to solve if we are to switch entirely to a fuel cell energy world but, with current research, the cost per kilowatt generated by fuel cells has reduced about 10-fold in the last 10 years!

Set 4. Exercises and Problems

Multiple Choice Questions

1. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ E=+1.51V

   $Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$ E=+1.60V

   Given the listed standard electrode potentials above, what is the E^0 for the cell below, in volts:

   $Mn^{2+}(aq) + 5Ce^{4+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 5Ce^{3+}(aq) + 8H^+(aq)$?

   (a) +3.12 (b) +2.16 (c) +0.50 (d) +1.21 (e) +0.09

2. $N_2(g) + 5H^+(aq) + 4e^- \rightarrow N_2H_5^+(aq)$ $E^o = -0.23V$

   $BiO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Bi(s) + H_2O(l)$ $E^o = +0.32V$

   Given the listed standard electrode potentials above, what is the E^o for the cell below.

   $4BiO^+(aq) + 3N_2H^{5+}(aq) \rightarrow 4Bi(s) + 3N_2(g) + 4H_2O(l) + 7H^+(aq)$?

   (a) +1.88V (b) +0.34 (c) -0.09 (d) +0.09 (e) +0.55

3. Based on the cell notation for a spontaneous reaction, the reaction at the anode is:

   $Mg(s)/Mg^{2+}(aq)//Sn^{2+}(aq)/Sn(s)$

   (a) Mg is oxidised (b) Sn^{2+} is oxidised

   (c) Mg^{2+} is reduced (d) Sn is reduced

4. Based on the cell notation for a spontaneous reaction,

   $Mg(s)/Mg^{2+}(aq)//H^+(aq)/H_2(g)/Pt$

   (a) Electrons flow in the external circuit toward the platinum electrode

   (b) H_2 is oxidised

   (c) Mg is the anode

   (d) Mg^{2+} is reduced

   (e) None of the above is correct

5. $I_2(s) + 2e^- \rightarrow 2I^-(aq)$ $E^o = +0.536$ V

   $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^o = +1.36$ V

   From the listed standard electrode potentials above, what would be the E^o for the cell:

   $I^-/I_2 // Cl_2/Cl^-$?

   (a) +0.948 (b) -0.824 (c) +1.896 (d) +0.824 (e) -1.896

6. $Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$ $E^o = -0.74$ V

$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$ $E^o = -0.44$ V

From the listed standard electrode potentials above, what is the E^o for the cell:

$Cr_{(s)}/Cr^{3+}_{(aq)}\ //\ Cd^{2+}_{(aq)}/Cd_{(s)}$?

(a) +1.80 (b) -1.18 (c) + 1.34 (d) +0.30 (e) -0.16

7. In a copper/zinc electrochemical cell, which uses copper sulfate and zinc sulfate electrolytes (the copper half cell is called Y and the zinc half cell is X) which of the following can be used as the solution in the salt bridge?

1) 1 mol L^{-1} NaCl 2) 1 mol L^{-1} KNO_3 3) 1 mol L^{-1} Na_2SO_4

(a) 1 only (b) 2 only (c) 3 only (d) 1 and 2 only (e) all three

8. In the cell referred to in question 7, cell X is zinc sulfate solution and cell Y is copper (II) sulfate solution. In this cell, what is the function of the salt bridge?

(a) To complete the circuit by allowing electrons to move from cell Y to cell X.

(b) To complete circuit by allowing ions to move between the two solutions.

(c) To complete the circuit by allowing electrons to move from cell X to cell Y.

(d) To complete the circuit by allowing electric current to flow from cell Y to cell X.

(e) To complete the circuit by allowing electric current to flow from cell X to cell Y.

9. Referring to the cell indicated in question 7, what happens when the zinc rod and zinc sulfate in cell X are replaced by magnesium rod and magnesium sulfate?

(a) A lamp connected to the external circuit will go out.

(b) A lamp connected to the external circuit will become brighter.

(c) A lamp connected to the external circuit will become dimmer.

(d) The cell gives smaller emf.

(e) The current flow reverses its direction.

10. Two clean metal foils are connected by means of wires to a small lamp and then dipped into dilute sulfuric acid as shown.

Which of the following metals in dilute sulfuric acid makes the lamp brightest?

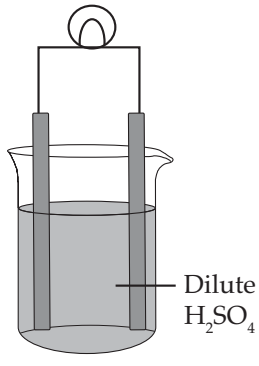
(a) magnesium/zinc.

(b) magnesium/copper.

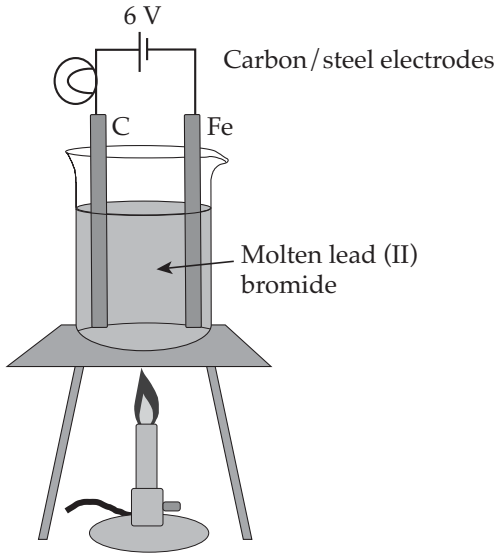
(c) zinc/copper.

(d) silver/copper.

(e) copper/copper.



Questions 11, 12 and 13 are based on the sketch of the circuit shown below



11. The lead (II) bromide in the beaker is kept molten by using the Bunsen flame. During the experiment, which of the following can be observed?

    1) The lamp lights up.
    2) Reddish brown fumes are evolved near the carbon electrode.
    3) A silvery solid is coated on steel electrode.

    (a) 1 only (b) 2 only (c) 3 only (d) 2 and 3 only (e) 1, 2 and 3.

12. The experiment should be performed in a fume cupboard because:

    (a) the reaction takes place at high temperatures.
    (b) poisonous bromine vapours are evolved.
    (c) carbon electrode reacts with the cations.
    (d) steel electrode reacts with the cations.
    (e) molten lead (II) bromide evaporates to give poisonous vapours.

13. The molten compound lead (II) bromide conducts electricity because:

    (a) molten lead (II) bromide contains delocalised electrons.
    (b) lead is a metal which conducts.
    (c) lead (II) bromide is very unstable.
    (d) bromine is ionic.
    (e) The liquid contains ions.

Longer Questions

1. Study the Standard Reduction Potentials on the Data Sheet and answer the following questions:

   (a) Which species is the strongest oxidant?

   _____

   (b) Which species is the strongest reductant?

   _____

   (c) Which species is weakest reductant?

   _____

   (d) Which species is the weakest oxidant?

   _____

   (e) What is the cell emf of the galvanic reaction, $Zn/Zn^{2+}//Fe^{2+}/Fe$?

   _____

   (f) Identify a reaction that has a galvanic voltage of 1.14 V. (There could be several)

   _____

   (g) Identify a galvanic cell reaction which occurs in the rusting of iron in moist air.

   _____

2. Will a reaction occur in the following cases? Justify your answer.

   (a) Water and calcium metal

   _____

   _____

   (b) Aqueous acidified solution of potassium permanganate and tin (II) nitrate

   _____

   _____

   (c) Potassium metal and an aqueous solution of sodium nitrate

   _____

   _____

3. Using the Standard Reduction Potential, predict the theoretical emf for the following reactions:

   (a) $Ni / Ni^{2+} // Ag^{+} / Ag$

   _____

   _____

   (b) $Cr^{3+}/Cr_2O_7^{2-}//H_2O_2/H^{+}/H_2O$

   _____

   _____

(c) $Zn/Zn^{2+}//Ni^{2+}/Ni$

_____

_____

4. Standard electrode potentials for the following two metals are given below:

$Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = 0.34V$ $Zn^{2+} + 2e^- \rightarrow Zn$ $E^o = -0.76$ V

(a) Why is the copper reaction assigned a positive potential?

_____

(b) Why is zinc reaction assigned a negative potential?

_____

(c) For a galvanic cell using the above reactions, what will be the cell potential?

_____

(d) Which one will be the oxidant?

_____

(e) If the half-reaction $Zn^{2+} \rightarrow Zn$ is assigned an arbitrary value of 0 V, what will be the electrode potential for the half reaction with copper?

_____

(f) What will be the new cell potential for the Cu^{2+}/Zn cell?

_____

5. Assuming that the electrode potential for the half-reaction $K^+(aq) + e^- \rightarrow K(s)$ is assigned a E^0 value of 0.00V, how will the electrode potential values assigned to all the other half-reactions change?

_____

_____

_____

_____

6. Note the following information:

$AuBr_4^-(aq) + 3e^- \rightarrow Au(s) + 4Br^-(aq)$	$E^0 = -0.858$ V
$Eu^{3+}(aq) + e^- \rightarrow Eu^{2+}(aq)$	$E^0 = -0.43$ V
$IO^-(aq) + H_2O(l) + 2e^- \rightarrow I^-(aq) + 2OH^-(aq)$	$E^0 = 0.49$
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	$E^0 = -0.14$ V

(a) Write the cell reaction that would give the largest cell emf.

_____

_____

_____

(b) Write the cell reaction that would give the smallest cell emf.

_____

_____

7. A galvanic cell that uses the reaction, $Fe^{2+}(aq) + Mg \rightarrow Fe + Mg^{2+}(aq)$ has a cell emf of 1.93 V under standard conditions.

   (a) What is meant by "under standard conditions"?

   _____

   _____

   _____

   (b) What are the E^{o} values for each of the two half reactions?

   _____

   _____

   _____

8. (a) Arrange the following species in order of increasing strength as oxidants:

   $Cr_2O_7^{2-}$, H_2O_2, Cu^{2+}, Cl_2, O_2

   _____

   (b) Arrange the following species in order of increasing strength as reducing agents:

   Zn, I^-, Sn^{2+}, H_2O_2, Al

   _____

9. Indicate which of the following reactions are spontaneous under standard conditions:

   (a) $H_2S(aq) + Cl_2(aq) \rightarrow S(s) + 2Cl^-(aq) + 2H^+(aq)$

   _____

   (b) $5H_2O_2(l) + Cl_2(aq) \rightarrow 4H_2O(l) + 2H^+(aq) + 2ClO_3^-(aq)$

   _____

   (c) $2Cl^-(aq) + Cu^{2+}(aq) \rightarrow Cu(s) + Cl_2(g)$

   _____

   (d) $10NO_3^-(aq) + 3I_2(s) + 4H^+(aq) \rightarrow 10NO(g) + 6IO_3^-(aq) + 2H_2O(l)$

   _____

10. The net cell reaction in a galvanic cell is $Sn(s) + Br_2(aq) \rightarrow Sn^{2+}(aq) + 2Br^-(aq)$

    What is the effect on the cell emf of each of the following changes?

    (a) The anode surface area is doubled?

    _____

    (b) The platinum electrode is replaced by a graphite electrode?

    _____

    (c) Tin (II) sulfate salt is dissolved in the anode half-cell?

    _____

    (d) Sodium bromide solution is added to the cathode half-cell?

    _____

11. In writing the notation for an electrochemical cell, what do the following mean:

(a) An oblique line

_____

(b) The formula of a substance in parentheses

_____

(c) A double oblique line

_____

12. Using the Standard Reduction Potential Table, identify an oxidising agent which will, under standard conditions, oxidise:

(a) I^- to I_2, but not Cl^- to Cl_2

_____

(b) $Fe_{(s)}$ to Fe^{2+}, but not $Pb_{(s)}$ to Pb^{2+}

_____

(c) $Zn_{(s)}$ to Zn^{2+} , but not $Cd_{(s)}$ to Cd^{2+}

_____

13. Use sketches to show the experimental arrangement by which the following galvanic half cells could be coupled together to produce a potential difference. Label the parts. Give the standard cell potentials for each of the cells.

(a) $Sn/Sn^{2+}//Ag^+/Ag$

(b) $Cl_2/Cl^-(Pt)//I^-/I_2(Pt)$

(c) $Fe/Fe^{2+}//Sn^{4+}/Sn^{2+}(Pt)$

14. Two common galvanic cells are the rechargeable nickel oxide-cadmium alkaline cell and the silver oxide-zinc button alkaline cell. Identify the anode and cathode reactions in the cells mentioned.

(a) $2NiO(OH)_{(s)} + Cd_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_2$

_____

(b) $Ag_2O_{(s)} + Zn_{(s)} + H_2O_{(l)} \rightarrow 2Ag_{(s)} + Zn(OH)_{2(s)}$

_____

15. A cell is represented by $Fe_{(s)}/Fe^{2+}_{(aq)}//H^+_{(aq)}/H_{2(g)}(Pt)$

(a) Identify the anode and write the anode half equation.

_____

(b) Identify the cathode and write the cathode half equation.

_____

(c) Draw a diagram to show the design of the galvanic cell below. Label the parts including all the chemicals and the direction of flow of electrons and ions.

16. A galvanic cell is represented by the equation:

$(Pt)\ Fe^{2+}_{(aq)}/Fe^{3+}_{(aq)}//Br_{2(aq)}/Br^-_{(aq)}\ (Pt)$.

(a) What is the anode half-reaction?

_____

(b) What is the cathode half-reaction?

_____

(c) Which electrode is to be labelled positive? Why?

_____

(d) Which electrode is to be labelled negative? Why?

_____

(e) What is the direction of the flow of bromide ions?

_____

(f) What is the direction of the flow of electrons?

_____

(g) What is the cell emf?

_____

(h) If you place a mixture of $Fe(NO_3)_2$ solution and bromine water in a container, will a reaction occur? How will you know?

_____

17. (a) Explain why hydrochloric acid reacts with zinc but not with copper:

_____

_____

_____

(b) Why is it necessary to regularly check the density of the electrolyte in the car battery?

_____

_____

_____

18. (a) Why are $NaNO_3$ or KNO_3 or NH_4NO_3 commonly used in salt bridges but not NaCl?

_____

_____

_____

(b) What is the purpose of a salt bridge in an electrochemical cell?

_____

_____

(c) Why is sodium chloride unsuitable for a salt bridge for a cell which uses zinc and silver electrodes?

_____

_____

19. Ethanol and methane are fuels suitable for fuel cells.

Fuel cells can operate either in an acidic environment or in an alkaline environment.

(a) Derive the anode and cathode reactions in a fuel cell which uses ethanol in an acidic environment?

_____

_____

_____

(b) What are the anode and cathode reactions in a fuel cell which uses methane in an acidic environment?

_____

_____

_____

20. Electrolysis is used to purify impure copper, either from blister copper extracted from copper ore, or from scrap metal that contains copper.

(a) Draw a labelled diagram of an electrolytic cell used for purifying copper.

(b) Give the anode and cathode half equations for the purification of copper in the above cell.

Anode:

Cathode:

(c) Impure copper may contain reactive metal impurities such as zinc, iron and nickel, which are below copper on the standard reduction potential table. To prevent these impurities frombeing reduced at the cathode a small voltage is used in the electrolytic cell. Using iron as an example explain why a small voltage is used. Include equations and E^{o}s in your answer.

(d) Impurities like gold, silver and platinum may also be present in impure copper. What happens to these impurities during the purification of the copper?

Notes

Unit 3 Examination Questions

CHEMICAL EQUILIBRIUM, ACIDS & BASES AND REDOX REACTIONS

Multiple-choice Questions

1. Consider the following 1.00 mol L^{-1} aqueous solutions.

   I Sodium chloride

   II Ethanol

   III Acetic acid

   IV Sulfuric acid

   Which of the following options lists these solutions from greatest conductivity to lowest conductivity?

   (a) $NaCl > H_2SO_4 > CH_3COOH > CH_3CH_2OH$

   (b) $CH_3CH_2OH > CH_3COOH > H_2SO_4 > NaCl$

   (c) $H_2SO_4 > NaCl > CH_3COOH > CH_3CH_2OH$

   (d) $CH_3COOH > NaCl > H_2SO_4 > CH_3CH_2OH$

2. When solid silver chromate is added to water, the following equilibrium is established:

   $Ag_2CrO_4(s) \leftrightarrows 2\ Ag^+(aq) + CrO_4^{2-}(aq)$

   A small quantity of sodium chromate solid is added to the solution. Assuming there is no change in the volume of the system, which of the following statements is correct?

   (a) The concentration of $CrO_4^{2-}(aq)$ will increase and the concentration of $Ag^+(aq)$ will not change.

   (b) The concentration of $CrO_4^{2-}(aq)$ will decrease and the concentration of $Ag^+(aq)$ will increase.

   (c) The concentration of $CrO_4^{2-}(aq)$ will increase and the concentration of $Ag^+(aq)$ will decrease.

   (d) The concentrations of $CrO_4^{2-}(aq)$ and $Ag^+(aq)$ will not change.

3. Consider the following system, which is at equilibrium:

   $C_2H_4(g) + HCl(g) \leftrightarrows CH_3CH_2Cl(g) \qquad \Delta H = -70\ kJ\ mol^{-1}$

   Which of the following statements about this system is true?

   (a) The rate of the forward reaction and the rate of the reverse reaction are both zero.

   (b) The concentrations of the reactants will remain constant over time.

   (c) The concentration of C_2H_4 will equal the concentration of CH_3CH_2Cl.

   (d) The sum of the concentrations of C_2H_4 and HCl will equal the concentration of CH_3CH_2Cl.

4. In a chemical reaction at constant temperature, which one of the following statements best describes the result of the addition of a catalyst?

   (a) Addition of a catalyst increases the amount of products formed.

   (b) Addition of a catalyst decreases the time taken to reach equilibrium.

   (c) Addition of a catalyst decreases the amount of energy released in the reaction.

   (d) Addition of a catalyst increases the amount of energy released in the reaction.

5. Solubility rules apply at modest concentrations of about 0.1 mol L^{-1} or higher. In each of the following instances, 0.2 mol of each of the four named substances is added to 1 L of water and the mixture stirred. In which of these will a precipitate remain after stirring?

   I $NaCH_3COO$, $(NH_4)_2CO_3$, $MgCl_2$, KNO_3

   II $Pb(NO_3)_2$, K_2S, $NaCl$, NH_4NO_3

   III $BaCl_2$, KCH_3COO, $CuSO_4$, LiBr

   IV KI, NH_4Cl, NaBr, $CuSO_4$

   (a) III only

   (b) II and III only

   (c) I, II and III only

   (d) I, II, III and IV

6. Which one of the following statements about the addition of a catalyst to a chemical reaction is false?

   (a) It increases the rate of the reaction relative to the uncatalysed reaction.

   (b) It provides a reaction pathway that has a smaller activation energy than that for the uncatalysed reaction.

   (c) It causes a greater fraction of collisions between reaction particles to result in a reaction relative to the uncatalysed reaction.

   (d) It causes particles involved in a reaction to move faster than those in the uncatalysed reaction.

7. A small rise in temperature of gaseous reactants in a system results in an increase in the rate of reaction. Which one of the following is the main reason for this change?

   (a) an increase in the speed of reactant particles, leading to a higher rate of collision

   (b) an increase in the pressure inside the reaction vessel, leading to a higher rate of collision

   (c) an increase in the proportion of collisions with more than the activation energy

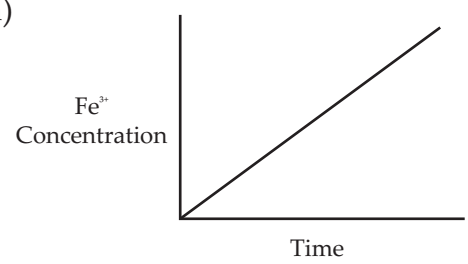
   (d) an increase in the activation energy of the reaction

8. When aqueous solutions of Ag^+ and Fe^{2+} are mixed, Ag and Fe^{3+} form according to the following equilibrium.

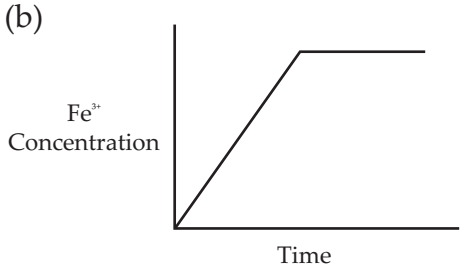
   $Ag^+(aq) + Fe^{2+}(aq) \leftrightarrows Ag(s) + Fe^{3+}(aq)$

   Which one of the following concentration versus time graphs best represents the way in which the Fe^{3+} concentration varies as the reaction proceeds to equilibrium?

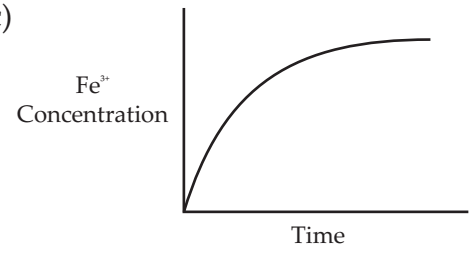
(a)



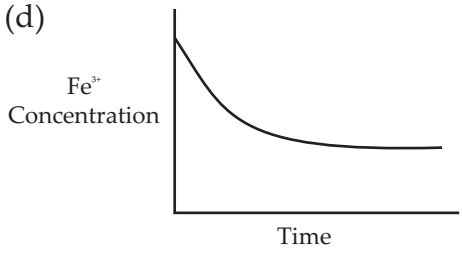
(b)



(c)



(d)



9. Ammonium chloride (NH_4Cl) dissolves readily in water at room temperature. If a sample of ammonium chloride is dissolved in a beaker of water, the beaker becomes cold to the touch. Which one of the following is the best explanation for this observation?

   (a) The reaction is exothermic with a small activation energy.

   (b) The reaction is exothermic with a large activation energy.

   (c) The reaction is endothermic with a small activation energy.

   (d) The reaction is endothermic with a large activation energy.

The next two questions refer to the following reaction.

$CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g) \quad \Delta H = 178.3 \text{ kJ mol}^{-1}$

10. Which one of the following is the equilibrium constant expression for this reaction?

    (a) $K = [CO_2]$

    (b) $K = \dfrac{[CaO][CO_2]}{[CaCO_3]}$

    (c) $K = \dfrac{[CaO] + [CO_2]}{[CaCO_3]}$

    (d) $K = \dfrac{1}{[CO_2]}$

11. Consider a sealed system in which $CaCO_3$, CaO and CO_2 are at equilibrium. Now consider the following actions:

    I Add more $CO_2(g)$ to the system.

    II Add more $CaCO_3(s)$ to the system.

    III Decrease the volume of the system.

    IV Increase the temperature of the system.

    One or more of these actions lead to a change in $CO_2(g)$ concentration (after equilibrium is re-established).

    Which statement below is true?

    (a) All actions lead to a change in $CO_2(g)$ concentration.

    (b) Only II, III and IV lead to a change in $CO_2(g)$ concentration.

    (c) Only III and IV lead to a change in $CO_2(g)$ concentration.

    (d) Only IV leads to a change in $CO_2(g)$ concentration.

12. When silver sulfide is added to water, the following equilibrium is established.

    $Ag_2S(s) \leftrightarrows 2Ag^+(aq) + S^{2-}(aq)$

    The value of the equilibrium constant for this reaction is very small. What does this suggest?

    (a) Adding more silver sulfide will increase the amount of ions in solution.

    (b) Silver sulfide reacts extensively with water.

    (c) Silver sulfide has a very low solubility.

    (d) This reaction is endothermic.

13. When $CoCl_2$ is dissolved in dilute hydrochloric acid, the following equilibrium is established.

$Co(H_2O)_6^{2+}(aq) + 4\ Cl^-(aq) \leftrightarrows CoCl_4^{2-}(aq) + 6\ H_2O(l)$

red deep blue

The solution appears purple in colour because of the mixture of the blue and red colours. Which one of the following changes will cause the solution to become more blue in colour?

(a) A catalyst is added.

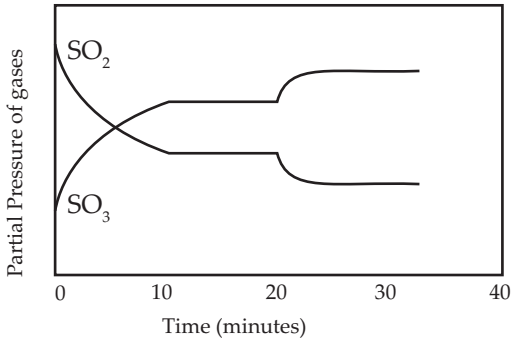
(b) A few drops of concentrated HCl are added.

(c) A few millilitres of $AgNO_3$ solution are added.

(d) The solution is diluted by the addition of water.

Questions 14 and 15 refer to the following graph, which represents the partial pressures of SO_2 and SO_3 in the reaction shown below.

$SO_2(g) + NO_2(g) \leftrightarrows SO_3(g) + NO(g) \qquad \Delta H = -42\ kJ$



14. At what time is equilibrium first established?

(a) 5 minutes

(b) 10 minutes

(c) 15 minutes

(d) 30 minutes

15. At the 20-minute mark, what changes could have been made to the system to produce the effects shown by the graph?

(a) The system temperature is increased or the partial pressure of NO is increased.

(b) The system temperature is increased or the partial pressure of NO_2 is increased.

(c) The system temperature is decreased or the partial pressure of NO is decreased.

(d) The system temperature is decreased or the partial pressure of NO_2 is decreased.

Questions 16 and 17 refer to the following chemical reaction taking place in a sealed container:

$2NO(g) + 2H_2(g) \leftrightarrows N_2(g) + 2H_2O(g) \qquad \Delta H = -664$ kJ

16. Which of the following changes made to the system would increase the equilibrium yield of N_2?

    I adding a catalyst

    II increasing the temperature

    III increasing the pressure

    IV cooling to cause the $H_2O(g)$ to condense to liquid water

    (a) I and II only

    (b) III and IV only

    (c) II and IV only

    (d) I, II and III only

17. In the changes referred to in question 16 which would increase the rate of the production of N_2?

    (a) I and II only

    (b) III and IV only

    (c) I, II and III only

    (d) II, III and IV only

18. The equilibrium utilised in the Haber Process can be represented as:

$$N_2(g) + 3H_2(g) \overset{\mathbf{Fe_2O_3\ catalyst}}{\leftrightarrows} 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1} \text{ (at } 25°C)$$

    What will happen if the quantity of catalyst is halved?

    (a) The temperature drops to half the original value.

    (b) The rate drops to half the original value.

    (c) The yield of product drops to half the original value.

    (d) None of the above will occur.

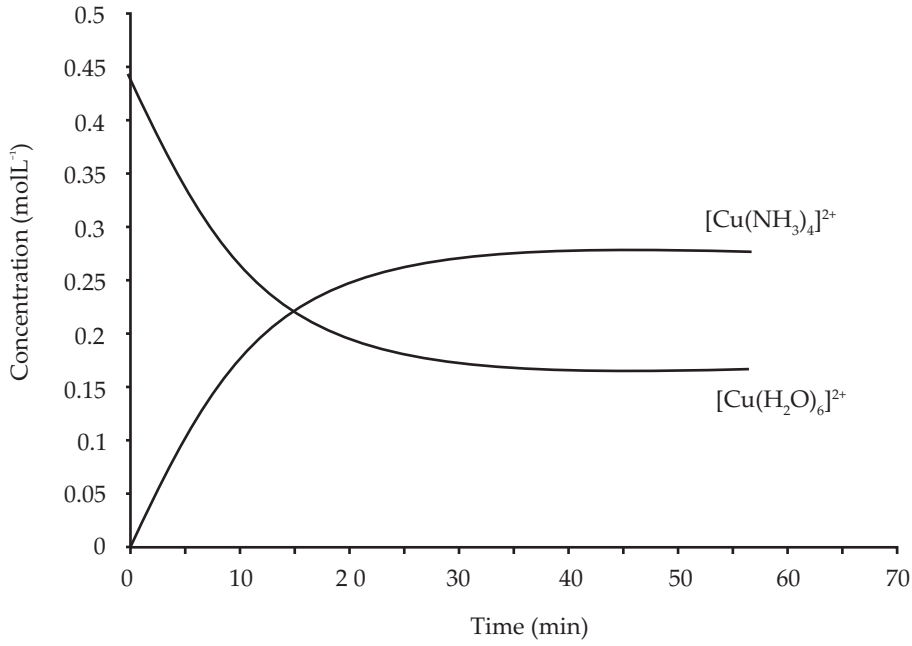
Questions 19 and 20 refer to the following equilibrium system.

Aqueous solutions of copper(II) ions and ammonia form the equilibrium represented below.

$[Cu(H_2O)_6]^{2+}(aq) + 4\ NH_3(aq) \leftrightarrows [Cu(NH_3)_4]^{2+}(aq) + 6\ H_2O(l)$

pale blue deep royal blue

The following graph shows the changes in concentration with time for $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ ions when solutions of copper(II) nitrate and ammonia are mixed.



19. Which one of the following statements is true for this equilibrium system?

    (a) The system reaches equilibrium at approximately 35 minutes.

    (b) At equilibrium, the concentration of NH_3 will always be four times greater than the concentration of $[Cu(NH_3)_4]^{2+}$.

    (c) Adding ammonia to the system will decrease the equilibrium constant.

    (d) At equilibrium, the rate of the forward reaction is less than the rate of the reverse reaction.

20. Which one of the following would be observed if a small quantity of concentrated nitric acid was added to the system after it had reached equilibrium?

    (a) The solution would be a deeper royal blue colour.

    (b) The solution would be a paler blue colour.

    (c) There would be no change in the colour of the system.

    (d) Copper(II) nitrate crystals would precipitate from solution.

21. 20.0 mL of a 0.0100 mol L^{-1} solution of NaOH is added to 20.0 mL of a 0.0300 mol L^{-1} solution of NaC*l*. What is the pH of the resulting solution?

    (a) 2.00

    (b) 7.00

    (c) 11.70

    (d) 12.00

22. Which one of the following equations does not represent the donation and acceptance of protons?

    (a) $2H^+ + 2\,e^- \leftrightarrows H_2$

    (b) $H^+ + OH^- \leftrightarrows H_2O$

    (c) $H_2O_2 + OH^- \leftrightarrows HO_2^- + H_2O$

    (d) $H_2C_2O_4 + CO_3^{2-} \leftrightarrows HC_2O_4^- + HCO_3^-$

23. Solid sodium ethanoate is added to water. Which one of the following statements best describes what happens?

    (a) The pH decreases because the ethanoate ions react with water to produce ethanoic acid.

    (b) The pH decreases because the sodium ions react with water to produce hydrogen ions.

    (c) The pH increases because the ethanoate ions react with water to produce hydroxide ions.

    (d) The pH increases because the sodium ions react with water to produce hydroxide ions.

24. Ammonia is classified as a weak electrolyte. Which of the following statements best explains this?

    (a) A water-solution of ammonia contains more hydroxide ions than hydrogen ions.

    (b) Ammonia is very soluble in water.

    (c) Hydrogen bonding exists between ammonia molecules.

    (d) In a water-solution only some of the ammonia molecules have reacted with water molecules.

25. In which one of the following will each listed compound dissolve in water to give a basic solution?

(a) carbon dioxide, sodium chloride, potassium hydroxide, ammonia

(b) ammonia, sodium oxide, potassium carbonate, barium hydroxide

(c) potassium acetate, sodium carbonate, ammonia, ammonium chloride

(d) sodium sulfate, potassium chloride, magnesium oxide, aluminium oxide

26. The water in a seriously neglected swimming pool is tested and found to have a pH of 3. By what factor must the hydrogen ion concentration be changed to increase the water pH to 6?

(a) decrease the hydrogen ion concentration by 1000 times.

(b) double the hydrogen ion concentration.

(c) halve the hydrogen ion concentration.

(d) increase the hydrogen ion concentration by 1000 times.

27. Sulfuric acid is a stronger acid than ethanoic acid. Which one of the following statements best explains this?

(a) Concentrated sulfuric acid has a concentration of 18 mol L^{-1}, while concentrated ethanoic acid has a concentration of 17 mol L^{-1}.

(b) Sulfuric acid has two hydrogen atoms available for ionisation per molecule, while ethanoic acid has only one hydrogen atom available for ionisation per molecule.

(c) Sulfuric acid ionises to a greater extent than ethanoic acid.

(d) Sulfuric acid is more soluble in water than ethanoic acid.

28. Household vinegar can be produced by adding 250 mL of glacial (nearly pure) ethanoic acid to 10 L of pure water. Which one of the following best describes the glacial ethanoic acid?

(a) a dilute solution of a strong acid;

(b) a concentrated solution of a weak acid;

(c) a dilute solution of a weak acid;

(d) a concentrated solution of a strong acid.

29. Methyl violet produces the following colours when added to solutions of known pH.

pH	Colour
0	Yellow
1	Green
2	Violet
3	Violet

Methyl violet is added to 1.0 mol L^{-1} solutions of hydrochloric acid, ethanoic acid and nitric acid. Which one of the following correctly identifies the colours the indicator will produce in each solution?

	Hydrochloric acid	Ethanoic acid	Nitric acid
(a)	Yellow	Yellow	Yellow
(b)	Yellow	Violet	Green
(c)	Green	Green	Green
(d)	Yellow	Violet	Yellow

30. Which one of the following correctly identifies the acidity of the listed salts when dissolved in water?

	Potassium chloride	Sodium nitrate	Ammonium sulfate	Sodium carbonate
(a)	Neutral	Acidic	Acidic	Neutral
(b)	Acidic	Acidic	Basic	Acidic
(c)	Neutral	Neutral	Acidic	Basic
(d)	Acidic	Neutral	Neutral	Basic

31. Which one of the following substances is the most suitable as a primary standard for acid–base titrations?

(a) sodium hydroxide

(b) hydrochloric acid

(c) oxalic acid

(d) sodium carbonate

32. 20.00 mL of a 0.0100 mol L^{-1} solution of NaOH is added to 20.00 mL of a 0.0300 mol L^{-1} solution of HC*l*. What is the pH of the resulting solution?

(a) 1.52

(b) 1.70

(c) 2.00

(d) 12.00

33. Which one of the following solutions would have a pH of 10?

(a) 1×10^{-10} mol L^{-1} sodium hydroxide

(b) 5×10^{-5} mol L^{-1} barium hydroxide

(c) 1×10^{-4} mol L^{-1} calcium hydroxide

(d) 1×10^{-10} mol L^{-1} nitric acid

34. Which one of the following statements is true?

(a) Only organic acids are weak.

(b) H_2O and OH^- are a conjugate acid-base pair.

(c) Weak acid solutions do not contain H_3O^+.

(d) Diluting a strong acid produces a weak acid.

35. A group of students conducted a series of titrations using the following steps:

I Washed burette with distilled water and a small quantity of acid before filling with acid.

II Washed the pipette with distilled water before filling with base.

III Washed the conical flasks with distilled water and a small quantity of base before adding the base from the pipette.

IV Rinsed the sides of the conical flasks with distilled water during the titrations.

V Added two drops of indicator to each conical flask.

The students found they could not obtain consistent results. Which of the above steps could have been responsible for the errors?

(a) I and V only

(b) II and III only

(c) II, III and IV only

(d) I, II and IV only

Use the following information to answer the next two questions.

A student has 20.0 mL of 0.15 mol L^{-1} $Ba(OH)_2$ solution and 30.0 mL of 0.223 mol L^{-1} HC*l* solution.

36. What is the pH of the $Ba(OH)_2$ solution?

    (a) 0.52

    (b) 2.52

    (c) 13.18

    (d) 13.48

37. If the two solutions are mixed, what is the pH of the resulting solution?

    (a) 1.13

    (b) 1.86

    (c) 2.43

    (d) 3.16

38. Which one of the following statements best explains why water is classified as a weak electrolyte?

    (a) A strong acid or strong base is required to ionise water molecules.

    (b) The rate of ionisation of water molecules is very slow.

    (c) When water ionises, the concentration of $OH^-(aq)$ is equal to the concentration of $H^+(aq)$.

    (d) A small proportion of the water molecules will form $H^+(aq)$ and $OH^-(aq)$.

39. In which one of the following is water acting as a base?

    (a) $H_2O(l) + NH_3(aq) \leftrightarrows NH_4^+(aq) + OH^-(aq)$

    (b) $H_2O(l) + CO_2(g) \leftrightarrows H_2CO_3(aq)$

    (c) $H_2O(l) + HSO_4^-(aq) \leftrightarrows H_3O^+(aq) + SO_4^{2-}(aq)$

    (d) $2H_2O(l) + 2Na(s) \leftrightarrows 2NaOH(aq) + H_2(g)$

40. The pH of a solution formed by adding 200 mL of distilled water to 20.0 mL of 2.00 mol L^{-1} hydrochloric acid is

    (a) 0.39

    (b) 0.70

    (c) 0.74

    (d) 1.39

41. A 20.0 mL aliquot of 0.100 mol L^{-1} sodium carbonate solution is titrated with hydrochloric acid with an approximate concentration of 0.1 mol L^{-1} in the presence of methyl orange indicator. The colour for methyl orange over a range of pH values is given below.

pH	1 – 3.3	3.3 – 4.4	4.4 - 14
Colour	red	orange	yellow

Which one of the following describes what will be observed?

(a) The colour changes from yellow to orange after about 40 mL of the acid has been added.

(b) The colour changes from yellow to orange after about 20 mL of the acid has been added.

(c) The colour changes from yellow to red after about 20 mL of the acid has been added.

(d) The colour changes from red to yellow after about 40 mL of the acid has been added.

42. Hydrochloric acid (HC*l*) is a stronger acid than the ammonium ion (NH_4^+). Which one of the statements below is true?

(a) The equilibrium constant for the hydrolysis of HC*l* is smaller than that for NH_4^+.

(b) Cl^- (aq) is a weaker base than NH_3(aq).

(c) Solutions of HC*l* will always have more hydrogen ions than solutions of NH_3.

(d) The pH of a 0.1 mol L^{-1} solution of HC*l* will be greater than the pH of a 0.1 mol L^{-1} solution of NH_3.

43. Which one of the following pairs of substances forms a buffer in aqueous solution?

(a) HC*l* and NaC*l*

(b) H_2SO_4 and Na_2SO_4

(c) NH_4Cl and $NaNH_2$

(d) $NaHCO_3$ and Na_2CO_3

44. Bromophenol blue is an acid-base indicator that has a colour change from yellow to blue between pH 3.0 and 4.6. A sodium hydroxide solution (in a conical flask) is titrated with an ethanoic acid solution (in a burette), using bromophenol blue indicator.

Which one of the following statements about this titration is true?

(a) The end point and the equivalence point occur at the same time.

(b) The end point occurs after the equivalence point.

(c) The end point occurs before the equivalence point.

(d) The indicator will be yellow at the equivalence point of the titration.

45. Which one of the following species cannot act as a Brønsted-Lowry acid and a Brønsted- Lowry base?

(a) $H_2PO_4^-$

(b) CH_3COCH_3

(c) H_2O

(d) HCO_3^-

46. Which one of the following is not true of this equation?

$HS^-(aq) + CO_3^{2-}(aq) \leftrightarrows S^{2-}(aq) + HCO_3^-(aq)$

(a) HCO_3^- is acting as a Brønsted-Lowry acid.

(b) CO_3^{2-} is acting as a conjugate base.

(c) HS^- is acting as a conjugate base.

(d) S^{2-} is acting as a Brønsted-Lowry base.

47. Consider the following list of compounds:

(i) KNO_3

(ii) Na_3PO_4

(iii) Fe_2O_3

(iv) Na_2S

(v) $Ba(OH)_2$

(vi) $AlCl_3$

(vii) $Ca(NO_3)_2$

Which of the above compounds will dissolve in water to give a basic solution?

(a) (i), (ii), (iii), (iv) and (v)

(b) (ii), (iii), (iv), (v), (vii)

(c) (ii), (iv), (v)

(d) (ii), (iv)

48. A buffer solution is prepared by mixing equal moles of sodium ethanoate and ethanoic acid in water. Which one of the following statements applies to the buffer?

(a) Addition of a few drops of concentrated nitric acid will produce more ethanoic acid molecules.

(b) The sodium ions play a significant role in the buffering action.

(c) Addition of water to the buffer will reduce its buffering capacity.

(d) Most of the hydrogen ions will be supplied by water.

49. An electrolytic cell with inert electrodes was operated in turn with each one of the following electrolyte solutions.

I 1 mol L^{-1} $CuSO_4$

II 1 mol L^{-1} H_2SO_4

III 1 mol L^{-1} NaOH

IV 1 mol L^{-1} NaCl

For which of the solutions would hydrogen gas be produced at the cathode and oxygen gas at the anode?

(a) I, II, III and IV

(b) II only

(c) II and III only

(d) II, III and IV only

50. In which one of the following does manganese have an oxidation state of +6?

(a) Mn_2O_3

(b) MnO_2

(c) MnO_4^{2-}

(d) MnO_4^-

51. What is the change in the oxidation number of bromine in the following reaction?

$2\ BrO_3^-(aq) + 10\ I^-(aq) + 12\ H^+(aq) \leftrightarrows 5\ I_2(aq) + Br_2(aq) + 6\ H_2O(l)$

(a) +7 to 0

(b) +7 to –1

(c) +5 to 0

(d) +5 to –1

52. Consider the elements A*l*, Cr, F, Fe, N, and Zn.

Which of the elements exhibit variable oxidation states in their compounds?

(a) all six of the elements.

(b) A*l*, Cr, Fe and Zn.

(c) A*l*, Cr, Fe, N and Zn.

(d) Cr, Fe and N.

53. A mixed solution containing both 1 mol L^{-1} $ZnSO_4$ and 1 mol L^{-1} $CuSO_4$ was electrolysed in an electrolytic cell using inert electrodes.

Which one of the following statements is correct?

(a) Copper is produced at the cathode and zinc is produced at the anode.

(b) Copper is produced at the cathode and oxygen gas is produced at the anode.

(c) Hydrogen gas is produced at the cathode and oxygen gas is produced at the anode.

(d) Zinc is produced at the cathode and oxygen gas is produced at the anode.

54. An electrochemical cell has a positive value of E°. Which one of the following statements about the two half cells forming the cell is true?

(a) Both half cells must have positive standard reduction potentials.

(b) The cathode half cell must have a positive standard reduction potential, while the anode half cell must have a negative standard reduction potential.

(c) At least one of the half cells must have a positive standard reduction potential.

(d) Both half cells may have a negative standard reduction potential.

55. A solution containing 1 mol L^{-1} $MgSO_4$ was electrolysed using copper electrodes. Which one of the following statements is correct?

(a) Hydrogen gas is produced at the cathode and copper ions are produced at the anode.

(b) Copper is produced at the cathode and copper ions are produced at the anode.

(c) Hydrogen gas is produced at the cathode and oxygen gas is produced at the anode.

(d) Magnesium is produced at the cathode and copper ions are produced at the anode.

56. A 'dry cell' contains a zinc anode and a carbon cathode. Which one of the following statements best describes the role of these electrodes?

(a) The zinc is reduced and the carbon is oxidised.

(b) The zinc is oxidised and the carbon is reduced.

(c) The zinc is oxidised and reduction of another component occurs at the carbon.

(d) The carbon is reduced and oxidation of another component occurs at the zinc.

57. When the following 1 mol L^{-1} solutions are electrolysed with inert electrodes, which one of them will not produce oxygen at the anode?

(a) $NaNO_3$ solution

(b) NaI solution

(c) NaOH solution

(d) KF solution

58. A garden water feature made of cast iron was observed to be severely corroded. Which one of the following measures would decrease the rate of corrosion?

(a) Attach a piece of copper to the iron.

(b) Attach a piece of magnesium to the iron.

(c) Apply an anodic current to the iron.

(d) Add bleach (sodium hypochlorite) to the water.

59. Consider the statements about the following reaction:

$2\ H_2O_2(l) \leftrightarrows 2\ H_2O(l) + O_2(g)$

I H_2O_2 is reduced.

II H_2O_2 is oxidised.

III H_2O_2 acts as a reducing agent.

IV This is not a redox reaction.

Which of the above statements are true?

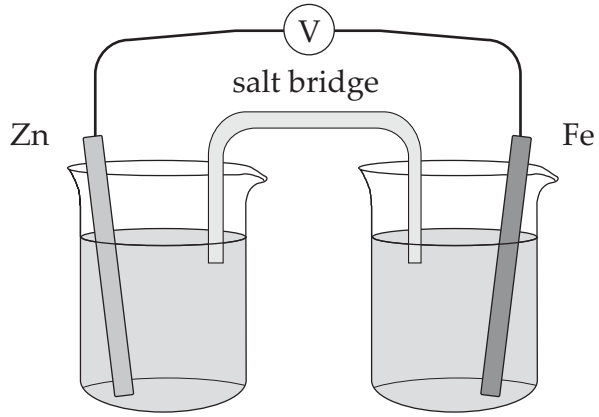
(a) IV only

(b) II and III only

(c) I only

(d) I, II and III only

Use the following information to answer the next two questions.



60. Which one of the following will be true for this cell?

(a) The mass of the zinc electrode will increase.

(b) Electrons will flow from the zinc electrode to the iron electrode.

(c) The concentration of Fe^{2+} ions in the electrolyte will increase.

(d) Iron will be deposited on the zinc electrode.

61. Which one of the following will be the closest to the cell EMF, at 25°C?

(a) 0.32 V

(b) 1.20 V

(c) 1.53 V

(d) 1.59 V

62. In which one of the following will a metal displacement reaction occur?

(a) a zinc rod is dipped in a 1.0 mol L^{-1} solution of sodium sulfate

(b) a copper rod is dipped in a 1.0 mol L^{-1} solution of cobalt(II) nitrate

(c) a silver rod is dipped in a 1.0 mol L^{-1} solution of gold(III) nitrate

(d) a tin rod is dipped in a 1.0 mol L^{-1} solution of manganese(II) sulfate

63. How many moles of electrons must be exchanged to oxidise 1 mole of hypophosphorous acid, H_3PO_2, to phosphoric acid, H_3PO_4?

(a) 2

(b) 3

(c) 4

(d) 5

64. Corrosion is a redox process. Which one of the following explains why coating iron with nickel protects the iron from corrosion?

(a) Nickel accepts electrons from iron.

(b) Iron and nickel form an alloy that is particularly resistant to redox processes.

(c) Nickel is a stronger oxidising agent than iron.

(d) The thin coating of nickel prevents iron from reacting.

65. Identify the oxidant in the following reaction:

$2\ Al(s) + Cr_2O_3(s) \leftrightarrows Al_2O_3(s) + 2\ Cr(s)$

(a) Al

(b) Cr_2O_3

(c) O

(d) Cr

66. Which one of the following is commonly used as an oxidising agent?

(a) $PbSO_4(s)$

(b) $H_2O(l)$

(c) $MnO_4^-(aq)$

(d) $CO_2(g)$

67. Which one of the reactions below is most likely to occur spontaneously?

(a) $H_2(g) + PbSO_4(s) \leftrightarrows 2H^+(aq) + Pb(s) + SO_4^{2-}(aq)$

(b) $Zn^{2+}(aq) + Fe(aq) \leftrightarrows Zn(s) + Fe^{2+}(aq)$

(c) $Cu^{2+}(aq) + Ni(s) \leftrightarrows Cu(s) + Ni^{2+}(aq)$

(d) $2Fe^{3+}(aq) + H_2O_2(aq) \leftrightarrows O_2(g) + 2Fe^{2+}(aq) + 2H^+(aq)$

68. Predict in which of the following a reaction would occur. Assume all solutions are 1.0 mol L^{-1}.

I Acidified potassium permanganate is mixed with potassium iodide solution.

II Chlorine gas is bubbled through hydrogen sulfide solution.

III Acidified potassium dichromate is mixed with potassium fluoride.

IV An iron(II) sulfate solution is placed in a nickel container.

V A piece of copper metal is placed in a hydrochloric acid solution.

(a) I and II only

(b) I, II and III only

(c) II and V only

(d) II, III and V only

69. Carbonated 'soft' drinks are made fizzy by dissolving $CO_2(g)$ into the flavoured liquid. Which one of the following statements relating to the volume of $CO_2(g)$ that can be dissolved in 1 L of soft drink liquid is true?

(a) It does not vary with temperature or pressure.

(b) It increases with increasing temperature.

(c) It decreases with increasing temperature.

(d) It decreases with increasing pressure.

Short Answer, Written and Calculation Questions

1. Write the equation for the reaction that occurs in each of the following procedures. If no reaction occurs, write 'no reaction'.

   Following this, describe in full what you would observe in each case, including any

   - colours
   - odours
   - precipitates (give the colour)
   - gases evolved (give the colour or describe as colourless). If no change is observed, you should state this.

   (a) Chlorine gas is bubbled through a sodium iodide solution.

   Equation: _____

   Observations:_____

   _____

   _____

   _____

   (b) Iron(III) nitrate solution is added to sodium sulfide solution.

   Equation: _____

   Observations:_____

   _____

   _____

   _____

   (c) Solid sodium carbonate is added to an excess of acetic acid solution.

   Equation: _____

   Observations:_____

   _____

   _____

   _____

   (d) A sample of iron metal is added to a solution of lead(II) nitrate.

   Equation: _____

   Observations:_____

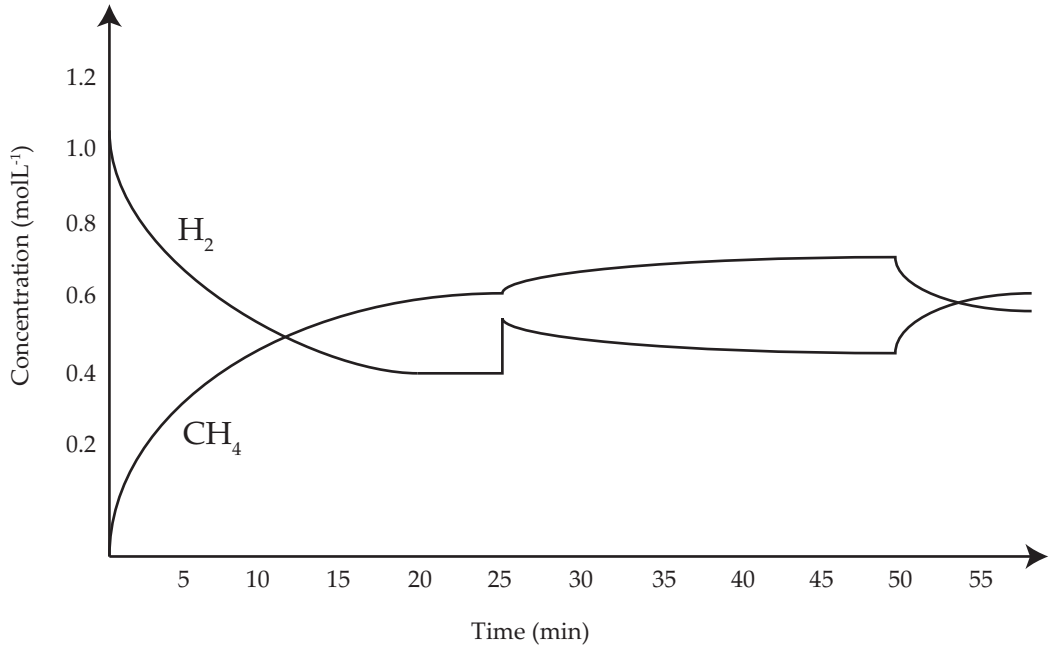
   _____

   _____

2. The reaction between carbon and hydrogen gas to form methane can be represented by the following equation.

$C(s) + 2H_2(g) \leftrightarrows CH_4(g) + 75\ kJ$

The concentrations of hydrogen and methane were plotted over time and the following graph produced.



(a) About what time was equilibrium first established?

_____

_____

(b) Suggest what could have caused the change at the 25 minute mark.

_____

_____

(c) Suggest what change to the system occurred at the 50 minute mark.

_____

_____

(d) What would be the effect on the equilibrium if more C(s) was added to the system?

_____

_____

(e) Explain, using Le Chatelier's Principle, what would be the effect of halving the volume of the reaction container.

_____

_____

_____

3. The following equilibrium is set up by adding solid silver chloride to dilute ammonia solution in three test tubes:

$AgCl(s) + 2\ NH_3(aq) \leftrightarrows [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

(a) Write an equilibrium constant expression for this equation.

(b) The following changes are made to the equilibrium system. Each change is applied to a separate test tube and equilibrium is re-established. Complete the table below, indicating the changes in the forward reaction rate, and the concentration of $[Ag(NH_3)_2]^+(aq)$, compared to the original equilibrium system. Use the terms 'increase', 'decrease' or 'no change'.

Also describe what you would observe as equilibrium is re-established in the system.

	At new equilibrium		
Imposed change	**Effect on forward reaction rate**	**Effect on $[Ag(NH_3)_2]^+(aq)$**	**Observation**
$NH_3(g)$ is bubbled through the solution.			
NaCl(s) is added to the solution.			
A few drops of concentrated HNO_3 (aq) are added to the solution.			

4. Solid magnesium hydroxide is added to a beaker of water. The water is stirred, and the contents of the beaker left to settle. A saturated solution is formed, with undissolved magnesium hydroxide at the bottom of the beaker. The system can be shown by the following equation:

$Mg(OH)_2(s) \leftrightarrows Mg^{2+}(aq) + 2\ OH^-(aq)$

(a) The system is allowed to come to equilibrium. Explain why the amount of solid present remains constant.

_____

_____

_____

_____

_____

_____

(b) The changes indicated in the table below are now imposed on the system. Predict and explain the effect these changes have on the amount of solid magnesium hydroxide in the beaker once equilibrium is re-established.

Imposed change	**Effect on solid $Mg(OH)_2$ (write 'increase', 'decrease' or 'no change')**	**Explanation**
A little concentrated sodium hydroxide solution is added to the beaker		
Some sodium phosphate solution is added to the beaker		
More water is added to the beaker		

5. Consider the following system:

$CO(g) + 2\ H_2(g) \leftrightarrows CH_3OH(g) \quad \Delta H = -92\ kJ$

Predict whether the following changes will increase, decrease or have no effect on the rate of attainment of equilibrium.

Change	Effect
Decreasing the temperature	
Increasing the pressure of hydrogen	
Adding a catalyst	

Predict whether the following changes will increase, decrease or have no effect on the equilibrium yield of the reaction.

Change	Effect
Increasing the temperature	
Increasing the pressure of the system	
Adding a catalyst	

6. Aluminium salts are acidic due to the presence of the hexaaqualuminate ion, $[Al(H_2O)_6]^{3+}$ which is formed when a soluble aluminium salt is dissolved in water. This ion undergoes hydrolysis as follows:

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \leftrightarrows [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^{+}(aq)$$

(a) Write the equilibrium constant (K) expression for this reaction. _____

_____

(b) A solution of an aluminium nitrate had a pH of 5.6.

(i) Using the above equilibrium reaction, explain how the pH of the solution would change when more solid aluminium nitrate was dissolved into the solution.

_____

_____

_____

(ii) When more water was added to the original solution, the pH initially rose from 5.6 to 6.0, and then dropped to 5.8. Explain these observations.

_____

_____

_____

(c) It was found that when the aluminium nitrate solution was warmed, the pH of the solution decreased. From this information, deduce whether the forward reaction in the above equilibrium is endothermic or exothermic. Explain your reasoning.

_____

_____

_____

_____

(d) Draw an electron dot diagram to show the bonding present in the H_3O^+ ion.

(e) In the complex ion: $[Al(OH)(H_2O)_5]^{2+}$ what is the oxidation number of the *Al*?

_____

_____

_____

7. Write the equilibrium constant expression for the following equilbria:

(a)

Equation	$BaSO_4(s) \leftrightarrows Ba^{2+}(aq) + SO_4^{2-}(aq)$
Equilibrium constant expression	

(b)

Equation	$2CrO_4^{2-}(aq) + 2H^+(aq) \leftrightarrows Cr_2O_7^{2-}(aq) + H_2O(l)$
Equilibrium constant expression	

8. The white solid bismuth oxychloride reacts with concentrated hydrochloric acid to establish the following equilibrium:

$BiOCl(s) + 2H^+(aq) \leftrightarrows Bi^{3+}(aq) + Cl^-(aq) + H_2O(l)$

Three test tubes of the equilibrium system, 'A', 'B' and 'C' were prepared by adding excess BiCl to concentrated hydrochloric acid.

Complete the table below by indicating the direction of the expected shift in equilibrium immediately following the changes stated in the table. Give the reason for the shift.

Test tube	Change	Direction of shift in equilibrium ('left', 'right' or 'no change')	Reason for shift
A	3 mL of water is added		
B	A few drops of concentrated nitric acid are added		
C	A few drops of concentrated silver nitrate solution are added		

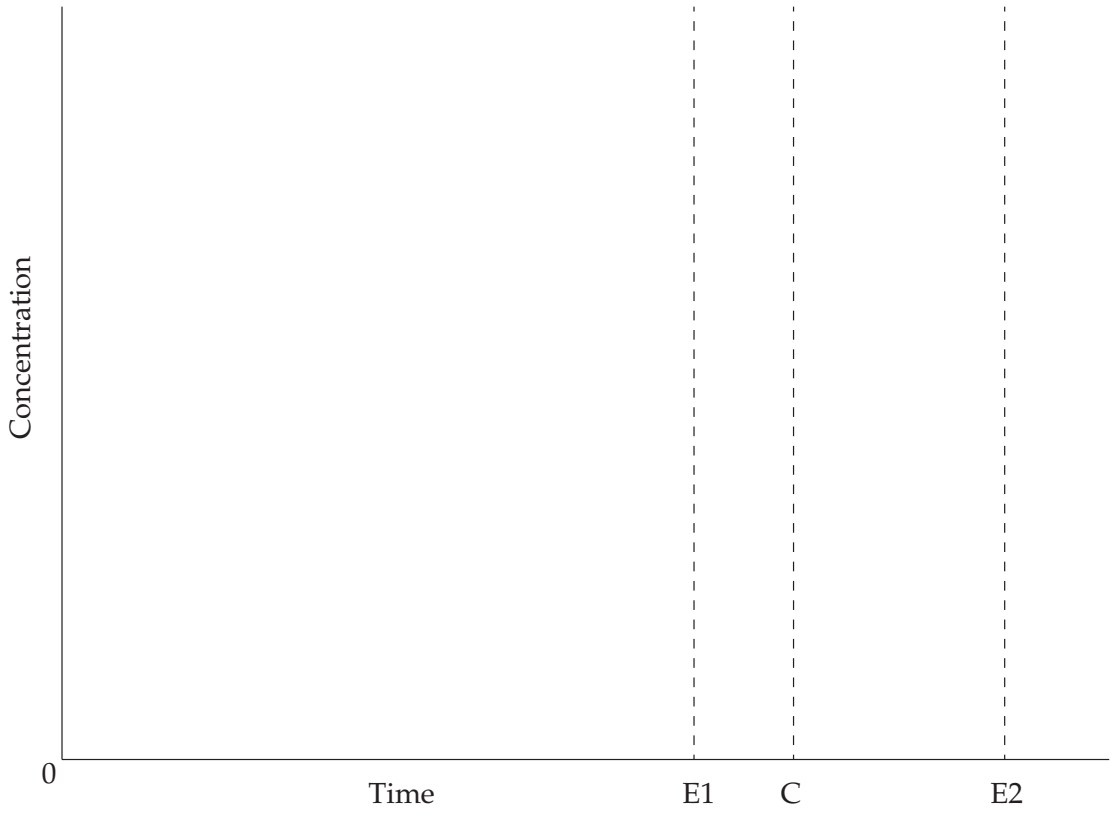
9. Silver chloride, Ag*Cl*(*s*), is very sparingly soluble in water. However, it is soluble in ammonia solutions, due to the formation of the $[Ag(NH_3)_2]^+$ ion as shown in the equilibrium below:

$AgCl(s) + 2NH_3(aq) \leftrightarrows [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

The equilibrium constant, K, for this system is greater than 1

A student mixes the reactants at time t = 0.

(a) On the axes below, draw separate curves to show how the concentrations of $NH_3(aq)$ and $[Ag(NH_3)_2]^+(aq)$ change with time as the system approaches, and finally reaches, equilibrium (Time E1). Clearly label your curve for $NH_3(aq)$ and your curve for $[Ag(NH_3)_2]^+(aq)$. Continue your curves from Time E1 to Time C.



(b) At Time = C, as shown on the axis, a small quantity of concentrated Na*Cl* solution is added to the system, and the system is then again allowed to reach equilibrium at Time E2. On the same axes above, show how the concentrations of $NH_3(aq)$ and $[Ag(NH_3)_2]^+(aq)$ would change in response to the addition of Na*Cl* solution from Time C until equilibrium is reached at Time E2.

10. Consider the following system at equilibrium.

$4NH_3(g) + 5O_2(g) \leftrightarrows 4NO(g) + 6H_2O(g) + 920\ kJ$

Indicate in the table below whether there would be an increase, decrease, or no change in the concentration of $NH_3(g)$ after the changes given in the table are imposed on the system and **equilibrium has been re-established**. Provide a brief explanation for the observation.

Change	**Change in concentration of $NH_3(g)$ (circle the correct response)**	**Brief explanation**
The volume of the reaction vessel is doubled	• increase • decrease • no change	
The temperature of the reaction system is doubled	• increase • decrease • no change	
$N_2(g)$ is injected into the reaction system while keeping the volume constant	• increase • decrease • no change	
Water vapour is injected into the reaction system while keeping the volume constant	• increase • decrease • no change	

11. Sodium carbonate is used as a primary standard in acid–base titrations, while sodium hydroxide is not.

(a) Explain why this is so.

Sodium hydrogencarbonate is often used to increase the pH in swimming pools.

(b) Explain, with the aid of suitable equations, how adding sodium hydrogencarbonate affects the pH of the water.

(c) Briefly explain why methyl orange is an inappropriate indicator to use in a titration between sodium hydroxide and acetic (ethanoic) acid.

12. A student was given a 0.100 mol L^{-1} sulfuric acid solution and a 0.200 mol L^{-1} hydrochloric acid solution. She tested the pH of the solutions using a pH meter and found that the pH of the sulfuric acid solution was higher than that of the hydrochloric acid solution. Explain this observation. Include equations in your answer.

13. Astudent titrated an approximate 0.1 mol L^{-1} solution of hydrochloric acid against a standard solution of 0.200 mol L^{-1} sodium carbonate in order to determine the exact concentration of the acid.

The reaction occurring in the titration is shown below:

$Na_2CO_3 + 2\ HCl \leftrightarrows 2\ NaCl + CO_2 + H_2O$

The student rinsed a 50 mL burette with distilled water and filled it with hydrochloric acid. He also rinsed a conical flask with distilled water and pipetted 25.0 mL of the sodium carbonate solution into the conical flask. A few drops of phenolphthalein were then added to the conical flask. He added the hydrochloric acid from the burette into the conical flask until there was a permanent colour change.

The student made two mistakes in his method. Complete the table below by stating

- each mistake
- the effect the mistake had on the volume of HC*l* delivered from the burette
- why the volume of HC*l* was affected in the way stated
- the correct technique

	Mistake 1	**Mistake 2**
Description of mistake		
Effect on volume of HCl		
Reason HCl volume is affected as stated above		
Correct technique		

14. Like water, ammonia is able to react with itself, in the process known as 'self-ionisation'. The equation for the self-ionisation of ammonia is below.

$NH_3(aq) + NH_3(aq) \leftrightarrows NH_4^+(aq) + NH_2^-(aq)$

(a) Identify the conjugate acid and base pairs in the reaction.

$NH_3(aq) \quad + \quad NH_3(aq) \quad \leftrightarrows \quad NH_4^+(aq) \quad + \quad NH_2^-(aq)$

_____

_____

(b) At standard temperature and pressure, the equilibrium constant, K, for this reaction is about 1×10^{-30}. The self-ionisation of ammonia is an endothermic process. Will the value of K be less than or greater than 1×10^{-30} at temperatures greater than 0°C? Explain.

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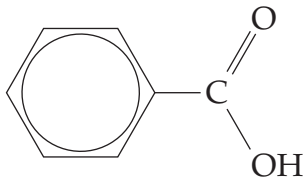
15. Benzoic acid is found in many berries and some other fruits and is used as a food preservative. The structure of benzoic acid is shown below. In an aqueous environment, benzoic acid ionises and exists in equilibrium with the benzoate ion.



(a) Write the equation for the reaction between benzoic acid and water.

(b) Draw the structure (either benzoic acid or the benzoate ion) that would predominate in the acidic environment of the stomach.

(c) Explain, using equations and the principles of equilibrium, how a solution of benzoic acid and the benzoate ion may behave as a buffer.

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(d) The ease with which a substance is excreted from the body is determined in part by its solubility in water. Is benzoic acid more or less miscible with water than acetic (ethanoic) acid, and hence more or less readily excreted from the body? Explain.

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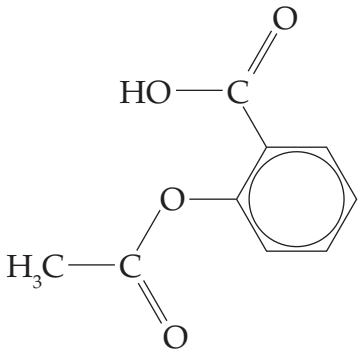
16. Write a relevant equation or equations to explain each of the observations shown in the table below.

Observation	Explanatory equation(s)
The pH of a $NaHSO_4$ solution is 5	
$Mg(OH)_2$ is basic	
A solution of Na_2HPO_4 is basic, while a solution of KH_2PO_4 is acidic	

17. The active ingredient in aspirin tablets (acetylsalicylic acid) has the structure shown below. When acetylsalicylic acid is placed in water, some of it dissolves and ionises to form its conjugate base.



(a) Write the equation for the ionisation of acetylsalicylic acid in the space below, and identify the conjugate acid and base pairs in the reaction. Connect the acid-base pairs with a line and label the conjugate acid in the pair 'A', and the conjugate base 'B'.

(b) Acetylsalicylic acid is a weak acid, and only partly ionises in water. It is poorly soluble in water, and far less soluble than a related compound, acetic acid (CH_3COOH). Explain why the water solubility of molecular acetylsalicylic acid is poor relative to that of CH_3COOH.

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18. Water is able to react with itself in the process known as 'self-ionisation' or 'auto-ionisation'.

(a) Write the equation for the self-ionisation of water.

_____

_____

(b) At 25°C, the value of K_w is approximately 1.0×10^{-14}. At 10°C, the value of K_w is approximately 2.9×10^{-15}.

What are the relative concentrations of H^+ and OH^- ions in a neutral water solution at 25°C? Circle the correct answer.

$[H^+] > [OH^-]$ $[H^+] < [OH^-]$ $[H^+] = [OH^-]$

What are the relative concentrations of H^+ and OH^- ions in a neutral water solution at 10°C? Circle the correct answer.

$[H^+] > [OH^-]$ $[H^+] < [OH^-]$ $[H^+] = [OH^-]$

(c) Consider the values of K_w at 10°C and 25°C, and state whether the self-ionisation of water is an endothermic or exothermic process. Give a reason to support your answer.

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19. Oxalic acid dihydrate ($H_2C_2O_4.2H_2O$) is a primary standard used to standardise potassium permanganate solutions, which can be used for volumetric analysis.

(a) List two properties of oxalic acid that make it a good primary standard.

_____

_____

(b) A student was asked to prepare a standard solution of oxalic acid of approximate concentration 0.05 mol L^{-1}. The equipment listed below was available.

- electronic balance
- distilled water (20 L)
- beakers (20 mL, 50 mL, 100 mL, 250 mL)
- stirring rod
- volumetric flasks (250 mL, 500 mL)
- wash bottle
- oxalic acid ($H_2C_2O_4.2H_2O$) (5 g)
- weighing boats

Give a step-by-step, detailed description of a procedure for preparing the standard oxalic acid solution. Perform and include any necessary calculations

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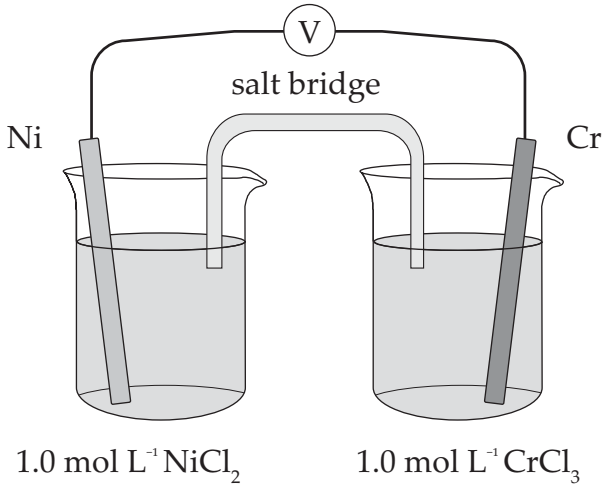
20. Consider the following diagram of an electrochemical cell consisting of a potassium nitrate salt bridge and half cells containing:

I a 1 mol L^{-1} nickel(II) chloride solution and a nickel electrode;

II a 1 mol L^{-1} chromium(III) chloride solution and a chromium electrode.



(a) Label the cell diagram, showing anode, cathode, direction of electron flow and direction of flow of ions (both positive and negative) in the salt bridge.

(b) Write an equation for the overall reaction in the cell.

_____

_____

(c) Calculate the EMF (voltage) for the cell at standard conditions.

_____

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(d) Why would a potassium carbonate salt bridge be an inappropriate choice for this electrochemical cell?

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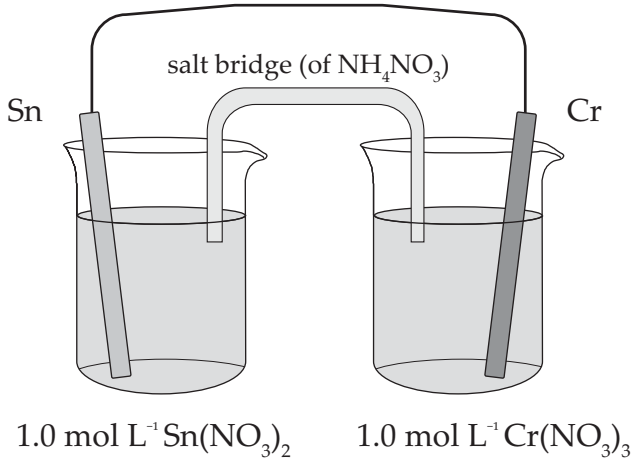
21. An electrochemical cell consists of a tin electrode in a solution of 1.0 mol L^{-1} tin(II) nitrate, to create a Sn/Sn^{2+} half cell, and a similarly constructed half cell composed of a chromium electrode in a solution of 1.0 mol L^{-1} chromium(III) nitrate. The two electrodes are joined by a piece of copper wire. A salt bridge, as shown in the diagram below, joins the two solutions.



(a) On the diagram, label

(i) the anode

(ii) the direction of electron flow

(iii) the direction of cation flow in the salt bridge.

(b) Write the balanced anode and cathode reactions.

(i) Anode: _____

(ii) Cathode: _____

(c) Why does the rate of production of electrical current from an electrochemical cell decrease as it operates?

_____

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(d) During the operation of an electrochemical cell, why is it important that the anode and cathode do not come into contact with each other?

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22. A nickel-cadmium cell consists of a positive nickel(III) oxide-hydroxide, NiO(OH), electrode and a negative metallic cadmium electrode plate. The following processes occur during discharge:

    (i) metallic cadmium reacts in the presence of hydroxide ions to produce cadmium(II) hydroxide; and

    (ii) nickel(III) oxide-hydroxide reacts in the presence of water to produce nickel(II) hydroxide and hydroxide ions.

    (a) Write the half-equations for the reactions occurring at the anode and cathode and the overall redox equation for the Ni-Cd cell.

Anode half-equation:
Cathode half-equation:
Overall equation:

    (b) The electrolyte in the Ni-Cd cell is usually a solution of potassium hydroxide. State the role of an electrolyte in an electrochemical cell. _____

_____

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    (c) The standard reduction potential for cadmium metal is –0.4 V. Explain the role of the hydrogen half-cell in determining this value. Comment on the significance of the negative value. You may use diagrams to aid your explanation.

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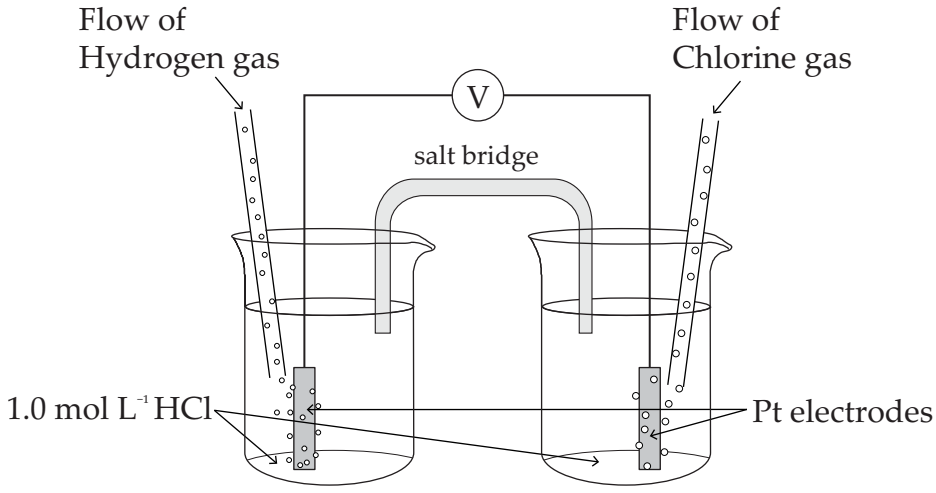
23. Below is a representation of an electrochemical cell, which involves the reaction of hydrogen and chlorine:



(a) Give the half equation for the reactions occurring at the anode and at the cathode and write an overall redox equation for the reaction occurring in the cell.

Anode half-equation:
Cathode half-equation:
Overall equation:

(b) Using the standard reduction potential values from the data sheet, calculate the maximum voltage (e.m.f.) that could be produced by this cell.

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(c) Show the direction of flow of electrons in the external circuit by means of an arrow on the above diagram

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(d) Suggest a reason why platinium is used for the electrodes.

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24. When a few drops of concentrated sodium bismuthate solution, $NaBiO_3(aq)$, are added to a small volume of manganese(II) chloride solution, a deep purple solution is formed. The purple colour of the solution suggests that manganese is transformed to the +7 oxidation state as the permanganate ion, MnO_4^-. The colourless bismuth ion, $Bi^{3+}(aq)$, is also formed.

(a) Write the oxidation and reduction half equations, and the overall redox equation, for this reaction.

Oxidation half-equation:

_____

Reduction half-equation:

_____

Overall redox equation:

_____

(b) In redox titrations involving permanganate or dichromate, the permanganate and dichromate must often be acidified. State why concentrated HC*l* is not suitable for acidifying permanganate or dichromate solutions in redox titrations.

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25. A student was given three bottles, A, B and C. Each bottle was labelled with its contents as shown in the table below.

Bottle	Contents
A	46.5 mL of 0.010 mol L^{-1} HCl
B	65.7 mL of 0.0555 mol L^{-1} HNO_3
C	20.9 mL of 0.4161 mol L^{-1} NaOH

(a) Calculate the pH of the NaOH solution. _____

_____

_____

_____

(b) The contents of all three bottles are placed in one beaker and mixed thoroughly. Calculate the pH of the final mixture.

26. A bottle of anhydrous oxalic acid ($H_2C_2O_4$) was found to be contaminated with potassium chloride. 2.05 g of the mixture was dissolved in distilled water and the volume made up to 250.0 mL in a volumetric flask. 20.0 mL aliquots of the solution were titrated against 0.115 mol L^{-1} sodium hydroxide solution and the following results were obtained:

Titration Results	Trials (mL)			
	1	2	3	4
Final volume	32.05	32.10	31.11	33.25
Initial volume	0.50	2.45	1.40	3.65
Titre				

(a) Write an equation for the reaction between oxalic acid and sodium hydroxide.

(b) Complete the table and calculate the average titre.

(c) Calculate the concentration of the oxalic acid solution.

(d) Calculate the percentage purity of the oxalic acid mixture.

(e) What would be an appropriate indicator for this titration? Justify your answer.

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27. An experiment was carried out to calculate the purity of a sample of calamine ($ZnCO_3$).

4.54 g of impure calamine was added to 50.0 mL of 2.00 mol L^{-1} HC*l*.

The resulting solution was filtered into a volumetric flask and made up to 250.0 mL.

25.00 mL aliquots of this solution were then titrated against 0.105 mol L^{-1} of NaOH solution and the results shown below:

Burette readings (mL)	Titrations			
	1	2	3	4
Final volume	32.50	37.25	43.15	38.40
Initial volume	0.00	5.50	11.30	6.60
Titre				

(a) Complete the table and calculate the titration volume.

_____

_____

(b) Calculate the number of moles of hydrochloric acid present in the 25.00 mL aliquots.

_____

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(c) Calculate the total number of moles of hydrochloric acid present in the 250.0 mL flask and hence calculate the % purity of the calamine.

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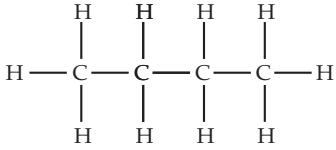
Chapter

4

Organic Chemistry

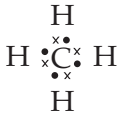
4.1 HYDROCARBONS

Organic chemistry is the chemistry of carbon compounds (other than metallic carbonates, hydrogencarbonates and the oxides of carbon). These compounds are called **hydrocarbons**.



The electron configuration of carbon is $1s^2\ 2s^2\ 2p^2$, or 2, 4, and as such, carbon atoms form four very strong covalent bonds in order to obtain a stable electron configuration.

Example



In methane, carbon has four single bonds

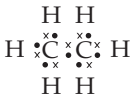
In carbon dioxide, carbon has two double bonds

In hydrogen cyanide, carbon has a triple bond and a single bond

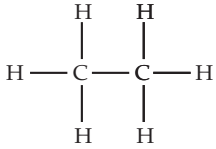
The central role of carbon in organic chemistry depends on the fact that carbon atoms can form a virtually unlimited number of straight chain, branched chain and ring molecules with a succession of strong covalent carbon-carbon bonds.

Saturated hydrocarbons are those which contain carbon and hydrogen atoms with only single bonds between carbon atoms. There are several ways to show the molecule.

Example ethane, C_2H_6



electron dot diagram



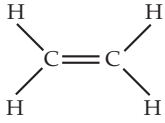
structural formula

CH_3CH_3

condensed formula (semi structural)

Unsaturated hydrocarbons contain one or more double or triple bonds between carbon atoms.

Example ethene, C_2H_4



ethyne, C_2H_2

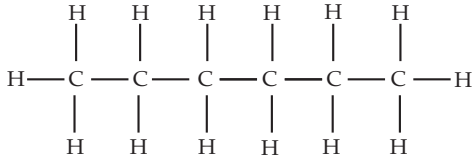
Aliphatic, alicyclic and aromatic hydrocarbons are the different types of hydrocarbons.

Aliphatic hydrocarbons

Aliphatic hydrocarbons are those with open chains of carbon atoms.

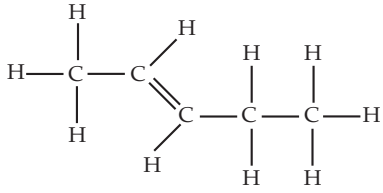
Alkanes are saturated aliphatic hydrocarbons with chain-like molecules.

Example hexane, C_6H_{14}



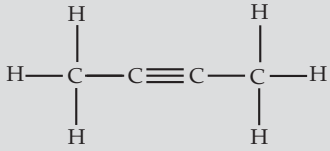
Alkenes are unsaturated and contain at least one double bond between carbon atoms.

Example pent-2-ene



Alkynes contain at least one triple bond between carbon atoms.

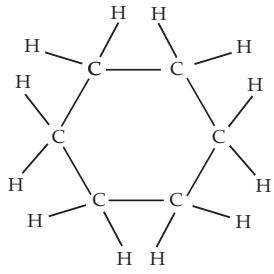
Example but-2-yne



Alicyclic hydrocarbons are formed when the ends of a chain are bonded to each other in a ring.

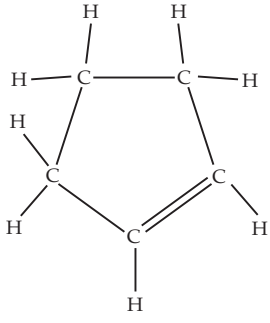
Cycloalkanes are saturated and have ring-like molecules.

Example cyclohexane, C_6H_{12}

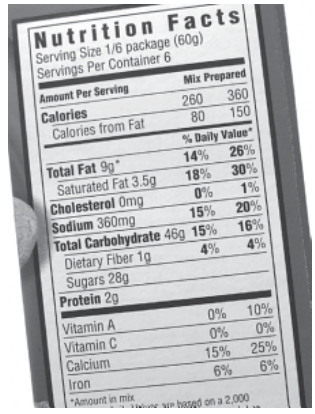


Cycloalkenes are unsaturated and have ring like molecules.

Example cyclopentene, C_5H_8



Margarine is a butter substitute that contains both saturated and unsaturated hydrocarbons.

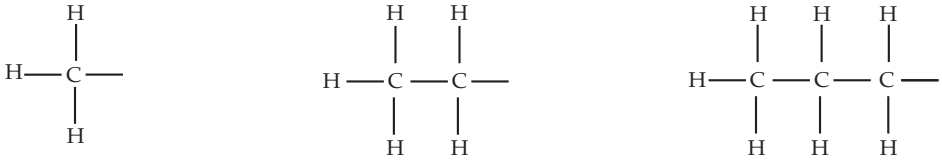


Aromatic hydrocarbons are hydrocarbons which contain a benzene ring.

Example Benzene methyl benzene

An alkyl group, or hydrocarbon radical, is one which has lost one hydrogen atom with its associated electrons. It acts as a substituent to a carbon chain or ring.

Example methyl ethyl propyl



Valence electrons not involved in bonding within the carbon-carbon chains are often used in forming bonds with other atoms, i.e. H, N and O or even in multiple bonds with other carbon atoms.

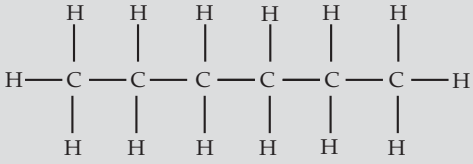
The principal classes of oxygen-containing organic compounds are alcohols, aldehydes, ketones, carboxylic acids and esters. The principal classes of nitrogen containing organic compounds are amines and amides. α-amino acids contain both the amine and carboxylic acid functional groups.

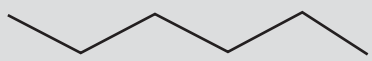
Line structures, or skeletal structures (not examinable)

In addition to structural and condensed formulae it is possible to depict hydrocarbons using line structures. Here, a line represents a single bond. Junctions between lines are carbon atoms and it is assumed that each carbon atom has sufficient hydrogen atoms attached to it to give it four bonds. NB: These structures are not accepted in the examination. You should show all atoms and bonds.

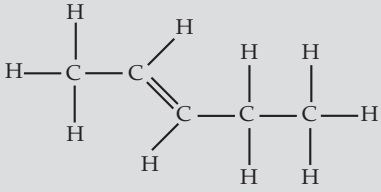
Examples

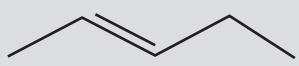
hexane



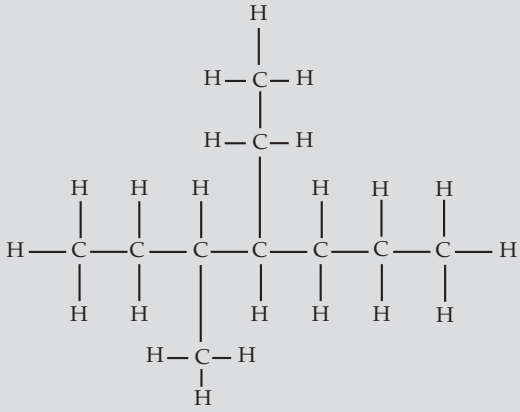


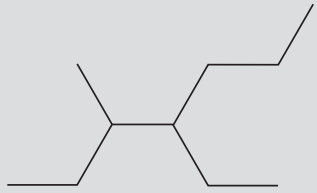
2-pentene (pent-2-ene)



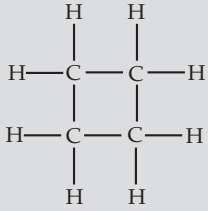


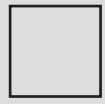
4-ethyl-3-methylheptane



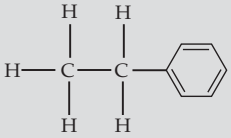


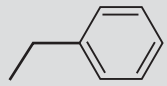
cyclobutane



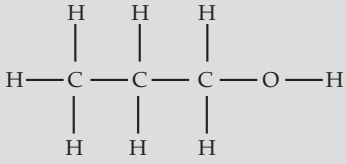


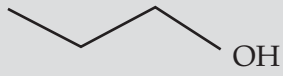
ethylbenzene



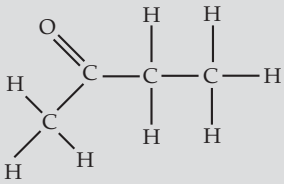


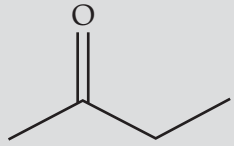
propan-1-ol



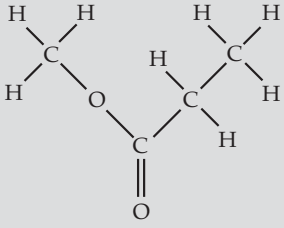


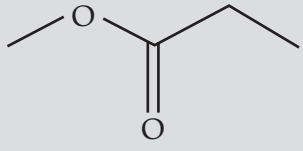
butanone





methylpropanoate



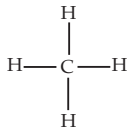
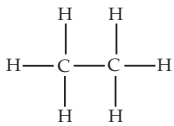
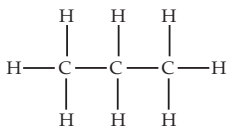
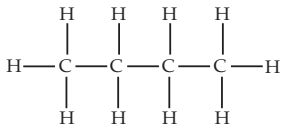
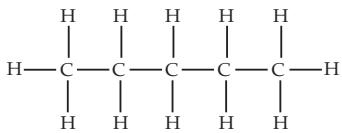
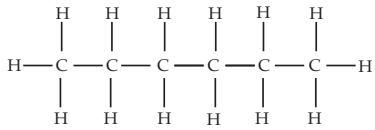
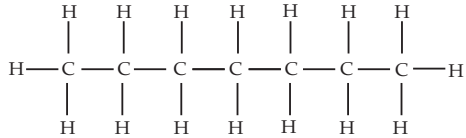
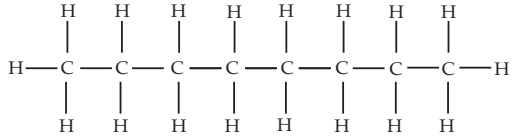


4.2 HOMOLOGOUS SERIES

A group or class of compounds related to each other by a general molecular formula constitutes an homologous series.

Each member of the series differs from the next member in the series by having an extra CH_2 in their formula and is called a Homologue.

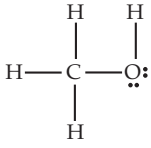
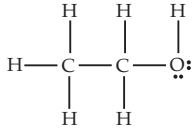
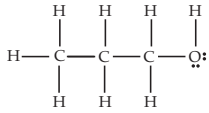
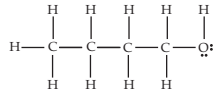
All the members of the series, or homologues, have the same general molecular formula. For example alkanes, C_nH_{2n+2} which refers to the alkane chain.

	Full structural formulae	Semi-structural formulae and condensed formulae
Methane		CH_4
Ethane		CH_3CH_3
Propane		$CH_3CH_2CH_3$
Butane		$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$
Pentane		$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$
Hexane		$CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_4CH_3$
Heptane		$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_5CH_3$
Octane		$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_6CH_3$

Homologues have the same functional group(s) and similar chemical properties

There is a regular trend in their physical properties, such as the increase in melting points and boiling points. This is due to increased dispersion forces as the molar mass increases.

Example

	methanol	ethanol	propan-1-ol	butan-1-ol
				
Boiling point (°C)	64.7	78.3	97.2	117.7

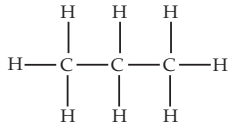
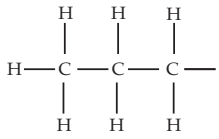
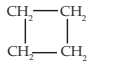
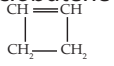
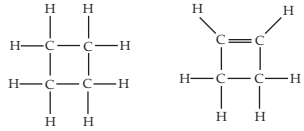
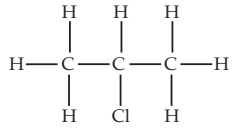
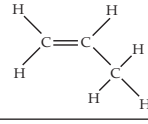
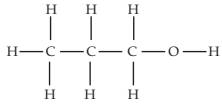
Alcohols have hydrogen bonding as their predominant intermolecular forces, but increasing chain length increases dispersion forces so their boiling points increase accordingly.

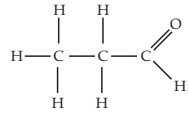
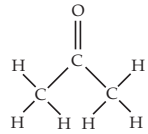
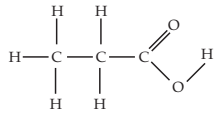
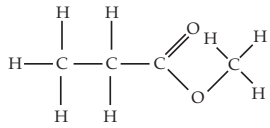
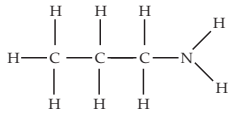
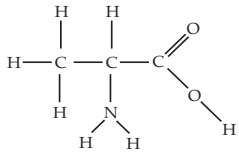
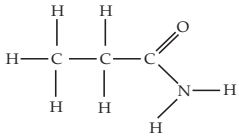
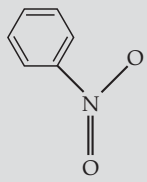
They also become less soluble in water as the proportion of the molecule that is non-polar increases with increasing chain length, i.e. butan-1-ol is less soluble than methanol.

4.3 FUNCTIONAL GROUPS

Each homologous series is characterised by a particular group which is specific to that particular series only. This characteristic is known as the Functional Group.

A functional group is a non-hydrocarbon part of an organic molecule or an alkyl group. These functional groups can contribute to the organic molecule's characteristic chemical properties. In addition they can influence physical properties, since they dictate the intermolecular forces present.

	General formulae	Naming suffix (prefix)	Example	Structural formula (showing bonds)
Alkanes	C_nH_{2n+2}	-ane	propane $CH_3CH_2CH_3$	
Alkyl group	C_nH_{2n+1}	-yl	propyl $CH_3CH_2CH_2$-	
Alicyclic cycloalkanes cycloalkenes	C_nH_{2n} C_nH_{2n-2}	cyclo- -ane cyclo- -ene	cyclobutane  cyclobutene 	
Halogenoalkanes (alkyl halides)	R-X X is a halogen	halo-	2-chloropropane $CH_3CHClCH_3$	
Alkenes	C_nH_{2n}	-ene	propene CH_2CHCH_3	
Alcohols	R-OH	-ol (hydroxy)	propan-1-ol $CH_3CH_2CH_2OH$	

	General formulae	Naming suffix (prefix)	Example	Structural formula (showing bonds)
Aldehydes	R-CHO	-al (formyl-)	propanal CH_3CH_2CHO	
Ketones	R-COR′	-one (oxo-)	propanone CH_3COCH_3	
Carboxylic acids	R-COOH	-oic acid	propanoic acid CH_3CH_2COOH	
Esters	R-COOR′	-yl -oate	methyl propanoate $CH_3CH_2COOCH_3$	
Amines	R-NH_2	-amine (amino-)	1-propanamine $CH_3CH_2CH_2NH_2$	
α-amino acids	R(NH_2)COOH	amino- -oic acid	2-amino-propanoic acid $CH_3CH(NH_2)COOH$	
Amides	R-$CONH_2$	-amide (amido)	propanamide $CH_3CH_2CONH_2$	
Nitro	R-NO_2	nitro-	nitrobenzene $C_6H_5NO_2$	

4.4 NOMENCLATURE (NAMING OF ORGANIC COMPOUNDS)

Many organic compounds have names derived from the names of their corresponding alkanes.

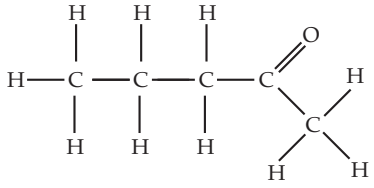
The Rules

1. Count the longest continuous chain of carbon atoms that contains the main functional group. This give you the stem name:

No of C's	1	2	3	4	5	6	7	8
Stem	meth-	eth-	prop-	but-	pent-	hex-	hept-	oct-

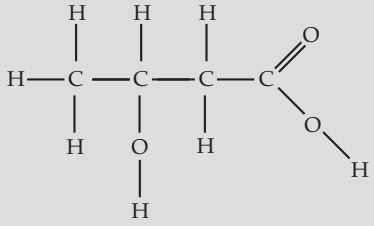
2. The main functional group of the molecule provides the end of the name, or the suffix.
3. Number the longest carbon chain so that it gives the functional group the lowest number.

Example pentan-2-one rather than pentan-4-one

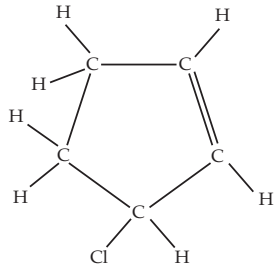


4. Any side chains (alkyl groups) or less important functional groups are included alphabetically as prefixes at the start of the name and given numbers corresponding to the carbon to which they are attached.

Example 3-hydroxybutanoic acid, since, –COOH take precedence over –OH



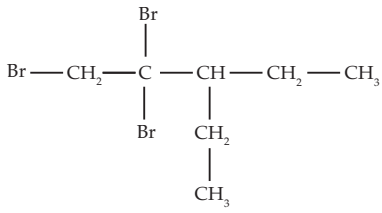
Example 3-chlorocyclopentene



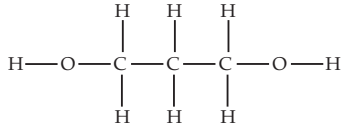
N.B. With unsaturated cyclic compounds counting starts before the double or triple bond.

5. If there is more than one of the same side chains or functional groups use di-, tri-, tetra- etc.. before their part of the name. These do not count towards the alphabetical order.

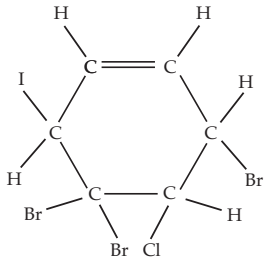
Example 1,2,2-tribromo-3-ethylpentane



Example propane-1,3-diol



Example 4,4,6-tribromo-5-chloro-3-iodocyclohexene



IUPAC priority of functional groups

most important

carboxylic acids
esters
amides
aldehydes
ketones
alcohols
amines
alkenes
alkynes
alkanes

4.5 ISOMERS

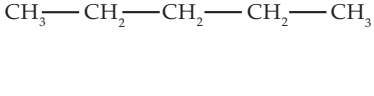
Isomers are substances that have the same molecular formula, but a different structural formula.

4.5.1 Structural isomers

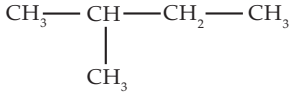
There are two main types of structural isomers.

Chain structural isomers have the same molecular formula but different chain length.

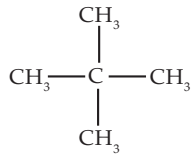
Example



pentane



methylbutane

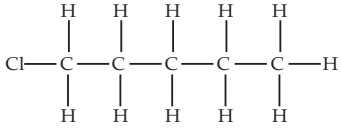


dimethylpropane

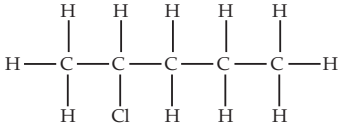
These have similar chemical properties but different physical properties because their molecules are a different shape.

Position structural isomers have the same molecular formula but with functional groups attached at different parts of the chain.

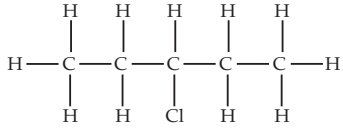
Examples



1-chloropentane



2-chloropentane



3-chloropentane

These have different physical properties and their chemical properties are often different too.

4.5.2 Cis-trans isomerism (Geometric isomers)

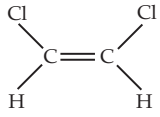
Geometric isomers have the same molecular formula and the atoms are connected in the same way but they are arranged differently in space.

They can only exist where there is a carbon to carbon double bond (as this restricts rotation) and where there are two different radicals attached to each of the double bonded carbon atoms.

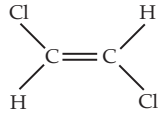
cis isomers have similar groups on the same side of the double bond.

trans isomers have similar groups attached diagonally opposite across the double bond.

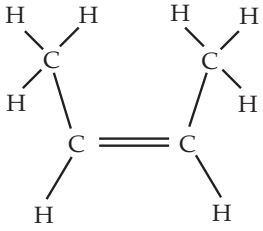
Example



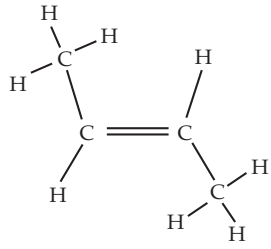
cis-1,2-dichloroethene



trans-1,2-dichloroethene



cis-but-2-ene



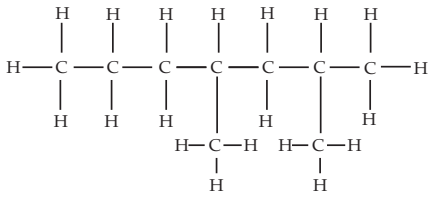
trans-but-2-ene

Geometric isomers have different physical properties because the different positions of the groups affect the shape and hence the intermolecular forces present.

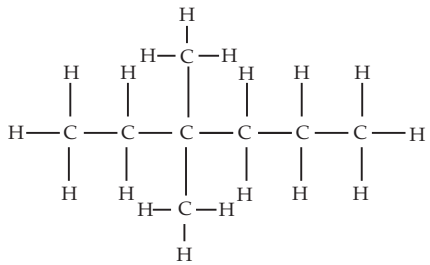
Their chemical properties are usually similar, but this depends upon the relative position of the groups present.

Set 1. Nomenclature

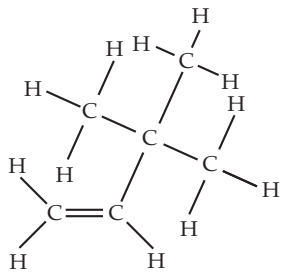
1. Classify the following hydrocarbons as saturated or unsaturated and name them:
   (a) $CH_3CH_2CH_2CH_3$
   (b) $CH_2CHCH_2CH_3$
   (c) $CH_3CH_2CH(CH_3)CH_2CH_3$
   (d) $CH_3CH_2CH_2C(CH_3)C(CH_3)CH_2CH_3$
2. Write condensed formulae for the following hydrocarbons and name them:
   (a)



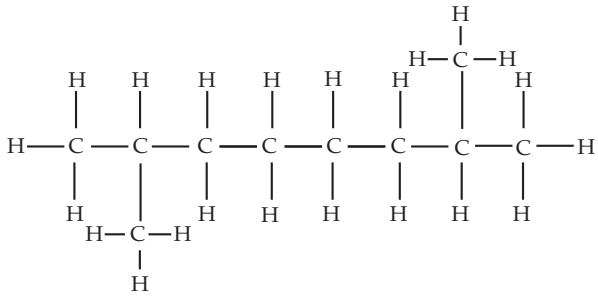
   (b)



   (c)



   (d)



3. Draw structural formulae for the following hydrocarbons, showing all bonds and hydrogen atoms, and name them:

   (a) $CH_3(CH_2)_2CH(CH_2CH_3)CH_2CH_3$

   (b) $CH_3CH(CH_3)(CH_2)_3CH(CH_3)CH_3$

   (c) $CH_3CH(CH_3)CH(CH_3)CH_3$

   (d) $CH_3(CH_2)_4CH(CH_3)CH_3$

4. Draw structural formulae for the following hydrocarbons and classify them as aliphatic, alicyclic or aromatic:

   (a) methylpropene

   (b) cyclopentene

   (c) 3-ethyl-2-methylheptane

   (d) 1,4-dimethylbenzene

5. Identify the functional group(s) in each of the following then name them using IUPAC conventions.

   (a) $CH_3CH_2CH_2CH_2OH$

   (b) $CH_3CH_2CHCHCH_2CH_3$

   (c) $CH_3CH_2CH_2CH(CH_2CH_3)CH_2CH(CH_3)CH_3$

   (d) $CH_2Cl(CH_2)_3CHBrCHBrCH_2CH_3$

   (e) $CH_3CH_2CH_2CH_2CHO$

   (f) $CH_3CH_2CH(OH)CH_2CH_3$

   (g) $CH_3CH_2COCH_2CH_2CH_3$

   (h) $CH_3CH_2CH_2CH_2COOH$

   (i) $CH_3CH_2CH_2CH_2NH_2$

   (j) $CH_3CH_2COOCH_2CH_2CH_3$

   (k) $CH_3CH_2CH_2CONH_2$

   (l) $CH_3CH_2CH(NH_2)COOH$

   (m) $CH_3CH_2CH_2C(CH_3)_2CH_2COOH$

   (n) $CH_3CH_2CHCHCH_2CH_2Cl$

   (o) $CH_3CHClCH(CH_3)CH_2NH_2$

   (p) $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_2CH_3$

   (q) $CH_3CH_2COCH_2CH_2CH_2OH$

   (r) $CH_3CH_2OOCCH_2CH_3$

   (s) $CH_2ClCH(CH_3)CH_2CH_2CONH_2$

(t) $CH_3CH(OH)(CH_2)_3CH(OH)CH_2CH_3$

(u) $OHCCH_2CH_2CH_2Br$

(v) $CH_3CH_2CH(NH_2)(CH_2)_2CH(NH_2)CH_2CH_3$

(w) $CH_2(OH)CH_2CH_2COOH$

6. Write condensed structures for the following:

(a) butan-2-ol

(b) 2,3,3-triiodopentane

(c) propanal

(d) 3,3-dimethylhexan-2-ol

(e) butanoic acid

(f) pentylamine / 1-pentanamine

(g) 3-hydroxyheptanoic acid

(h) pentan-3-one

(i) 4-aminohexanoic acid

(j) butanamide

(k) 5,6-dichlorohepta-2,4-diene

(l) 4-oxo-pentanoic acid

7. Draw full structures for the following:

   (a) chlorocyclobutane

   (b) methylbenzene

   (c) *cis*-pent-2-ene

   (d) 1,2,4-triiodocyclohexene

   (e) methylpropanoate

   (f) 3-chlorobutanoic acid

   (g) 4,4-dimethylpentanal

   (h) 1,1,2-tribromopropene

   (i) 3-iodo-1-propanamine

   (j) butan-2-one

   (k) ethanedioic acid

   (l) pentane-1,2,4-triol

   (m) 1,3,5-triethylbenzene

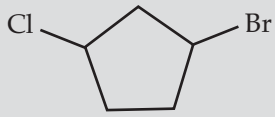
   (n) 3-aminopropanoic acid

   (o) hexanamide

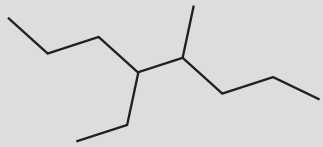
8. Name the following hydrocarbons from their line structures:

(a)

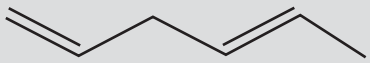
(b)



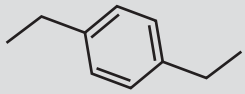
(c)



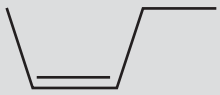
(d)



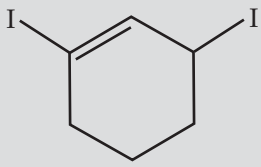
(e)



(f)



(g)



9. Draw line structures for the following:

(a) methylcyclopropane

(b) 1,3-diethylbenzene

(c) *trans*-3-hexene

(d) 1,2-cyclopentanediol

(e) ethylpentanoate

(f) 2-hydroxypropanoic acid

(g) 2,3-dibromopropanal

(h) tetrachloroethene

(i) ethylamine (ethanamine)

(j) propanone

(k) propanedioic acid

(l) 1-penten-3-one

(m) nitrobenzene

(n) 3-ethyl-2,4-dimethylpentan-1-ol

(o) propanamide

(p) 1-chloro-3-methylbenzene

(q) 2-aminopropanoic acid

(r) butylbutanoate

Set 2. Isomers

1. Draw structural formulae and name all isomers with the molecular formula C_6H_{14}.

2. Draw structural formulae and name all isomers with the molecular formula C_5H_{10}.

3. Draw all of the isomers of trimethylbenzene.

4. Draw the following and determine which ones exhibit cis/trans isomerism.

   (a) pent-2-ene

   (b) 1,1,2-trichlorobut-1-ene

   (c) 2,4-dimethylhex-1-ene

   (d) 1,2,3-tribromopropene

   (e) buta-1,3-diene

4.6 PROPERTIES, PREPARATION AND REACTIONS OF THE HYDROCARBONS

4.6.1 Alkanes

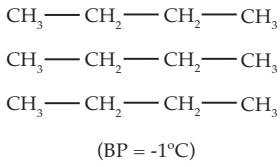
Alkanes are hydrocarbons with the general formula C_nH_{2n+2}.

Every carbon atom has four single bonds connected to other atoms.

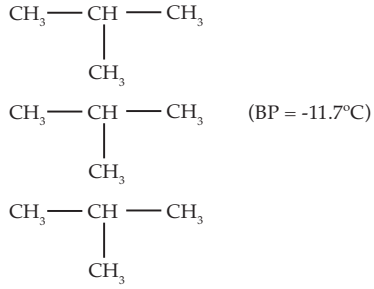
The melting and boiling points of alkanes increases as their molecular mass increases since dispersion forces become greater with increasing chain length.

Their melting and boiling points decrease as their chains become more branched. There is less opportunity for dispersion forces to have an effect as the molecules aren't able to get close enough together.

Example butane versus methylpropane



Dispersion forces are most effective when molecules can get close together



Branching prevents molecules from getting close together so dispersion forces are less effective

Reactions of alkanes

Combustion

Alkanes combust in air to produce water and carbon dioxide (or carbon monoxide in limited oxygen).

Example complete and incomplete combustion of methane

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g)$$

Halogenation

Alkanes undergo substitution reactions with halogens in the presence of UV light.

Example substitution of methane by chlorine

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

then $$CH_3Cl + Cl_2 \xrightarrow{UV} CH_2Cl_2 + HCl$$

then $$CH_2Cl_2 + Cl_2 \xrightarrow{UV} CHCl_3 + HCl$$

then $$CHCl_3 + Cl_2 \xrightarrow{UV} CCl_4 + HCl$$

With plenty of Cl_2 and UV light the reaction is very difficult to stop and will proceed until all hydrogens have been substituted. So products are fairly unpredictable.

Cracking

The larger alkanes obtained from the distillation of petroleum can be split (or 'cracked') into smaller, more useful ones by thermal and catalytic cracking. This also produces unsaturated hydrocarbons like alkenes, used to make polymers.

Example

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \xrightarrow{\text{catalyst}} CH_2CH_2 + CH_3CH_2CH_2CH_2CH_2CH_3$$

octane ethene hexane

4.6.2 Alkenes

Alkenes are unsaturated hydrocarbons with the general formula C_nH_{2n}.

Their names are based on alkanes, but with the suffix –ene.

They possess at least one carbon-to-carbon double bond.

Alkenes have physical properties similar to alkanes.

Their chemical properties are largely influenced by the double bond, so they are more reactive than alkanes.

The presence of the double bond also gives rise to the possibility of geometric (cis-trans) isomerism.

Reactions of alkenes

Combustion

Alkenes combust in air to produce water and carbon dioxide (or carbon monoxide in limited oxygen).

Example

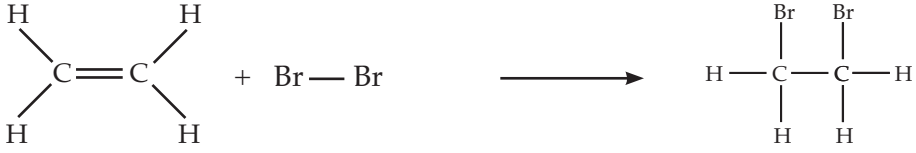
$$CH_2CH_2(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

Addition reactions

Alkenes can undergo a variety of addition reactions, where two new atoms are added across the double bond, converting unsaturated compounds into saturated compounds.

Halogenation

Example

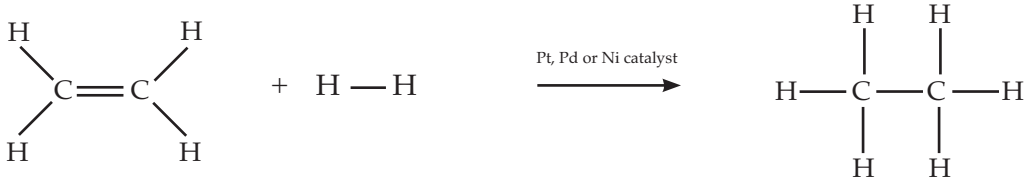


ethene bromine 1,2-dibromoethane

N.B. Bromine water will be decolourised when shaken with an alkene (Br_2 is absorbed). This is a test for unsaturation.

Hydrogenation (catalysts Pt, Pd, Ni)

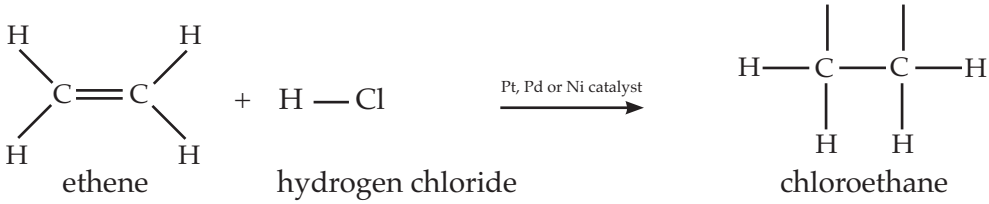
Example



ethene hydrogen ethane

Hydrohalogenation

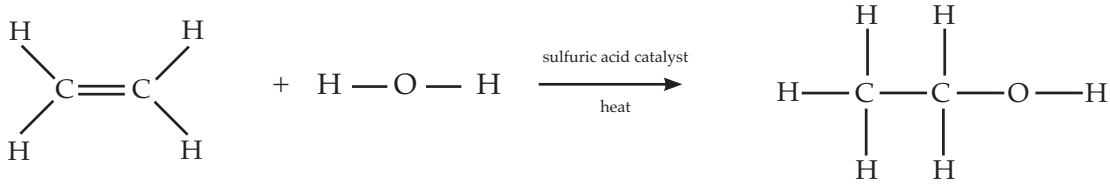
Example



ethene hydrogen chloride chloroethane

Hydration (heat and conc. H_2SO_4 or H_3PO_4)

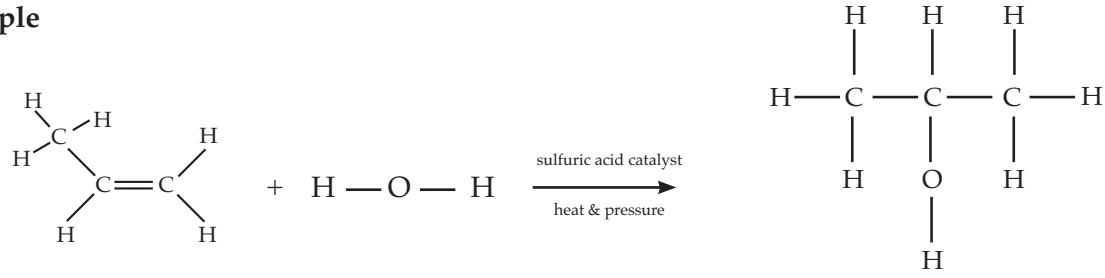
Example



ethene water ethanol

N.B. When hydrohalogens and water are added to asymmetrical alkenes, Markovnikov's rule is applied to predict the predominant product. The hydrogen atom of the added molecule will attach to the carbon with the greater number of hydrogens.

Example



propene water propan-2-ol (not propan-1-ol)

In nature, unsaturated fatty acids in vegetable oils generally consist of hydrocarbon chains with cis double bonding. These unsaturated fatty acids are often hydrogenated to produce saturated fatty acids which are softer and have lower melting points. Unfortunately, this process can result in cis double bonds becoming trans double bonds which are thought to contribute to heart disease.

4.6.3 Halogenoalkanes (alkyl halides/haloalkanes)

Halogenoalkanes are hydrocarbons which contain one or more halogen atoms attached in place of hydrogen.

Example

chloromethane dichloromethane trichloromethane tetrachloromethane

The presence of halogen atoms can produce polar or non-polar molecules, depending upon their position and the molecule's shape. Chloromethane, dichloromethane and trichloromethane are polar since they have polar bonds and are asymmetrical. Tetrachloromethane is symmetrical, so its four polar bonds do not contribute to an overall polarity.

Some halogenoalkanes can have dipole-dipole bonding in addition to dispersion forces. These generally exhibit low melting and boiling points and make good solvents.

Preparation of halogenoalkanes

Halogenation of alkanes (see 4.6.1)

This substitution is difficult to control and multiple substitutions often occur.

Hydrohalogenation of alkenes (see 4.6.2)

Set 3. Reactions and properties of the aliphatic hydrocarbons

Combustion

1. (a) Using condensed structural formulae, write balanced equations for the complete combustion of the following:

   i) butene

   _____

   ii) methylpropane

   _____

   (b) Using condensed structural formulae, write balanced equations for the incomplete combustion of the following:

   i) pentane

   _____

   ii) cyclohexane

   _____

Substitution

2. For each of the following reactions write balanced equations, using structural diagrams for all reactants and products. Name any organic products.

   (a) chloromethane is produced by reacting methane and chlorine under UV light

   (b) (i) A limited supply of bromine and cyclobutane react in the presence of UV light

   (ii) Excess bromine reacts with cyclobutane in UV light

   (c) propane reacts with fluorine gas under UV light

Addition

3. For each of the following reactions write balanced equations using structural diagrams for all reactants and products. Name any organic products.

   (a) the addition of hydrogen bromide to prop-1-ene

   (b) the hydration of *cis*-but-2-ene using sulfuric acid as a catalyst

   (c) the hydrogenation of *trans*-but-2-ene

   (d) the chlorination of ethene

Markovnikov's rule

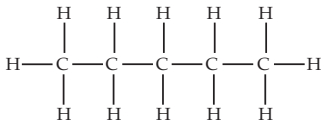
4. Name the predominant product when HCl is added to each of the following alkenes.

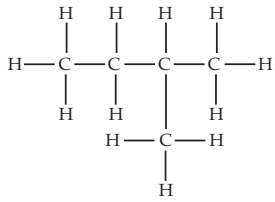
   (a) CH_3CHCH_2

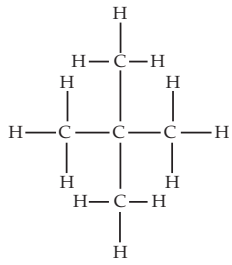
   (b) $CH_3(CH_3)CCH(CH_3)$

   (c) $CHCCH_2CH_3$

5. The isomers of pentane are shown below:







They have the same molar masses but their boiling points decrease from left to right. Explain with reference to the strength of intermolecular forces present in each.

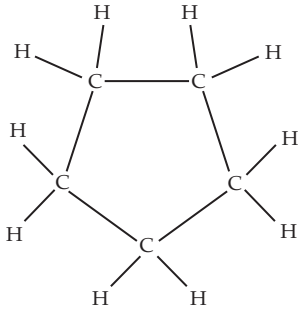
6. Tetrachloroethene is used in dry cleaning and is an excellent solvent for organic substances but it's solubility in water is low (0.150 g/L @25°C). Trichloroethene is a lot more soluble in water (1.23 g/L @25°C). Explain this difference in solubility with reference to the intermolecular forces present in each and also those that need to form for each to dissolve in water.

4.6.4 Alicyclic hydrocarbons

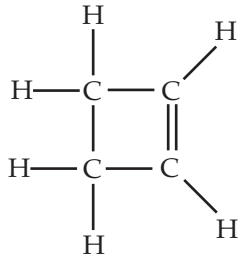
Alicyclic hydrocarbons form closed rings with as few as 3 carbon atoms.

They can be saturated cycloalkanes or unsaturated cycloalkenes.

Example



cyclopentane



cyclobutene

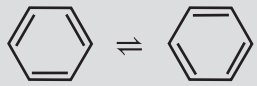
Alicyclic hydrocarbons have similar physical properties to their corresponding straight chain and branched hydrocarbons.

They undergo similar chemical reactions to those of their corresponding straight chain and branched chain hydrocarbons.

4.6.5 Aromatic hydrocarbons (arenes)

Aromatic hydrocarbons are cyclic hydrocarbons containing the characteristic benzene ring.

Benzene is a planar molecule of six carbon atoms in a ring. Kekule's original structure below suggested that there must be alternating single and double bonds, but he found each of the carbon to carbon bonds to be equivalent. He later proposed that benzene resonates between two structures, with the bonds being single half the time and double half the time.

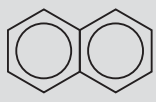


Benzene's stability and inability to readily undergo addition reactions indicates a different bonding arrangement. It is thought to be a structure with six identical carbon to carbon bonds having a bond length somewhere between that of a single bond and a double bond, with an additional six delocalised electrons not linked to any particular carbon atom.

We represent it in equations as C_6H_6 or structurally as:

Aromatic compounds have relatively low melting and boiling points due to their predominantly weak dispersion forces. They tend to be insoluble in water as the benzene ring is non-polar.

Naphthalene is a benzene derivative consisting of two joined benzene rings.



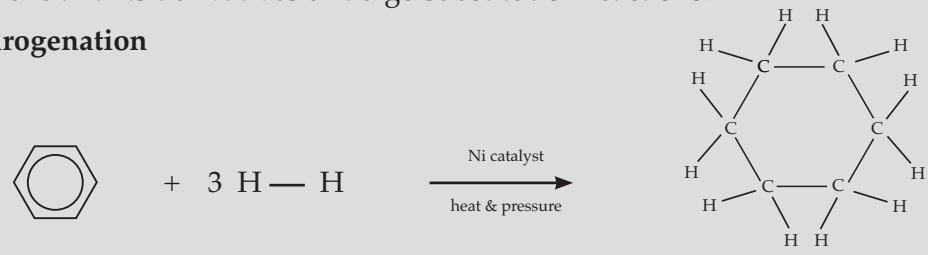
Moth balls contain naphthalene which is toxic to insects. It sublimes directly from solid to gas due to its having weak dispersion forces.

Reactions of aromatic hydrocarbons

Benzene and molecules containing the benzene ring do not readily undergo the addition reactions characteristic of alkenes.

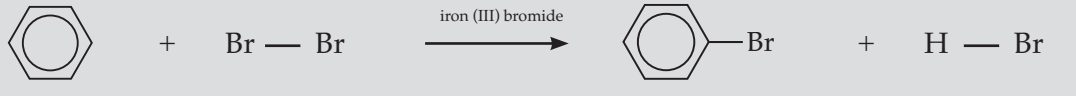
Benzene and its derivatives undergo substitution reactions.

Hydrogenation



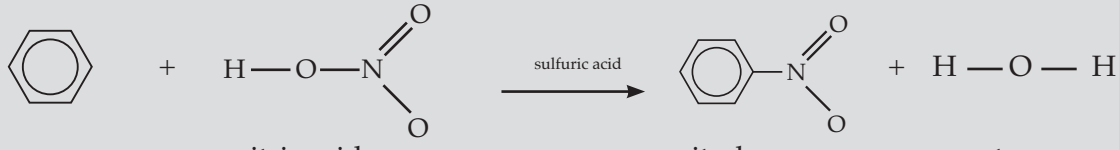
benzene hydrogen cyclohexane

Halogenation



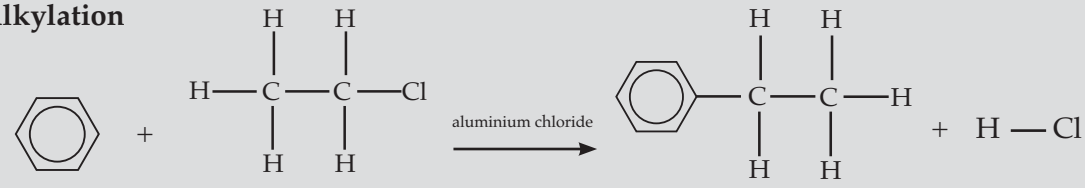
benzene bromine bromobenzene hydrogen bromide

Nitration



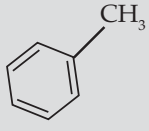
benzene nitric acid nitrobenzene water

Alkylation

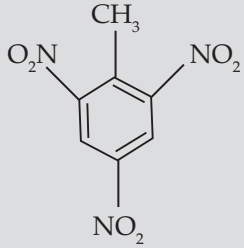


benzene chloroethane ethylbenzene hydrogen chloride

Methyl benzene is also known as toluene, commonly used as a paint thinner.



Trinitrotoluene, or TNT, is methylbenzene with three NO_2 functional groups substituted onto the benzene ring. Its IUPAC name is 2-methyl-1,3,5-trinitrobenzene and it is an explosive.



Set 4. Reactions of the alicyclic and aromatic hydrocarbons

1. For each of the following reactions write equations, using line structural diagrams for all organic reactants and products. Name any organic products.

   (a) cyclopentane and limited chlorine react under UV light

   (b) bromine water is added to cyclohexene

2. Write equations for the production of the following compounds. Use line structural diagrams for all organic reactants and products.

   (a) nitrobenzene

   (b) propylbenzene

   (c) cyclohexane

   (d) chlorobenzene

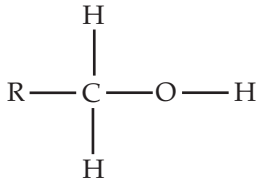
4.7 PROPERTIES, PREPARATION AND REACTIONS OF ALCOHOLS

Alcohols are alkanes containing the hydroxyl group, -OH.

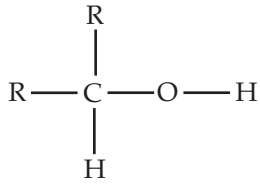
The homologous series has the general formula $C_nH_{2n+1}OH$

Alcohols are classified as primary (1°), secondary (2°) or tertiary (3°) depending upon how many alkyl groups (R) are attached to the carbon atom the hydroxyl group –OH is bonded to.

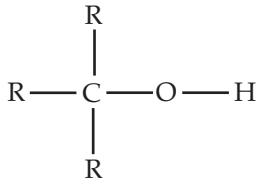
Example



1° has one alkyl group attached



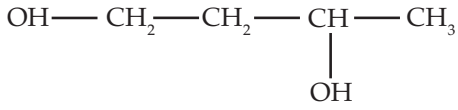
2° has two alkyl groups



3° has three alkyl groups

Alcohols may contain more than one hydroxyl group.

Example



butan-1,3-diol

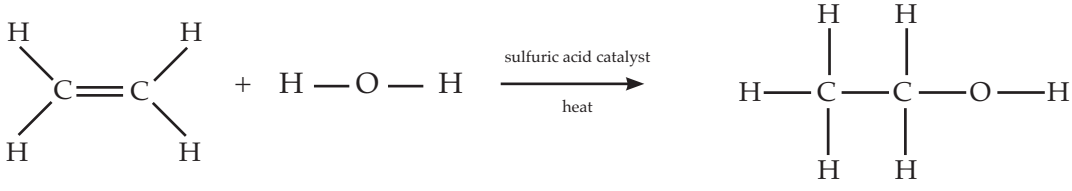
The physical properties of alcohols are influenced by the presence of the polar –OH group which allows them to form hydrogen bonds between molecules. The presence of hydrogen bonding gives alcohols higher boiling points than non-polar hydrocarbons.

Alcohols with a smaller carbon chain (e.g. methanol, ethanol and propanol) are miscible with water since hydrogen bonds can form between the –OH and H_2O, allowing them to mix.

Larger alcohols are mainly non-polar due to the long carbon chain and so form mainly dispersion forces with water. So as alcohols increase in size they become less miscible with H_2O.

Preparation of alcohols

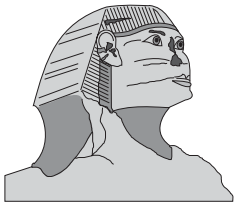
In industry, alcohols can be prepared by the hydration of alkenes. (see 4.6.2)



Ethanol is also made by the fermentation of carbohydrates, catalysed by enzymes from yeast.

Example Glucose fermenting to form ethanol and carbon dioxide.

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2CH_3CH_2OH + 2CO_2$$



The fermentation of plant sugars to form ethanol is utilised in the production of alcoholic drinks like beer and spirits, where the sugars are from grain. With wine and ciders, the sugars are from fruits. The oldest documentation referring to the fermentation of alcohol for human consumption can be traced back at least six thousand years! In Egyptian times workers were paid in beer which was offered to the gods and consumed several times per day by men, women and children.

Reactions of alcohols

Combustion

All alcohols can undergo complete combustion in excess oxygen to produce carbon dioxide and water.

Example Ethanol burning in oxygen

$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

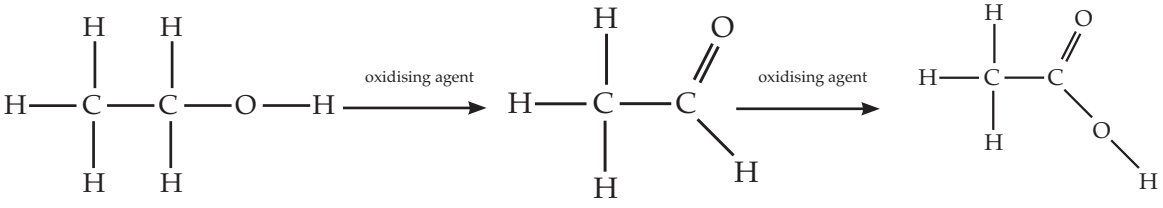
Oxidation

Primary and secondary alcohols can be oxidised by oxidising agents, including acidified MnO_4^- and $Cr_2O_7^{2-}$. Oxidation of primary alcohols firstly produces aldehydes and further oxidation results in the formation of carboxylic acids. The oxidation of secondary alcohols produces ketones. Remember oxidation is defined as a rise in oxidation number, addition of oxygen or loss of hydrogen. Reduction is the lowering of oxidation number, loss of oxygen or gain in hydrogen. In this section we will make extensive use of these full definitions.

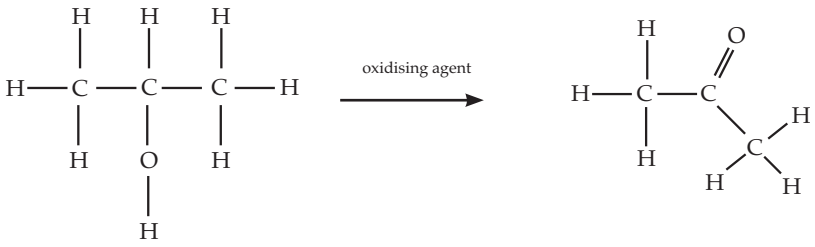
With primary and secondary alcohols there is at least one hydrogen atom attached to the carbon atom attached to the –OH. The oxidising agent can remove this hydrogen and the hydrogen from the –OH group which enables oxidation to occur. It allows the carbon-to-oxygen double bond, or a carbonyl group, to form.

Tertiary alcohols do not have any hydrogen atoms attached to the carbon so they are not oxidised at all. The carbonyl group cannot form.

Examples



ethanol ethanal ethanoic acid



propan-2-ol propanone

Vinegar is a solution of roughly 3-5% ethanoic acid in water. It is commonly used nowadays as a cooking ingredient but is making a resurgence as a mild household cleaning agent as people look to use less harsh chemicals in their homes. The ethanol in wines, ciders and even beer can be fermented to produce a great variety of flavoured vinegars, like white wine vinegar, red wine vinegar, apple cider vinegar and balsamic vinegar.

To write full balanced ionic equations for the oxidation of alcohols first write and balance the oxidation and reduction half equations (see Redox section) and then combine them in order to balance the number of electrons given out with those received.

Example

$CH_3CH_2OH_{(l)} \rightarrow CH_3CHO_{(aq)} + 2H^+ + 2e^-$ (x5)

$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$ (x2)

$5CH_3CH_2OH_{(l)} + 2MnO_4^-{}_{(aq)} + 6H^+_{(aq)} \rightarrow 5CH_3CHO_{(aq)} + 2Mn^{2+} + 8H_2O_{(l)}$

Reaction with sodium

Alcohols can react with sodium to produce hydrogen gas and a sodium alkoxide.

Example sodium added to ethanol produces sodium ethoxide and hydrogen

$2CH_3CH_2OH_{(l)} + 2Na_{(s)} \rightarrow 2CH_3CH_2ONa_{(aq)} + H_{2(g)}$

This reaction can be used to test for the presence of the hydroxy group in alcohols.

The order of reactivity of alcohols with sodium metal is primary > secondary > tertiary.

This is due to the decreased exposure of the hydroxy group for reaction as more alkyl groups are attached to the carbon bearing the hydroxy group.

Sodium also reacts with carboxylic acids to give the sodium salt.

e.g. $2CH_3COOH_{(l)} + 2Na_{(s)} \rightarrow \underbrace{2CH_3COO^-_{(aq)} + 2Na^+_{(aq)}}_{\text{sodium ethanoate}} + H_{2(g)}$

Set 5. Reactions and properties of alcohols

1. Classify the following as primary, secondary or tertiary alcohols, and name them.

   (a) $CH_3CH_2C(CH_3)_2OH$

   _____

   (b) $HOCH_2CH_2CH_2CH_3$

   _____

   (c) $CH_3CH(CH_3)(CH_2)_3CH(CH_3)OH$

   _____

   (d) $CH_3CH_2CHOHCH_2CH_3$

   _____

2. Butanol has four chain and positional isomers. Draw and name these.

3. Write an equation for the complete combustion of propan-2-ol.

4. Write an equation for the preparation of propan-2-ol. Use full structural formulae and name all reactants and products.

5. Write a balanced redox equation for the oxidation of butan-2-ol using acidified potassium dichromate. Name the products.

Reduction half equation	
Oxidation half equation	
Overall equation	
Names	

6. Write a balanced redox equation for the oxidation of pentan-1-ol using potassium permanganate. Name the products.

Reduction half equation	
Oxidation half equation	
Overall equation	
Names	

7. a) Draw each of the following alcohols and list them in order of increasing boiling point:

butan-1-ol, ethanol, methyl propan-1-ol, methanol, methyl propan-2-ol

(b) With reference to intermolecular bonding explain why you have placed them in this order.

8. Write a balanced equation for the reaction between sodium and propan-1-ol to produce sodium propoxide.

9. Describe how potassium dichromate could be used to determine whether an alcohol is secondary or tertiary. Include observations.

_____

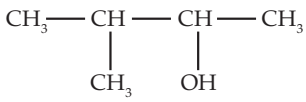
_____

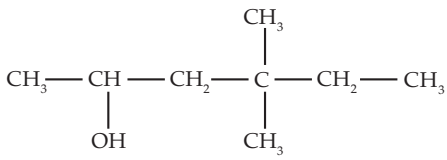
_____

_____

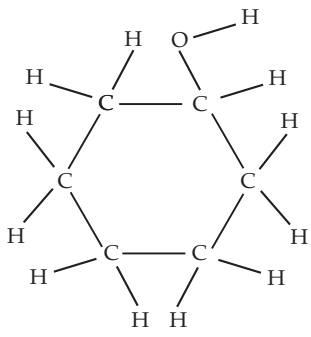
_____

10. Name the following alcohols:

(a) 

(b) 

(c) $CH_3CH(CH_3)CHOHCH_2CH_3$

(d) 

4.8 PROPERTIES, PREPARATION AND REACTIONS OF ALDEHYDES AND KETONES

The carbonyl group

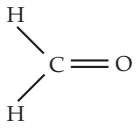
The carbonyl group is a functional group with a carbon atom double bonded to an oxygen atom. Carboxylic acids, aldehydes, ketones, esters and amides contain the carbonyl group and it largely influences the properties of these compounds.

The oxygen atom is more electronegative than the carbon atom and produces a polar bond so dipole-dipole interactions between molecules can occur. Molecules that have a hydrogen atom bonded directly to a nitrogen, oxygen or fluorine atom can form hydrogen bonds with the oxygen of the carbonyl group.

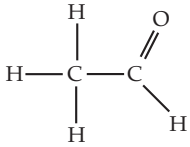
4.8.1 Aldehydes

Aldehydes are oxidised products of primary alcohols and have a carbonyl group (C=O) at their terminal (end) carbon atom. They have the general formula R-CHO.

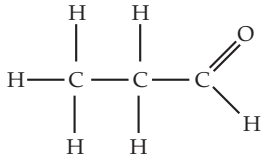
Examples



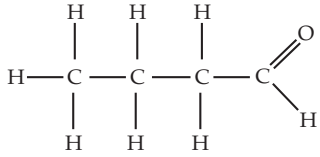
methanal



ethanal



propanal



butanal

Lower molar mass aldehydes are typically gases at room temperature but larger ones are liquids due to increased dispersion forces from longer chains.

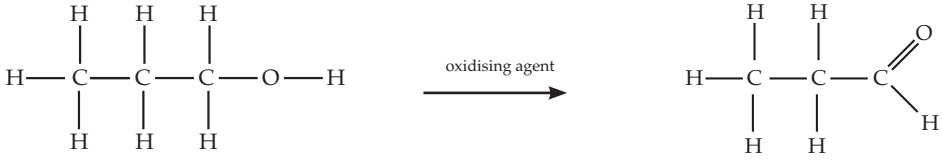
Aldehydes are polar molecules due to the presence of the carbonyl group. In addition to dispersion forces they can have dipole-dipole interactions with neighbouring molecules. Their melting and boiling points are low but still higher than similarly-sized hydrocarbons due to their polarity. Since they cannot hydrogen bond with each other they have lower melting and boiling points than corresponding alcohols.

Smaller aldehydes are soluble in water but, as the chain gets longer, their miscibility decreases. Their carbonyl group enables them to hydrogen bond with water molecules. As the hydrocarbon portion of the molecule increases in length it can only form dispersion forces with water, which do not provide enough energy on formation to break the hydrogen bonds between water molecules.

Preparation of aldehydes

Aldehydes are prepared in the laboratory by oxidation of primary alcohols, but they must be isolated once produced so that they do not oxidise further to carboxylic acids.

Example

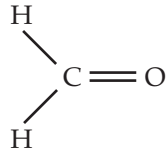


1-propanol propanal

Methanal is the simplest aldehyde commonly known as formaldehyde.

Formalin is a solution of formaldehyde in water used as a disinfectant and for the preservation of biological specimens.

It is also used in nail varnish as a solvent, but it is a known carcinogen.



Reactions of aldehydes

Combustion

Aldehydes can burn completely in oxygen to produce carbon dioxide and water.

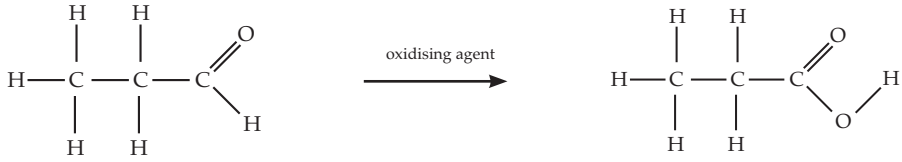
Example

$$HCHO(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Oxidation

Aldehydes can be oxidised to form carboxylic acids.

Example



propanal propanoic acid

N.B. No numbering is required to place the aldehyde and carboxylic acid groups as they must be on the end.

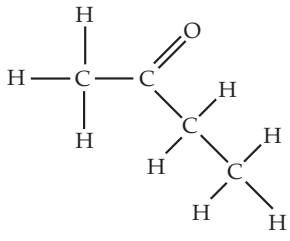
Reduction

Aldehydes can also be reduced to form primary alcohols using reducing agents such as $LiAlH_4$ and $NaBH_4$.

4.8.2 Ketones

Ketones are oxidation products of secondary alcohols which have a carbonyl group within their carbon chain. They have the general formula R-COR'.

Example



butan-2-one

N.B. Numbering is required for ketones longer than three carbon atoms.

Ketones are liquids at room temperature with boiling points that increase with increasing chain length due to increased dispersion forces as the chains get longer.

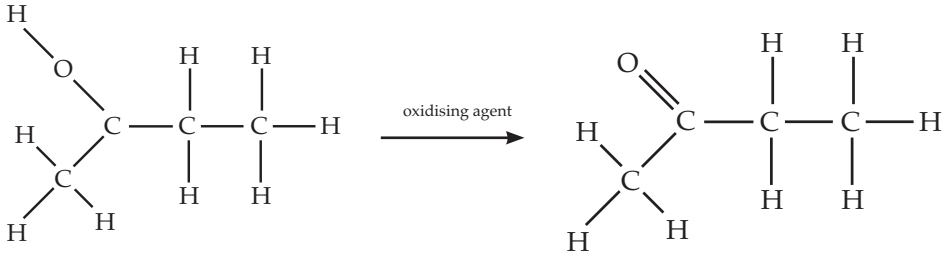
Ketones are polar molecules due to the presence of the carbonyl group (C=O). Like aldehydes, they can have dipole-dipole interactions with neighbouring molecules and have melting and boiling points higher than similarly-sized hydrocarbons. They have lower melting and boiling points than corresponding alcohols.

Like aldehydes, smaller ketones are soluble in water but as the chain gets longer their miscibility decreases. The smallest ketone is propanone (nail-varnish remover) which is an important solvent for organic compounds and is also miscible with water.

Preparation of ketones

Ketones are prepared in the laboratory by the oxidation of secondary alcohols. Unlike aldehydes, they are very difficult to oxidise further.

Example



2-butanol 2-butanone

Reactions of ketones

Combustion

Ketones can burn completely in oxygen to produce carbon dioxide and water.

Example

$$2CH_3COCH_2CH_{3(l)} + 11O_{2(g)} \rightarrow 8CO_{2(g)} + 8H_2O_{(g)}$$

Reduction

Ketones can be reduced to secondary alcohols using reducing agents such as $LiAlH_4$ and $NaBH_4$.

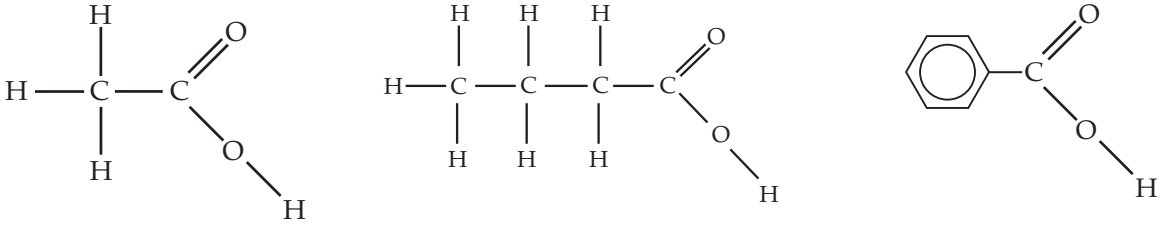
Ketones and oxoacids (carboxylic acids with an additional carbonyl group within the chain) are produced in the liver when the body burns fats for energy. This can occur in people who have diabetes when there is not enough insulin in their bodies to obtain energy from sugar. A build-up of ketones can lead to ketoacidosis which can be fatal if not treated.

4.9 PROPERTIES, PREPARATION AND REACTIONS OF CARBOXYLIC ACIDS AND ESTERS

4.9.1 Carboxylic acids

Carboxylic acids are formed by the replacement of a hydrogen atom with a carboxyl functional group -COOH group. The carboxyl group is always at the end of the molecule and it is the most important of the functional groups, so takes precedence when naming.

Example

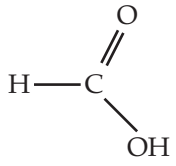


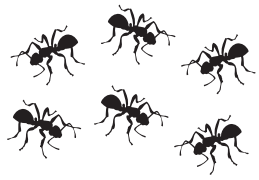
ethanoic acid butanoic acid benzoic acid

Carboxylic acids are polar molecules due to the presence of the carbonyl group (C=O) and can form hydrogen bonds with water. They are typically soluble in water. Once again their solubility decreases with the increasing length of their carbon chain. If the strength of the dispersion forces between these larger carboxylic acid molecules is greater than that of the possible hydrogen bonds that could form with water then the carboxylic acid will not dissolve.

They have high melting and boiling points due to hydrogen bonding.

Methanoic acid, commonly called formic acid, is a pungent, clear liquid which was originally distilled from ants since it occurs naturally in their venom. 'Formica' is the Latin word for ant.

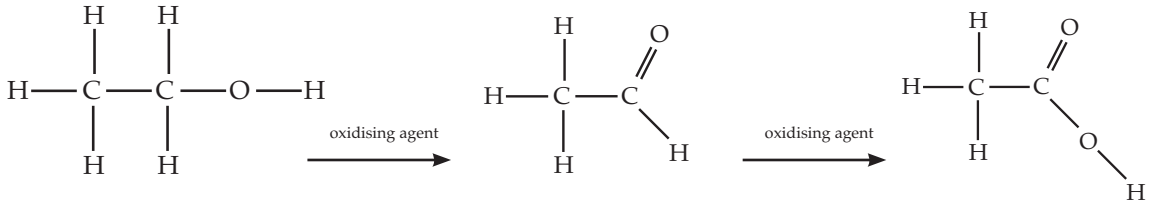




Preparation of carboxylic acids

Carboxylic acids can be prepared by the oxidation of primary alcohols or aldehydes.

Example

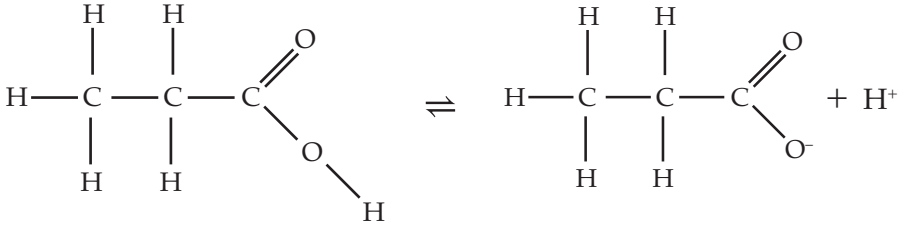


ethanol ethanal ethanoic acid

Reactions of carboxylic acids

Carboxylic acids are weak acids and dissociate to a small extent into the H^+ ion and a carboxylate ion. They have the chemical properties of weak acids.

Example



propanoic acid the propanoate ion

Neutralisation

Carboxylic acids undergo neutralisation reactions with alkalis to produce a salt and water.

Example $CH_3COOH_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H_2O_{(l)}$

They react with carbonates and hydrogencarbonates to produce a salt, water and carbon dioxide.

Example $2CH_3COOH_{(aq)} + Na_2CO_{3(aq)} \rightarrow 2Na^+_{(aq)} + 2CH_3COO^-_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

With reactive metals

They react with reactive metals to produce a soluble salt and hydrogen gas.

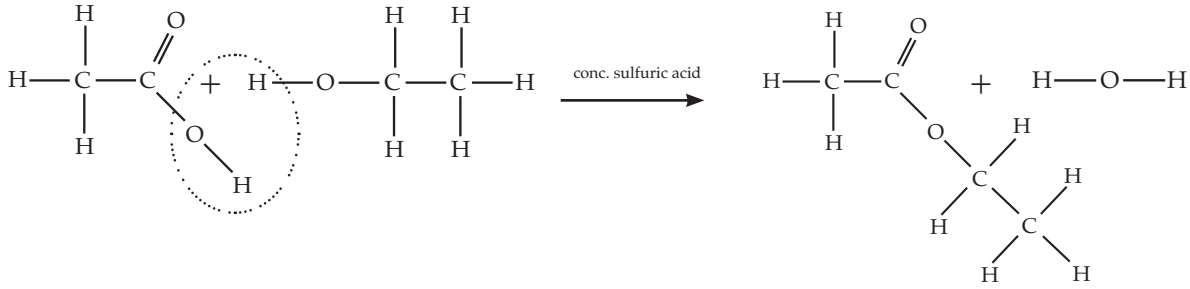
Example

$$2CH_3COOH_{(aq)} + 2Na_{(s)} \rightleftharpoons 2Na^+_{(aq)} + 2CH_3COO^-_{(aq)} + H_{2(g)}$$

Esterification

Carboxylic acids react with alcohols to produce esters. This reaction is called esterification. Concentrated sulfuric acid is used to link the alcohol and the carboxylic acid together by removing a water molecule. The H comes from the alcohol and the OH from the carboxylic acid.

Example



ethanoic acid ethanol ethyl ethanoate water

Reduction

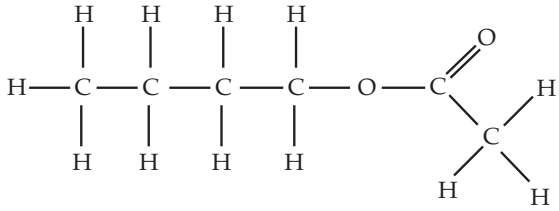
Carboxylic acids can be reduced back to alcohols using a very strong reducing agent like $LiAlH_4$.

4.9.2 Esters

Esters have a sweet fruity smell and are found in nature in fruits and flowers. As such, they are used in perfumes and cosmetics and to flavour foods.

Esters contain the functional group -COO- and have the general formula R-COOR-.

Example



butyl ethanoate

N.B. the alkyl prefix comes from the alcohol and the carboxylate suffix comes from the carboxylic acid. Butyl ethanoate is prepared by reacting butanol and ethanoic acid.

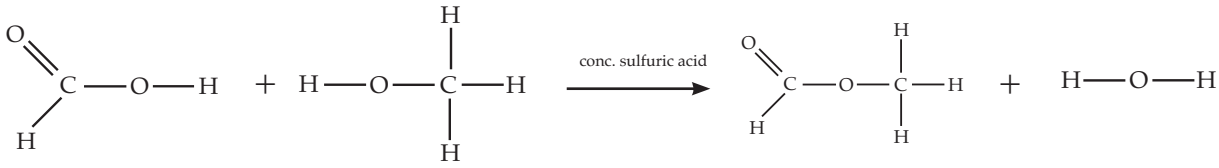
Esters are polar molecules though their melting and boiling points are quite low due to their having considerable non-polar chains. Dispersion and dipole-dipole forces exist between molecules. They tend to be liquids at room temperature but evaporate easily.

They are typically insoluble in water because their long non-polar chains overcome any hydrogen bonding. However, being polar, they are powerful solvents for many polar organic compounds. This makes them good solvents in paints and lacquers.

The ester functional group is also used in condensation polymerisation in the formation of polyesters.

Preparation of esters

Example



methanoic acid methanol methyl methanoate water

Esters are sweet smelling and are used in perfumery for their characteristic aromas.

pentyl ethanoate	pears
octyl ethanoate	oranges
pentyl butanoate	apricots / strawberries
3-methyl butyl ethanoate	bananas
methyl propyl methanoate	raspberry
ethyl butanoate	pineapple
methyl butanoate	apple
methyl salicylate	oil of wintergreen (Dencorub)

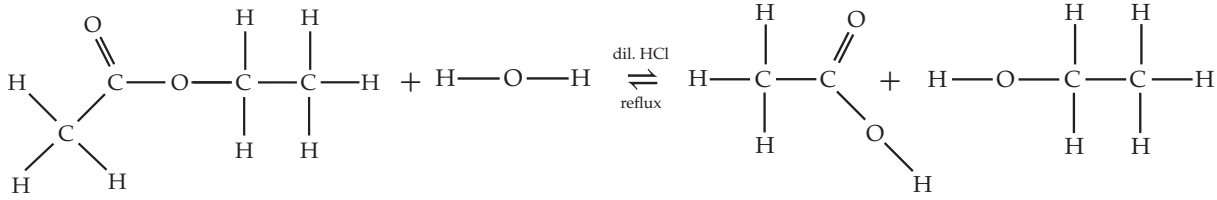
Reactions of esters

Hydrolysis

Esters can be hydrolysed to form alcohols and carboxylic acids.

Acid hydrolysis splits the ester into an acid and an alcohol which is the reverse of the esterification reaction. The ester is refluxed with a dilute acid like hydrochloric or sulfuric acid.

Example



ethyl ethanoate water ethanoic acid ethanol

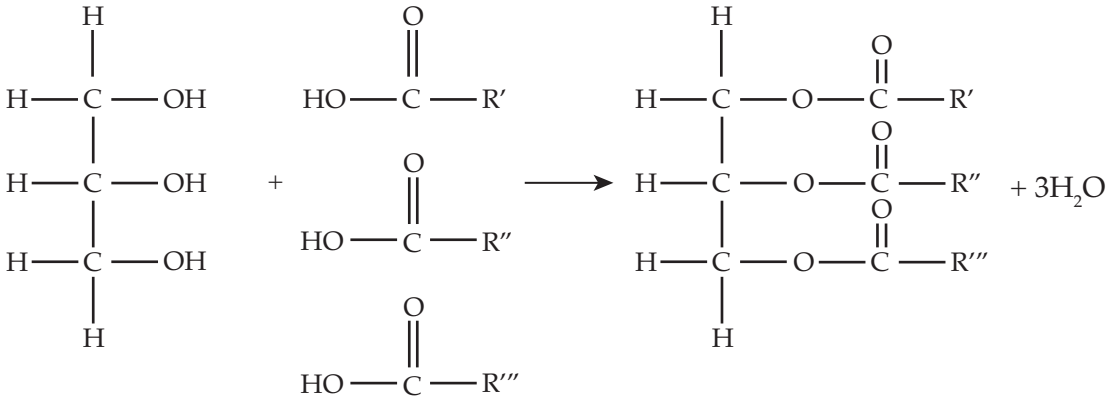
Alkaline hydrolysis splits the ester into an alcohol and a carboxylate ion. The ester is refluxed with a dilute alkali like sodium hydroxide.

Example

$$CH_3COOH_2CH_3 + OH^- \underset{\text{reflux}}{\rightleftharpoons} CH_3COO^- + HOCH_2CH_3$$

Fats and oils

Fats and oils (triglycerides) are esters of glycerol and fatty acids. Triglycerides can be made into soaps (see Soap Making).



glycerol 3 fatty acids triglyceride (triester of glycerol)

Set 6. Aldehydes, ketones, carboxylic acids and esters

1. Identify the following as aldehydes, ketones, carboxylic acids or esters:
   (a) $CH_3COCH_2CH_3$ _____
   (b) $CH_3CH_2CH_2COOCH_2CH_2CH_3$ _____
   (c) $CH_3CH_2CH_2CHO$ _____
   (d) $CH_3(CH_2)_4COOH$ _____
   (e) $CH_3(CH_2)_5COCH_3$ _____
   (f) $CH_3CH_2OOCCH_2CH_3$ _____
   (g) $CH_3COCH_2CH_2CH_2COOH$ _____

2. Name each of the compounds in Q1 above.
   (a) _____
   (b) _____
   (c) _____
   (d) _____
   (e) _____
   (f) _____
   (g) _____

3. Write an equation for the complete combustion of propanone.

4. Write an equation for the incomplete combustion of butanoic acid (in limited O_2).

5. Write a balanced redox equation for the oxidation reaction which produces butanal using acidified potassium permanganate.

Reduction half equation	
Oxidation half equation	
Overall equation	
Names of all species	

6. Write a balanced redox equation for the oxidation reaction which produces pentan-3-one using acidified potassium dichromate.

Reduction half equation	
Oxidation half equation	
Overall equation	
Names of all species	

7. Name the starting materials required to produce butanoic acid in the laboratory.

8. Write an equation for the production of propyl butanoate in the laboratory.

9. Write a balanced equation for the reaction between propanoic acid and the following substances. Give full observations.

(a) magnesium carbonate

equation:

_____

_____

observations:

_____

_____

(b) sodium

equation:

_____

_____

observations:

_____

_____

(c) potassium hydroxide

equation:

_____

_____

observations:

_____

_____

(d) ethanol and concentrated sulfuric acid

equation:

_____

_____

observations:

_____

_____

(e) acidified potassium dichromate

equation:

_____

_____

observations:

_____

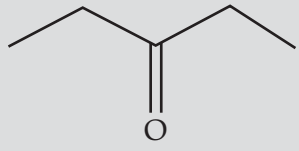
_____

10. The following compounds are all of similar molecular mass. Place them in order of increasing boiling point and explain your logic, with reference to their shapes and the intermolecular forces present in each.

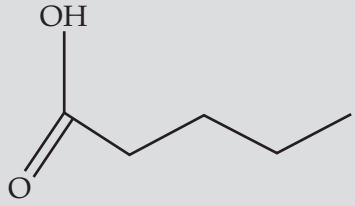
    1-butanol, butanoic acid, butanal, butane

11. Match each line structure to its major functional group with arrows.

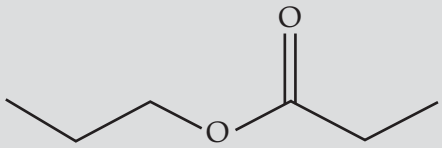
ester



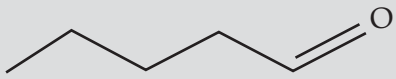
aldehyde



ketone



carboxylic acid

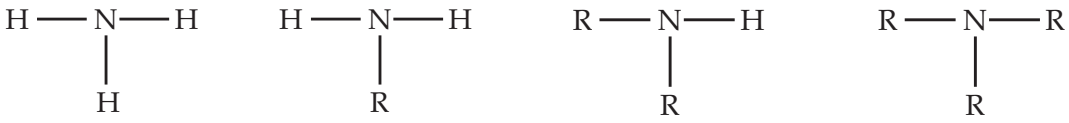


4.10 PROPERTIES, PREPARATION AND REACTIONS OF AMINES, AMIDES AND α-AMINO ACIDS.

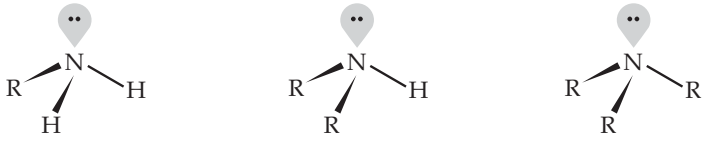
4.10.1 Amines

Amines are organic derivatives of ammonia, where one or more hydrogens are replaced by an organic group. They have the general formula R-NH_2.

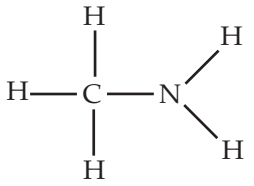
They are classified by the number of carbons attached to the nitrogen atom. R represents an alkyl group.



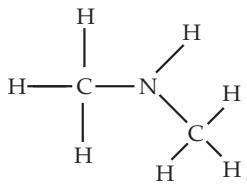
ammonia 1° primary amine 2° secondary amine 3° tertiary amine



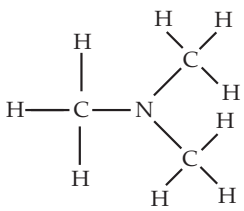
1° primary amine 2° secondary amine 3° tertiary amine



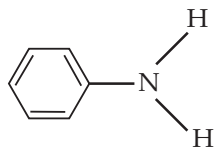
methylamine (1°)



dimethylamine (2°)

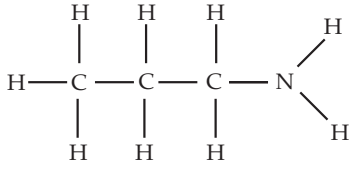


trimethylamine (3°)

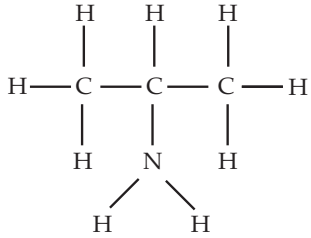


phenylamine (1°)

Alternative nomenclature

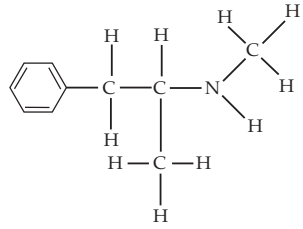


1-propanamine, propylamine or amino propane



2-propanamine, 2-propylamine or 2-amino propane

Methylamine is used in the synthesis of many compounds including herbicides, fungicides and insecticides. It is also a precursor for the manufacture of the extremely dangerous addictive drug, methamphetamine or crystal meth shown.



Amines have relatively high melting and boiling points since they can form hydrogen bonds with each other, as well as dispersion forces and dipole-dipole interactions.

The boiling points of secondary amines are lower than the corresponding primary amines. Secondary amines form hydrogen bonds but have the nitrogen atom in the middle of the chain rather than at the end, which decreases dipole-dipole interactions and dispersion forces.

Tertiary amines do not have any hydrogen atoms attached directly to the nitrogen. They cannot form hydrogen bonds with each other and so their boiling points are much lower than both primary and secondary amines of similar size.

Small amines are soluble in water since the amine group can form hydrogen bonds with water molecules. Solubility decreases with increasing chain length, since the strength of the dispersion forces between these larger amine molecules is greater than that of the possible hydrogen bonds that could form with water.

Amines are found in nature as amino acids. Many are used as catalysts and solvents or in the manufacture of dyes, medicines and polymers.

Reactions of amines

Amines that are able to dissolve act as weak bases. They form alkaline solutions by accepting a proton from water, leaving hydroxide ions.

Example Hydrolysis of methylamine

$$CH_3NH_{2(g)} + H_2O_{(l)} \rightleftharpoons CH_3NH_3^+{}_{(aq)} + OH^-{}_{(aq)}$$

Neutralisation

Amines react with acids to produce a salt and water.

Example

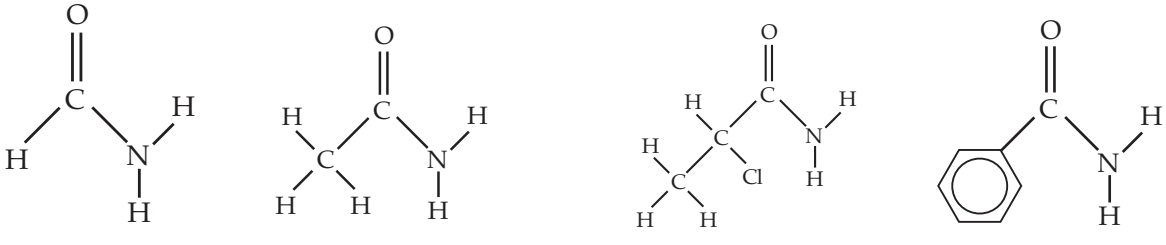
$$CH_3CH_2CH_2NH_{2(aq)} + H_3O^+{}_{(aq)} + Cl^-{}_{(aq)} \rightleftharpoons CH_3CH_2CH_2NH_3^+{}_{(aq)} + Cl^-{}_{(aq)} + H_2O_{(l)}$$

propylamine hydrochloric acid propylammonium chloride water

4.10.2 Amides

Amides are carboxylic acid derivatives, where the hydroxy group (-OH) is replaced by an amine group (-NH_2). They contain the functional group –$CONH_2$ and have the general formula R-$CONH_2$.

Examples



methanamide ethanamide 2-chloropropanamide benzamide

Preparation of amides

Amides can be prepared in the laboratory by reacting carboxylic acids with ammonium carbonate to produce an ammonium salt and then heating it to remove water. Excess acid is required to stop any dissociation of the ammonium salt as it is heated.

Example Preparation of ethanamide

$$2CH_3COOH(aq) + (NH_4)_2CO_3(s) \rightleftharpoons 2CH_3COO^-NH_4^+(aq) + H_2O(l) + CO_2(g)$$

ammonium ethanoate

$$CH_3COO^-NH_4^+(aq) \rightarrow CH_3CONH_2(s) + H_2O(l)$$

ethanamide

Reactions of amides

Amides do not behave as bases since proximity to the carbonyl group causes the lone pair of electrons on the nitrogen to become delocalised and not attractive to protons.

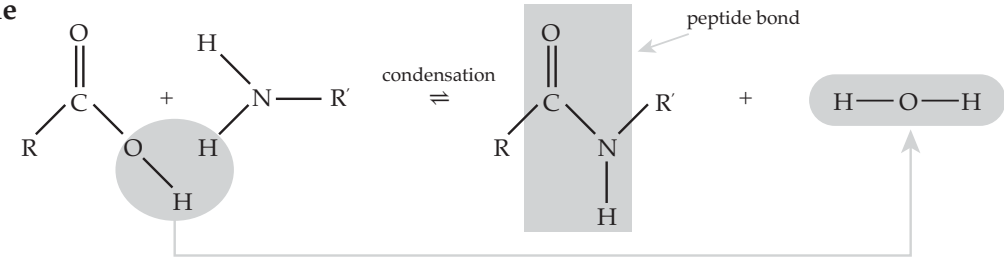
Reduction

Amides can be reduced to amines using reducing agents such as $LiAlH_4$ and $NaBH_4$.

The amide bond

The amide bond occurs when the amine functional group reacts with the carboxylic acid functional group.

Example



When dicarboxylic acids or diamines react they can form polymers with long chains held together by amide bonds. They are called polyamides. Nylons and Kevlar are synthetic polyamides. (see 4.11.2)

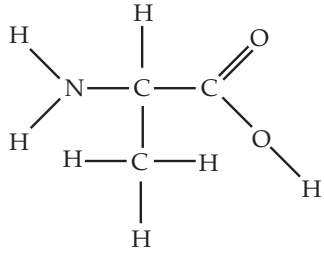
The amide bond can also form between amino acid molecules since they contain both amine and carboxylic acid functional groups at different ends of the molecule. In this case it is called a peptide bond and it produces proteins, which are natural polyamides. (see 4.11.3)

4.10.3 α-amino acids

Amino acids are naturally occurring and are molecules that contain both the basic amine group $–NH_2$ and the acidic carboxyl group –COOH. This makes them amphoteric, i.e. they can both accept and donate protons.

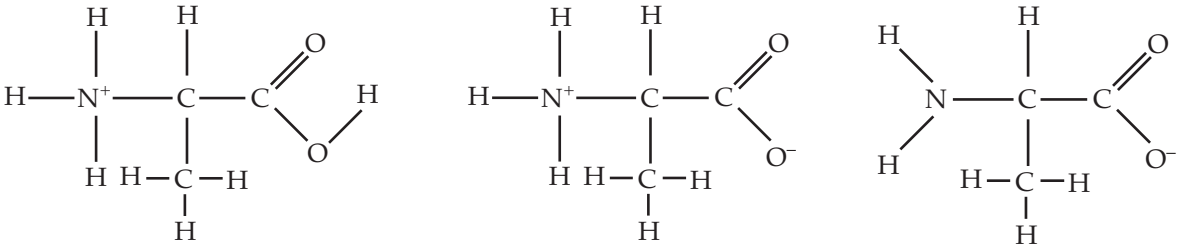
If both the amino and the carboxyl groups are attached to the first or alpha (α) carbon atom they are called α-amino acids.

Example



2-aminopropanoic acid

When solid and in solution they can exist as 'zwitterions' which are dipolar ions (have a positive and negative end). This explains their high melting and boiling points and their solubility in water.

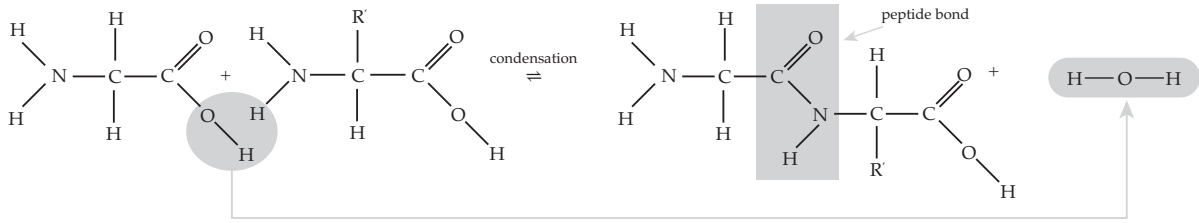


acidic conditions (proton accepted) | the zwitterion | alkaline conditions (proton donated)

α-amino acids are the building blocks of proteins

About 20 α-amino acids occur naturally and it is these that produce proteins essential to life. Amino acids join to make dipeptides in condensation reactions as shown below. Many amino acids produce polypeptides and these form proteins. (see 4.11.3).

Example

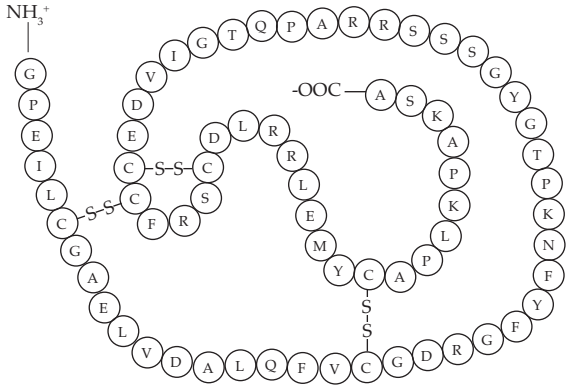


Peptides in sport

Peptides are small chains of amino acids not long enough to be considered full proteins. They are the building blocks that produce proteins.

In recent times athletes and body builders (and footballers) have been taking peptides as supplements. They enable the athlete to build muscle mass quickly and also assist in recovery from injuries. Peptides don't come with the side effects of steroids but many haven't yet been cleared for human use. They are difficult to detect in urine tests.

IGF, MGF and SARMs are some of the commonly used peptides. IGF is a chain of amino acids including isoleucine (I), glycine (G), alanine (A) and glutamic acid (E) shown using their one letter symbols below.



Set 7. Amines, amides and amino acids

1. Identify the following as amines, amides or amino acids and name them:

   (a) $CH_3CH(CH_3)CH_2CONH_2$

   (b) $CH_3CH(NH_2)CH_2CH_3$

   (c) $H_2NCH_2(CH_2)_6CH_3$

   (d) CH_3CHNH_2COOH

   (e) $CH_3CH_2CH_2CH_2CONH_2$

   (f) $H_2NCH_2CH_2COOH$

2. Classify the following as primary, secondary or tertiary amines and draw them using full structural formulae.

   (a) H_3CNH_2

   (b) $CH_3CH_2N(CH_3)_2$

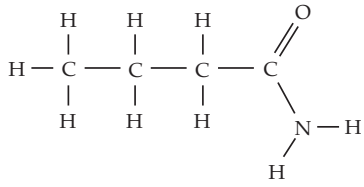
   (c) $H_2NCH(CH_3)_2$

   (d) $H_3CN(CH_3)_2$

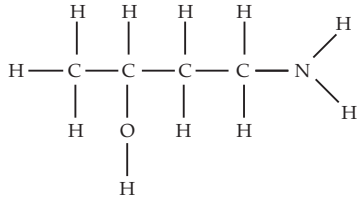
   (e) $CH_3CH_2CH_2NHCH_3$

3. Name the following:

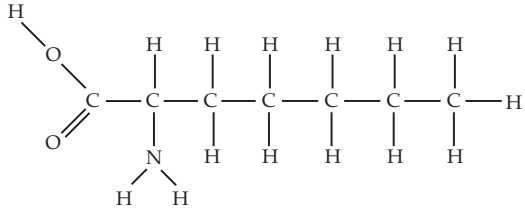
(a)



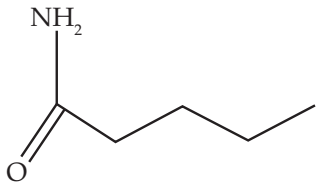
(b)



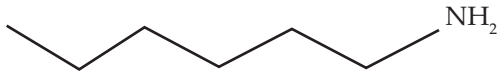
(c)



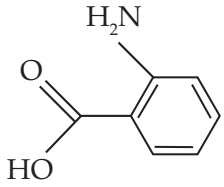
(d)



(e)



(f)



4. Prepare full structural formulae for the following:

(a) ethyldimethylamine

(b) propanamide

(c) 3-aminobutanoic acid

(d) 3-methylpentan-2-amine

(e) 3-aminopentanoic acid

5. Which of the following are α-amino acids? (You may need to sketch them).

(a) $H_3CC(CH_3)(NH_2)COOH$

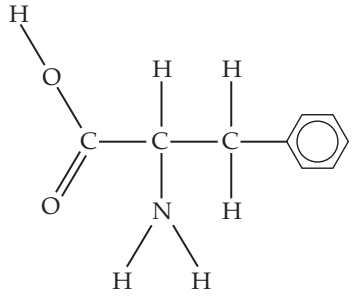
(b) $H_3CCH(NH_2)COOH$

(c) $H_3CCH(NH_2)CH_2COOH$

(d) $H_3CC(CH_3)(NH_2)CH_2CH_2COOH$

(e) $HOOCCH(NH_2)CH_3$

6. Phenylalanine is an amino acid shown below:



(a) Draw phenylalanine in its zwitterionic form under neutral conditions.

(b) Draw phenylalanine when in acidic conditions.

(c) Draw phenylalanine when in alkaline conditions.

4.11 POLYMERS

Polymers are large organic molecules with very long chains, formed by joining up smaller units called monomers. This process is called polymerisation.

Natural polymers include proteins and starch. The synthetic polymers (often called plastics) include Teflon, polyethene, Nylon and polystyrene.

The physical properties of polymers can be explained from the type of bonding between the large polymer molecules.

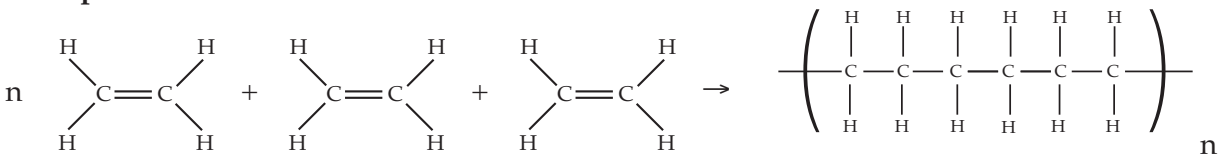
There are two main types of polymers: Addition polymers and Condensation polymers.

4.11.1 Addition polymers

Addition polymers are formed from addition reactions, where the double bonds in alkenes open up to form long chains of carbon atoms. The structure of the alkene monomer contributes to the final structure and, therefore, the properties of the polymer.

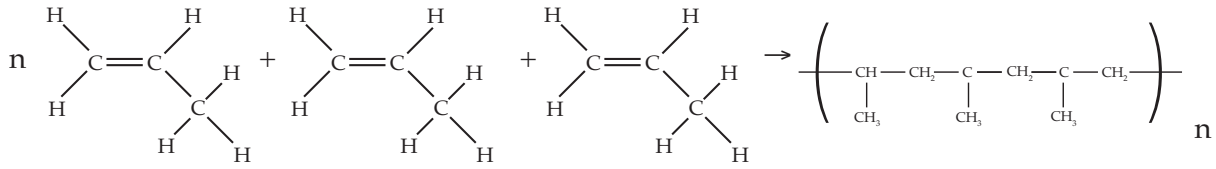
In the example 'n' represents the number of monomers and the chain will be 'n' units long.

Example



ethene monomers polyethene

Branched chains

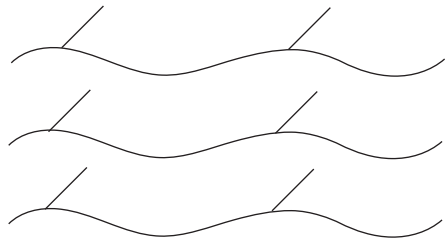


propene monomers polypropene

If the addition polymer is regular and unbranched the chains can get close together providing a larger surface area for dispersion forces between chains to occur. This contributes to higher melting points and greater strength.

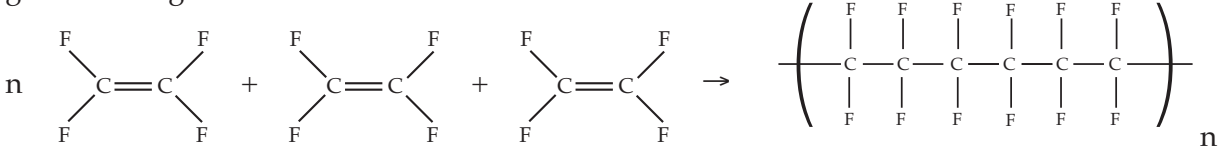
If the polymer chains have branching along the chain this decreases the strength of dispersion forces, as the chains can't get closer together.

Unbranched chains can get closer which increases dispersion forces



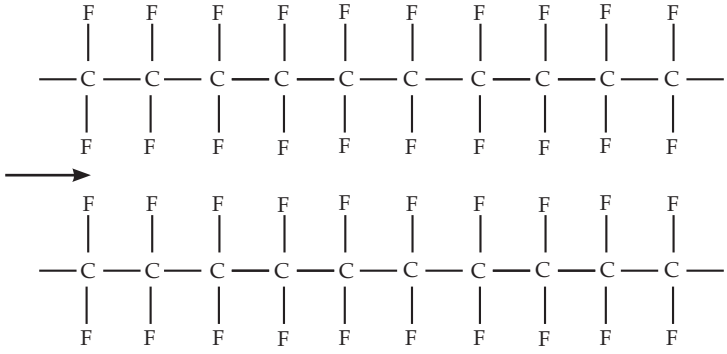
Branched chains are further apart so dispersion forces are decreased

If there are groups like halogens attached to the chains this can allow dispersion forces of even greater strength.

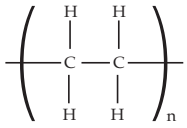
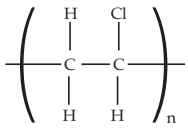
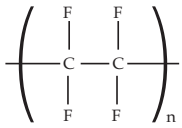
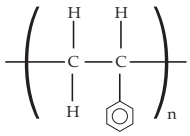


tetrafluoroethene monomer polytetrafluoroethene

Dispersion forces are possible between polymer chains



Examples and uses of addition polymers

Name	Structure & bonding		Properties	Uses
Polyethene (polythene)		Low density polyethene has random branched chains and low dispersion forces. High density polyethene is more regularly arranged and larger dispersion forces.	LDPE's have low melting points, and are weak and flexible. HDPE's have higher melting points and are stronger.	• Plastic bags • Ice cream containers • Drink bottles
Polychloroethene (polyvinylchloride) PVC		Polar C-Cl bonds allow for dipole-dipole interactions.	Hard and rigid. Can be made softer with plasticisers.	• Plumbing pipes • Door and window frames • Imitation leather and inflatable products
Polytetrafluoroethene PTFE		Highly polar C-F bonds cause increased dispersion forces.	Non-stick, high melting point and very strong.	• Non-stick coatings • Corrosion protection
Polyphenylethene (polystyrene)		Benzene rings along the chains keep chains apart but contribute to dispersion forces.	Can be expanded on production to low density. Brittle.	• Coffee cups • Packaging • Insulation

4.11.2 Condensation polymers

Condensation polymerisation usually occurs between two different types of monomers that contain two functional groups. Water is eliminated through a condensation reaction and bonds are formed to join monomers together.

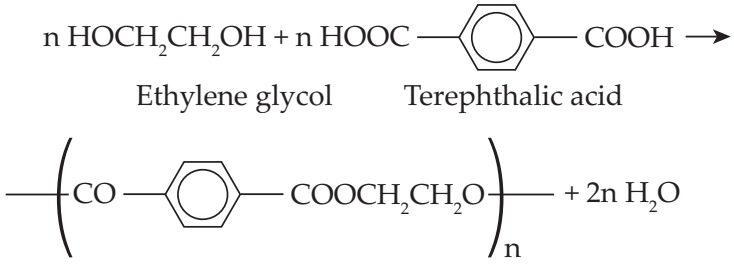
Condensation reactions can be used to produce polyesters and polyamides.

Polyesters

Polyesters result from condensation reactions between diols (alcohols with two hydroxyl groups) and dicarboxylic acids (carboxylic acids with two carboxyl groups). The carboxyl groups and the hydroxyl groups form ester links to produce the polymer chain.

Example

Polyethylene terephthalate [PET] is a strong polyester used in fibres for clothing, transparent drink bottles and food containers.



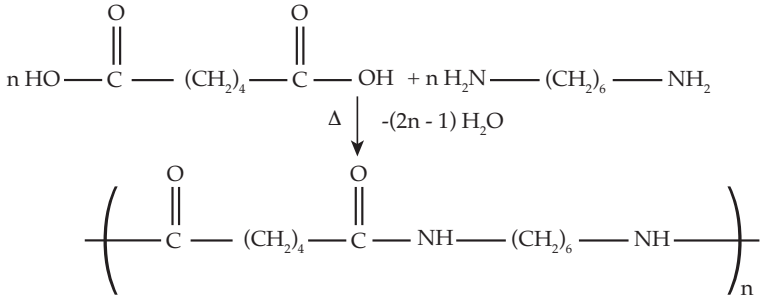
Polyethylene terephthalate

Like addition polymers, the properties of a condensation polymers are determined by the structure of the polymer. Polyester chains contain the carbonyl group, C=O, at regular intervals along the chain which allows dipole-dipole interactions between chains. These contribute to the strength of the polymer.

Polyamides

Polyamides result from the condensation reactions between dicarboxylic acids and diamines (amines with two amino groups). The amino groups and the carboxyl groups form amide links to produce the polymer chain.

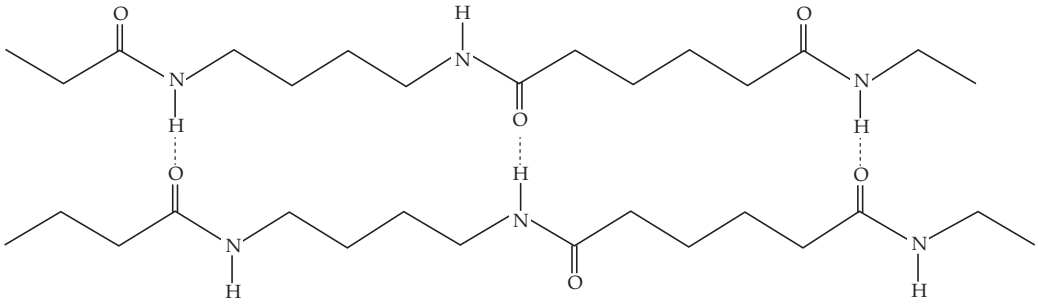
Example Nylon 6,6



Nylon

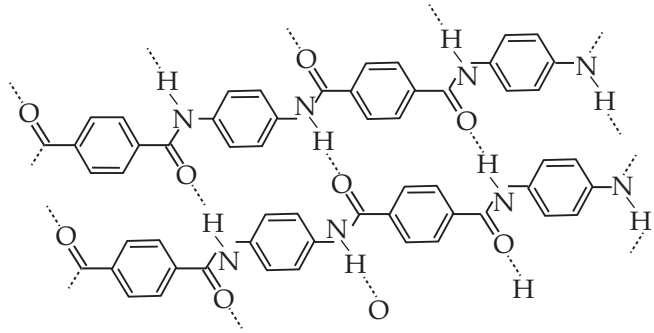
In the 1930's women's silk stockings were very popular, but in the depression years the price became prohibitive. Nylon was invented at around the same time and nylon stockings were marketed as a cheaper replacement. It is thought that the name nylon was coined because ladies from New York to London were wearing these fashionable modern items. Hence NY-LON.

Polyamide chains contain the C=O and N-H groups and so can form hydrogen bonds and dipole-dipole interactions between chains.



Generally the smaller the monomers the greater the proportion of C=O and/or N-H there are in the polymer. This increases the polymer's strength as these enable more hydrogen bonding and dipole-dipole interactions.

Kevlar is a very strong polyamide used to make sails and body armour. The amide bond enables the polymer chains to form hydrogen bonds with one another.



4.11.3 Polypeptides and proteins from a bonding perspective

Polypeptides and proteins are natural polyamide condensation polymers that form when amino acids (which contain both the amino and carboxyl groups) form amide links to produce the polymer chain.

The α-amino acid monomers are joined by peptide bonds (amide links) to form polypeptides. Each protein contains at least one long polypeptide. Polypeptides are said to contain amino acid residues.

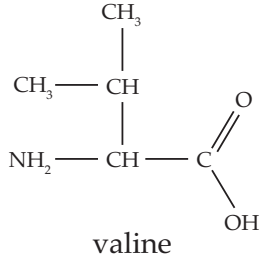
Proteins have four levels of structure. These levels are called primary, secondary, tertiary and quaternary. Quaternary structure is beyond the scope of this course.

The hydrogen bonds and dipole-dipole interactions that protein chains exhibit contribute to the structure of the protein.

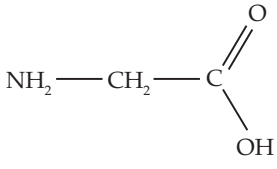
In addition, there are dispersion forces between polymer chains which increase with the increasing molecular mass of attached groups.

The specific sequence of α-amino acids that makes up a protein is called its **primary structure**.

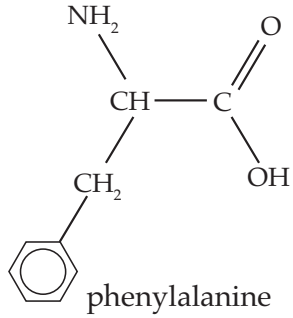
Examples



valine

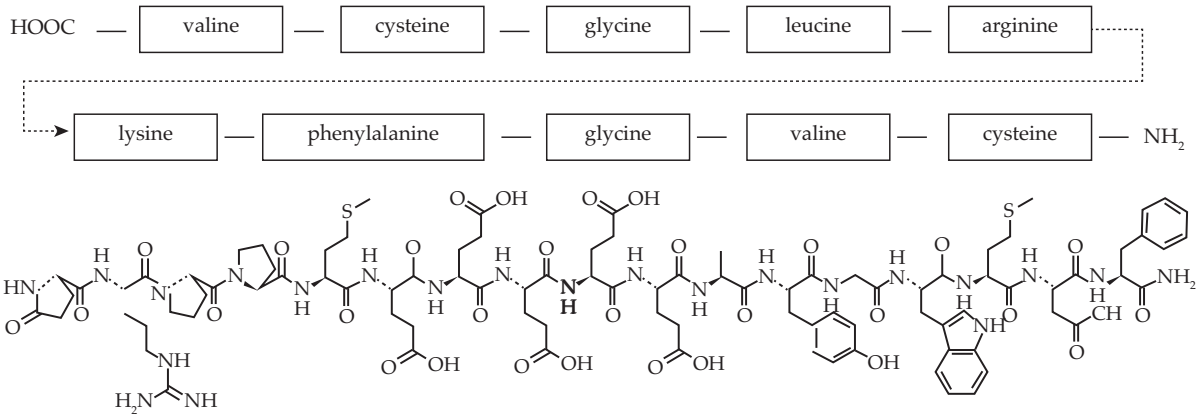


glycine



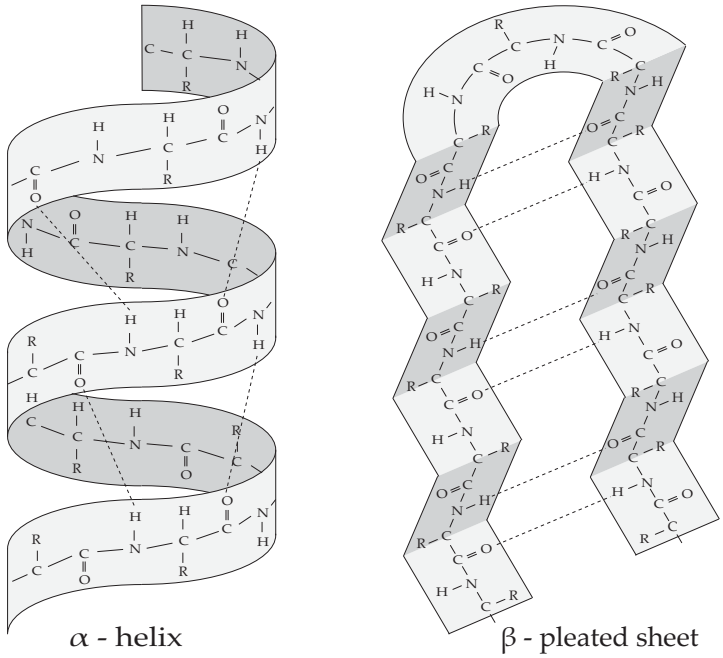
phenylalanine

These amino acids form peptide links with each other to form polypeptides.



The peptide links in the chain can form hydrogen bonds with each other and these cause the chain to cross-link, coil into a helix and fold into pleats. This is the secondary structure of proteins. Hydrogen bonding between amide and carbonyl functional groups within a peptide chain leads to α-helix structures while hydrogen bonding between adjacent polypeptide chains leads to β-pleated sheets.

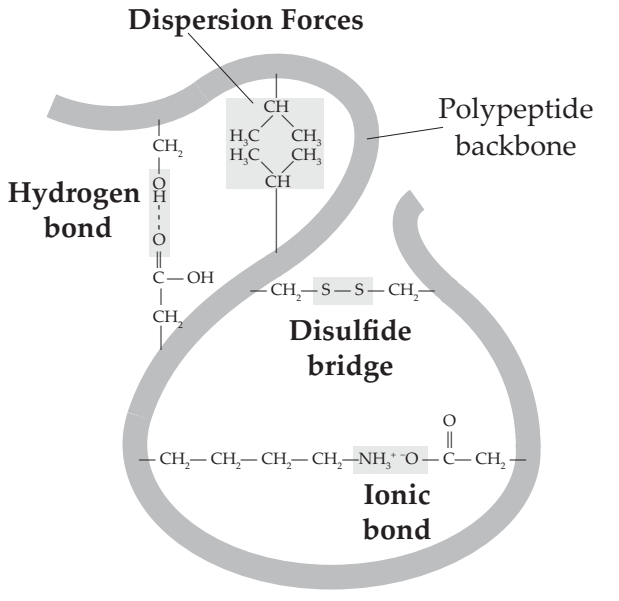
Secondary structure is the result of hydrogen bonding



The tertiary structure of a protein is its overall three-dimensional shape. This shape is produced by further interactions between the side chains of the polypeptides. These interactions include disulfide bridges, hydrogen bonding, dipole-dipole interactions, dispersion forces and ionic interactions and they give rise to a protein's characteristic shape.

- Disulfide bridges are covalent bonds between two sulfur-containing side groups. This forms a very strong bond.
- Hydrogen bonding occurs between groups like –OH and –NH_2.
- Dipole-dipole interactions occur between polar side groups.
- Dispersion forces are weak interactions between non-polar side groups like methyl, CH_3.
- Ionic interactions are between charged side groups like CO_2^- and NH_3^+

Interactions contributing to tertiary structure



The Protein Data Bank (PDB)

The Protein Data Bank (PDB) houses an international repository of the structural data of known proteins. Most of the data has been determined by X-ray crystallography which provides the 3-D coordinates of the atoms within a protein. Other methods including nuclear magnetic resonance (NMR), vibrational spectroscopy and cryo-electron microscopy have enabled more structures and many of higher resolution to be recorded. When a new protein is discovered, comparison to other proteins through databases like the PDB can help to predict its function.

The function of a protein is dependent on its 3-D structure. Proteins contain a wide range of functional groups. When combined in various sequences, these functional groups determine the structure and can account for the protein's function.

Structural proteins are proteins that are more rigid than others and can form structural parts of cells, e.g. collagens provide support for connective tissues such as tendons and ligaments.

Contractile proteins have more flexibility and their function is due to their ability to act as springs, levers or hinges, e.g. myosin which is involved in muscle contraction and movement.

Hormonal proteins are messenger proteins which help to coordinate certain bodily activities, e.g. insulin which controls blood-sugar concentration.

Transport proteins move molecules from one place to another around the body, e.g. haemoglobin transports oxygen through the blood via red blood cells.

Storage proteins store metals ions and amino acids, e.g. ferritin stores iron in the body.

Enzymes are proteins that have functional groups and shapes that are essential to their function of catalysing specific chemical reactions in biological systems. (See 4.11.4 below)

Antibodies are proteins are used by the immune system to identify and defend against antigens like bacteria and viruses, e.g. Immunoglobulin A (IgA) prevents colonization of mucosal areas by pathogens.

4.11.4 Enzymes

Enzymes are biological catalysts that accelerate chemical reactions. They are required to catalyse most of the metabolic processes that occur in cells. Most enzymes are proteins and their 3D structure makes them specific to certain biological reactions. They allow substrates to react and form products at the rate necessary for the cell to survive. Being catalysts, they aren't used up in the reaction and work by providing an alternative pathway to lower activation energy.

Enzyme activity can be affected by inhibitors, like drugs and poisons, which decrease their activity. There are also enzyme activators that increase their activity.

Enzymes activity is also affected by changes in temperature and pH.

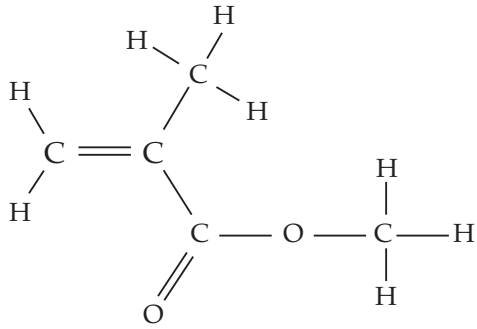
Examples of Enzymes

Proteases break down or hydrolyse peptide bonds of proteins. They aid digestion. Lipases hydrolyse fats or lipids. Amylase hydrolyses dietary starch into disaccharides and trisaccharides, enabling them to be converted by other enzymes into glucose. Catalase catalyses the decomposition of hydrogen peroxide into water and oxygen.

Commercially, enzymes are used in biological washing powders to remove protein, fat or starch stains on clothing. Enzymes are also used to make antibiotics.

Set 8. Polymers and amino acids

1. Perspex is a clear, colourless polymer. Methyl methacrylate, shown below, is the only monomer used in its synthesis.



(a) Would Perspex be an addition or condensation polymer?

(b) Draw a section of the Perspex polymer showing at least two repeating units.

2. Write an equation for the synthesis of polychloroethene (PVC) from its monomer chloroethene.

3. PVC is a hard, rigid polymer. Explain this with reference to the intermolecular forces present between polymer chains.

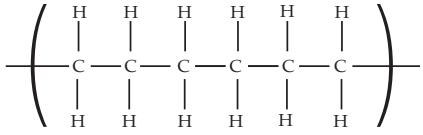
4. Which of the polymers below would be best suited for making:

   (a) a coffee cup.

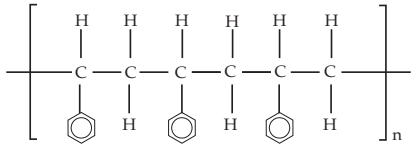
   (b) a water bottle.

   (c) gutter pipes.

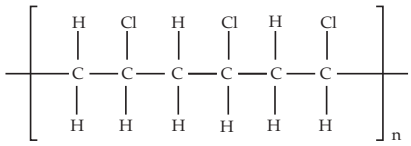
i)



ii)



iii)



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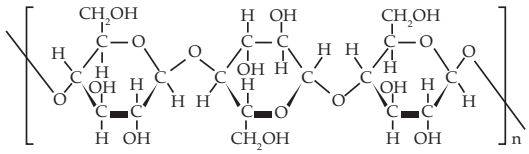
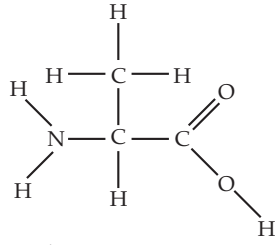
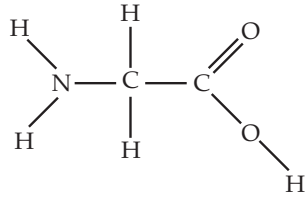


5. Silks produced by insects are natural protein fibres or polypeptides. They consist of amino acid residues. One such silk was found to consist mainly of alternating glycine and alanine residues.



alanine



glycine

   (a) Draw a section of this natural protein fibre showing at least four amino acid residues.

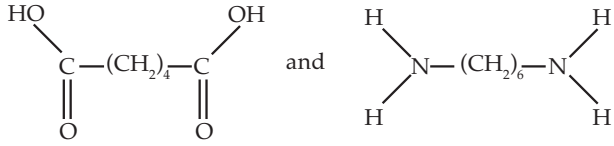
(b) What type of polymerisation reaction is this?

(c) What is the name of the link between each amino acid residue in the silk?

(d) State the bonding type that contributes to the α-helix structure of the silk.

6. The monomers below are used to produce Nylon 6,6.

(a) Name these monomers.



(b) Draw a section of Nylon 6,6 showing at least two repeating units.

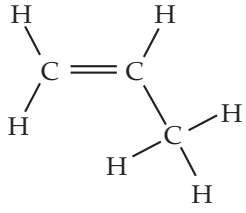
7. Cysteine is an α-amino acid found in many high protein foods. Its condensed chemical formula is:

$$HSCH_2CH(NH_2)COOH$$

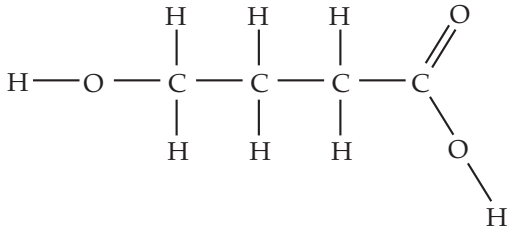
(a) Draw the structural formula of cysteine.

(b) Draw the structural formula of cysteine in its zwitterionic form.

8. Draw diagrams of an addition polymer and a condensation polymer which uses one of the monomers below. Show a minimum of two repeating units.



Monomer 1

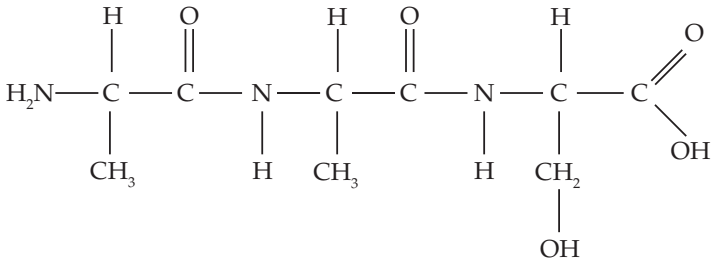


Monomer 2

(a) Addition polymer

(b) Condensation polymer

9. A tripeptide is a peptide consisting of three amino acids joined by peptide bonds.



(a) Circle the peptide bonds in the tripeptide shown above.

(b) Draw the structures of the two amino acid (peptide) monomers that produced this tripeptide.

(c) Using this tripeptide as an example, explain what determines its primary structure.

(d) Which parts of the tripeptide could contribute to α-helix structures or β-pleating secondary structures in a protein?

(e) Explain the difference between α-helix structures and β-pleating.

(f) The tertiary structure of proteins determines their shape and also function. Give examples of side chains and functional groups on polypeptides that can contribute to a protein's tertiary structure and name the type of bonding that occurs between each.

10. Carbonic anhydrases are enzymes that help maintain the pH balance in blood. The reversible reaction that they catalyse is shown below:

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

The forward reaction is fast but the reverse reaction takes about 15s without a catalyst.

(a) Explain why it is important that this reaction can move in either direction at a rapid rate.

(b) How do carbonic anhydrases catalyse this reaction?

4.11.4 Empirical and molecular formulae of organic compounds

The empirical formula of a compound is the formula which shows the simplest ratio of the atoms of different elements present in the molecule. Quantitative information about the elements in the compound is collected empirically by experiment.

In simple empirical formula calculations the percentages or masses of elements in a sample of a compound are provided. These can be converted to moles and then the simplest ratio of moles of the elements found.

When finding empirical formulae of organic compounds, products of reactions of the compound provide information about the quantities of elements present. Typically the organic compound will contain carbon, hydrogen and oxygen. Other elements like nitrogen, sulfur or even halogens like chlorine may also be present.

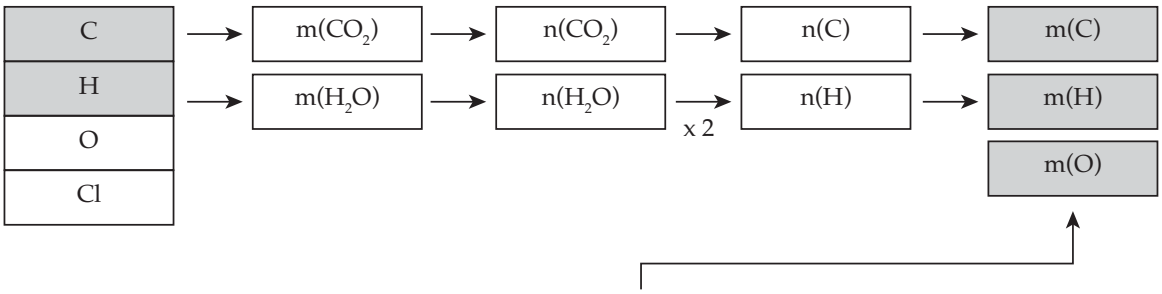
The masses of carbon and hydrogen in the compound can be found using combustion analysis, where the compound is burned completely in excess oxygen. The mass of carbon dioxide produced provides information about the mass of carbon in the compound. The mass of water produced tells us the mass of hydrogen in the compound.

Separate samples of the compound can then be subjected to other reactions to collect products containing any other elements present. Often these include products like ammonia, sulfur dioxide and silver chloride. These masses can provide information about the masses of the other elements contained in the compound.

Oxygen is often present, but the mass of this in the compound can only be determined by subtracting the masses of all other elements, once determined, from the original mass of the analysed sample.

Once the masses of all elements in the sample are known the empirical formula can be determined.

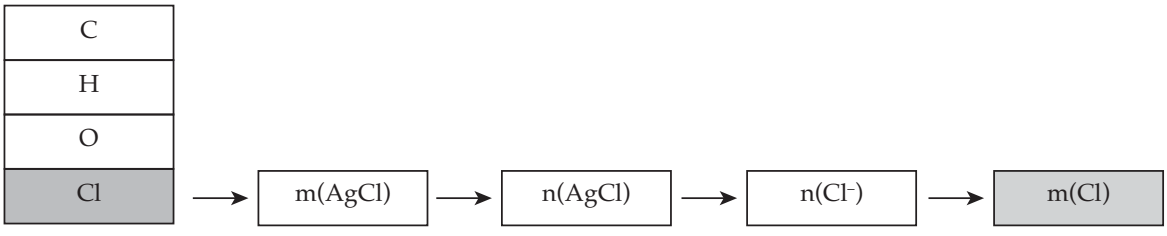
Sample 1



Once the masses of carbon and hydrogen in Sample 1 are known, and the mass of chlorine in Sample 2 is adjusted to determine its mass in Sample 1, these can be subtracted from the original mass of sample to determine the mass of oxygen.

$$m(Cl)_{Sample\ 1} = \frac{m(Sample\ 1)}{m(Sample\ 2)} \times m(Cl)_{Sample\ 2}$$

Sample 2



Then determine the simplest ratio of moles for each element:

Example

		C	H	O	Cl
Mass (g)	m	14.92	3.130	9.935	22.01
Molar mass ($g\ mol^{-1}$)	M	12.01	1.008	16.00	35.45
Moles (mol)	n = m/M	$\frac{14.92}{12.01}$ = 1.242	$\frac{3.130}{1.008}$ = 3.105	$\frac{9.935}{16.00}$ = 0.6209	$\frac{22.01}{35.45}$ = 0.6209
Simplest ratio of moles	Divide by smallest	$\frac{1.242}{0.6209}$ = 2	$\frac{3.105}{0.6209}$ = 5	$\frac{0.6209}{0.6209}$ = 1	$\frac{0.6209}{0.6209}$ = 1

The empirical formula is C_2H_5OCl.

The molecular formula of a compound shows its actual formula so if E.F. is CH_2O, M.F. could be $C_2H_4O_2$, $C_3H_6O_3$ etc. It will either be the same as the empirical formula, or a whole number multiple of it. To determine the molecular formula from the empirical formula one must be provided with the molar mass of the compound, or be given information to calculate it. Then the molar mass of the empirical formula can be compared with the molar mass of the molecular formula.

Empirical determination of the molar mass of the compound is often done by weighing a sample of the compound, turning it into a gas, and then measuring its pressure, temperature and volume. From PV = nRT, the number of moles of sample can be obtained, and then using the mass of sample the molar mass can be calculated.

$$n(\text{sample}) = \frac{P \times V}{R \times T}$$

where P = pressure in kPa
V = volume in L
R = gas constant, 8.314
T = temperature in Kelvin

$$M(\text{sample}) = \frac{m}{n}$$

Example

A 1.622 g of an organic compound X containing only carbon, hydrogen and bromine was analysed in the laboratory. The compound was divided into equal samples for testing. The first sample was combusted in plenty of oxygen and produced 0.535 g carbon dioxide. The water produced in the reaction escaped as steam and was unable to be measured. The second sample was reacted with concentrated nitric acid and then treated with silver nitrate to yield 1.525 g of silver bromide.

(a) Determine the empirical formula of compound X.

Sample 1:

$n(CO_2)$ in sample 1 = $m(CO_2) / M(CO_2)$
= 0.535 / 44.01
= 0.01216 mol

n(C) in sample 1 = $n(CO_2)$
= 0.01216 mol

m(C) in sample 1 = n(C) × M(C)
= 0.01216 × 12.01
= 0.1460 g

Sample 2:

$n(AgBr)_{\text{in sample 2}} = m(AgBr) / M(AgBr)$ $\quad M(AgBr) = 107.9 + 79.90$

$= 1.525 / 187.8$

$= 8.12 \times 10^{-3}$ mol

$n(Br)_{\text{in sample 2}} = n(AgBr)$

$= 8.12 \times 10^{-3}$ mol

$m(Br)_{\text{in sample 2}} = n(Br) \times M(Br)$

$= 8.12 \times 10^{-3} \times 79.90$

$= 0.6488$ g

Since samples are the same size, 0.811g

$m(H) = 0.8110 - m(C) - m(Br)$

$= 0.8110 - 0.1460 - 0.6488$

$= 0.01619$ g

		C	H	Br
Mass (g)	m	0.1460	0.01619	0.6488
Molar mass ($g\ mol^{-1}$)	M	12.01	1.008	79.90
Moles (mol)	n = m/M	0.01216	0.01606	0.00812
Simplest ratio of moles	Divide by smallest	$\frac{0.01216}{0.00812} = 1.497$	$\frac{0.01606}{0.00812} = 1.993$	$\frac{0.00812}{0.00812} = 1$
		3	4	2

The empirical formula is $C_3H_4Br_2$.

(b) A further 0.500 g sample of compound X was heated to above its boiling point and turned into a gas. At 135.0°C and a pressure of 101.3 kPa its volume was measured to be 83.7 mL. What is its molecular formula?

$n(X) = \frac{PV}{RT}$

$= \frac{101.3 \times 0.0837}{8.314 \times (135.0 + 273.15)}$

$= 2.499 \times 10^{-3}$ mol

$M(X) = m(X) / n(X)$

$= 0.500 / 2.499 \times 10^{-3}$

$= 200.11\ g\ mol^{-1}$

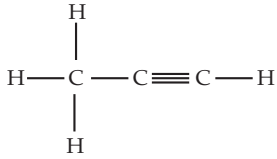
$M(C_3H_4Br_2) = (3 \times C) + (4 \times H) + (2 \times Br)$

$= 199.862\ g\ mol^{-1}$

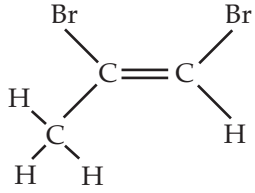
Since the molar mass of the molecular formula is essentially the same as the molar mass of the empirical formula, the molecular formula is also $C_3H_4Br_2$.

(c) It is discovered that compound X was the product of the addition of bromine to an alkyne. Draw the structure of both compound X and the original alkyne from which it was prepared.

An alkyne with three carbon atoms will be propyne.

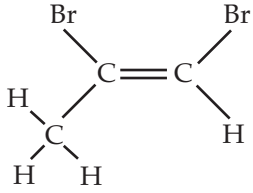


The addition of bromine to propyne produces 1,2-dibromopropene.

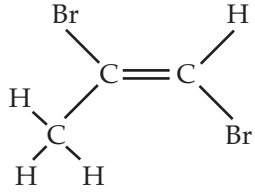


(d) Give the two possible IUPAC names for compound X.

1,2-dibromopropene has two geometric isomers.



cis-1,2-dibromopropene



trans-1,2-dibromopropene

Set 9. Empirical and molecular formulae

1. An organic compound contains 40.67% of carbon, 8.54% of hydrogen, 27.09% of oxygen, and the rest is nitrogen. Determine its empirical formula.

2. An organic compound containing carbon, hydrogen, oxygen and chlorine gave on analysis 16.30% of carbon and about 0.68% of hydrogen. On reacting with $AgNO_3$, 0.295 g of the compound gave 0.861 g of silver chloride. Another sample of mass 0.295 g was heated and had a volume of 49.2 mL at 101.3 kPa pressure at 27.0°C.

   Determine the molecular formula of the compound.

3. An organic compound containing only carbon, hydrogen and oxygen is analysed by combusting a 2.323 g sample in excess oxygen. All the carbon in the compound is converted to carbon dioxide, and all the hydrogen it contains is converted to water.

   (a) Given that the mass of carbon dioxide produced is 5.281 g and the mass of water is 2.162 g, calculate the empirical formula of the compound.

   (b) When a 1.503 g sample of the compound is vaporised in the absence of air, the vapour occupies 579.7 mL at S.T.P. From this data, calculate the molecular formula of the compound.

   (c) Further analysis shows the presence of a CHO group. From this information, draw the structural formula of the compound.

4. A sample of 4.121 g of a chlorofluorocarbon (a compound containing carbon, fluorine and chlorine only) was analysed as follows:

   All the carbon in the sample was converted into carbon dioxide gas, and all its chlorine was converted into hydrochloric acid. The carbon dioxide weighed 1.320 g, and the hydrochloric acid formed required 85.70 mL of 1.050 mol L^{-1} ammonia solution for complete neutralisation. Another sample of the same gaseous compound of mass 3.661 g occupied 0.6068 L at S.T.P.

   (a) Determine the empirical formula of the compound.

   (b) Determine the molecular formula of the compound.

   (c) Name and draw a possible structure of the compound.

5. 15.00 g of an alkyl hydrogen sulfate containing only carbon, hydrogen, oxygen and sulfur was completely combusted to produce 10.50 g of carbon dioxide and 6.421 g of water. A second sample weighing 10.00 g was reacted with concentrated sodium hydroxide and all of its sulfur was reacted to form 9.980 g of sodium sulfite.

   (a) Determine the empirical formula of the alkyl hydrogen sulfate.

   (b) To deduce its molecular formula 2.000 g was heated to 220.0ºC, beyond its boiling point at 100.0 kPa, and it had a volume of 0.651 L. What is its molecular formula?

   (c) How might its formula be written in condensed form?

6. A chlorofluorocarbon (a compound containing only chlorine, fluorine and carbon) is analysed by preparing two identical samples of the compound of mass 2.320 g. The first sample is burnt in excess oxygen gas to convert all the carbon it contains into carbon dioxide. The second sample of the compound is chemically treated to convert all the chlorine it contains into hydrochloric acid.

   (a) Given that the mass of carbon dioxide produced is 0.9267 g and the hydrochloric acid produced requires 17.20 mL of 3.062 mol L^{-1} ammonia solution for complete neutralisation, calculate the empirical formula of the chlorofluorocarbon.

   (b) When a 1.503 g sample of the compound is vaporised in the absence of air, the vapour occupies 152.8 mL at S.T.P. From this data, calculate the molecular formula of the compound.

   (c) Draw full structural formula for the chlorofluorocarbon.

7. 0.450 g of an organic compound containing carbon, hydrogen, nitrogen and possibly oxygen was combusted to produce 0.792 g of carbon dioxide and 0.324 g of water. 0.240 g of the same compound was analysed to determine its nitrogen content. It was heated with sulfuric acid to produce ammonium sulfate and this was then distilled with sodium hydroxide to produce ammonia. The ammonia formed was absorbed into 50.0 mL of 0.100 M sulfuric acid. The excess acid required 76.5 mL of 0.100 M sodium hydroxide for complete neutralisation.

   Determine the empirical formula of the compound.

8. An organic compound containing only carbon, hydrogen and oxygen is analysed by combusting a 3.605 g sample in excess oxygen. All the carbon in the compound is converted to carbon dioxide, and all the hydrogen it contains is converted to water.

   (a) Given that the mass of carbon dioxide produced is 8.802 g and the mass of water is 3.603 g, calculate the empirical formula of the compound.

   (b) When a 2.466 g sample of the compound is vaporised in the absence of air, the vapour occupies 441.8 mL at 22.0°C and 95.0 kPa. From this data, calculate the molecular formula of the compound.

   (c) Further analysis shows the compound is an hydroxy aldehyde. From this information, draw a possible structural formula of the compound.

9. Hexamethylene glycol is an organic compound used in the production of polyesters and polyurethane. Elemental analysis of hexamethylene glycol has shown it to be composed of carbon, hydrogen and oxygen only.

   In order to find the empirical formula of hexamethylene glycol, a 0.7870 g sample of the compound was burned in a plentiful supply of oxygen, causing the carbon and hydrogen to be converted into carbon dioxide and water respectively. The mass of carbon dioxide formed was 1.759 g, whilst the mass of water was 0.8436 g.

   Further analysis of hexamethylene glycol showed that a 0.8980 g sample when heated to gaseous state occupied 198.0 mL at a pressure of 101.3 kPa and a temperature of 45.0ºC.

   (a) Calculate the empirical formula hexamethylene glycol.

   (b) Determine the molecular formula of hexamethylene glycol.

   (c) Given that hexamethylene glycol is a diol, or an alcohol with two hydroxyl groups (-OH), draw a possible structure showing all atoms and bonds.

   (d) Hexamethylene glycol is not an IUPAC name. Give the IUPAC name for the structure that you have drawn above.

Chapter

5

Chemical synthesis

In industry companies employ scientists to design chemical synthesis pathways in order to make or synthesise new substances, and to refine existing substances.

Chemical synthesis often requires a sequence of chemical reactions and chemists select reagents and reaction conditions in order to optimise the rate and yield of the product. Collision theory, the use of catalysts and the careful manipulation of systems in equilibrium are utilised. For example the production of ammonia via the Haber process and the production of sulphuric acid via the Contact process (See Chapter 1 section 1.12).

Chemists begin by researching in the laboratory with small quantities in order to determine most efficient way to turn a raw material into the desired product. Small scale pilot plants are often built to test the process and once optimised then large scale production can commence.

5.1 ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS

Chemists designing chemical synthesis pathways must take into account the sustainability of the process. They should aim to meet current demand and production requirements whilst ensuring that the process does not prevent future needs being met. Use of renewable resources, both for raw materials and for the energy requirements of the process would be ideal but is often difficult to achieve. This is a challenge for chemists catering for the modern consumer world and an increasing population.

For both economic and environmental reasons, which go hand in hand, chemists look to the availability of **local resources** to meet their raw material and energy requirements. This minimises transport costs and also the use of fuels.

Minimising waste is very important and chemists work to ensure that raw materials are used fully and energy losses are avoided. Unused reactants can be recycled back into the process to achieve greater conversion to products.

Energy recycling should be employed wherever practicable. Here energy that might leave the system is recovered and reused in the process e.g. excess heat can be used to generate electrical energy or simply be returned to the process where required. This reduces energy costs and also minimises greenhouse gas pollution by reducing fuel consumption.

The **Atom economy** can be used in green chemistry as an alternative to yield. It is given as a percentage and represents the proportion of reactant atoms that make their way into the final product. It is a measure of

$$\text{Atom economy } \% = \frac{\text{Relative molecular/formula mass of desired products} \times 100}{\text{Relative molecular/formula mass of all reactants}}$$

Catalysts can be used to decrease energy requirements whilst maintaining a sufficient rate.

Often processes involve toxic reactants or by-products. These should be kept from entering the natural environment. Processes should be designed with safety in mind.

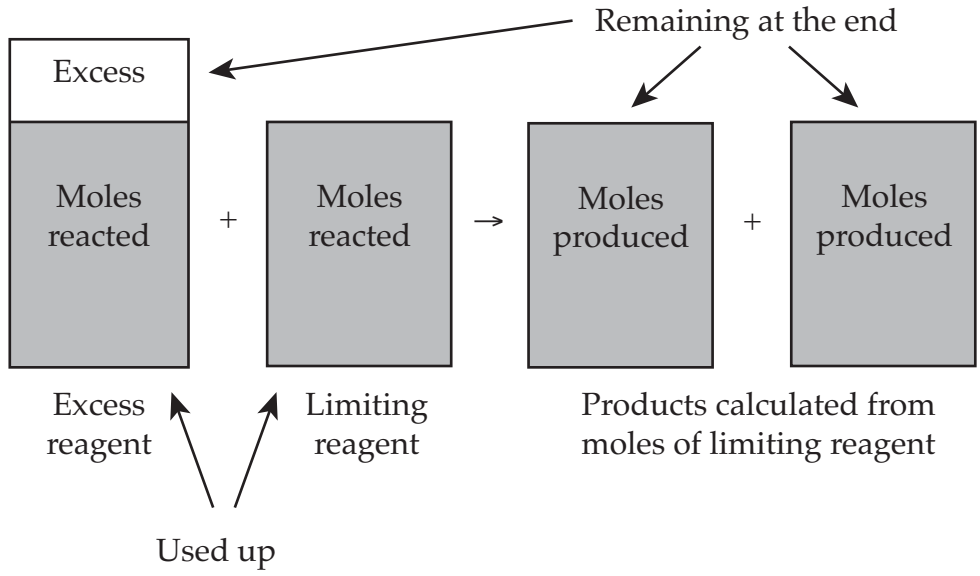
5.2 CALCULATIONS IN CHEMICAL SYNTHESIS

5.2.1 Limiting reagent calculations

Quantities of products required in a chemical synthesis reaction can be calculated by comparing stoichiometric quantities with actual quantities and by determining the limiting reagent.

In a typical calculation, using a chemical equation, information is provided about one of the reactants or products. It could be the mass, moles, concentration or gaseous volume of this species. In a limiting reagent problem information is provided about two of the reactants. The chemist must then determine which reactant is the limiting reagent (the one that runs out) and which is the excess reagent. The limiting reagent is always all used up.

Once the limiting reagent is determined it can be used to calculate the mass, moles, concentration or gaseous volume of any of the other species in the chemical equation, including the amount of the excess reactant that actually reacted.



Example

Hydrogen gas is produced by the reaction between zinc and hydrochloric acid, according to the equation below.

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$

If 10.94 g of hydrochloric acid is added to 13.08 g of zinc, calculate the limiting reagent, the mass of hydrogen gas produced and also the mass of excess reactant.

Step 1. Determine the limiting reagent.

Calculate the number of moles of each reactant.

n(Zn) = m/M

= 13.08/65.38

= 0.2000 mol of Zn

n(HCl) = m/M

= 10.94/36.458

= 0.3000 mol of HCl

Step 2. Compare the stoichiometric and actual amounts

Stoichiometric		n(Zn)	:	n(HCl)
		1	:	2
Actual		n(Zn)	:	n(HCl)
		0.2000	:	0.300
	or	1	:	(1.50) ← *not enough as it needs to be 2*

Therefore HCl is the limiting reagent!

Now you can use the limiting reagent to work out product produced and excess reagent.

Step 3. Calculate moles of H_2 produced

$n(H_2) = ½ \times n(HCl)$

$= ½ \times 0.3000$

$= 0.1500$ mol

Step 4. Calculate mass of H_2 produced

$m(H_2) = n \times M$ $\quad M(H_2) = 2 \times 1.008$

$= 0.150 \times 2.016$ $\quad = 2.016$ g mol^{-1}

$= 0.3024$ g

Step 5. Calculate the moles of excess reactant that reacted.

$n(Zn) = ½ \times n(HCl)$

$= ½ \times 0.300$

$= 0.1500$ mol

Step 6. Calculate the mass of excess reactant that reacted.

$m(Zn) = n \times M$ $\quad M(Zn) = 65.38$ g mol^{-1}

$= 0.1500 \times 65.38$

$= 9.809$ g

Step 7. Calculate the mass of excess reactant remaining.

$m(Zn)_{remaining} = m(Zn)_{initial} - m(Zn)_{reacted}$

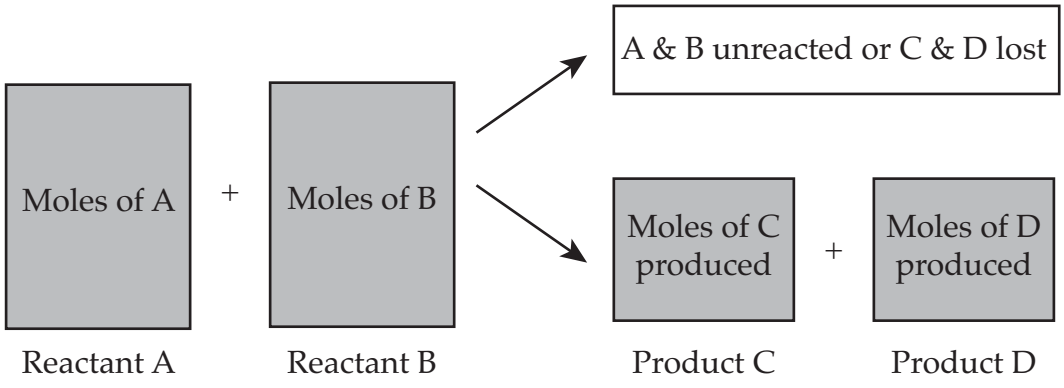
$= 13.08 – 9.809$

$= 3.371$ g

5.2.2 Percentage yield calculations

Chemists calculate the percentage yield of a chemical synthesis reaction by comparing theoretical versus actual product quantities.

In most industrial examples the process is not 100% efficient. If this is the case, the mass of products will be less than that predicted by stoichiometric calculations, as some is lost in production. It is important for chemists to be able to calculate losses for economic reasons.



Example

The fertiliser, ammonium sulfate, is produced by the following reaction:

$$2NH_{3(aq)} + H_2SO_{4(aq)} \rightarrow (NH_4)_2SO_{4(aq)}$$

What mass of ammonium sulfate could be produced from 30.0 kg of ammonia, assuming that the sulfuric acid is in excess and the process is 75.0% efficient?

This problem is solved as with other mass to moles to moles to mass problems.

$n(NH_3) = m(NH_3) / M(NH_3)$ $M(NH_3) = 17.034 \text{ g mol}^{-1}$

$= 30000 / 17.034$

$= 1761.18 \text{ mol}$

$n((NH_4)_2SO_4) = ½ \times n(NH_3)$

$= 880.59 \text{ mol}$

$m((NH_4)_2SO_4) = n((NH_4)_2SO_4) \times M((NH_4)_2SO_4)$ $M((NH_4)_2SO_4) = 132.144 \text{ g mol}^{-1}$

$= 880.59 \times 132.144$

$= 116364.92 \text{ g}$

If the process is only 75% efficient then,

$m((NH_4)_2SO_4) = 75/100 \times 116364.92$

$= 87273.69 \text{ g}$

$= 87.3 \text{ kg produced}$

It is also possible for chemists to alter the reactant amounts for an inefficient process to ensure that a maximum quantity of product is obtained.

Example

With the previous example, assume that the chemist needs to obtain 100.0 kg of ammonium sulfate.

What mass of ammonia is required to ensure that 100.0 kg of ammonium sulfate is obtained assuming that the process is 75.0% efficient?

This problem is solved as with other mass to moles to moles to mass problems.

$n((NH_4)_2SO_4) = m((NH_4)_2SO_4) / M((NH_4)_2SO_4)$

$= 100000 / 132.144$

$= 756.75 \text{ mol}$

$n(NH_3) = 2 \times n((NH_4)_2SO_4)$

$= 2 \times 756.75$

$= 1513.50 \text{ mol}$

$m(NH_3) = n(NH_3) \times M(NH_3)$

$= 1513.50 \times 17.034$

$= 25780.97 \text{ g}$

So 25780.97 g of ammonia is required to produce 100.0 kg if the process was 100% efficient

Since it is only 75% efficient,

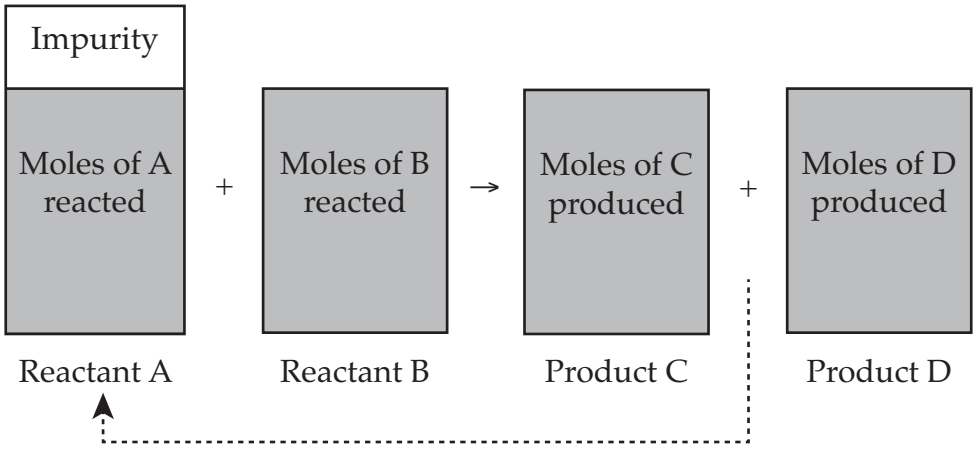
$m(NH_3)_{\text{required}} = 100/75 \times 25780.97$

$= 34374.62 \text{ g}$

Mass of NH_3 required is 34.4 kg (to 3 s.f.)

5.2.3 Percentage purity calculations

Often one of the reactants in a chemical synthesis is impure. If an impure reactant is used, it is possible to calculate the percentage purity of the reactant using stoichiometry and information about the products of the reaction.



Example

A sample of iron wire is oxidised to iron (III) oxide by reaction with oxygen. If 5.70 g of iron wire produces 8.00 g of iron (III) oxide, calculate the percentage purity of the iron wire.

Here the iron (III) oxide product is the known and the original impure iron wire is the unknown.

Step 1: Write the balanced equation.

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$$

Step 2: Calculate the number of moles of product.

$n(Fe_2O_3)$ = $m(Fe_2O_3) / M(Fe_2O_3)$ $M(Fe_2O_3) = (2 \times Fe) + (3 \times O)$

= 8.00 / 159.7 $= 159.7 \text{ g mol}^{-1}$

= 0.0501 mol

Step 3: Calculate the moles of iron in the impure reactant.

$n(Fe) = 4/2 \times n(Fe_2O_3)$

= 0.1002 mol

Step 4: Calculate the mass of iron in the impure reactant.

$m(Fe) = n(Fe) \times M(Fe)$ $M(Fe) = 55.85 \text{ g mol}^{-1}$

$= 0.1002 \times 55.85$

= 5.60 g

Step 5: calculate the percentage purity

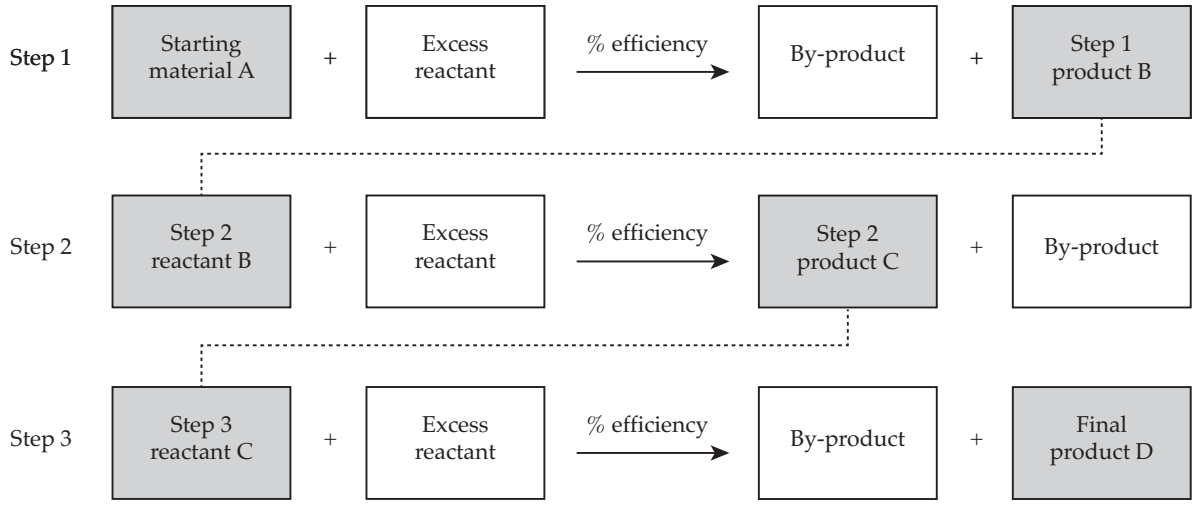
% purity = m(Fe) / m(impure sample) × 100

$= \frac{5.595}{5.70} \times 100$

= 98.2%

5.2.4 Multiple step stoichiometry calculations

Many industrial processes involve a series of reactions to produce the final product. When attempting calculations involving several steps the stoichiometry of each equation must be taken into account. One product of an earlier reaction becomes a reactant in the next. Efficiencies of each reaction can also be included for each step.



n(B) = stoichiometric ratio × n(A) × % efficiency

n(C) = stoichiometric ratio × n(B) × % efficiency

n(D) = stoichiometric ratio × n(C) × % efficiency

Example

The Ostwald Process for the production of nitric acid is an example of a multiple step process.

Calculate the mass of nitric acid produced when 300.0 kg of ammonia is reacted with excess oxygen. The first reaction is 96.0% efficient and the second reaction is 87.0% efficient. Assume that the final reaction is 100% efficient.

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$

$n(NH_3) = m(NH_3) / M(NH_3)$

$= 300000 / 17.034$

$= 17611.84$ mol

$n(NO) = 4/4 \times n(NH_3) \times 96/100$

$= 16907.36$ mol

$n(NO_2) = 2/2 \times n(NO) \times 87/100$

$= 14709.40$ mol

$n(HNO_3) = 4/4 \times n(NO_2)$

$= 14709.40$ mol

$m(HNO_3) = n(HNO_3) \times M(HNO_3)$

$= 14709.40 \times 63.018$

$= 926957.27$ g

$= 927$ kg (3 sfs)

$M(HNO_3) = (1 \times H) + (1 \times N) + (3 \times O)$

$= 63.018$ g mol^{-1}

5.3 EXAMPLES OF CHEMICAL SYNTHESIS

Industrial production of ethanol

Ethanol can be produced via the fermentation of carbohydrates like sugar from sugar cane. This reaction is catalysed by enzymes from yeast. Biological catalysts are often used to provide cheaper, lower energy, chemical synthesis pathways which are an alternative to more expensive pathways that require high temperature or pressure conditions.

Example Glucose fermenting to form ethanol and carbon dioxide.

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2CH_3CH_2OH + 2CO_2$$

Ethanol can also be produced by the direct hydration of ethene. Here, high temperatures and pressures are required. Conditions of 70 atm, 300°C and the use of a phosphoric acid catalyst are chosen to maximise yield.

Example

$$CH_2CH_2(g) + H_2O(g) \xrightarrow[\text{heat and pressure}]{\text{phosphoric acid catalyst}} CH_3CH_2OH(l)$$

Multiple step chemical synthesis

The production of ethyl ethanoate is an example of a multiple-step chemical synthesis.

Ethanol, once produced, can be oxidised to ethanoic acid as described in the Carboxylic Acid section. This ethanoic acid can then be reacted with more ethanol to produce the ester, ethyl ethanoate, as described in the Ester section.

Step 1: $$CH_2CH_2 + H_2O \xrightarrow[\text{heat and pressure}]{\text{phosphoric acid catalyst}} CH_3CH_2OH$$

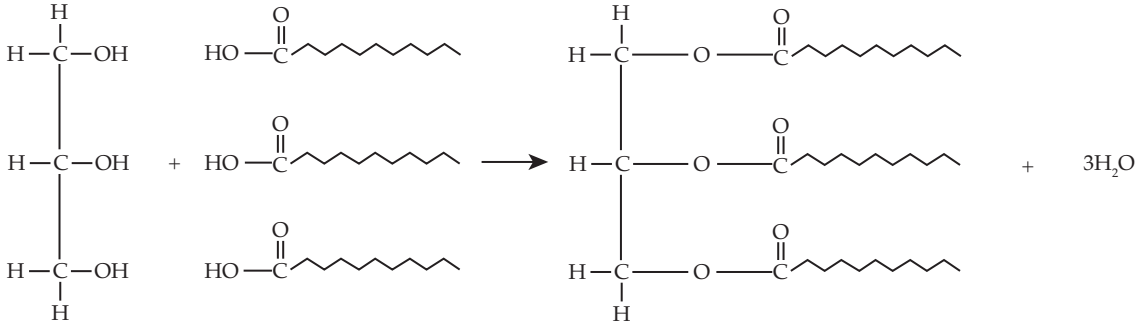
Step 2: $$CH_3CH_2OH \xrightarrow{[\text{oxidising agent}]} CH_3COOH$$

Step 3: $$CH_3COOH + CH_3CH_2OH \xrightarrow{\text{conc. sulfuric acid}} CH_3COOCH_2CH_3 + H_2O$$

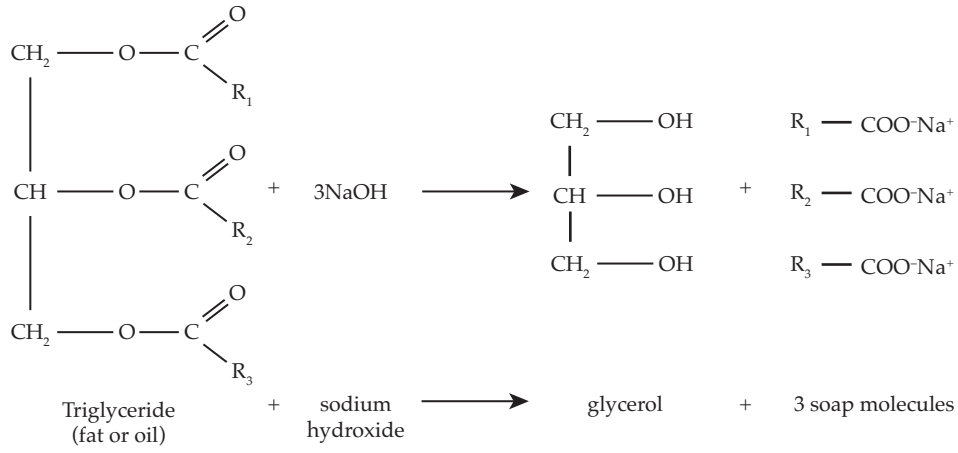
Soap making or saponification

Fatty acids are long chain carboxylic acids. If the chain contains no double bonds it is called a saturated fatty acid. If it contains double bonds it is called an unsaturated fatty acid. If it contains many double bonds it is called polyunsaturated.

Typical fats are triglycerides or lipids and these are formed when three fatty acids react with glycerol in a condensation reaction. Triglycerides contain ester linkages and so the reaction is an example of an esterification reaction.



Soap-making, or saponification, involves the basic hydrolysis of fats. It produces glycerol and soap, which is a sodium or potassium salt of a long chain fatty acid.

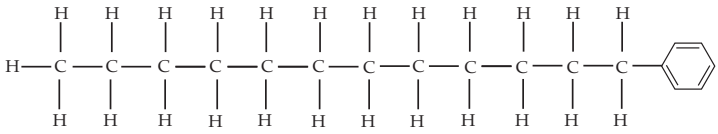


Detergents

Detergents are typically alkylbenzene sulfonates.

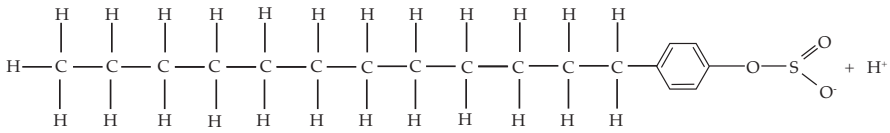
They are produced in a three-step process:

1. Alkylbenzenes are produced from the reaction between benzene and a halogenoalkane.



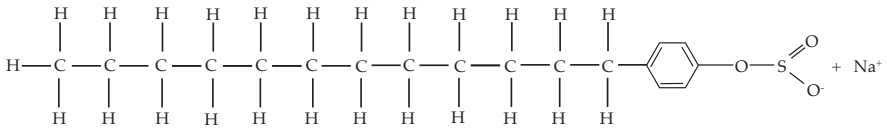
dodecylbenzene

2. The alkylbenzene is reacted with concentrated sulfuric acid to produce an alkylbenzene sulfonic acid.



dodecylbenzenesulfonic acid

3. The alkylbenzene sulfonic acid is neutralised with sodium hydroxide to produce the detergent, sodium alkylbenzene sulfonate.



sodium dodecylbenzenesulfonate – the Detergent

How do soaps and detergents work?

Soaps and detergents are surfactants or wetting agents. They enable water to wash away oils, grease and dirt.

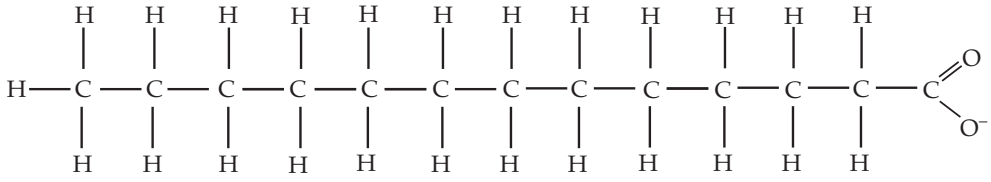
Oil and grease are non-polar and do not dissolve in water.

Once soaps and detergents dissolve they have a hydrophobic non-polar, hydrocarbon end which will bond with oil and grease, and a hydrophilic, polar charged end which will bond with water.

With soaps, the non-polar end is a hydrocarbon chain and the polar end is the carboxylate group.

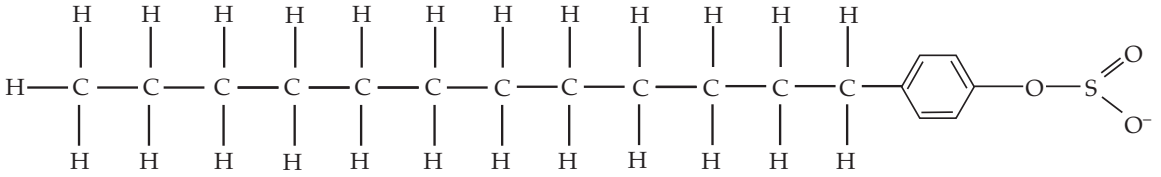
With anionic detergents the non-polar end is a hydrocarbon chain containing a benzene ring (often dodecylbenzene) and the polar end is the sulfonate group.

Typical soap



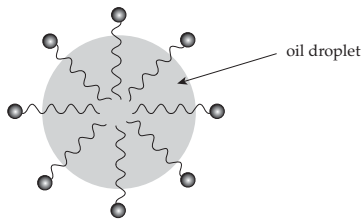
non-polar end polar end

Typical detergent



non-polar end polar end

On agitation in water, the surfactant molecules can surround small droplets of oil and grease forming micelles. The hydrophobic end dissolves in the oil and the hydrophilic end in water. These small droplets can now be washed away as they are effectively dissolved in water.



Soaps are not effective in hard water as it contains calcium and magnesium ions and these form a precipitate, or scum, with the soap ions, removing them from solution.

$$2CH_3(CH_2)_{16}COO^-Na^+ + Ca^{2+} \longrightarrow (CH_3(CH_2)_{16}COO^-)_2Ca^{2+} + 2Na^+$$

soap scum

Detergents in contrast do not form scum with calcium or magnesium ions and so can be used in hard water.

Biodiesel

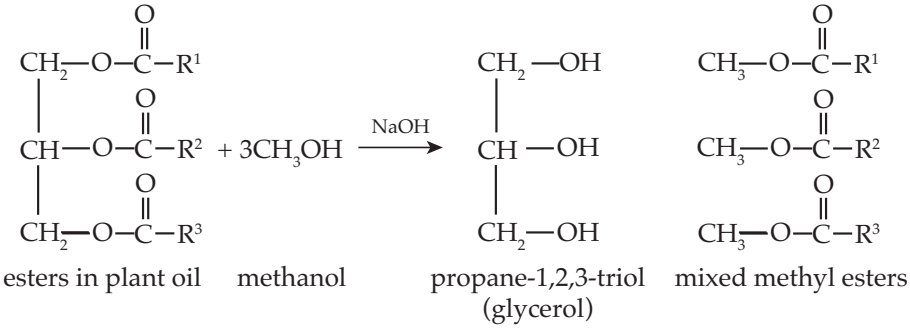
Biodiesel is non-toxic, biodegradable and a renewable fuel source. It is considered a carbon-neutral fuel as the carbon dioxide produced in its combustion is equivalent to that which was absorbed by the plant from which it was made.

Diesel or petrodiesel is different from biodiesel in that it is a mixture of alkenes rather than methyl esters.

Biodiesel can be manufactured by converting the triglycerides obtained from animal fats or vegetable oils into methyl esters. The fatty acids are subjected to a process of condensation called transesterification.

Base-catalysed transesterification

Transesterification is similar to the saponification reaction for soap making. If this base catalysed reaction is performed in the presence of methanol it transforms the triglycerides into biodiesel rather than soap.



Lipase catalysed transesterification

Biodiesel can also be prepared by a lipase-catalysed process. Lipase is an enzyme that catalyses the hydrolysis of fats (lipids). Enzymatic transesterification has advantages over the chemical catalysis of transesterification as it is less energy intensive and allows easy recovery of glycerol. Limitations of the enzyme-catalysed reactions include high cost of enzyme, low yield and long reaction time.

Set 1. Chemical synthesis

1. Mn_3O_4 is found in nature as the mineral hausmannite. It can be reduced with carbon monoxide to produce MnO according to the equation:

$$Mn_3O_{4(s)} + CO_{(g)} \rightarrow 3MnO_{(s)} + CO_{2(g)}$$

If 2.62 tonnes of hausmannite is reacted with 871 kL of carbon monoxide at 100.0 kPa and 600.0ºC determine the mass of manganese (II) oxide produced.

2. Chalcopyrite, $CuFeS_2$, is an ore of copper. The first step when extracting the copper is to roast the impure chalcopyrite in oxygen to produce copper (I) sulfide according to the equation:

$$2CuFeS_{2(s)} + 4O_{2(g)} \rightarrow 2FeO_{(s)} + Cu_2S_{(s)} + 3SO_{2(g)}$$

1.25×10^4 tonnes of impure chalcopyrite is roasted in excess oxygen. The mass of copper (I) sulfide produced was found to be 5.10×10^3 tonnes. If the process is assumed to be 100% efficient, determine the percentage purity of the chalcopyrite.

3. The Bayer process is used to purify bauxite, Al_2O_3, prior to electrolysis in the production of aluminium. It proceeds via the following series of reactions:

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2NaAl(OH)_{4(aq)}$$

$$NaAl(OH)_{4(aq)} \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)}$$

$$2Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)} + 3H_2O_{(l)}$$

The first reaction is 97.0% efficient. The second reaction is 83.0% efficient.

If 1.10×10^4 tonnes of ore are initially reacted and the final mass of bauxite produced is 7.50×10^3 tonnes, what is the efficiency of the final reaction?

4. Rutile, TiO_2, is the ore from which titanium is extracted. It is first heated with chlorine and coke at a temperature of about 900ºC to produce titanium (IV) chloride. The titanium (IV) chloride is then reduced in a batch process to produce very pure titanium by reacting it with sodium metal.

$$TiO_{2(s)} + 2Cl_{2(g)} + 2C_{(s)} \rightarrow TiCl_{4(s)} + 2CO_{(g)}$$

$$TiCl_{4(s)} + 4Na_{(l)} \rightarrow Ti_{(s)} + 4NaCl_{(s)}$$

In a small scale pilot plant operating at 95.0% efficiency chemists tested the purity of a sample of rutile. They reacted 10.0 kg of rutile with excess chlorine and coke, and then purified it through reduction with excess sodium. They produced 5.076 kg of pure titanium.

Determine the purity of their rutile sample.

5. The Solvay process is a multi-step synthesis for the production of sodium carbonate and calcium chloride from the raw materials sodium chloride, ammonia and calcium carbonate (limestone).

   Step 1: $CaCO_3(g) \rightarrow CaO(s) + CO_2(g)$

   Step 2: $NaCl(aq) + NH_3(g) + H_2O(l) + CO_2(g) \rightarrow NH_4Cl(aq) + NaHCO_3(aq)$

   Step 3: $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$

   Step 4: $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

   Step 5: $2NH_4Cl(aq) + Ca(OH)_2(aq) \rightarrow 2NH_3(g) + CaCl_2(aq) + 2H_2O(l)$

   (a) A company produces 325 000 tonnes per year of sodium carbonate. How many tonnes of calcium carbonate are needed to produce this?

   (b) Salt is the raw material for the process and is mined from evaporative basins in salt lakes. This is purified, then dissolved to form a saturated brine solution that is pumped to the Solvay plant for Step 2. If 60.0% of the original salt is sodium chloride what mass of salt must be mined in order to maintain production?

   (c) What mass of ammonia is required to ensure that all of the sodium chloride reacts?

   (d) Calcium hydroxide is made from the calcium oxide produced in Step 1. This is then reacted with the ammonium chloride from Step 2 to produce calcium chloride. What mass of calcium chloride is produced if Step 4 is only 85.0% efficient?

6. An analytical chemist is required to determine the percentage by mass of methanol in a sample of methylated spirits (a mixture of ethanol and methanol). The chemist takes a 20.0 g sample of the methylated spirits, adds concentrated sulfuric acid and reacts the resulting liquid with excess pure ethanoic acid. After the resulting esterification reaction is complete, the chemist removes any residual ethanoic acid, dries the remaining liquid and finds it to be a mixture of methyl ethanoate and ethyl ethanoate. The mass of ethyl ethanoate was found to be 35.76 g. Assume that complete recovery of both organic compounds was achieved.

   (a) Determine the percentage by mass of methanol in the sample of methylated spirits.

   (b) Determine the mass of water produced during the complete esterification of the 20.0 g sample of methylated spirits.

7. Iron pyrites FeS_2 can be used to produce small quantities of sulfuric acid via the following sequence of reactions:

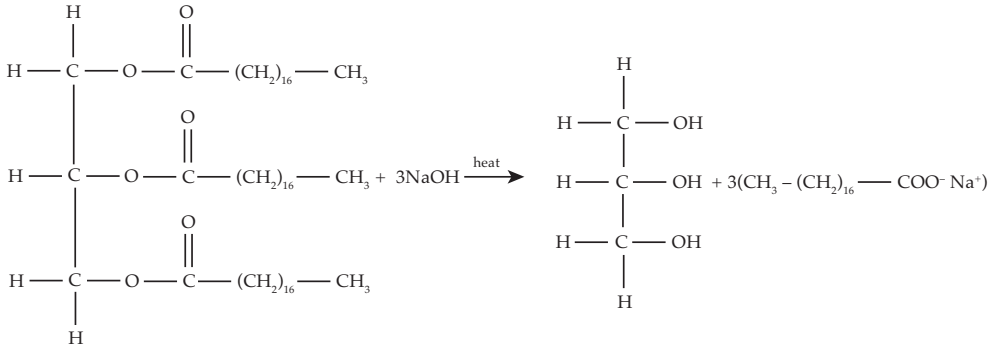
$$4FeS_{2(s)} + 11O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$
$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$
$$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$$

Step 1 is 95.0% efficient, step 2 is 85.0% efficient and step 3 is only 67.0% efficient.

If 2.550 kg of impure iron pyrites is reacted in excess oxygen and 15.00 L of 1.500 mol L^{-1} sulfuric acid is produced, what is the percentage purity of the original sample?

8. Some chemistry students decided to prepare some soap, $CH_3(CH_2)_{16}COO^-Na^+$, in the laboratory by the reaction between a pure vegetable oil and sodium hydroxide.

   The reaction is:



   The students weighed out 50.0 g of the vegetable oil.

   (a) Calculate the mass of sodium hydroxide needed to react with the vegetable oil.

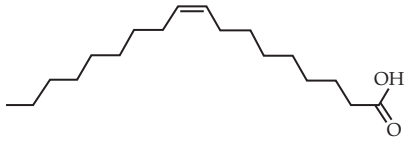
   (b) Calculate the mass of glycerol produced as a by-product of this reaction.

   (c) The soap which was prepared was then dissolved in excess 'hard' water containing Ca^{2+} ions and HCO_3^- ions. This produced a grey insoluble scum, $(CH_3(CH_2)_{16}COO^-)_2\ Ca^{2+}$.

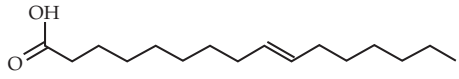
   What mass of scum is formed by dissolving 10.0 g of the soap in excess 'hard' water?

9. Products from olive oil

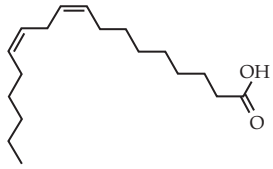
A sample of olive oil was found to consist of triglycerides containing the fatty acids oleic acid, palmitic acid and linoleic acid in various combinations.



oleic acid, $CH_3(CH_2)_7CHCH(CH_2)_7COOH$



palmitic acid, $CH_3(CH_2)_5CHCH(CH_2)_7COOH$



linoleic acid, $CH_3(CH_2)_4CHCHCH_2CHCH(CH_2)_7COOH$

(a) Which of these fatty acids is saturated?

(b) The most prevalent triglyceride in olive oil is the oleic-oleic-oleic (or OOO) triglyceride. Write a condensed formula for the methyl ester biodiesel molecule formed in the production of biodiesel from OOO triglyceride.

_____

_____

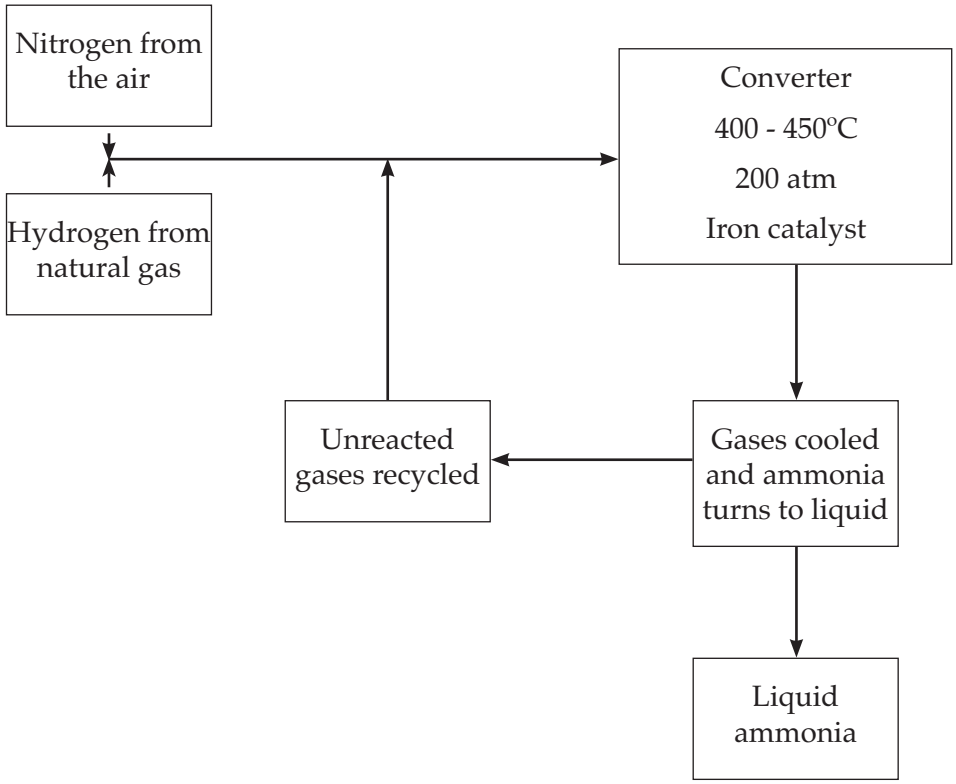
(c) If oleic-linoleic-palmitic (or OLP) triglyceride from olive oil was used to prepare soap, draw diagrams of the soap molecules formed, labelling their polar hydrophilic and the non-polar hydrophobic sections.

(d) Describe, with reference to the micelle, how soaps are able to lift oil and grease from fabrics.

(e) How are detergents different from soaps?

10. Describe how you might prepare ethylpropanoate in the laboratory starting with ethene and propan-1-ol. Give equations showing each step and include the reagents required for each step.

11. You have studied the Haber process from an equilibrium perspective. Examine the flowchart of the Haber process below:



(a) Does this process utilise local and renewable resources?

_____

_____

_____

_____

(b) How is waste kept to a minimum?

_____

_____

_____

_____

(c) Can you identify a part of the process where energy cycling or heat recovery could be implemented?

_____

_____

(d) From your equilibrium studies what are the conditions that are employed to maximise yield? Is there a compromise in the chosen conditions?

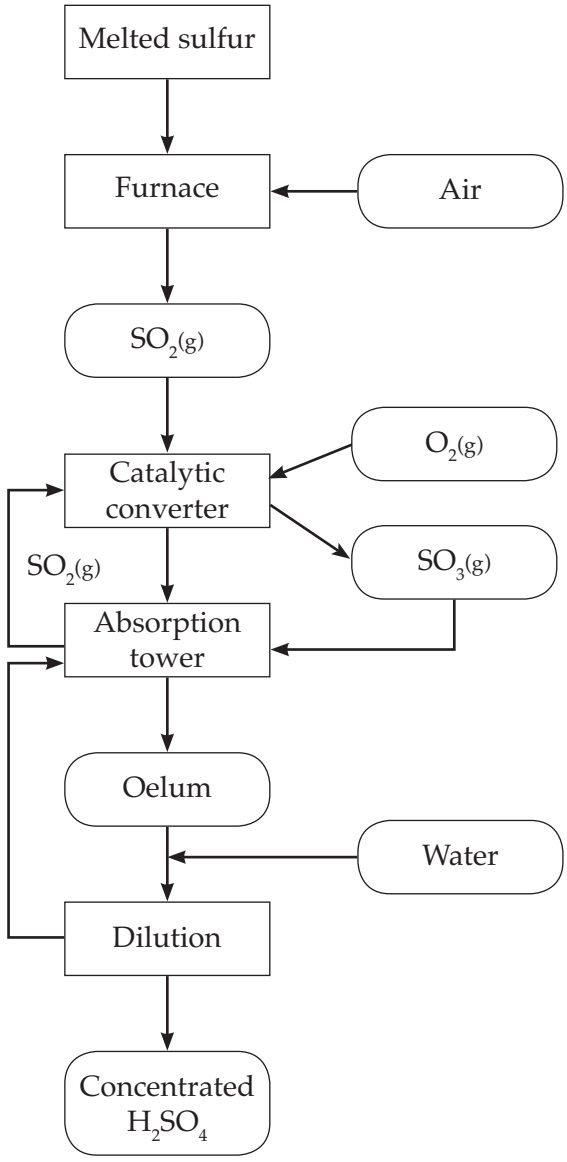
_____

_____

_____

_____

12. Below is a flowchart for the Contact process to manufacture sulfuric acid:



(a) Write equations for each step of the process.

Step 1: Sulfur is melted and heated in the furnace with air to produce sulfur dioxide.

_____

Step 2: Sulfur dioxide and oxygen are reacted together to produce sulfur trioxide.

_____

Step 3: Sulfur trioxide is added to sulfuric acid to produce oleum, $H_2S_2O_7$.

_____

Step 4: Oleum is added to water to produce sulfuric acid.

_____

(b) Discuss this process with reference to its economic and environmental sustainability. Refer to Chapter 1 section 1.12 for the conditions of the process.

13. Atom economy can be used in green chemistry as an alternative to yield. It is given as a percentage and represents the proportion of reactant atoms that make their way into the final product.

$$\text{Atom economy } \% = \frac{\text{Relative molecular/formula mass of desired product} \times 100}{\text{Relative molecular/formula mass of all reactants}}$$

(a) Write an equation for the production of chloroethane by the addition of hydrogen chloride to ethene and calculate the atom economy % of this reaction.

(b) Write an equation for the production of chloroethane from the reaction between chlorine gas and ethane and calculate the atom economy % of this reaction.

(c) Which of the two reactions has the best atom economy, the addition or the substitution reaction?

Chapter

6

Science Inquiry Skills

Sample Electrolysis Investigation illustrating good experimental techniques and error estimation

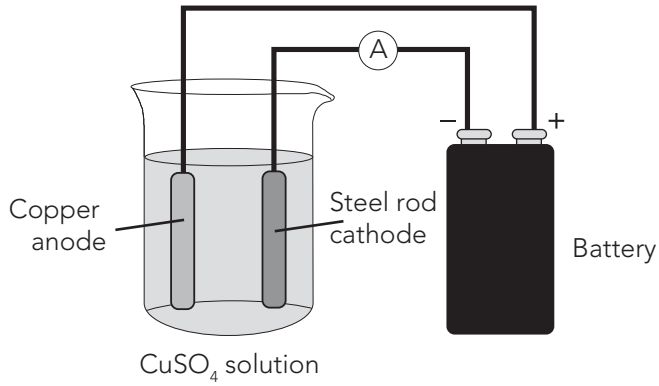
A teacher has set a class investigation which involved electroplating a piece of steel rod with copper.

The task was to find out how the amount of copper deposited depended on the variables:

- Current flowing
- Concentration of the electrolyte
- Time the current was flowing.

Students must arrange for the experiment to be a Fair Test i.e. variables must be controlled rigorously.

The experimental set-up is shown below.



The students were asked to do the following:

- Clean any grease off the electrodes
- Weigh the steel electrode on a balance
- Connect the steel rod into the circuit above and pass a known current for up to 10 minutes
- Record the average ammeter reading, the concentration of the copper sulfate solution and the time for electrolysis
- Remove the steel rod from the circuit. Wash, dry and reweigh it.
- Calculate the gain in mass of the steel rod.
- Tabulate values for electrolyte concentration, current, run time and mass gain.

Hypothesising

Students were asked to make a hypothesis about the gain in mass during electrolysis.

A hypothesis is a tentative proposition or assertion that links the dependent variable/s with an independent variable. Hypotheses are not just guesses, but have to have some factual experiences as a basis, e.g. a hypothesis about the best washing powder might be: "OMO is best because I know it costs more".

An Independent Variable in an investigation is the factor that can be deliberately changed e.g. in this experiment the independent variables are:

Concentration of electrolyte; Current used; Time of electrolysis.

The Dependent Variable is the factor that is being measured by the experiment – in this case it is the mass m gained by the steel rod.

Below are some of the hypotheses proposed by several students:

Student #1

"I think the more concentrated the electrolyte is, the greater the gain in mass of the rod".

Reason: If there are more copper ions in solution there will be a great mass of copper deposited.

Mathematically expressed: mass is directly proportional to concentration i.e. **m** α **c**.

Student #2

"I think the greater the current, the greater the gain in mass of the rod".

Reason: More current means more electrons are passing, which will deposit more copper ions.

Mathematically expressed: mass is directly proportional to current i.e. **m** α **I**.

Student #3

"I think the greater the time of electrolysis, the greater the gain in mass of the rod".

Reason: The more time the current flows the more electrons that have been produced to deposit the copper ions.

Mathematically expressed: mass is directly proportional to time i.e. **m** α **t**.

Student #4

"The total number of electrons passed in a given time depends on both the current and the time for which they have been running i.e. the total charge. The more charge passed, the greater the mass of copper that will be deposited.

Reason: The product of current multiplied by time is the total quantity of electrons or Charge (Q), measured in coulombs.

Mathematically expressed: mass is directly proportional to charge i.e. **m** α **Q**.

Results

The students performed their experiments individually and Student #1 used his and the results of 2 others to test his hypothesis. This student controlled all other variables, apart from concentration to make a Fair Test. Concentration is the Dependent Variable here.

The Concentration results are shown in Table 1 for three of the students.

Table 1 Concentration and mass gain

Student	Current I (A)	Time t (s)	Concentration c (mol L^{-1})	Mass gain (g)
#1	1.7	6000	0.1	6.7
#8	1.7	6000	0.2	4.2
#9	1.7	6000	0.3	1.9

Hypothesis testing for Student #1

1. Is there an underlying mathematical trend linking c and m in these results?

   _____

2. What can you say about the hypothesis proposed by Student #1 from these data?

   _____

Hypothesis testing for Students #2, #3, #4

To test these hypotheses the students collected results from 7 students in the class (shown below).

Table 2 Combined students' results of current, time and mass gain.

Student #	Current I (A)	Time t (s)	Mass gain m (g)
1	1.7	6000	6.7
2	2.2	3000	4.3
3	0.7	15000	6.4
4	2.0	9000	11.9
5	0.5	12000	3.9
6	0.4	24000	6.3
7	1.6	9000	9.5

Hypothesis testing for Student #2

3. Looking at the values of current and mass gain, does there seem to be a direct proportionality? Give your evidence.

_____

_____

4. Find two results for the table where one current value is a whole multiple of the other (e.g. 2x, 3x the value, etc). Which two students' results have you chosen? _____

Look at the corresponding values of mass gain for these two current results. Are these masses in the same ratio as the currents ratio? _____.

What does your finding tell you about the whether mass gain is proportional to current?

_____

Hypothesis testing for Student #3

5. Find two student results where the time for which the current flowed was the same.

Which two results were these? _____

Here the two times taken were the same but were the two mass gains identical? _____

Can Hypothesis #3 be accepted or not? Explain.

_____

_____

Hypothesis testing for Student #4

For this hypothesis test we need to have a table showing total charge passed (Q) and mass gain. Total charge Q = current x time.

Table 3 Table showing total charge passed and mass gain.

Student #	Current I (A)	Time t (s)	Charge Q = I x t, (coulomb)	Mass gain m (g)
1	1.7	6000	10200	6.7
2	2.2	3000	6600	4.3
3	0.7	15000	10500	6.4
4	2.0	9000	18000	11.9
5	0.5	12000	6000	3.9
6	0.4	24000	9600	6.3
7	1.6	9000	14400	9.5

"*Is m directly proportional to Q*" is the test for this hypothesis. If this statement is true then each value of m/Q should be about the same (m/Q represents the proportional constant k in the equation m = kQ)

6. Take 3 values of m and its corresponding Q value from Table 3 and see if m/Q values are similar.

   Q = _____, m = _____ $m_{(i)}/Q_{(i)} = k_{(i)}$ = _____

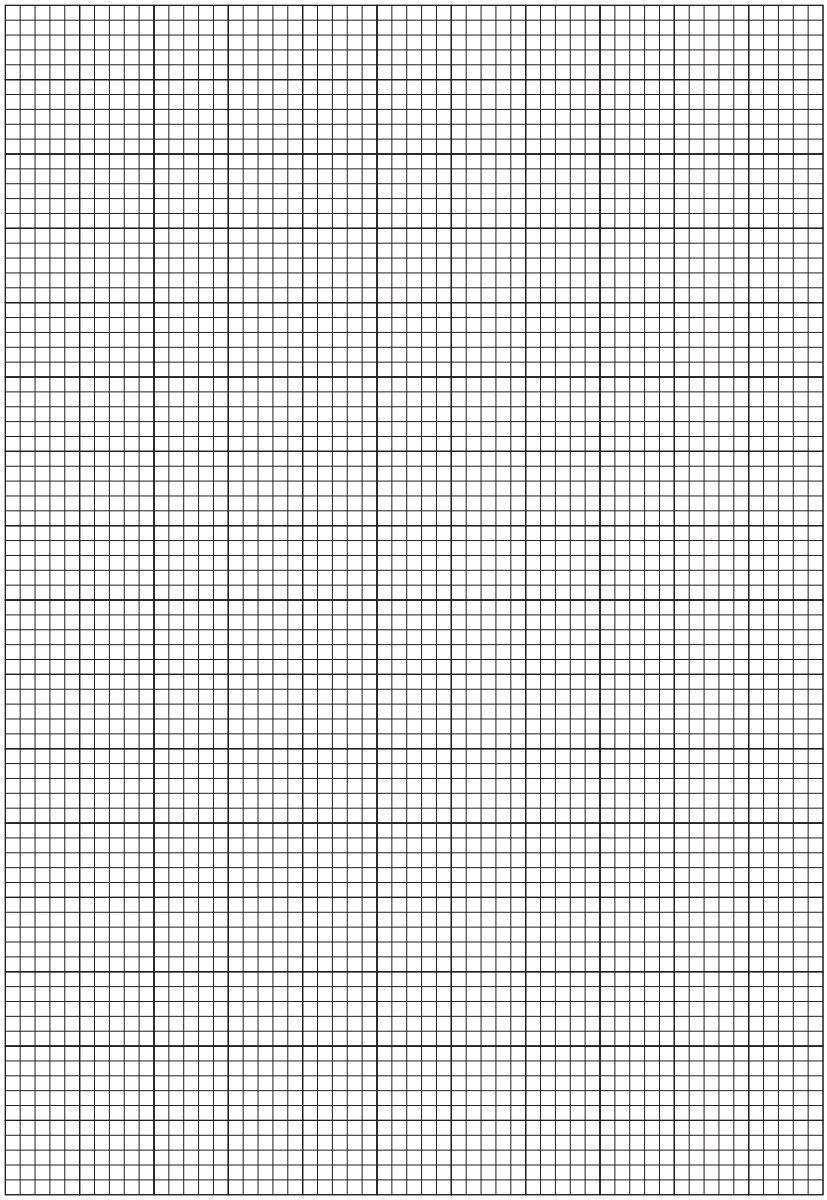
   Q = _____, m = _____ $m_{(ii)}/Q_{(ii)} = k_{(ii)}$ = _____

   Q = _____, m = _____ $m_{(iii)}/Q_{(iii)} = k_{(iii)}$ = _____

7. How do the 3 values of k compare – quite close or not? _____

   It is possible that you may have chosen one or more results from the table that are subject to a large amount of systematic or random error. The way scientists allow for and evaluate these errors is to draw a line of best fit through the points and then make a judgement as to whether the line represents the true trend, within reason.

8. Plot a graph of m (up) against Q (along) on the grid below.

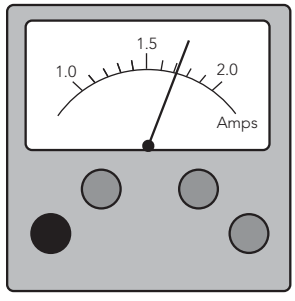


9. From the graph, would you say that there is a good fit of the data to a straight line relationship, meaning that variance from random errors is small?

_____

Note: Random errors are always present in any experiment and are due to slight inaccuracies in reading the instruments, e.g. interpretation of the current reading on the ammeter or balance.

The closest interpreted reading below is 1.7 amps but there could be as much as ± 0.05 A variance, which is plus or minus ½ of the smallest scale division of 0.1 amp.



0.05 A is said to be the Absolute Error in current reading. The Absolute Error in any instrument reading is defined as half the least measurement division on the scale.

The percentage difference in reading is called the Relative Error.

Here, Relative Error, RE = 0.051.7 × 100 = 3% error.

Error in timings

The least reading on this digital timer is 1 second.

10. What is the Absolute Error in all the timings for this experiment?

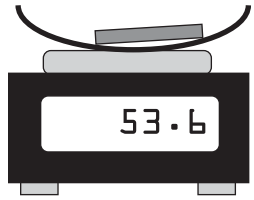
    _____ s.

11. What is the Relative Error in the reading on the digital timer shown above? (All values must be in seconds) _____%.

Error in weighings

12. What would be the Absolute Error in the value of mass of the steel rod shown?

    _____ g



13. What is the Relative Error in mass?

    _____%

14. A Systematic Error is an inaccuracy caused by a mistake in experimental procedure or poor technique.

    Is there any point on the graph that might indicate a Systematic Error in the data? If so, circle that point.

15. Looking at the experimental procedure outlined, suggest some possible Systematic Errors that the student could have made.

    _____

    _____

    _____

16. Calculate the gradient of the graph which will a value for k in the equation m = kQ.

    _____

    Theory shows that the Relative error in k will be equal to the sum of the relative errors in each of the variables I, t and m.

17. Using the results of Student #1, calculate a value for k and its Relative Error.

    _____

Unit 4 Examination Questions

HYDROCARBONS AND CHEMICAL SYNTHESIS

Multiple-choice Questions

1. In a series of experiments the following observations were made about a colourless liquid.

Experiment	Observation
Liquid was added to potassium dichromate solution	No visible reaction
Liquid was added to sodium metal	Colourless, odourless gas evolved, silvery solid dissolved
Liquid was added to ethanol and heated with concentrated sulfuric acid	Fruity smell produced

Which one of the following substances would produce all of these observations?

(a) 2-methyl-2-butanol

(b) butanoic acid

(c) 1-butanol

(d) 2-butanone

2. Ionisation of ethanoic acid can be represented by the following equation

$$CH_3COOH(aq) + H_2O(l) \leftrightarrows CH_3COO^-(aq) + H_3O^+(aq)$$

Which one of the following would increase the concentration of ethanoate ions?

(a) addition of a strong base

(b) addition of a strong acid

(c) addition of a weak acid

(d) dilution with water

3. How many aldehydes and ketones are there with the molecular formula C_4H_8O?

(a) 2

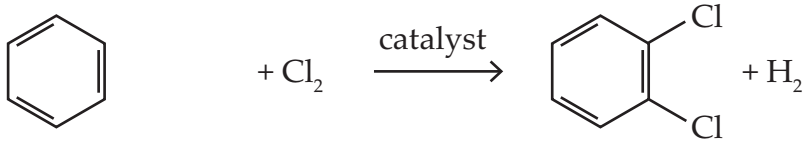
(b) 3

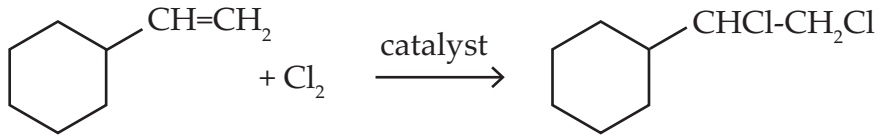
(c) 4

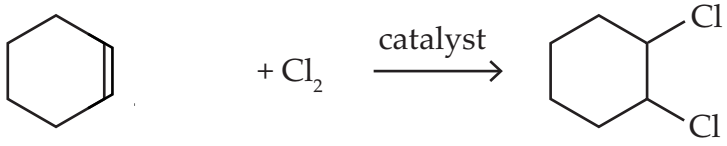
(d) 5

4. Which of the following are examples of addition reactions?

I 

II 

III 

IV 

(a) III and IV only

(b) III only

(c) I and IV only

(d) All of I, II, III and IV

5. 0.100 mol of a compound has a mass of 9.00 g. Its empirical formula is CHO_2. What is the molecular formula of the compound?

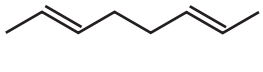
(a) CHO_2

(b) $C_2H_2O_4$

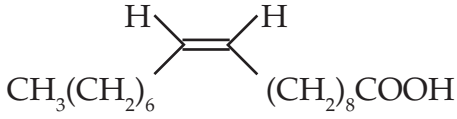
(c) $C_3H_3O_6$

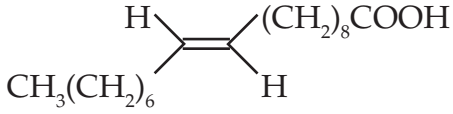
(d) $C_4H_4O_8$

6. Fatty acids are important in our diet and can be saturated or unsaturated. The unsaturated fatty acids can have cis or trans forms. Which one of the following representations of various fatty acids best shows the structure of a cis type unsaturated fatty acid?

(a) $CH_3(CH_2)_2$  $(CH_2)_8COOH$

(b) $CH_3(CH_2)_5CH{=}CH(CH_2)_6COOH$

(c) 

(d) 

7. Which of the following can be produced by the oxidation of propan-1-ol?

I CH_3CH_2CHO

II CH_3CH_2COOH

III CH_3COCH_3

IV CO_2

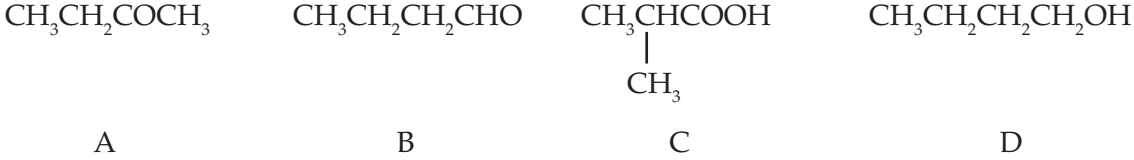
(a) I and II only

(b) I, II and III only

(c) I, II and IV only

(d) all of them

The next three questions refer to the structures shown below.



8. Which of the following will react to form an ester?

(a) A and B

(b) B and C

(c) A and C

(d) C and D

9. Which of the following, if any, are isomers of each other?

   (a) A and B

   (b) B and C

   (c) C and D

   (d) none of the above

10. Which of the following will react with sodium, giving hydrogen gas?

   (a) A and B

   (b) B and C

   (c) B and D

   (d) C and D

11. Which one of the following compounds has an empirical formula different from the other three?

   (a) ethanal

   (b) propyl methanoate

   (c) ethanol

   (d) butanoic acid

12. Consider the compounds below.

   I $CH_3CH_2CH_2CH_3$

   II $CH_3CH_2CH_2OH$

   III CH_3CH_2CHO

   IV $CH_3CH_2CH_2CH_2OH$

   Which one of the following lists these compounds in order of increasing boiling point?

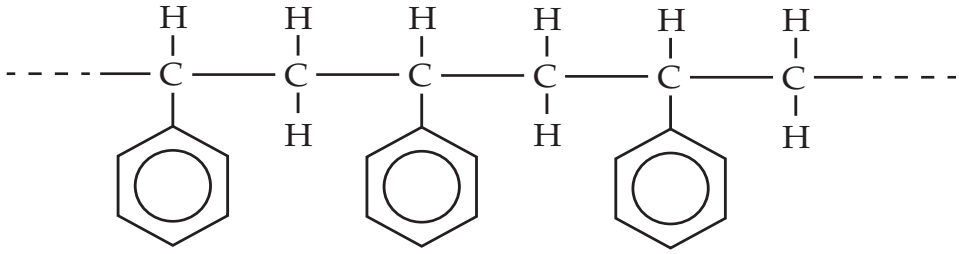
   (a) IV < III < II < I

   (b) I < II < III < IV

   (c) I < III < IV < II

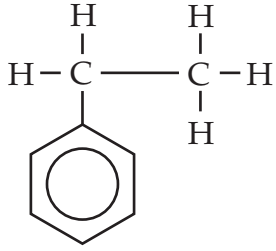
   (d) I < III < II < IV

13. Below is a section of the structure of an addition polymer:

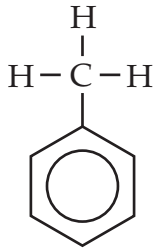


Which one of the following compounds could polymerise to form this chain?

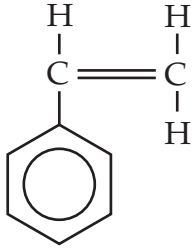
(a)



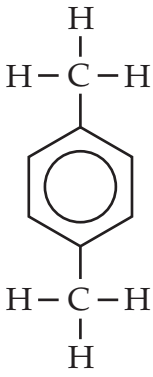
(b)



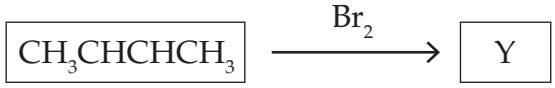
(c)



(d)



14. The hydrocarbon $CH_3CHCHCH_3$ reacts with bromine as indicated below. Which one of the following gives the correct formula for the product Y?



(a) $CH_3CHBrCHBrCH_3$

(b) $CH_3CHBrCHCH_2Br$

(c) $CH_2BrCH_2CH_2CH_2Br$

(d) $CH_2BrCHCHCH_2Br$

15. Which of the following compounds can exist as a pair of geometric (cis-trans) isomers?

I $CH_3CH_2CH_2CH=CH_2$

II $CH_3CH=CHCH_2CH_3$

III $CH_3C=CCH_2CH_3$

IV $CH_3CH=C(CH_3)$

(a) II and III only

(b) IV only

(c) I, II and III only

(d) II only

Questions 16 and 17 refer to the compounds, numbered I to IV, below.

I $CH_3CH_2CH_2CH_2COOH$

II $CH_3CH_2CH_2CH_2CH_2OH$

III $CH_3CH_2CH_2CH_2CHO$

IV $CH_3CH_2CH_2CH_2CH_2CH_3$

16. Which one of the following lists the compounds in order of decreasing solubility in water?

(a) IV > III > II > I

(b) I > II > III > IV

(c) I > III > II > IV

(d) II > I > III > IV

17. Which two of the compounds will react to form an ester?

(a) I and II

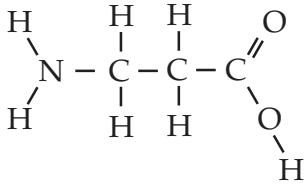
(b) I and III

(c) II and III

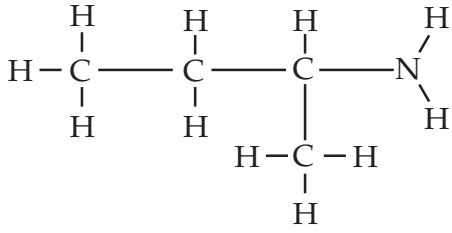
(d) I and IV

18. Which one of the following compounds is an α-amino acid?

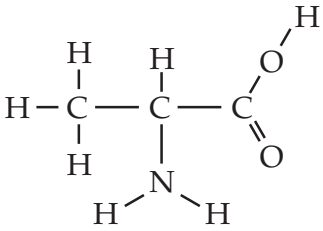
(a)



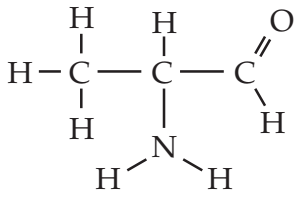
(b)



(c)



(d)



Use the information below to answer questions 19 and 20

19. Which one of the following is the formula for the product B from the reaction of A with hydrogen chloride?

(a) $CH_3CHCHCH_2Cl$

(b) $CH_3CHClCHClCH_3$

(c) $CH_3CH_2CHClCH_3$

(d) $CH_3CH_2CH_2CH_2Cl$

20. Which one of the following is the formula for the product C from the reaction of A with chlorine?

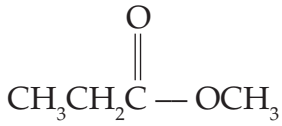
(a) $CH_3CHCHCH_2Cl$

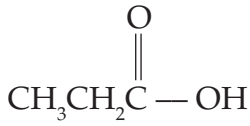
(b) $CH_3CHClCHClCH_3$

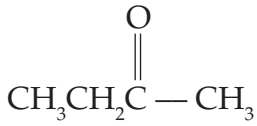
(c) $CH_3CH_2CHClCH_3$

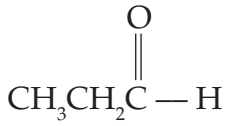
(d) $CH_2ClCHCHCH_2Cl$

The next two questions refer to the compounds shown below.

I. 

II. 

III. 

IV. 

21. Which one of the following lists places these compounds in their correct class?

	I	II	III	IV
(a)	Ester	Aldehyde	Ketone	Carboxylic acid
(b)	Carboxylic acid	Ketone	Aldehyde	Ester
(c)	Ketone	Carboxylic acid	Ester	Aldehyde
(d)	Ester	Carboxylic acid	Ketone	Aldehyde

22. Which of these compounds can be prepared by oxidation of propan-1-ol, $CH_3CH_2CH_2OH$?

(a) I only

(b) I and II

(c) II and III

(d) II and IV

23. Which one of the following is a substitution reaction?

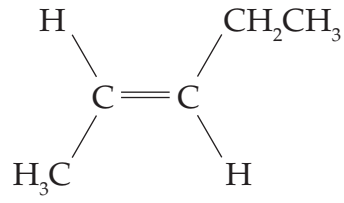
(a) $CH_3CH_2CH_2CH_2Br + Br_2 \rightarrow CH_3CH_2CH_2CHBr_2 + HBr$

(b) $CH_3CH_2CHCH_2 + Br_2 \rightarrow CH_3CH_2CHBrCH_2Br$

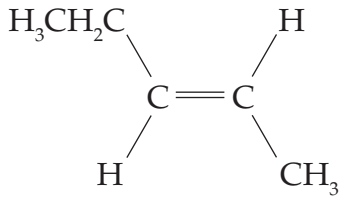
(c) $CH_3CH_2CH_2COOH + CH_3OH \rightarrow CH_3CH_2CH_2COOCH_3 + H_2O$

(d) $CH_3CH_2CHCH_2 + H_2 \rightarrow CH_3CH_2CH_2CH_3$

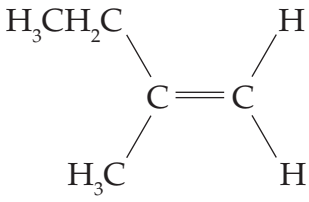
Examine the structures for compounds (i), (ii), (iii) and (iv) below to answer Questions 24, 25 and 26.



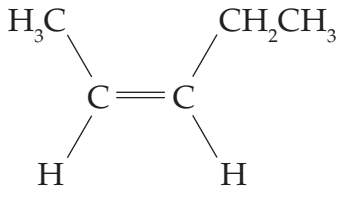
(i)



(ii)



(iii)



(iv)

24. Which of these compounds are geometric isomers?

    (a) (i) and (ii)

    (b) (i), (ii) and (iii)

    (c) (i) and (iv)

    (d) (iii) and (iv)

25. How many moles of oxygen will be consumed in the complete combustion of 1 mole of compound (i)?

    (a) 1 mol

    (b) 3.5 mol

    (c) 5 mol

    (d) 7.5 mol

26. Which one of the following is the product from the reaction of bromine with Compound (iii)?

    (a) $CH_3CH_2CBr(CH_3)CH_2Br$

    (b) $CH_3CH_2BrCH(CH_3)CH_3$

    (c) $CH_3CH_2BrCH(CH_3)CH_2Br$

    (d) $CH_3CH_2CH(CH_3)CH_2Br$

27. Which one of the following will react with acidified potassium dichromate to give a ketone?

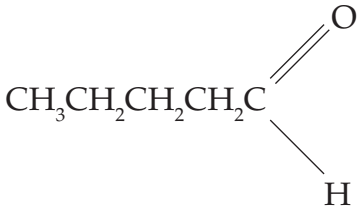
    (a) $CH_3CH_2CH_2OH$

    (b) CH_3CH_2CHO

    (c) $CH_3CH(OH)CH_3$

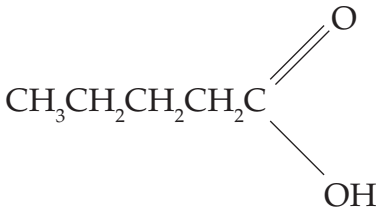
    (d) $(CH_3)_3COH$

Questions 28, 29 and 30 refer to Compounds I to IV below.

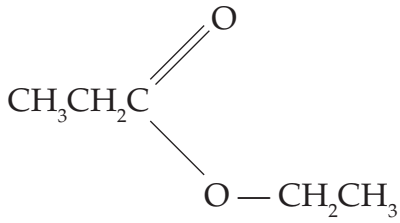


I

II



III



IV

28. Which one of the following lists the functional groups for Compounds I to IV correctly?

	I	II	III	IV
(a)	aldehyde	ketone	ester	carboxylic acid
(b)	carboxylic acid	aldehyde	ester	ketone
(c)	aldehyde	ketone	alcohol	carboxylic acid
(d)	aldehyde	ketone	carboxylic acid	ester

29. Which one of the alcohols below can be oxidised to produce Compound II?

(a) $CH_3CH_2CH_2CH_2CH_2OH$

(b) $CH_3CH_2CH_2CHOHCH_3$

(c) $CH_3CH_2CHOHCH_2CH_3$

(d) $CH_3C(OH)(CH_3)CH_2CH_3$

30. Which one of Compounds I to IV will react with an alcohol in the presence of an acid?

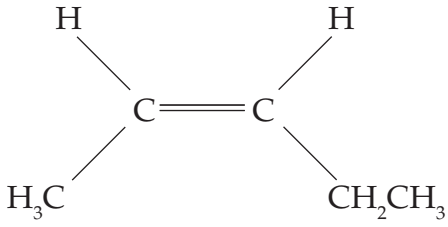
(a) I

(b) II

(c) III

(d) IV

31. Consider the following statements about the compound shown below.



I It will decolourise iodine water.

II If 1 mol of the compound is mixed with 2 mol of chlorine, all of the chlorine can react.

III Its systematic name is *cis* pent-2-ene.

IV It is soluble in hexene.

Which of the statements are correct?

(a) I and III only

(b) II and IV only

(c) II, III and IV only

(d) I, II, III and IV

32. Which one of the following will show hydrogen bonding between neighbouring molecules?

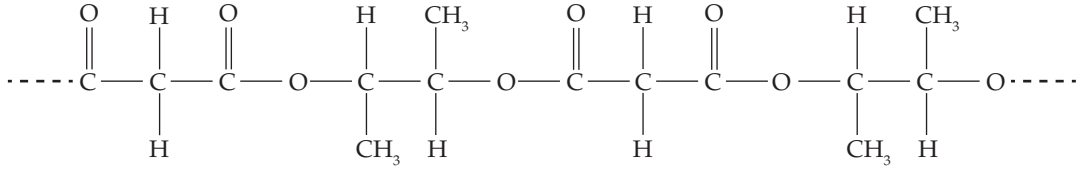
(a) Ethane

(b) Ethanol

(c) Ethene

(d) Ethanal

33. Which one of the following pairs of monomers could be used to produce the polymer shown below?



(a) $HOCH_2CH_2CH_2CH_2OH$ and $HOOCCH_2COOH$

(b) $CH_3CH{=}CHCH_3$ and HOOCCOOH

(c) $CH_3CH(OH)CH(OH)CH_3$ and $HOOCCH_2CH_2COOH$

(d) $CH_3CH(OH)CH(OH)CH_3$ and $HOOCCH_2COOH$

34. Amino acids contain

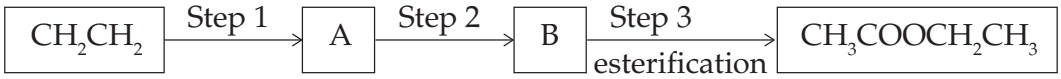
(a) a carboxylic acid group and a hydroxyl group

(b) an amine and an alcohol group

(c) an alcohol group and an aldehyde group

(d) an amine group and a carboxylic acid group

35. Ethene (CH_2CH_2) can be used to manufacture ethyl ethanoate, $CH_3COOCH_2CH_3$, in three steps, as indicated below:



Which one of the following is the correct sequence of steps 1 and 2?

	Step 1	Step 2
(a)	substitution with water	oxidation
(b)	addition of water	oxidation
(c)	oxidation	addition of water
(d)	oxidation	substitution with water

36. An esterase is an enzyme that splits esters into an acid and an alcohol in a chemical reaction with water called hydrolysis.

$$\text{ester + water} \overset{\text{esterase}}{\rightleftharpoons} \text{carboxylic acid + alcohol}$$

In the presence of esterase which one of the following statements is true for this process?

(a) The position of the equilibrium for this reaction is shifted to the right.

(b) The rate of forward reaction and rate of reverse reaction both increase equally.

(c) The rate of forward reaction increases more than the rate of reverse reaction.

(d) The rate of forward reaction increases and the rate of reverse reaction decreases.

37. The Contact process which is used to produce sulfuric acid is an important industrial process. The process contains several steps, one of which is the production of sulfur trioxide shown below.

$2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$

Which one of the following changes will increase the concentration of $SO_3(g)$ in the mixture when equilibrium is re-established?

(a) decreasing the concentration of SO_2 at constant temperature and pressure

(b) decreasing the concentration of O_2 at constant temperature and pressure

(c) decreasing the temperature of the system

(d) decreasing the pressure of the system

38. Ammonia is an important industrial chemical. It is produced by the Haber Process. The reaction used in the production of ammonia gas is shown below.

$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$

Addition of a catalyst will increase the rate of this reaction. Which one of the following will occur on the addition of a catalyst?

(a) The equilibrium yield of ammonia remains constant.

(b) The rate of the forward reaction increases relative to the rate of the reverse reaction.

(c) The proportion of successful collisions remain constant.

(d) The endothermic reaction is favoured.

39. Ethanol can be produced by the hydration of ethene with steam as per the reaction below.

$C_2H_4(g) + H_2O(g) \leftrightarrows CH_3CH_2OH(g) \quad \Delta H = -45 \text{ kJ mol}^{-1}$

Which of the following statements about this system is true?

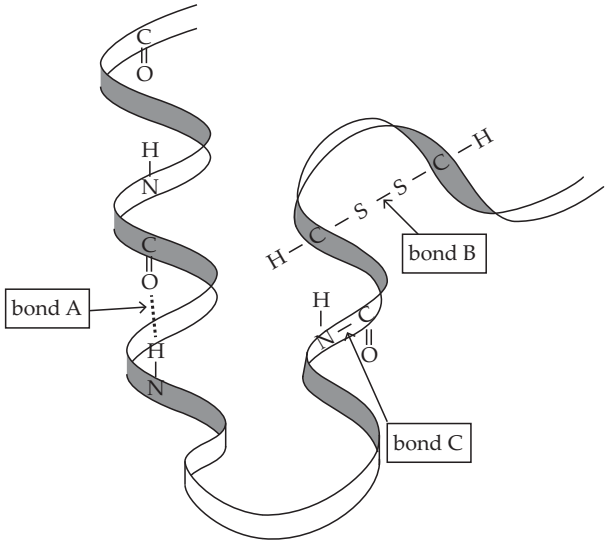
(a) The hydration of ethene is a substitution reaction.

(b) The hydration of ethene to produce ethanol utilizes enzymes to increase reaction rate.

(c) The hydration reaction requires higher temperatures than those used in the production of ethanol via fermentation.

(d) The hydration reaction requires lower pressures than those used in the production of ethanol via fermentation.

40. Enzymes, which are composed mostly of protein, catalyse many chemical reactions. The structure of a portion of an enzyme with some of its constituent atoms shown, is represented below.



Which level of the protein structure is each of the labelled chemical bonds involved in?

	Bond A	**Bond B**	**Bond C**
(a)	secondary	primary	tertiary
(b)	secondary	tertiary	primary
(c)	tertiary	primary	secondary
(d)	primary	secondary	tertiary

41. Which of the following statements is true of soap?

(a) Soap is a polymer.

(b) Soap produced from the saponification of oils and fats is usually coloured and fragrant.

(c) Each molecule of soap is made up of one part consisting of a long chain hydrophilic hydrocarbon and another part that is charged and hydrophobic.

(d) Soap is produced by means of the hydrolysis of triglyceride esters by a concentrated alkali solution.

42. The formula of a stearate ion is $CH_3(CH_2)_{16}COO^-$. Which of the following is the best explanation of why this ion can act as a surfactant, and therefore help to remove grease from a surface.

(a) The long chain within the ion enables them to form a layer on the surface preventing the grease from attaching to the surface.

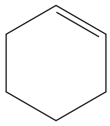
(b) The stearate ion acts a catalyst for the chemical breakdown of the molecules that make up the grease.

(c) The stearate ion contains separate polar and non-polar sections.

(d) The stearate group is able to form an ester linkage to the molecules in the grease and hence they can be removed when the stearate ion is washed away.

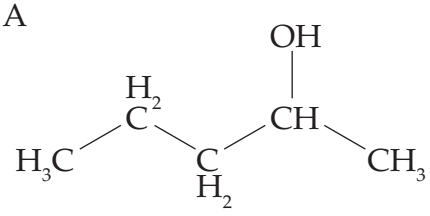
Short Answer, Written and Calculation Questions

1. Use structural formulae to show the organic products of the following reactions:

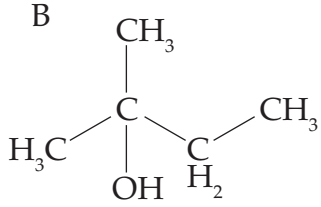
$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3 + Na_2Cr_2O_7 \xrightarrow{H^+}$
$CH_3CH{=}CH_2 + Br_2 \longrightarrow$
$CH_4 + Cl_2 \xrightarrow{\text{UV light}}$
 $+ \quad H_2 \xrightarrow{\text{Metal catalyst}}$
$nCH_2{=}CHCl \xrightarrow{\text{Catalyst}}$

2. Two isomers of $C_5H_{12}O$ have the following structures.

A



B



Both are colourless liquids. Describe a chemical test that could be used to distinguish between the two compounds.

3. (a) Explain the differences between a covalent bond (intramolecular force) and an intermolecular force.

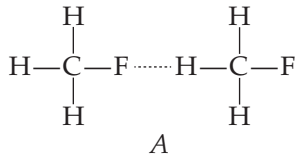
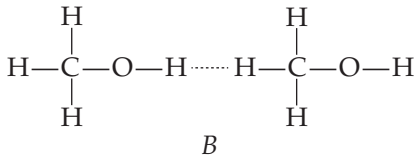
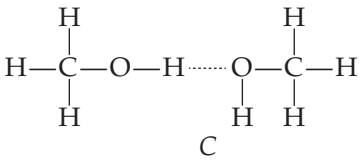
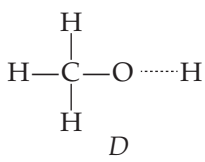
(b) Mixtures of propan-2-ol and propanone can be separated by distillation due to their different boiling points. Explain why these compounds have such different boiling points even though they have very similar molar masses.

	2-propanol	propanone
Boiling point (^{o}C)	82	56
Molar mass (g mol^{-1})	60	58

4. Describe a chemical test that can be used to distinguish between each substance in the following pairs of substances. Describe fully the chemical test and the observations expected for each substance.

Substances	Chemical Test	Expected observations
Cyclohexane (C_6H_{12}) and cyclohexene (C_6H_{10})		C_6H_{12}
		C_6H_{10}
1 mol L^{-1} sulfuric acid solution (H_2SO_4) and 1 mol L^{-1} hydrochloric acid solution (HCl)		H_2SO_4
		HCl
Propanone (CH_3COCH_3) and propanal (CH_3CH_2CHO)		CH_3COCH_3
		CH_3CH_2CHO

5. Which one of the following diagrams best represents a hydrogen bond? Circle A, B, C or D.

 *A*	 *B*
 *C*	 *D*

Explain your choice.

_____

_____

_____

_____

_____

_____

6. Chloromethane can be produced industrially by the reaction of methanol and hydrogen chloride at high temperature in the presence of a catalyst. The equation for this reaction is shown below:

$$CH_3OH + HCl \leftrightarrows CH_3Cl + H_2O$$

The boiling points and melting points for each of the species involved in the reaction are shown below.

Species	Boiling point (°C)	Melting point (°C)
CH_3OH	65	–98
HCl	–85	–114
CH_3Cl	–24	–98
H_2O	100	0

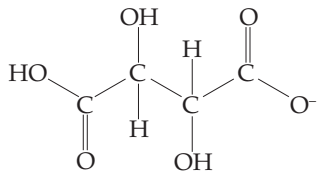
Write the phase, i.e., solid (*s*), liquid (l) or gas (*g*), of each species in this system at the temperatures shown in the table below and predict the effect of an increase in total pressure on this equilibrium at each of the temperatures.

Temperature (°C)	Phase (*s*, l or *g*)				Shift in equilibrium (right, left or no change)
	CH_3OH	HCl	CH_3Cl	H_2O	
–50					
40					
70					
110					

7. Complete the table below by giving a brief description of a chemical test that could be used to distinguish between the substances listed. List the observations relating to the test for each of Substance 1 and Substance 2.

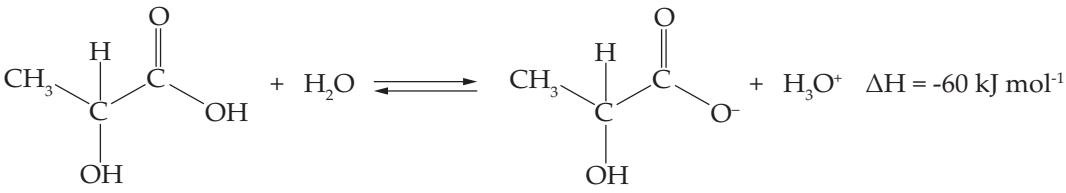
Substances to be distinguished		Description of chemical test	Observation with Substance 1	Observation with Substance 2
Substance 1	**Substance 2**			
butan-2-ol	2-methylpropan-2-ol			
zinc nitrate solution	zinc sulfate solution			
solid magnesium hydroxide	solid lead sulfate			
methanol	methanal			

8. Complete the table by writing the formula or drawing the structure for the conjugate base, species X or conjugate acid in the blank spaces as appropriate. Species X is the species that is able to form both a conjugate base and a conjugate acid.

Conjugate base	Species X	Conjugate acid
		$CH_3NH_3^+$
$C_2O_4^{2-}$		
		

9. Lactic acid produced by muscles during exercise, is found in many milk products and is used in the brewing of beer. It is also added to a number of canned food items as a buffer.

The equation for the reaction of lactic acid with water is shown below.



The value of the equilibrium constant for the above reaction, at 25°C, is approximately 7.9×10^{-5}.

(a) State whether the ratio of organic products to organic reactants will be equal to one, less than one (< 1) or greater than one (> 1) for this system at equilibrium at 25°C. Explain your choice.

_____

_____

_____

_____

_____

_____

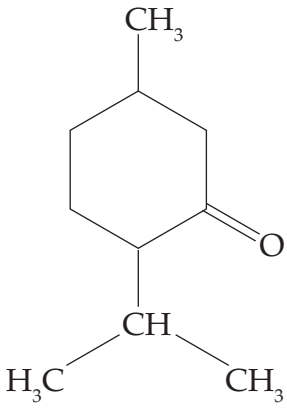
_____

_____

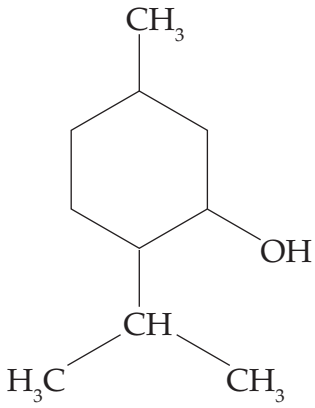
(b) Predict the direction in which the equilibrium will shift immediately after the changes indicated in the table below. Write 'left', 'right' or 'no change'.

Change	Direction of initial equilibrium shift
Decreasing the temperature	
Adding hydrochloric acid	
Adding sodium hydroxide	

10. The structures and melting points are provided for two similarly-sized organic substances. Explain the difference in their melting points.

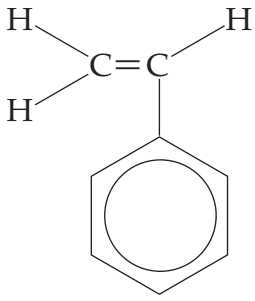


Menthone
-6°C

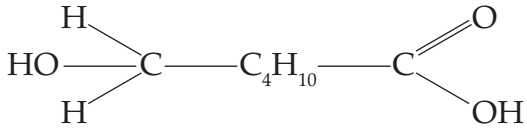


Menthol
35°C

11. In the boxes below draw diagrams of an addition polymer and condensation polymer using the monomers provided. You may use one or both monomers in both polymers. (You must show a minimum of two repeating units.)



Monomer 1



Monomer 2

Addition polymer	
Condensation polymer	

12. Draw the structure and give the IUPAC name of the organic compounds that match the following descriptions. **Show all atoms in the structure**

(a) A primary amine containing 9 hydrogen atoms.

Structure	Name
	_____

(b) The product of the oxidation of 2-pentanol

Structure	Name
	_____

(c) A compound X has the molecular formula C_5H_8. When X is warmed with excess hydrogen in the presence of powdered nickel, it forms a compound with the molecular formula C_5H_{10}.

Give the structure and name of compound X

Structure	Name
	_____

(d) The compound formed when butan-1-ol is added to propanoic acid in the presence of an acid catalyst.

Structure	Name
	_____

13. Consider the following reactions and complete the tables that follow.

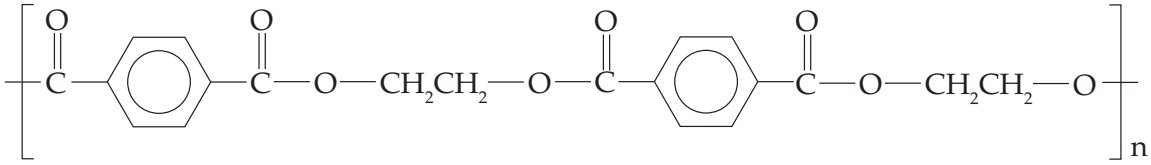
(a) An excess of butan-2-ol is oxidised by acidified $Na_2Cr_2O_7$.

Observations	
Structural formula of organic product Show all atoms	
Name of organic product	

(b) Butanoic acid reacts with methanol in the presence of H_2SO_4.

Observations	
Structural formula of organic product Show all atoms	
Name of organic product	

14. Condensation polymers form from two monomers, each with functional groups at their terminal carbon atoms (that is, the monomers are difunctional). Examine the polyester structure below.



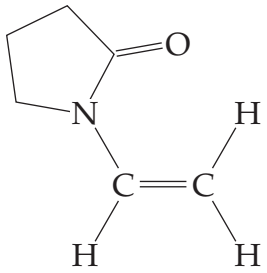
(a) Circle **all** the ester linkages (functional groups that link the monomers) represented in the above structure.

(b) Identify the two monomer compounds (A and B) used in the production of this polymer and draw their molecular structures.

Monomer A

Monomer B

15. Polyvinyl pyrrolidone is a polymer with a wide range of applications including as a binder in tablets and hair styling agents. It is made from the monomer shown below.



(a) Draw three units in the polymer formed from this monomer.

(b) What type of polymerisation reaction occurs to form the polymer from the above monomer?

_____

_____

_____

16. An organic compound is known to be an ester. Its molar mass is 74 g mol^{-1}.

(a) Draw the structural formula for the compound. Show all atoms in the structure.

(b) Write the name for the compound you have drawn.

_____

_____

_____

17. (a) Write an equation for the preparation of a soap from a fat.

(b) Describe how soap acts to remove grease from a shirt when it is washed.

_____

_____

_____

_____

_____

(c) Briefly explain why sulfonate detergents sometimes perform better than soaps.

_____

_____

_____

18. For each of the following reactions draw the structural formula of the organic product.

Reaction	Structural formula
Acidified butanoic acid is added to methanol and heated	
Hydrogen gas is bubbled through but-2-ene	
Acidified potassium dichromate is added to ethanol	
Chlorine gas is added to excess propane and exposed to UV light	

19. Give the IUPAC name and draw the structural formula for each of the following:

(a) An amine containing three carbon atoms per molecule.

Name:

Structural formula:

(b) A tertiary alcohol containing four carbon atoms per molecule.

Name:

Structural formula:

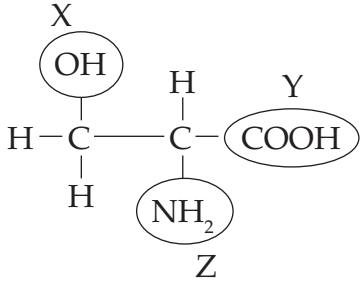
(c) An aromatic hydrocarbon containing seven carbon atoms per molecule.

Name:

Structural formula:

20. Serine, whose structure is shown below, is required for production of antibodies. It contains three functional groups labelled X, Y and Z in the structural formula below.

Name the class of compounds associated with each of these functional groups

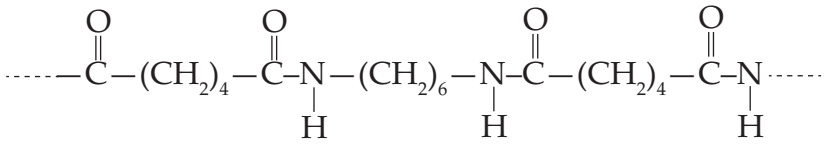


X_____

Y_____

Z_____

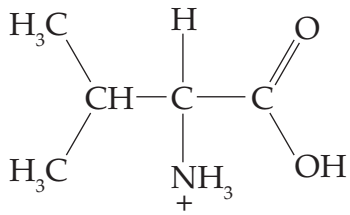
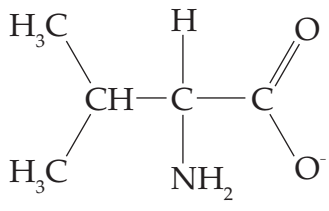
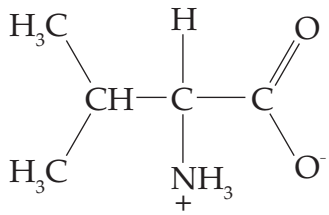
21. The structure below shows part of the chain of a polymer:



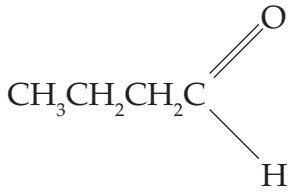
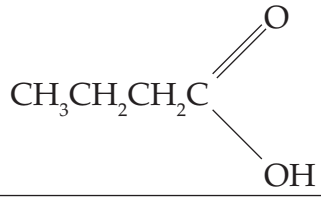
In the boxes below, show the structures for each of the monomers used to form the polymer.

To which class of polymer does this belong?

22. Below are the structures for the amino acid valine under different pH conditions. In the spaces provided, give the approximate pH range (acidic, basic or neutral) under which each valine structure would exist.

Valine structure	pH range
	
	
	

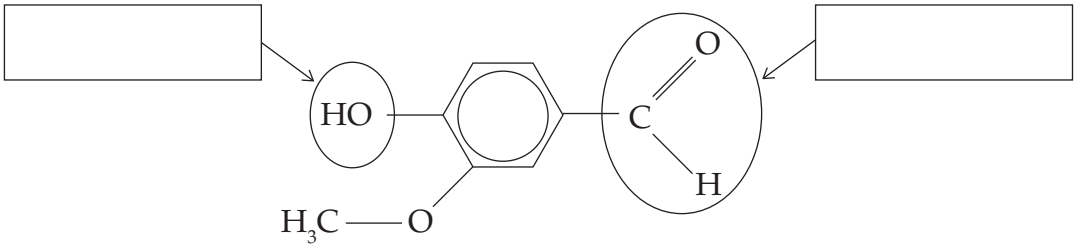
23. Examine the data in the table below. Use your knowledge of intermolecular forces to explain the differences in boiling points of the three compounds listed in the table.

Compound	Structure	Molar mass ($g\ mol^{-1}$)	Boiling point (°C)
Butan-1-ol	$CH_3CH_2CH_2CH_2OH$	74.24	118
Butanal		72.22	75
Butanoic acid		88.22	163

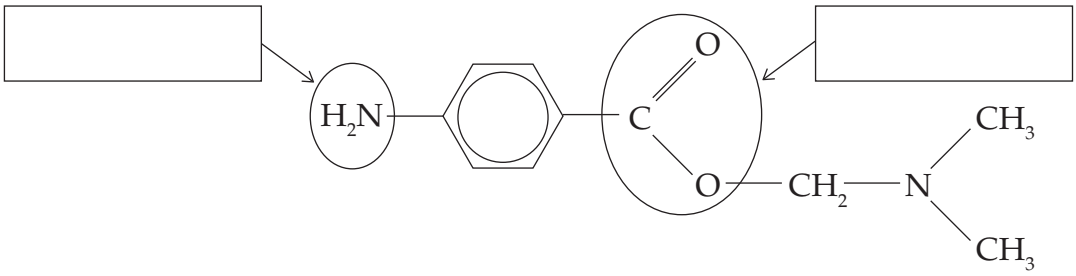
24. The chemical formula of the α-amino acid glycine is $C_2H_5NO_2$

Draw the structure of glycine, showing all atoms.

25. Examine the two compounds below. Compound 1 is the naturally occurring flavouring agent vanillin. Compound 2 is the local anaesthetic procaine. Name the functional groups circled in these two compounds.

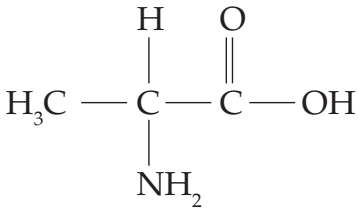


Compound 1: Vanillin



Compound 2: Procaine

26. The structure for the α-amino acid alanine is given below.



(a) Give the structure for alanine under acidic, neutral and basic conditions by completing the table below:

pH	Structure of alanine
acidic	
neutral	
basic	

(b) When crystallised from a neutral solution, alanine exists as a white crystalline solid. The solid has a melting point of 258°C. This contrasts with a melting point of –47°C for 2-methylpropanoic acid (molar mass 87 g mol^{-1}), a molecule of similar size to alanine. With reference to the appropriate structure in (a), explain why alanine has such a high melting point.

27. A polyester polymer was analysed to determine its empirical formula. Combustion of a 9.76 g sample of the polyester in excess oxygen produced 17.9 g of carbon dioxide and 4.88 g of water.

(a) Calculate the empirical formula of the polyester.

The polymer was then hydrolysed using sulfuric acid to split it into the diol and dicarboxylic acid monomers used in its preparation. The flow diagram below illustrates this.

2.20 g of the dicarboxylic acid monomer was isolated and dissolved in 250.0 mL of distilled water. 50.0 mL of the diacid solution required 15.3 mL of 0.487 mol L^{-1} sodium hydroxide solution for complete neutralisation.

(b) Calculate the molar mass of the dicarboxylic acid monomer.

(c) Draw a possible structure of the dicarboxylic acid that is consistent with your answer to part(b).

28. Diet soft drinks contain artificial sweeteners. A combustion analysis of a 1.021 g sample of an artificial sweetener produced 1.715 g CO_2, 0.2521 g H_2O, 0.2558 g NO_2 and 0.3568 g SO_2. The sweetener contains the elements C, H, O, N and S. Determine its empirical formula.

29. Sevoflurane is a gaseous compound (at room temperature) used for inducing and maintaining general anaesthesia. It contains carbon, hydrogen, oxygen and fluorine.

    Analysis of a 1.6328 g sample of sevoflurane yielded, on combustion, 866.0 mL of carbon dioxide at 50.0°C, 101.3 kPa and 0.220 g of water. The fluorine was released as hydrogen fluoride and absorbed by alkaline solution, revealing 5.71 x 10^{-2} mole of hydrogen fluoride. Determine the empirical formula of sevoflurane.

30. Qualitative analysis of an organic compound showed that it contained only carbon, hydrogen and oxygen. A quantitative study of the same compound was performed, in which a 0.5096 g sample was burnt in excess oxygen to produce 0.4160 g of water and 700.7 mL of carbon dioxide, collected at 100.0°C and 102.8 kPa.

(a) Determine the empirical formula of the compound.

(b) A second 0.4832 g sample of the compound was heated to 261°C. The vaporised sample was found to exert a pressure of 241 kPa in a 100.0 mL container. Use this information to determine the molecular formula of the compound.

(c) When the original compound was reacted with acidified ethanol it produced a fruity smelling liquid. Infer the structure of the original compound and draw its structure below. Name the original compound.

(d) Describe briefly and give observations for an additional chemical test to confirm the identity of the functional group in the original compound.

31. Soaps function because their molecules dissolve in both grease and water. Water containing significant quantities of calcium and magnesium ions will not lather properly with soap and will form an insoluble 'scum' according to the reaction below. Water that does not lather effectively is referred to as 'hard' water, and calcium ions are the primary cause of water hardness:

$Ca^{2+}(aq) + 2CH_3(CH_2)_{16}COO^-(aq) \rightarrow (CH_3(CH_2)_{16}COO)_2Ca(s)$

If water is hard due to the presence of calcium ions together with hydrogencarbonate ions (temporary hardness), then the hardness can be reduced by boiling the water. The calcium ions are removed from solution by precipitating as calcium carbonate:

$Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$

Boiling hard water causes the build-up of 'scale', and can lead to failure of the heating elements in kettles and other devices.

(a) The domestic water supply in Perth contains 65.0 mg L^{-1} calcium ions together with hydrogencarbonate ions. A large, tea-drinking family boils and consumes, on average, 4.20 L of water per day. Determine the mass of scale that will deposit in the household kettle during a 365-day year. Assume all calcium ions are removed from solution during boiling.

(b) What volume of $CO_2(g)$, measured at the boiling point of water, is produced during the boiling of 1.00 L of this water at standard pressure?

Water containing calcium and magnesium together with sulfates and/or chlorides cannot be made 'soft' by boiling. There are a number of methods that may be used to soften such water. One of these involves the addition of $Ca(OH)_2$ to the water in the process known as 'liming'. In the liming process, the pH of water is raised when $Ca(OH)_2(s)$ is added.

(c) Calculate the pH of 1.05×10^3 L of water solution to which 125 mg of $Ca(OH)_2$ have been added. Assume all added $Ca(OH)_2$ dissolves.

The increase in pH (i.e., addition of OH^-) of the water shifts the equilibria of the carbonate species in the water so that first HCO_3^- predominates, and as the pH is raised further, CO_3^{2-} predominates.

(d) Hard water containing HCO_3^- has significant buffering capacity. Explain what is meant by the term 'buffering capacity'.

(e) Write two equations that demonstrate the buffering capacity of hard water containing HCO_3^-.

(f) Write equations to show how the addition of OH^- shifts the equilibria of the carbonate species in water.

32. The first step in the production of nitric acid involves a reaction between ammonia and oxygen which can be represented by the following equation:

$4NH_3(g) + 5O_2(g) \leftrightarrows 4NO(g) + 6H_2O(g)$

In a production run, a rigid container of capacity 4.49×10^6 L, fitted with an entry valve to prevent the exit of gas, initially contains only air at a pressure of 105.3 kPa and a temperature of 175°C. 457.3 kg of ammonia is injected and the oxidation reaction is catalysed by hot platinum. When the reaction is complete the mixture is cooled to 25.0°C.

Air contains 20.9% oxygen by volume.

(a) Determine the limiting reagent.

(b) What mass of NO will be produced?

(c) What will be the mass of the excess reagent in the reaction vessel after cooling to 25.0°C?

33. Basic copper(II) sulfate is used as a fungicide and has the formula $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$. It can be produced using the following reaction:

$$4CuSO_4 \cdot 5H_2O(s) + 6NH_3(aq) \leftrightarrows CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O(s) + 6NH_4^+(aq) + 3SO_4^{2-}(aq) + 13H_2O(l)$$

100.0 kg of copper(II) sulfate pentahydrate, with a purity of 95.5%, was added to 15.0 L of saturated ammonia solution, with a concentration of 0.880 g mL^{-1}.

(a) Determine which reactant is the limiting reagent.

(b) Calculate the mass of basic copper(II) sulfate that will be produced. Note that the relative formula mass of basic copper(II) sulfate is 470.334.

(c) Calculate the number of moles of excess reactant remaining.

34. A blast furnace is a large furnace operated at very high temperatures to convert iron(III) oxide (in iron ore) to iron using carbon monoxide, which is itself converted to carbon dioxide during the process.

(a) Write the equation for the reaction of iron(III) oxide with carbon monoxide.

_____

(b) Identify the oxidant and reductant in the above process.

Oxidant:_____ Reductant: _____

(c) 1.00 tonne of iron ore containing 96.5% iron(III) oxide is fed into the blast furnace with 2.70×10^{6} L of carbon monoxide at 113.46 kPa pressure and 1986°C.

(i) Determine the limiting reactant for this reaction.

_____

_____

_____

_____

_____

(ii) What mass of iron is theoretically produced in this reaction?

_____

_____

_____

_____

(iii) Calculate the mass of the reactant in excess.

_____

_____

_____

_____

(d) If 5.56×10^{-1} tonne of iron is actually produced, what is the overall percentage yield of the process?

_____

_____

_____

_____

_____

35. The sandy soils of Western Australia are deficient in several elements essential to the growth of plant life. One of these elements is nitrogen, and there are a number of nitrogen-containing fertilisers available on the market. Urea, $CO(NH_2)_2$, is a commonly used fertiliser that contains nitrogen. Urea is produced as crystals by the reaction of ammonia with carbon dioxide. Water is also produced in the reaction. The equation for this reaction is shown below.

$2NH_3(g) + CO_2(g) \leftrightarrows CO(NH_2)_2(g) + H_2O(g)$

A reaction vessel designed for the synthesis of urea is operated at 200.0°C and 1.50×10^4 kPa. It has a total volume capacity of 5000.0 L, and ammonia and carbon dioxide are fed into it in batches so that ammonia occupies 62.0% of the volume and carbon dioxide occupies the remainder.

(a) Determine the limiting reagent for the reaction under the above operating conditions. Show all your workings.

(b) What mass of urea is theoretically produced in this reaction?

(c) Calculate the mass of the excess reactant remaining after reaction.

(d) Calculate the pressure of the remaining gas in the reactor after it is allowed to cool to room temperature (25.0°C). (The volume occupied by the urea crystals and water formed can be ignored.)

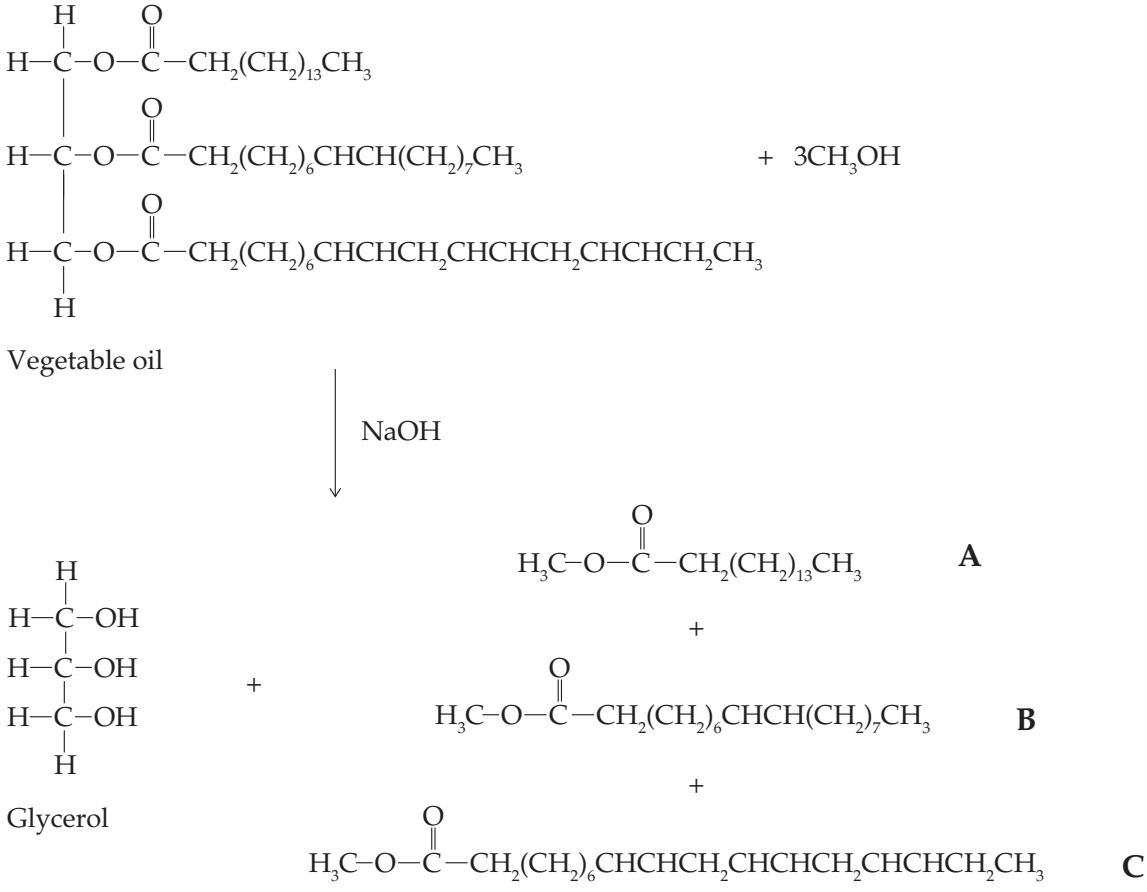
(e) 376 kg of impure crystals are formed in the above reaction and found, on analysis, to contain 83.0% urea. Calculate the percentage yield of the above process.

(f) Urea is added to fertiliser preparations at about 45.0% by mass. Ammonium sulfate is an alternative source of nitrogen often used in fertilisers.

(i) What mass of nitrogen is contained in 5.00 tonne of fertiliser that is 45.0% by mass urea? (1 tonne = 1×10^6 g)

(ii) What mass of ammonium sulfate, $(NH_4)_2SO_4$, is needed to prepare 5.00 tonne of fertiliser with the same mass of nitrogen as your answer in (i) above?

36. Biodiesel can be produced by a trans-esterification reaction between vegetable oil and an alcohol in the presence of sodium hydroxide catalyst. A typical trans-esterification reaction is shown below. The products are glycerol and three methyl esters.



(a) The vegetable oil in the reaction above has a molar mass of 855.334 g mol^{-1}. If 1.50 tonnes of vegetable oil is reacted, what mass of methanol will be required to react with this amount of oil? (1 tonne = 1 x 10^6 g)

(b) Three different methyl esters, denoted A, B and C, are produced from this reaction. What is the mass of Ester A produced in this process if the reaction is 78.0% efficient in production of this ester?

(c) Esters can also be produced by the reaction of a carboxylic acid with an alcohol. Draw the structure of the carboxylic acid that would be needed to produce Ester A in the reaction above. Show all H atoms.

(d) The glycerol produced from this process has a wide range of applications, including anti- freeze in the radiators of engines. A factor that contributes to its use as anti-freeze is its high water solubility. Explain, with the aid of a diagram, why glycerol has a high water solubility.

(e) Use your understanding of the collision theory to explain the role of sodium hydroxide in the reaction.

_____

_____

_____

_____

_____

37. The Pilbara iron ore industry uses vast amounts of ammonium nitrate explosive to break up the rock and ore. Much of the ammonium nitrate is produced in Kwinana, Western Australia, using the following process:

Step 1: Natural gas (from the North West Shelf) is reacted with steam.

$CH_4(g) + H_2O(g) \leftrightarrows 3H_2(g) + CO(g)$

Step 2: The hydrogen from the above process is reacted with nitrogen from the air using the Haber Process.

$3H_2(g) + N_2(g) \leftrightarrows 2NH_3(g)$

Step 3: Ammonia is reacted with oxygen in air.

$4NH_3(g) + 5O_2(g) \leftrightarrows 4NO(g) + 6H_2O(g)$

Step 4: Nitrogen monoxide is reacted with oxygen in air.

$2NO(g) + O_2(g) \leftrightarrows 2NO_2(g)$

Step 5: The nitrogen dioxide produced in the reaction above is reacted with water and oxygen to form nitric acid.

$4NO_2(g) + 2H_2O(l) + O_2(g) \leftrightarrows 4HNO_3(aq)$

Step 6: Finally, nitric acid is reacted with ammonia to form ammonium nitrate.

$HNO_3(aq) + NH_3(g) \leftrightarrows NH_4NO_3(aq)$

(a) How many moles of NH_4NO_3 are produced by the reaction of one mole of CH_4?

_____

_____

_____

_____

_____

_____

_____

(b) Calculate the mass of CH_4 required to produce 2.50×10^5 tonnes of NH_4NO_3. Assume all reactions are 100% efficient and express your answer to three significant figures.

(c) The equation for Step 3 of the process is reproduced below. It is an exothermic reaction ($\Delta H = -1130$ kJ) and is carried out at 900.0°C and atmospheric pressure. Use your understanding of reaction rates, collision theory and Le Chatelier's principle to explain why these conditions are employed for this reaction.

$4NH_3(g) + 5O_2(g) \leftrightarrows 4NO(g) + 6H_2O(g)$

38. Most food labels list the amount of protein in the food. Most of the nitrogen present in food is contained in the protein, so the quantity of protein in a food is determined from its nitrogen content. The standard approach to determining the amount of nitrogen in a sample is the Kjeldahl method, which consists of three steps:

1. A sample of food is heated in boiling sulfuric acid, which produces ammonium sulfate, among other products:

   Food sample + $H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq) + CO_2(g) + SO_2(g) + H_2O(g)$

   The ammonium ions contain the nitrogen that was initially present in the sample.

2. The ammonium ions are then converted into ammonia gas by adding sodium hydroxide to the solution of ammonium sulfate:

   $(NH_4)_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2NH_3(g)$

3. The ammonia gas goes inside a condenser and ends up in a flask that contains a solution of boric acid. The ammonia is neutralised by the boric acid, as follows:

   $B(OH)_3(aq) + H_2O(l) + NH_3(g) \rightarrow NH_4^+(aq) + B(OH)_4^-(aq)$

   When all the ammonia has reacted with the boric acid, the quantity of borate ions ($B(OH)_4^-$) is determined by titration with a strong acid such as hydrochloric acid.

   $B(OH)_4^-(aq) + H^+(aq) \rightarrow B(OH)_3(aq) + H_2O(l)$

   The protein content of the food is then calculated by multiplying the amount of nitrogen by a conversion factor appropriate to the food class being analysed. The conversion factor for milk and milk products is 6.38: that is, the mass of nitrogen is multiplied by a factor of 6.38 to get the mass of protein.

   An analytical chemist treated a 5.235 g sample of a powdered milk product as described above to determine its protein content. The borate solution from Step 3 was titrated with a standard 0.752 mol L^{-1} hydrochloric acid solution and the volume of acid used in the titration was 25.78 mL.

(a) Calculate the number of moles of ammonium ions formed from the treatment of the milk powder sample (Step 1).

(b) What was the mass of nitrogen in the sample? Express your answer to three significant figures.

(c) Calculate the mass of protein in the powdered milk product.

(d) Food labels usually give the protein content as the mass in a typical serving size. If the typical serving size for this product was 25.0 g, what mass of protein would be consumed in a single serving?

(e) Suggest what the chemist might do to increase the reliability of the value of the protein content he found for the milk product.

39. Lead-acid storage batteries use Pb and PbO_2 electrodes. Pb is the reducing agent, while PbO_2 is the oxidising agent. Sulfuric acid solution is used as the electrolyte.

(a) The overall battery reaction during discharge is given below. Write and balance the anode and cathode reactions for the lead-acid storage battery.

Overall reaction: $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

Anode reaction:

Cathode reaction:

(b) (i) With reference to the 'electrical potential' of a galvanic cell, describe how the lead-acid storage battery produces current.

_____

_____

_____

_____

_____

_____

_____

(ii) What determines the magnitude of the electrical potential of a cell?

_____

_____

_____

_____

_____

_____

_____

_____

(c) (i) Determine the number of moles of $H^+(aq)$ in a lead-acid battery that contains 4.50 L of 3.55 mol L^{-1} sulfuric acid solution.

(ii) Use the overall battery equation to determine the number of moles of $H^+(aq)$ consumed when discharge of this battery forms 138.1 g of $PbSO_4(s)$.

The molar mass of $PbSO_4$ is 303.27 g mol^{-1}.

(iii) Use your answers to (i) and (ii) to determine the concentration of $H^+(aq)$ in the electrolyte in the discharged battery. Assume that the electrolyte volume remains constant and ignore any changes due to the formation of water.

(iv) Use your answers to (i) and (iii) to show that when this battery discharges as described above, the change in pH of the electrolyte solution is negligible. Note that in any acid solution whose $H^+(aq)$ concentration is greater than 1 mol L^{-1}, the pH is negative.

(d) A flat (fully discharged) lead-acid battery can be 'jump started' by connecting it to a battery in a car whose engine is running. The current forced through the battery in this way causes the formation of a mixture of hydrogen and oxygen gas through the hydrolysis of water. State why the formation of the hydrogen and oxygen gas mixture may be dangerous.

40. Some baking soda (sodium hydrogencarbonate) is contaminated with sodium chloride. A sample of the contaminated baking soda was treated with dilute nitric acid to convert all of the sodium hydrogencarbonate into carbon dioxide, sodium nitrate and water. An excess of silver nitrate was then added to the solution to react with the chloride ions. A 12.45 g sample of the baking soda produced 1.02 g of silver chloride. Calculate the percentage purity of the baking soda.

41. The effervescence in indigestion tablets is due to the reaction between sodium hydrogen carbonate and citric acid. An indigestion tablet is found to contain 1.998 g of sodium hydrogencarbonate and 1.111 g of citric acid. Citric acid is a triprotic acid with the molecular formula $C_6H_8O_7$.

(a) What volume of carbon dioxide will be produced from the tablet at 37.0°C and 99.2 kPa?

(b) If the tablet has been dissolved in 120.0 mL of water, what will be the concentration (mol L^{-1}) of the excess reactant?

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H hydrogen 1.008																	2 He helium 4.003
3 Li lithium 6.968	4 Be beryllium 9.012											5 B boron 10.82	6 C carbon 12.01	7 N nitrogen 14.01	8 O oxygen 16.00	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium 24.31											13 Aℓ aluminium 26.98	14 Si silicon 28.09	15 P phosphorus 30.97	16 S sulfur 32.07	17 Cℓ chlorine 35.45	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.38	31 Ga gallium 69.72	32 Ge germanium 72.63	33 As arsenic 74.92	34 Se selenium 78.96	35 Br bromine 79.90	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.96	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 *La lanthanum 138.9	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tℓ thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radius	89–103 **Ac actinium	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium		114 Fℓ flerovium		116 Lv livermorium		

Key:

Atomic number
Symbol
Name
Standard atomic weight

* Lanthanide series	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
** Actinide series	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

[Data source: The International Union of Pure and Applied Chemistry Periodic Table of the Elements (May 2013)]

Formulae

Number of moles	n	=	$\frac{m}{M} = \frac{\text{mass}}{\text{molar mass}}$
Number of moles of solute	n	=	cV
Number of moles of a gas at STP	n	=	$\frac{V}{22.71}$
Ideal gas law	PV	=	nRT
Parts per million	ppm	=	$\frac{\text{mass of solute (mg)}}{\text{mass of solution (kg)}}$
pH of a solution	pH	=	$-\log [H^+]$

Units

Volumes are given in the units of litres (L), or millilitres (mL)
Temperatures are given in the units of degrees Celsius (°C) or kelvin (K).
It may be assumed that 0.0 °C = 273.15 K
Energy changes are given in kilojoules (kJ)
Pressures are given in kilopascals (kPa)
Solution concentrations are given in the units moles per litre (mol L^{-1}), grams per litre (g L^{-1}) or parts per million (ppm).

Constants

Universal gas constant, R = 8.314 J K^{-1} mol^{-1}
Avogadro constant, N = 6.022×10^{23} mol^{-1}
Volume of 1.00 mol of an ideal gas at 0.0 °C and 100.0 kPa is 22.71 L
S.T.P. is 0.0 °C and 100.0 kPa
Equilibrium constant for water at 25 °C, $K_w = 1.00 \times 10^{-14}$

Solubility rules for ionic solids in water

Soluble in water

Soluble	Exceptions	
	Insoluble	Slightly soluble
Most chlorides	AgCℓ	$PbCℓ_2$
Most bromides	AgBr	$PbBr_2$
Most iodides	AgI, PbI_2	
All nitrates	No exceptions	
All ethanoates		
Most sulfates	$SrSO_4$, $BaSO_4$, $PbSO_4$	$CaSO_4$, Ag_2SO_4

Insoluble in water

Insoluble	Exceptions	
	Soluble	Slightly soluble
Most hydroxides	NaOH, KOH, $Ba(OH)_2$ NH_4OH*, AgOH**	$Ca(OH)_2$, $Sr(OH)_2$
Most carbonates	Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$	
Most phosphates	Na_3PO_4, K_3PO_4, $(NH_4)_3PO_4$	
Most sulfides	Na_2S, K_2S, $(NH_4)_2S$	

* NH_3 dissolves in water to form both NH_3 (aq) and NH_4^+(aq)/OH^-(aq)
** Ag^+(aq) reacts with OH^-(aq) to form insoluble Ag_2O

Soluble = more than 0.1 mole dissolves per litre
Slightly soluble = between 0.01 and 0.1 mole dissolves per litre
Insoluble = less than 0.01 mole dissolves per litre

Colours of selected substances

In general, ionic solids have the same colour as that of any coloured ion they contain.
Two colourless ions in general produce a white solid.
Selected exceptions to these two basic rules are noted below.

Ionic Solid	Colour
copper(II) carbonate	green
copper(II) chloride	green
copper(II) oxide	black
copper(II) sulfide	black
lead(II) iodide	yellow
lead(II) sulfide	grey
manganese(IV) oxide	black
silver carbonate	yellow
silver iodide	pale yellow
silver oxide	brown
silver sulfide	black

Other coloured substances

Most gases and liquids are colourless, and most metals are silvery or grey. Selected exceptions to these basic rules are noted below.

Substance	State	Colour
copper	solid	salmon pink
gold	solid	yellow
nitrogen dioxide	gas	brown
sulfur	solid	yellow

Coloured halogens

Halogen	Colour of free element
$F_2(g)$	yellow
$C\ell_2(g)$	greenish-yellow
$Br_2(\ell)$	red
$I_2(s)$	purple

Halogen	Colour of halogen in aqueous solution
$C\ell_2(aq)$	pale yellow
$Br_2(aq)$	orange
$I_2(aq)$	brown

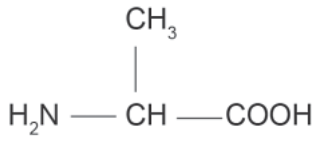
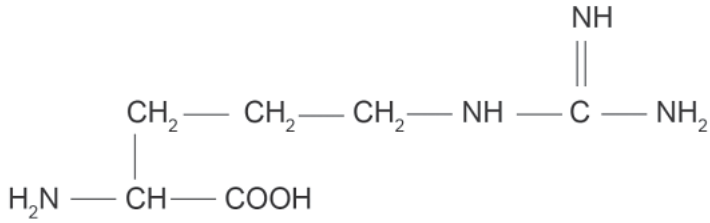
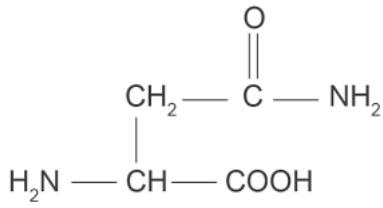
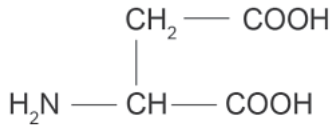
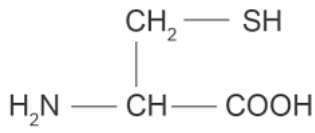
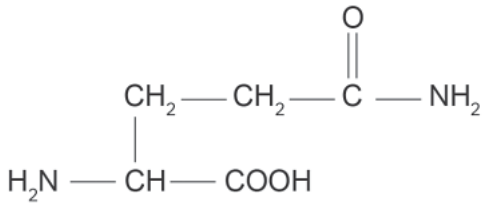
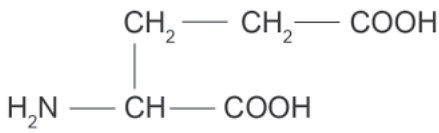
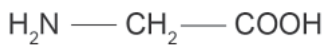
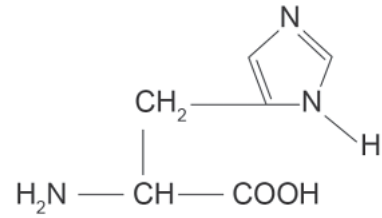
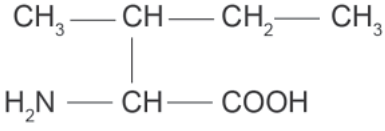
Halogen	Colour of halogen in organic solvent
Br_2	red
I_2	purple

Coloured ions in aqueous solution

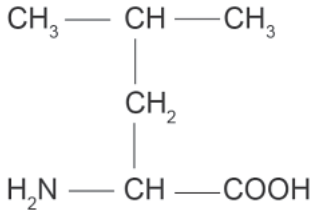
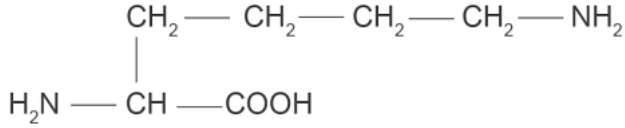
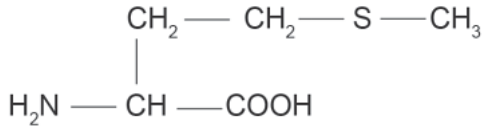
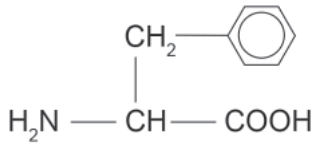
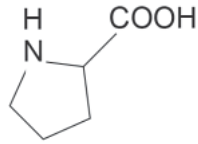
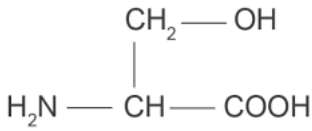
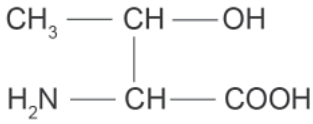
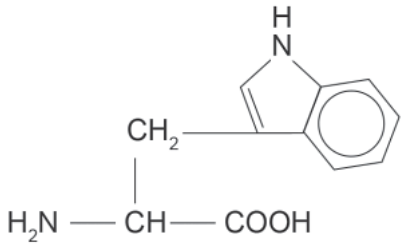
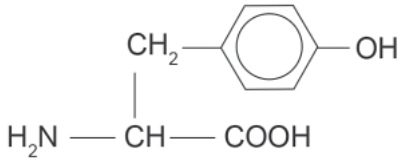
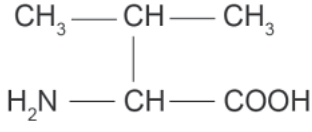
Cation	Colour
Cr^{3+}	deep green
Co^{2+}	pink
Cu^{2+}	blue
Fe^{2+}	pale green
Fe^{3+}	pale brown
Mn^{2+}	pale pink
Ni^{2+}	green

Anion	Colour
CrO_4^{2-}	yellow
$Cr_2O_7^{2-}$	orange
MnO_4^-	purple

α–amino acids

Name	Symbol	Structure
alanine	Ala	
arginine	Arg	
asparagine	Asn	
aspartic acid	Asp	
cysteine	Cys	
glutamine	Gln	
glutamic acid	Glu	
glycine	Gly	
histidine	His	
isoleucine	Ile	

α–amino acids

Name	Symbol	Structure
leucine	Leu	
lysine	Lys	
methionine	Met	
phenylalanine	Phe	
proline	Pro	
serine	Ser	
threonine	Thr	
tryptophan	Trp	
tyrosine	Tyr	
valine	Val	

Standard Reduction Potentials at 25 °C

Half-reaction	E°(volts)
$F_2(g) + 2\ e^- \rightleftharpoons 2\ F^-(aq)$	+ 2.89
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons 2\ H_2O(\ell)$	+ 1.76
$PbO_2(s) + SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons PbSO_4(s) + 2\ H_2O(\ell)$	+ 1.69
$2\ HC\ell O(aq) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons C\ell_2(g) + 2\ H_2O(\ell)$	+ 1.63
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightleftharpoons Mn^{2+}(aq) + 4\ H_2O(\ell)$	+ 1.51
$Au^{3+}(aq) + 3\ e^- \rightleftharpoons Au(s)$	+ 1.50
$HC\ell O(aq) + H^+(aq) + 2\ e^- \rightleftharpoons C\ell^-(aq) + H_2O(\ell)$	+ 1.49
$PbO_2(s) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons Pb^{2+}(aq) + 2\ H_2O(\ell)$	+ 1.46
$C\ell_2(g) + 2\ e^- \rightleftharpoons 2\ C\ell^-(aq)$	+ 1.36
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightleftharpoons 2\ Cr^{3+}(aq) + 7\ H_2O(\ell)$	+ 1.36
$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightleftharpoons 2\ H_2O(\ell)$	+ 1.23
$Br_2(\ell) + 2\ e^- \rightleftharpoons 2\ Br^-(aq)$	+ 1.08
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+ 0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+ 0.77
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2O_2(aq)$	+ 0.70
$I_2(s) + 2\ e^- \rightleftharpoons 2\ I^-(aq)$	+ 0.54
$O_2(g) + 2\ H_2O(\ell) + 4\ e^- \rightleftharpoons 4\ OH^-(aq)$	+ 0.40
$Cu^{2+}(aq) + 2\ e^- \rightleftharpoons Cu(s)$	+ 0.34
$S(s) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2S(aq)$	+ 0.17
$2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2(g)$	0 exactly
$Pb^{2+}(aq) + 2\ e^- \rightleftharpoons Pb(s)$	– 0.13
$Sn^{2+}(aq) + 2\ e^- \rightleftharpoons Sn(s)$	– 0.14
$Ni^{2+}(aq) + 2\ e^- \rightleftharpoons Ni(s)$	– 0.24
$Co^{2+}(aq) + 2\ e^- \rightleftharpoons Co(s)$	– 0.28
$PbSO_4(s) + 2\ e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	– 0.36
$Cd^{2+}(aq) + 2\ e^- \rightleftharpoons Cd(s)$	– 0.40
$2\ CO_2(g) + 2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2C_2O_4(aq)$	– 0.43
$Fe^{2+}(aq) + 2\ e^- \rightleftharpoons Fe(s)$	– 0.44
$Cr^{3+}(aq) + 3\ e^- \rightleftharpoons Cr(s)$	– 0.74
$Zn^{2+}(aq) + 2\ e^- \rightleftharpoons Zn(s)$	– 0.76
$2\ H_2O(\ell) + 2\ e^- \rightleftharpoons H_2(g) + 2\ OH^-(aq)$	– 0.83
$Mn^{2+}(aq) + 2\ e^- \rightleftharpoons Mn(s)$	– 1.18
$A\ell^{3+}(aq) + 3\ e^- \rightleftharpoons A\ell(s)$	– 1.68
$Mg^{2+}(aq) + 2\ e^- \rightleftharpoons Mg(s)$	– 2.36
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	– 2.71
$Ca^{2+}(aq) + 2\ e^- \rightleftharpoons Ca(s)$	– 2.87
$Sr^{2+}(aq) + 2\ e^- \rightleftharpoons Sr(s)$	– 2.90
$Ba^{2+}(aq) + 2\ e^- \rightleftharpoons Ba(s)$	– 2.91
$K^+(aq) + e^- \rightleftharpoons K(s)$	– 2.94

[Data source: Aylward, G.H., & Findlay, T. (2008). *SI Chemical Data* (6th ed.). Queensland: John Wiley & Sons Australia, Ltd.]

Solutions

Chapter 1.
Chemical Equilibrium

Set 1 Concentration Changes

1. *Yield rises, Rate rises. Forward collision rate rises so equilibrium moves right in order to partially compensate for the increase in O_2.*
2. *Yield falls, Rate drops. Forward collision rate drops so equilibrium moves left.*
3. *$[Ag^+]$ and $[Cl^-]$ returns to the same level although the number of ions increases – but so does the volume. Forward and reverse rates increase. Concentration of ions decreases initially, lowering Q. More AgCl dissolves to restore Q to the same value as K.*
4. *Concentration of all ions increases sending the equilibrium to the right and lowering Q so the amount of $PbCl_2$ increases. Rate increases then reduces but is still greater. More $PbCl_2$ precipitates to increase Q to the same value as K.*

   $$K = \frac{1}{[Pb^{2+}][Cl^-]^2}$$

5.
(i) *Yield of CH_3COO^- falls as it is used up but H^+ will still be higher at equilibrium. Rate increases overall.*

(ii) *Ethanoic acid is weak and K will not be affected by addition of H^+ as temperature is constant.*

6.
(i) *$[H^+]$ falls as it reacts with the OH^- to produce water. $[CH_3COO^-]$ rises as reaction shifts to the right.*
If H^+ is removed, reverse rate is less and so forward rate must also become less eventually.

(ii) *The acid is weak as K value is small. K will not change.*

7.
(i) *No change in yield but both forward and reverse rates increase equally as more surface area.*

(ii) *$K = [CO_2]$ which must stay constant, so yield is unaffected. Forward and reverse rates both increase.*

8. *Yield reduces and rate reduces as there are now less reactants.*

9.
(i) *All ions diluted so reaction moves left and yield will decrease. Rate reduces as there are now less collisions.*

(ii) *As equilibrium moves left, colour will become more yellow.*

10. *Yield will decrease as product is removed and equilibrium shifts right. Rate will decrease as less reactants present.*

Set 2 Changing Pressures

1. *Pressure increases as volume is now less. Yield increases as equilibrium shifts right. Forward rate increases more than the reverse rate as reactants are now more concentrated.*
2. *Pressure is decreased as volume becomes greater. Yield reduces as equilibrium shifts left. Forward rate decreases more than the reverse rate does.*
   K remains the same.
3. *Pressure remains the same as $K = [CO_2]$ which must stay constant. Yield of CO_2 would remain constant as equilibrium shifts to the left. Forward rate increases by the same amount as the reverse rate.*
   Mass of CaO would decrease as the equilibrium shifts to the left.
4. *Pressure increases as volume is now less. Yield becomes less as equilibrium shifts to the left. Forward rate increases but reverse rate increases more.*
5. *Pressure would initially decreased then goes back to the original value as $K = [As_4][CO]^6$ so concentration of products becomes constant. There will be more mass of products but the concentration would be the same but in a larger volume. Forward rate would increase as the equilibrium shifts right then returns to the original.*
   Mass of As_4O_6 decreases as reaction moves right.
6. *Pressure would increase as Cl_2 is now contained in a smaller volume.Equilibrium shifts right, giving more yield. Forward and reverse rates must become larger as all species' concentrations increase.*

   $$K = \frac{[HOCl][H^+][Cl^-]}{[Cl_2]}$$

7. *Pressure of air inside the vessel will be reduced. No change in yield or rate for solutions!*

8. *Pressure will increase. Mass of yield will remain the same but concentration of products will increase. Rate will increase but no equilibrium shift.*

9.

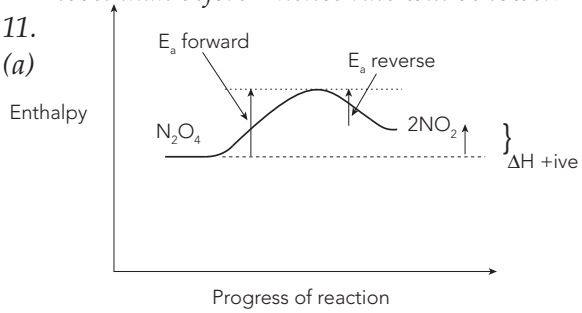
(i) *Pressure will increase as there are more particles. Yield and rate will remain constant as particle spacing remains the same.*

(ii) *For pressure to remain constant volume must increase therefore both rates decrease, but yield will increase as equilibrium shifts right.*

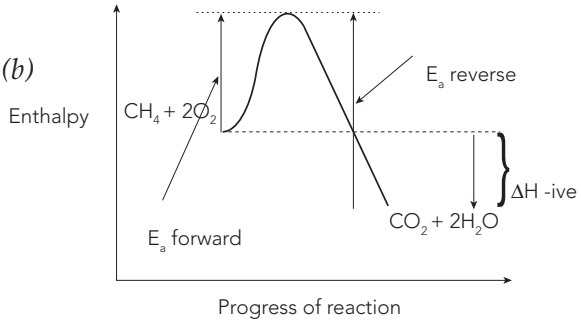
10. *Pressure will be reduced as volume increases. Yield will reduce as equilibrium shifts left and so $[SO_2]$ will increase but up to a lower level than before – hence rate will be lower.*

11.

(a)



(b)



Set 3 Changing Temperatures

1. *Pressure will decrease but equilibrium shifts to the right as exothermic and yield must increase. Forward rate will decrease as temperature is reduced and equilibrium shifts to the right because reverse rate decreases more than the forward rate.*
2. *Pressure must increase with temperature. Yield must decrease for exothermic reactions as equilibrium shifts to the left. Rate must increase with higher temperature.*
3.

(i) *Pressure must increase with temperature as K increases for endothermic reactions ($K = [CO_2]$).*
Yield will increase as equilibrium shifts to the right. Rate always increases with temperature.

(ii) *Mass of $CaCO_3$ will be reduced as equilibrium shifts to the right.*

(iii) *$K = [CO_2]$.*

4.

(i) *Pressure must increase with temperature. Yield must increase with temperature for the endothermic reaction. Rate must increase with temperature.*

(ii) *More iodine would be produced so colour becomes darker.*

5. *Pressure must increase with temperature. Yield must increase with temperature for an endothermic reaction. Rate must increase with temperature.*
6.

(i) *Exothermic equilibrium shifts to the left so mass of AgCl decreases. Forward rate must increase with higher temperature but reverse rate increases more.*

(ii) *Rate of forward reaction would decrease as the equilibrium shifts to the left. AgCl decreases.*

7.

(i) *Pressure must increase with temperature. Yield must decrease with temperature for an exothermic reaction. Forward rate must increase with higher temperature but reverse rate increases more so the equilibrium shifts to the left.*

(ii) *Mass and volume of bromine would increase.*

8.

(i) *Pressure must increase with temperature. Yield must increase with temperature for an endothermic reaction. Rate must increase with higher temperature.*

(ii) *Mass of ZnO would decrease as the equilibrium shifts to the right.*

9. *Pressure must increase with temperature. Yield must increase with temperature for an endothermic reaction. Rate must increase with higher temperature.*
10.

(i) *$[Cl_2]$ would decrease as the equilibrium shifts to the left.*

(ii) *$FeCl_2$ is a solid and so its concentration cannot change but mass would increase.*

(iii) *The mass of iron would decrease as the equilibrium shifts to the right.*

(iv) *Pressure must decrease with a temperature drop as Cl_2 molecules collide less.*

(v) *Total enthalpy change would be -342 + -57 = -399 kJ.*

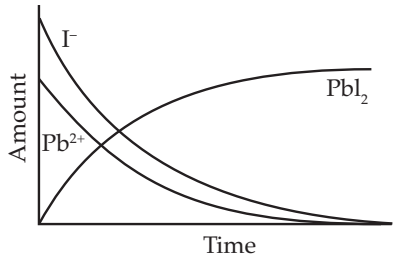
Set 4 Equilibrium

1. c, 2. b, 3. b, 4. a, 5. d, 6.a, 7. c, 8. d, 9. d, 10. e, 11. e, 12. a

Answers to longer questions

1. (a) $Pb^{2+}(aq) + 2I(aq) \rightarrow PbI_2(s)$

(b)



(c) The amount of the precipitate formed, its colour or intensity of the yellow colour, or any other observable changes have ceased.

(d) This could only be shown using tagged radioactive isotope mixed with normal iodine. It could be shown that the proportion of the radioactive isotopic iodine continues changing during the equilibrium even though the amounts remain constant.

2.

(a) N_2, H_2, and NH_3 are present at equilibrium.

(b) Final concentrations: $[N_2] = 1.60$ mol L^{-1}, $[H_2] = 1.00$ mol L^{-1}, $[NH_3] = 0.40$ mol L^{-1}

(c) Concentrations after 3 minutes: $[N_2] = 1.65$ mol L^{-1}, $[H_2] = 1.10$ mol L^{-1}, $[NH_3] = 0.25$ mol L^{-1}

(d) About 2 minutes after the reaction commences.

(e) At the seventh minute after the reaction commences.

(f) Same as given for b) above.

3.

(a) Increase the temperature of the reaction mixture.
Increase the pressure in gaseous reactions.
Increase the concentrations of the reactants.
Increase the surface area of any solids which are reacting.
Use a catalyst

(b) (i) Reaction would move to the right and colour would turn more yellow.
(ii) Reaction would move to the left and colour would turn more orange.
(iii) All ion concentrations would become less initially, then by LCP reaction would move to the left to increase the concentration of ions. More orange.

(c) When the bottle is opened CO_2 gas is lost from the left side of the equation, so, by LCP, the reaction will move right to replace it.

(d) (i) In an open container the CO_2 is lost and so by LCP reaction moves right to produce more. Eventually all the $CuCO_3$ will have decomposed.

(ii) In a sealed container the CO_2 cannot escape and an equilibrium is reached where the forward rate = reverse rate and the mass of $CuCO_3$ will become constant.

4.

(a) A decrease in pressure will shift the equilibrium to the left, forming more of the reactants from the products.

(b) A decrease in pressure has no effect because the number of gaseous moles are equal on both sides.

(c) A decrease in pressure will shift the equilibrium to the right (towards greater number of gaseous moles), forming more products from the reactants.

(d) A decrease in pressure will shift the equilibrium to the right (towards a greater number of gaseous moles), forming more products.

5.

(a) Raising the temperature will shift the equilibrium to the left, forming more reactants as this is an exothermic reaction.

(b) Raising the temperature will shift the equilibrium to the left, forming more reactants as this is an exothermic reaction.

(c) Raising the temperature will shift the equilibrium to the right, forming more products as this is an endothermic reaction.

6. The opposite effect to what is stated in question 5 will occur in each case.

7.

(a) $K = [Ca^{2+}][OH^-]^2$

(b) $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(c) $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$

(d) $K = \dfrac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$

(e) $K = \dfrac{[Mn^{2+}]^2[CO_2]^{10}}{[MnO_4^-]^2[H_2C_2O_4]^5[H^+]^6}$

8.

(a) $K = \dfrac{[Co(H_2O)_6^{2+}][Cl^-]^4}{[CoCl_4^{2-}]}$

(b) If you sprinkle some NaCl solution, the increased concentration of chloride ions will shift the equilibrium to the left and the solution will become blue.

(c) After microwaving the papers the blue paper will remain blue and the pink one will turn blue. The shift in equilibrium is to the left as water is removed from the paper.

9.

Change made	Change in rate	Change in yield
Increase in pressure	No change	No Change
Increase in temperature	Increase	Decrease
Add some NaCl solid	Increase	Increase
Divide the solution into 100 mL portions to increase the state of sub-division	No change	No change (not changing concentrations)

10.

(a) At the beginning of the reaction, SO_2, Cl_2, and SO_2Cl_2 are all present. (SO_2 = 0.05 M, Cl_2 = 0.068M, SO_2Cl_2 = 0.05 M)

(b) $K = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]}$

(c) Chlorine was pumped into the system. The increased concentration of one of the products shifts the equilibrium to the left. Chlorine starts reacting with SO_2, producing SO_2Cl_2. Therefore $[SO_2]$ begins to decrease and $[SO_2Cl_2]$ begins to increase.

(d) At t = 9 mins.

(e) Volume of vessel is increased so all concentrations decrease.

11.

(a) i) After $BaCl_2$ solution is added, the concentration of Ba^{2+} ions increases. Equilibrium shifts to the left. More $Ba(OH)_2$ is produced. The solution becomes cloudy initially, then becoming whiter.

ii) Addition of $Ba(OH)_2$ solid does not eventually produce any effect as K must stay constant.

(b) i) NaOH solution reacts and will dissolve acidic CO_2 gas. The equilibrium will shift to the right to produce more CO_2. More $CaCO_3$ will decompose.

ii) This is an endothermic reaction. Decrease in temperature will shift the equilibrium to the left, forming more $CaCO_3$. CO_2 gas is reduced because K reduces.

iii) The reaction moving to the right to produce some more CO_2, as some of this gas dissolves in the added water.

iv) A decrease in pressure will drive the reaction to the side of more number of gaseous moles. Equilibrium will shift to the right. More CO_2 will be produced but the concentration will remain the same so that K can stay the same. $K = [CO_2]$. $CaCO_3$ decreases.

(c) i) When the volume of the system is increased, the reaction moves in the direction of greater number of gaseous moles (left). More reactants are produced and the system gets cooler as a result.

ii) Introduction of an inert gas does not change the concentration of the gases and so K remains the same and there is no change in yield or rate.

12. $Cr_2O_7^{2-}(aq) + 2H^+(aq) + 3SO_2(g)$ *Orange* $\rightleftharpoons 2Cr^{3+}(aq) + H_2O(l) + 3SO_4^{2-}(aq)$ *Green*

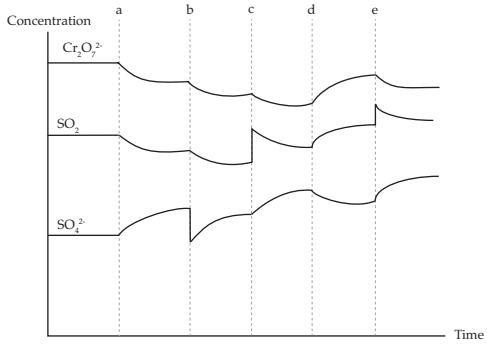
(a) When a solution of HCl is added to the mixture, $[H^+]$ increases. The equilibrium shifts to the right. More Cr^{3+} and SO_4^{2-} are produced and the mixture becomes greener..

(b) The added Ba^{2+} ions will react with SO_4^{2-} ions to produce $BaSO_4(s)$ and decrease its concentration. Equilibrium will shift to the right in order to produce more SO_4^{2-} ion. The mixture becomes more greenish.

(c) The reaction will then move to the right according to LCP to partially increase the concentrations again and so the colour will become greener.

(d) The added OH^- ions will react with the H^+ ions in the mixture to produce H_2O, thus decreasing its concentration. Equilibrium will shift to the left producing more reactants. The solution will become more orange.

(e) Increased concentration of the reactant SO_2 will shift the equilibrium to the right leading to the production of more Cr^{3+} and the other products. The solution will become greener.



13.

Tube No.	Change imposed	Shift in equilibrium	Explanation
A	5 mL of water added	None	All ions are diluted but no increase. Both rates reduced.
B	A few drops of HBr added	Left	Concentration of Br^- increases so reaction moves left by LCP to decrease Br^- concentration
C	A few drops of $AgNO_3$(aq) added	Right	Ag^+ ion reacts with the Br^- ion to form a precipitate of AgBr and removes Br^-. So reaction moves right by LCP to increase Br^- concentration.

14.

(i) The reaction has reached equilibrium.

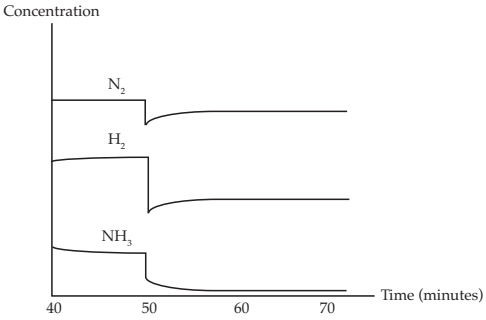
(ii) For every N_2 molecule used in the reaction 3 H_2 molecules are use up so the H_2 will decrease 3 times faster than the N_2.

(iii) More N_2 was introduced into the vessel.

(iv) Forward reaction rate and reverse reaction rate will have increased but forward rate increases more than the reverse rate.

(v) With more nitrogen present, the particles are closer and so there will be more collisions per second and the forward rate will go up producing more product. With more product, the reverse collision rate will then rise.

(vi)



15.

(a) $CO_{2(g)} \rightleftharpoons CO_{2(aq)}$

(b) Increasing oceanic temperatures would cause the equilibrium to shift in the reverse direction so more $CO_{2(g)}$ would be produced.

(c) $CO_{2(aq)} + H_2O_{(l)} \overset{1}{\rightleftharpoons} H^+_{(aq)} + HCO_3^-{}_{(aq)} \overset{2}{\rightleftharpoons} 2H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$
As carbon dioxide dissolves into the ocean LCP predicts that equilibrium 1 shifts in the forward direction to partially counteract the imposed change and the concentration of hydrogen ions and hydrogencarbonate ions increases. In turn, LCP predicts that equilibrium 2 will shift in the forward direction, further increasing the concentration of hydrogen ions. The pH decreases and acidity increases.

(d) Increasing the CO_2 concentration increases the collisions between CO_2 and H_2O molecules and so the rate of the forward reaction 1 increases relative to the rate of its reverse reaction. This in turn increases to collisions between hydrogen ions and hydrogencarbonate ions and so the rate of the forward reaction 2 increases relative to the rate of its reverse reaction. More hydrogen ions contribute to increased acidity.

(e) Increasing hydrogen ion concentration causes the equilibrium 2 above to shift in the reverse direction in order to partially counteract the imposed change. This causes the carbonate ion concentration to decrease.

(f) $CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

Chapter 2. Acids and Bases

Set 1 Brønsted-Lowry Acids and Bases

1.

(a)

(i) $2HCl_{(aq)} + Mg_{(s)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$
$2H^+_{(aq)} + Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$

(ii) $H_2SO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$
$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$

(iii) $2HNO_{3(aq)} + CaO_{(s)} \rightarrow Ca(NO_3)_{2(aq)} + H_2O_{(l)}$
$2H^+_{(aq)} + CaO_{(s)} \rightarrow Ca^{2+}_{(aq)} + H_2O_{(l)}$

(iv) $2HBr_{(aq)} + K_2CO_{3(aq)} \rightarrow 2KBr_{(aq)} + H_2O_{(l)} + CO_{2(g)}$
$2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)}$

(b) Davy identified acids as substances that contain hydrogen that could be replaced by metals. In equation (i) and (iii) the metal has replaced the hydrogen in the acid to produce the salt.

(c) Magnesium metal is not considered a 'Davy' base because when it reacts with an acid it does produce a salt, but not water. In our terms, the reaction is not a neutralisation.

2.

(a) Weak Arrhenius acid, since it does produce hydrogen ions in water but does not ionise completely.
$H_3PO_{4(aq)} \rightleftharpoons H^+_{(aq)} + H_2PO_4^-{}_{(aq)}$

(b) Weak Arrhenius base, since it does produce hydroxide ions in water but does not ionise completely.
$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons + NH_4^+{}_{(aq)} + OH^-_{(aq)}$

(c) Weak Arrhenius acid, since it does produce hydrogen ions in water but does not ionise completely.
$HF_{(aq)} \rightleftharpoons H^+_{(aq)} + F^-_{(aq)}$

(d) Strong Arrhenius base, since it dissociates completely to produce OH^- ions in solution.
$LiOH_{(s)} \rightarrow Li^+_{(aq)} + OH^-_{(aq)}$

(e) Strong Arrhenius acid, since its first ionisation occurs completely.
$H_2SO_{4(aq)} \rightarrow H^+_{(aq)} + HSO_4^-{}_{(aq)}$

3. (i) Acid = H_2O, Base is CN^-
(ii) Acid = CH_3COOH, Base = S^{2-}
(iii) Acid = HS^-, Base = CO_3^{2-}

4. (i) H_2O/ OH^-, HCN/ CN^-
(ii) CH_3COOH/ CH_3COO^-,
(iii) HS^-/ S^{2-}, HCO_3^-/ CO_3^{2-}

5. Theoretically the HCl solution should give the same number of H^+ ions as the H_2SO_4 as the latter is diprotic and the acids are both strong. However, not both of the hydrogens from the H_2SO_4 are fully ionised in solution. One is a strong ionisation and the second is weak so for HCl, moles of H^+ is $0.2 \times 1 = 0.2$

but for H_2SO_4 result is about 0.1 × 1.3 = 1.3, so less H^+ and higher pH.

6. *Answer is D.*
7. *Acidic compounds are CO_2, SO_3, OCl_2 and NO_2 (non-metal oxides).*
8. *$Ba(OH)_2$ is a strong base with 3 ions per formula unit.*
9. *OH^-, HCO_3^-, NH_3 (all can gain or lose a proton).*
10. *(i) CO_2 dissolves in water to produce H_2CO_3 which reacts with water:*
    $H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+$ (acidic pH < 7). When boiled, this reaction reverses the produce neutral water again and pH 7.
    (ii) The K value for water goes up because the reaction is endothermic so more H^+ ions.
    (iii) Although there are more H^+ ions if the pH is smaller, there is still an equal number of OH- ions so it is still neutral. N.B. The pH of water is 7 only at 25°C.
11. *(ii) and (v) are not Brønsted–Lowry reactions.*
12. *(i) The ammonia solution must have a much higher concentration than the HCl as it a weak base and a 0.05 M solution would not supply enough OH^- ions to neutralise it.*
    (ii) NH_3 ions would be most common as it "wants to" stay as a molecule.
13. *A Brønsted–Lowry acid is a species that donates a H^+ ion. To react with water, a proton must be exchanged which means the reactant must be a Brønsted–Lowry acid or base.*
14. *$NH_3 + H^+ \rightarrow NH_4^+$*
    $H_2O + H^+ \rightarrow H_3O^+$
    $HCO_3^- + H^+ \rightarrow H_2CO_3$
    $CO_3^{2-} + H^+ \rightarrow HCO_3^-$
    $CN^- + H^+ \rightarrow HCN$
    $OH^- + H^+ \rightarrow H_2O$
15. *$HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-}$*
    $HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$
    CO_3^{2-} is the conjugate base of HCO_3^- and H_2CO_3 is the conjugate acid of HCO_3^-.
16. *Acids: NH_4^+, H_2O, HBr, $AlCl_3$.*
    Bases: SO_3^{2-}, H_2O, Cl^-
17. *(i) HCl, HCN, HS^-, NH_4^+*
    (ii) O^{2-}, HSe^-, NH_2^-, CO_3^{2-}

Set 2 Acidity

Multiple Choice Answers

1. a, 2. c, 3. c, 4. d, 5. c, 6. d, 7. d, 8. b, 9. e, 10. a, 11. c, 12. b, 13. d. 14. a, 15. c.

Answers to Longer Questions

1. *Acid strength increases with increasing K_a, acid strength decreases with decreasing K_a.*
2. *I^- ion is the conjugate base of a strong acid. It will simply be hydrated and stay as I^-.*
   NO_2^- ion is the conjugate base of a weak acid, HNO_2, and would react to form a base.
   $NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$.
   K^+ ion does not react with water except to get hydrated because the ions stay as K^+.
   $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$
   $HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$
3. *KCl is the salt of the cation K^+, which is a weaker acid than water and the anion Cl^-, which is a weaker base than water. Because neither ion reacts with water to any extent, a KCl solution will be neutral.*
   NH_4NO_2 is the salt of a cation and anion both of which can react with water. The solution will be nearly neutral. The pH will depend on the relative degree of ionisation of the anion and cation in water.
   Na(HCOO) is the salt of a cation that does not react with water and an anion that is stronger base than water (because it is the anion of a weak acid). The solution will therefore be basic.
4. *NH_4CN: close to neutral, because both the parent acid and base are weaker than water*
   KI: close to neutral, because both the parent acid and base are stronger than water.
   $LiCH_3COO$: alkaline since the parent base $Li(OH)_2$ is a stronger base than water.
5. *(a) Acids: HNO_3, H_3O^+ Bases: H_2O, NO_3^-*
   (b) Acids: HCl, NH_4^+ Bases: NH_3, Cl^-
   (c) Acids: H_2SO_4, H_3O^+ Bases: H_2O, HSO_4^-
   (d) Acids: H_2O, H_3O^+ Bases: H_2O, OH^-
6. *$CO_2 + H_2O \rightarrow H_2CO_3$, and, $H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^-$*
   $Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$
7. *(a) Hydrolysis is a reaction in which a salt reacts with water to produce a H^+ (H_3O^+) or an OH^- ion. Acidic salts give H_3O^+ ions and basic salts give OH^- ions with water.*
   (b) Cations of the following acidic salts give H_3O^+ ions:
   $Fe^{3+} + 2H_2O \rightarrow Fe(OH)^{2+} + H_3O^+$
   $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$
   $HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$
   (c) Anions of the following basic salts give OH^- ions:
   $NH_2^- + H_2O \rightarrow NH_3 + OH^-$
   $CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$
   $PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^-$
8. *$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$*
   1 mol of H_2SO_4 reacts with 1 mole of $BaCl_2$.
   → mass of $BaCl_2$ = [0.1 × (137.3 + 70.9) × 0.032] = 0.667 g.

9. *All are strong acids and completely dissociated.*
(a) $[H^+] = 1 \times 10^{-1}$ M ∴ pH = 1.0
(b) $[H^+] = 1 \times 10^{-5}$ M ∴ pH = 5.0
(c) $[OH^-] = 1 \times 10^{-2}$ M ∴ $[H^+] = 1 \times 10^{-12}$ M ∴ pH = 12.0
(d) $[OH^-] = 2 \times 10^{-2}$ M ∴ $[H^+] = 5 \times 10^{-13}$ M → pH = 12.3
(e) $[H^+] = 1.72 \times 10^{-2}$ M ∴ $[H^+] = 1 \times 10^{-1.76}$ M ∴ pH = 1.76

10. *1.0 L of 0.1 M HCl contains 0.1 mol of HCl.*
(a) HCl left after reaction with 0.010 mol of KOH = 0.09 mol
$[H^+] = 0.09$ mol $L^{-1} = 9.0 \times 10^{-2}$M,
∴ pH = − log $9 \times 10^{-2} = 1.05$
(b) $[OH^-] = 2 \times 0.05 = 0.1$ mol ∴ HCl left after reaction is none ∴ pH = 7.
(c) $[OH^-] = 0.1$ mol ∴ HCl left after reaction is none ∴ pH = 7

11. *Assume 0.5 L of each solution is mixed.*
(a) Since $[H^+] = [OH^-]$ in the mixture, the pH is 7.
(b) Before reaction, there are 0.20 × 0.50 (0.1 mol) of HCl, and 0.10 × 0.500 = (0.05 mol) of NaOH.
After the reaction 0.05 mole of HCl is left. ∴ $[H^+] = 0.05/1.0 = 0.05$ mol L^{-1}
∴ pH= − log 0.05 = 1.30
(c) Before reaction, there are 0.40 × 0.50 (0.2 mol) of HCl, and 0.20 × 0.500 = (0.10 mol) of NaOH.
After the reaction 0.10 mole of HCl is left. ∴ $[H^+] = 0.10/1.0 = 0.1$ mol L^{-1}
∴ pH= − log 0.1 = 1.00
(d) Before reaction, there are 0.10 × 0.50 (0.05 mol) of HCl, and 0.20 × 0.50 = (0.10 mol) of OH^- ions.
After the reaction 0.05 mole of OH^- ions left.
∴ $[OH^-] = 0.05/1.0 = 0.05$ mol L^{-1}
∴ pOH= − log 0.05 = 1.30
so pH = 14 − 1.3 = 12.7.

12.
(i) *1.7×10^{-6} g in 1500 g of solution*
$= 1.13 \times 10^{-9}$ grams per gram
1.13×10^{-9} multiply by a million
$= 1.13 \times 10^{-3}$ ppm.

(ii) $n(HCl) = \dfrac{1.7 \times 10^{-6}}{36.45} = 4.664 \times 10^{-8}$ mol

$[H^+] = \dfrac{4.664 \times 10^{-8}}{1.5} = 3.109 \times 10^{-8}$ mol L^{-1}

(iii) *Calculated pH = $-\log(3.109 \times 10^{-8})$ = 7.50 but, this concentration of H^+ ions is lower than that for neutral water and so the contribution from water cannot be disregarded.*
Total concentration of $H^+ = 3.109 \times 10^{-8}$ (acid) + 1×10^{-7} (water) = 1.31×10^{-7} mol L^{-1}
pH = $-\log(1.31 \times 10^{-7}) = 6.88$ (acidic!)

13. *$n(H_2SO_4) = (4.90/ 98.086) = 0.050$ mol,*
∴ $[H_2SO_4] = (0.050/0.100) = 0.50$ M
∴ $[H^+] = 1.3 \times 0.5$ M = 0.65 M
∴ pH = −log [0.65] = 0.187

14. *$2\,NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$*
n (NaOH) = $0.025 \times 0.20 = 0.0050$ mol (limiting reagent)
$n(H_2SO_4)$ required to use up all the NaOH = ½ × 0.005 = 0.0025 mol
For H_2SO_4, n (H_2SO_4) = 0.030×0.175 = 0.00525 mol (excess reagent)
H_2SO_4 is left over and is in excess by (0.00525 − 0.0025) = 0.00275 mol
∴ Final $[H_2SO_4] = \dfrac{0.00275}{0.05} = 0.055$ M
∴ Final $[H^+] = 2 \times 0.055 = 0.959$ M
∴ pH = − log [0.182] = 0.74

15. *$Ba(OH)_2 + 2HNO_3 \rightarrow Ba(NO_3)_2 + 2H_2O$*
For $Ba(OH)_2$, n = $0.050 \times 0.200 = 0.010$ mol = (limiting reagent)
For HNO_3, n = $0.200 \times 0.400 = 0.080$ mol = (excess reagent)
HNO_3 is left over and is in excess.
∴ H^+ is in excess by 0.080 mol − 0.020 = 0.060 mol.
After dilution $[H^+] = 0.06/6.0 = 1 \times 10^{-2}$ M
pH = 2.

16. *(a) $[OH^-] = 2 \times 0.00500 = 0.0100$ M*
$= 1.00 \times 10^{-2}$M
∴ pOH = 2 pH = 14 − 2 = 12
∴ The pH of the original solution = 12.
(b) After making the final volume 1.0 L, the final concentration is calculated using the dilution relationship, $c_1V_1 = c_2V_2$.
0.010 L × 1.0×10^{-2} M = 1.99 L × c_2
∴ $c_2 = [(0.010 \times 1.0 \times 10^{-2})/ 1.0\ L]$
$= 1.0 \times 10^{-4}$ M
∴ $[OH^-] = 1.0 \times 10^{-4}$ M, and $[H^+]$
$= 1.0 \times 10^{-10}$ M
∴ pH = 10.
pH changes from 12 to 10.
(c) $n(Ca(OH)_2 = 0.00500 \times 0.010$
$= 5.00 \times 10^{-5}$ mol
m $[(Ca(OH)_2] = 5.00 \times 10^{-5} \times 74.09$
= 0.00370 g.
(d) $Ca(OH)_2 + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$
n (CO_2) = n$[(Ca(OH)_2] = 5.00 \times 10^{-5}$ mol
Using the relationship pV = nRT and V = nRT ÷ p, $V = [(5.00 \times 10^{-5} \times 8.314 \times 298)/ (110)] = 1.126 \times 10^{-3}$ L = 1.126 mL.

17. *$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$ (CO_3^{2-} is a stronger base than H_2O)*
$S^{2-} + H_2O \rightarrow HS^- + OH^-$ (S^{2-} is a stronger base than H_2O)

$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$
(CH_3COO^- is a stronger base than H_2O)

18. pH of 6 means $[H^+] = 1 \times 10^{-6}$ mol L^{-1} and a pH of 8 means $[H^+] = 1 \times 10^{-8}$ mol L^{-1} which is 100 times less than the first concentration.
19. (a) $(NH_4)_2CO_3(s) + water \rightarrow 2NH_4^+(aq) + CO_3^{2-}(aq)$
This reaction (reaction 1) is an ionisation reaction.
$NH_4^+(aq)$ produces H_3O^+ ions (reaction 2). It is from an acidic salt. Anions of basic salts produce H_3O^+ ions.
$CO_3^{2-}(aq)$ produces OH^- ions (reaction 3). It is from a basic salt. Cations of acidic salts produce OH^- ions.
Reactions 2 and 3 are hydrolysis reactions. NH_4^+ ion is a weak acid. It does not produce many H_3O^+ ions. Although the carbonate ion is in the minority, it has a higher K value so it will react with water to give an excess of OH^- ions.
20. In a series, acids such as H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-} the extent of dissociation decreases as H^+ ions had to be removed from negative ions and consequently their strength decreases also. (H_3PO_4 is the relatively strongest one of the three).

Set 3 Acids/Base Reactions

Multiple Choice Answers

1. a, 2. e, 3. e, 4. e, 5. b, 6. c, 7. c, 8. e, 9. d, 10. e, 11. b, 12. b, 13. c, 14. c, 15. b, 16. c, 17. c, 18. b, 19. b, 20. c.

Acid Base Calculations

1. No. of moles of $Ca(OH)_2 = cV = 0.015 \times 0.02 = 3.0 \times 10^{-4}$ mol
$n(OH^-) = 2 \times 3.0 \times 10^{-4}$ mol $= 6.0 \times 10^{-4}$ mol
($Ca(OH)_2 \rightarrow 2OH^-$).
$n(H^+)$ from $HNO_3 = 0.010 \times 0.080 = 8.0 \times 10^{-4}$ mol.
OH^- is the limiting reagent. So 6.0×10^{-4} moles of H_2O is formed and $n(H^+)$ left will be $8.0 \times 10^{-4} - 6.0 \times 10^{-4} = 2.0 \times 10^{-4}$ mol.
Total volume of mixed solution = 20 + 80 = 100 mL so
$[OH^-] = n/V = 2.0 \times 10^{-4}/0.10 = 2.0 \times 10^{-3}$ mol L^{-1}
pH = 2.7
2. $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$
$n(NaOH) = c \times V = 0.0250 \times 0.200 = 5.00 \times 10^{-3}$ mol
$n(HNO_3) = c \times V = 0.030 \times 0.175 = 5.25 \times 10^{-3}$ mol
From the equation 1 mol of NaOH reacts with 1 mol of HNO_3.
$\therefore$ 5.00×10^{-3} mol of NaOH will react with 5100×10^{-3} mol HNO_3.
$\rightarrow$ HNO_3 is in excess by 0.25×10^{-3} mol and $[H^+] = n/V = (0.25 \times 10^{-3}/ 0.055)$
$= 4.55 \times 10^{-3}$ mol L^{-1}
$\therefore$ pH = 2.35
3. $Ba(OH)_2 + 2HNO_3 \rightarrow Ba(NO_3)_2 + 2H_2O(l)$
$n(Ba(OH)_2) = 0.0500 \times 0.200 = 0.0100$ mol
$n(HNO_3) = 0.200 \times 0.400 = 0.0800$ mol
From the equation, 1 mole of $Ba(OH)_2$ reacts with 2 mols of HNO_3.
Accordingly, 0.0100 mol of $Ba(OH)_2$ reacts with 0.0200 mol of HNO_3.
HNO_3 is in excess by 0.0600 mol.
The final concentration after diluting to 6.00 L is [0.0600 /6.00 L] = 0.01 M
$[H^+] = 1.0 \times 10^{-2}$ M and, pH = 2.0
4.
(a) pH = 2
$\therefore$ $[H^+] = 1.0 \times 10^{-2}$ M; volume = 0.300 L
$\therefore$ $n(H^+)$ needed $= 1.0 \times 10^{-2} \times 0.300 = 3.00 \times 10^{-3}$ mol
Hence, n (HCl) needed $= 3.00 \times 10^{-3}$ mol
$\therefore$ $m(HCl) = 3.00 \times 10^{-3} \times 36.46 = 0.109$ g
(b) $n(HCl) = 0.0730 / 36.46 = 2.00 \times 10^{-3}$ mol.
$\therefore$ $n(H^+) = 2.00 \times 10^{-3}$ mol.
$[H^+] = (2.00 \times 10^{-3} /2.00 L) = 1.0 \times 10^{-3}$ M
$\therefore$ pH = 3.00
5.
(a) pH = 13, and hence $[H^+] = 1.0 \times 10^{-3}$ M and $[OH^-] = 1.0 \times 10^{-1}$ M
V = 0.600 L and,
$n(NaOH) = c \times v = 1 \times 10^{-1} \times 0.600 = 6.00 \times 10^{-2}$ mol
$m(NaOH) = 6.00 \times 10^{-2} \times 40.0 = 2.40$ g.
(b) m (NaOH) = 0.600 g and n (NaOH) = 0.600/40.0 = 0.0150 mol
[NaOH] = n/V = 0.0150/ 1.500 = 0.01 M, and $[OH^-] = 1.0 \times 10^{-2}$ M
$\therefore$ $[H^+] = 1.0 \times 10^{-12}$ M, thus pH = 12.0
6. $n(HCl) = 0.100 \times 0.020 = 2.00 \times 10^{-3}$ mol
pH required is 3. Therefore, $[H^+]$ should be 1.0×10^{-3} M.
Since the number of moles are the same before and after dilution,
$0.100 \times 0.020 = 1.0 \times 10^{-3} \times V$
$V = [(0.100 \times 0.020) /1.0 \times 10^{-3}] = 2.0$ L.
$\therefore$ Volume of water to be added $= 2.0 \text{ L} - 0.020 \text{ L} = 1.98$ L
7. pH = 4 and so $[H^+] = 1.0 \times 10^{-4}$ M.V = 1.00 L
$n(HCl) = n(H^+) = c \times V = 1.0 \times 10^{-4} \times 1.00 = 1.0 \times 10^{-4}$ mol
V (HCl @ STP) = n × 22.71
$= 1.0 \times 10^{-4} \times 22.71 = 2.27$ mL
8. All these hydrolyse to produce OH^- ions.

$CO_3^{2-}(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + OH^-(aq)$
$S^{2-} + H_2O(l) \rightarrow HS^-(aq) + OH^-(aq)$
$CH_3COO^-(aq) + H_2O \rightarrow CH_3COOH + OH^-(aq)$

9.

(a) $[Ca(OH)_2] = 0.0050$ M.
$[OH^-] = 2 \times 0.005 = 0.01$ so $pOH = 2$ and $pH = 12$

(b) Using the dilution formula, $0.010 \times 0.010 = c \times 1.0$ L.
Therefore, the final $[OH^-]$
$= 0.01 \times 0.010/1.0$ L $= 1.00 \times 10^{-4}$ M
$\therefore [OH^-] = 2 \times 5.00 \times 10^{-5} = 1.00 \times 10^{-4}$
$pOH = 4$ so $pH = 10.00$
Change is from 12.00 to 10.00

(c) $n(Ca(OH)_2 = cV = 0.00500 \times 0.010$ L
$= 0.000050$ mol
Number of moles of the substance does not alter during dilution.
$n(Ca(OH)_2 = n \times Mr = 0.0000500 \times 74.096$
$= 0.0037$ g

(d) $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$
$n(CO_2) = n(Ca(OH)_2 = 0.0000500$ mol
Using the relationship $PV = nRT$ and $V = nRT/P$:
$V = [(0.000050 \times 8.314 \times 298)/ 110]$
$= 0.0113$ L $= 11.3$ mL

10. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
$n(HCl) = 0.131 \times 0.0236 = 3.091 \times 10^{-3}$ mol
$n(NaOH) = n(HCl) = 3.091 \times 10^{-3}$ mol;
$V(NaOH) = 0.025$ L
$\therefore [NaOH] = n/ V = 3.091 \times 10^{-3}/0.025$
$= 0.124$ L

11. $m(\text{pure } Na_2CO_3) = 0.1223 \times 0.9995$
$= 0.1222$ g.
$n(Na_2CO_3) = 0.1222/105.9$
$= 1.153 \times 10^{-3}$ mol
$Na_2CO_3(aq) + 2HCl(aq) \rightarrow$
$2NaCl(aq) + H_2O(l) + CO_2(g)$
From the equation, 1 mole of Na_2CO_3 reacts with 2 moles of HCl.
$\therefore n(HCl) = 2 \times n(NaOH)$
$= 2 \times 1.153 \times 10^{-3} = 2.306 \times 10^{-3}$ mol
$\therefore [HCl] = n/V = 2.036 \times 10^{-3}/0.02265$
$= 0.090$ M

12. $CH_3COOH(aq) + NaOH(aq) \rightarrow$
$CH_3COONa + H_2O(l)$
$n(CH_3COOH) = c\ V = 0.100 \times 0.050$
$= 0.0050$ mol
$n(NaOH) = 0.100 \times 0.030 = 0.0030$ mol
(Since the reacting mole ratio is 1:1),
CH_3COOH is in excess by $(00.50 - 0.0030)$
$= 0.0020$ mol
$\therefore [CH_3COOH]$ final $= (0.0020/0.080)$
$= 0.0250$ M

13. $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$
$n(NaHCO_3) = 0.020 \times 0.050$
$= 1.0 \times 10^{-3}$ mol
$n(HCl) = 0.020 \times 0.0250 = 5.00 \times 10^{-4}$ mol
Since the reacting mole ratio between $NaHCO_3$ and HCl is 1:1, $NaHCO_3$ is in excess by $(1.0 \times 10^{-3} - 5.00 \times 10^{-4})$
$= 5.0 \times 10^{-4}$ mol
$[NaHCO_3$ left over$] = (5.0 \times 10^{-4}/ 0.075)$
$= 6.67 \times 10^{-3}$ M

14. $n(HNO_3) = 0.0305 \times 0.131 = 4.00 \times 10^{-3}$ mol
Each mole of HNO_3 requires ½ mole of Na_2CO_3 to react $= 2.00 \times 10^{-3}$ mol
So $n(Na_2CO_3) = 2.00 \times 10^{-3}$ mol and
$m(Na_2CO_3) = 2.00 \times 10^{-3} \times 105.99 = 0.212$ g
$\therefore m(H_2O) = 0.561 - 0.212 = 0.349$ g
$n(H_2O) = 0.349/ 18.016 = 0.0194$ mol.
Ratio of H_2O to Na_2CO_3 is
1.94×10^{-2}: 2.00×10^{-3} which is close to 10:1
Hence formula is $Na_2CO_3.\ 10H_2O$

15. The general reaction equation is: $NaOH(aq) + HBr(aq) \rightarrow NaBr(aq) + H_2O(l)$

(a) $HBr(1) = 20.0$ mL $n(NaOH)$
$= 0.100$ M $\times 0.0275$ L $= 0.00275$ mol
$\therefore n(HBr) = 0.00275$ mol
$c[HBr] = (0.00275/ 0.020) = 0.1375$ M

(b) $HBr(2) = 20.0$ mL
$n(NaOH) = 0.100 \times 0.0218 = 0.00218$
$n(HBr) = 0.00218$ mol
$[HBr] = n \div V = 0.00218/ 0.020 = 0.109$ M

(c) $HBr(3) = 20.0$ mL
$n(NaOH) = 0.100$ M $\times 0.0489$
$= 0.00489$ mol
$n(HBr) = 0.00489$ mol
$[HBr] = n/V = 0.00489/ 0.020 = 0.2445$ M

(d) $HBr(4) = 20.0$ mL
$n(NaOH) = 0.100 \times 0.0255 = 0.00255$ mol
$n(HBr) = 0.00255$
$[HBr] = n/V = 0.00255 \div 0.020 = 0.1275$ M

16. The general equation for the reaction is:
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
The reacting ratio is 1:1.

(a) $n(HCl) = 0.200 \times 0.020 = 4.00 \times 10^{-3}$ mol
$n(NaOH) = c \times V = 0.200 \times 0.0050$
$= 1.00 \times 10^{-3}$ mol
HCl is in excess by $(4.00 \times 10^{-3} - 1.00 \times 10^{-3})$
3.00×10^{-3} mol
$\therefore n(H^+)$ is in excess by 3.00×10^{-3} mol
$[H+] = (n/ v) = (3.00 \times 10^{-3}/0.025) = 0.12$ M
$\therefore pH = -\log 0.12 = 0.921$

(b) $n(HCl) = c \times v = 4.00 \times 10^{-3}$ mol
$n(NaOH) = c \times V = 0.200 \times 0.015$
$= 3.00 \times 10^{-3}$ mol
HCl is in excess by $(4.00 \times 10^{-3} - 3.00 \times 10^{-3})$
$= 1.00 \times 10^{-3}$ mol
$\therefore n(H^+)$ in excess $= 1.00 \times 10^{-3}$ mol
$[H^+] = (n/ v) = (1.00 \times 10^{-3}/0.035)$
$= 0.0286$ M

$pH = -\log 0.0286 = 1.54$

(c) $n(HCl) = 4.00 \times 10^{-3}$ mol
$n(NaOH) = 0.200 \times 0.0199$
$= 3.98 \times 10^{-3}$ mol
HCl is in excess by $(4.00 \times 10^{-3} - 3.98 \times 10^{-3})$
$= 0.02 \times 10^{-3} = 2.0 \times 10^{-5}$ mol
$\therefore n(H^+)$ is in excess by 2.0×10^{-5} mol
$[H^+] = (n/v) = (2.0 \times 10^{-5}/ 0.0399)$
$= 5.01 \times 10^{-4}$ M
$pH = -\log 5.01 \times 10^{-4} = 3.30$

17. The stated claim is that each contains 300 mg of aspirin. The equation for the reaction is: $C_6H_4(OCOCH_3)COOH + 2NaOH(aq) \rightarrow C_6H_4(OH)COONa(aq) + CH_3COONa(aq) + HCl(aq)$

(a) The tablets are reacted with 50.0 mL of 0.5090 M NaOH.
$n(NaOH)$ used in the first titration $= c \times V$
$= 0.5090 \times 0.050 = 0.02545$ mol $= n_1$
On back titration, the original 50.0 mL was diluted to 100.0 mL and 20.0 mL aliquot was used for the second titration.
Equation for the second titration:
$NaOH + HCl \rightarrow NaCl + H_2O$
$n(HCl)$ that reacted with the 20.0 mL aliquot
$= 0.1232 \times 0.02510 = 3.09232 \times 10^{-3}$ mol in 20 mL
$= 3.09232 \times 10^{-3}$ mol (reactant ratio is 1 to 1)
$\therefore n(NaOH)$ in the 100.0 mL
$= 3.09232 \times 10^{-3} \times (100/20)$
$= 0.0154616$ mol $= n_2$
$\therefore n(NaOH)$ that reacted in the first reaction (equation is supplied in the problem)
$= n_1 - n_2 = 0.02545$ mol $- 0.0154616$ mol
$= 0.0099884$ mol
According to the balanced equation supplied,
$n[C_6H_4(OCOCH_3)COOH] = n(NaOH)/2$
$= 0.0099884/2$
$= 4.9942 \times 10^{-3}$ mol
$m[C_6H_4(OCOCH_3)COOH]$
$= 4.9942 \times 10^{-3} \times 180.154 = 0.8997$ g
$\therefore$ Mass of this compound in one tablet $= 0.8997/ 3 = 0.2999$ g.
The average mass of the compound in each tablet = 299.9 mg.

(b) Within the limits of experimental or rounding off error, the claim is true.

18.

(a) Acid added to this cloudy ammonia
= 100.0 mL of 0.6342 M, HCl.
The mixture volume is made up to
= 250.0 mL.
Aliquot taken for titration purpose
= 20.0 mL.
The first reaction is between NH_3 in the "cloudy ammonia" and HCl.

(b) The reaction is $NH_3 + HCl \rightarrow NH_4Cl$
The second reaction is between the left over HCl and NaOH
The second reaction is
$HCl + NaOH \rightarrow NaCl + H_2O$

(c) $n(NaOH)$ that reacted with 20.0 mL of the excess HCl in reaction 2,
[Since, $n(HCl) = n(NaOH)] = c \times V =$
$0.6342 \times 0.01875 = 0.00205875$ mol
$n(NaOH)$ that would have reacted with 100.0 mL of the excess HCl in reaction 2,
$= 0.00205875 \times (100/ 20.0)$
$= 0.01029$ mol
$n(HCl)$ initially present before the reaction commenced,
$cV = 0.6342 \times 0.100 = 0.06342$ mol
$\therefore n(HCl)$ that actually reacted with 250.0 mL of original solution,
$= 0.06342 - 0.01029 = 0.05312$ mol
From the equation for the first reaction, $n(NH_3) = n(HCl) = 0.05312$ mol
$\therefore m(NH_3) = n \times Mr = 0.05312 \times 17.034 = 0.09048$ g
% of NH_3 in the cloudy ammonia
$= (0.09048 \text{ g}/ 15.4) \times 100$
$= 0.588\%$

(d) Not necessarily. If the calculated value is less than the claimed value and falls with in the limits of experimental error, the claim could still be true.

19.

(a) $H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow BaSO_4(s) + 2H_2O(l)$

(b) The back-titration reaction is: $Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O(l)$
$n(HCl)$ used $= c \times v = 0.100 \times 0.0345$
$= 0.00345$ mol
Therefore, according to the reacting mole ratio, the number of moles of $Ba(OH)_2$ that reacted in the back titration is $(0.00345/2)$
$= 0.001725$ mol

(c) Any indicator will be suitable for this back titration because the change of pH occurs over a pH range of 3 to 11. Any indicator with an end point change that occurs in this range would be suitable.

(d) Since the amount of $Ba(OH)_2$ used in the back titration is 0.001725 mol (0.2955 g), the mass of $Ba(OH)_2$ that reacted in the first titration is $= (3.0 - 0.2955) = 2.7045$ g.
$n(Ba(OH)_2$ that reacted in the first titration
$= (2.7045/ 171.316) = 1.58 \times 10^{-2}$ mol.
According to the mole ratio in equation 1,
$n(H_2SO_4) = n(Ba(OH)_2$
$= 1.58 \times 10^{-2}$ mol
$[H_2SO_4] = (n/V) = (1.58 \times 10^{-2}/ 0.020)$
$= 0.79$ M

20.

(a) *The burette should be rinsed with the filling solution (HCl). Rinsing with distilled water reduces the concentration of the filling solution. This makes [HCl] appear greater.*

(b) *This is not a mistake and there is no effect as there are the same no. of moles, even if diluted.*

(c) *The pipette should be rinsed with the filling solution (Na_2CO_3). Rinsing it with water will dilute the concentration of the filling solution. This makes [Na_2CO_3] appear weaker and less HCl will be used so [HCl] appears greater.*

(d) *The correct indicator – methyl orange, should be used. Using phenolphthalein would produce colour change soon, so the volume of HCl needed would decrease. This makes [HCl] appear greater.*

21.

(a) *i) Calculate the amount of Na_2CO_3 needed (106 g).*
ii) Weigh out close to 1.06 g; not necessarily the exact mass.
iii) Transfer the Na_2CO_3 to a clean 250.0 mL volumetric flask. Often this is done using a clean, dry funnel, carefully rinsing all traces of solid into the flask using distilled water.
iv) Fill the flask about one half with distilled water and swirl until all the solid is dissolved.
v) Add distilled water exactly up to the 250 mL calibration mark. Often the last few drops are added from a pipette or eye-dropper.
vi) Mix the solution thoroughly by inverting the flask. Then calculate the exact concentration from the actual mass used.

(b) *Note: The dilution is ten times the original volume. Remember that you should always add acid to water and not the other way otherwise 'spitting' occurs!*
i) Put a small amount of water in the flask first.
ii) Transfer the 25.0 mL of 5.0 M sulfuric acid to a graduated cylinder, which has a volume of 250.0 mL.
iii) Add distilled water to about half the volume of the flask. Stopper it and swirl it a few times until the bubbles die out.
iv) Add distilled water up to the 250 mL calibration mark. Add the last few drops with a pipette or eye-dropper.

(c) *Note: Because the concentration of this solution does not need to be accurately known, you can use a graduated cylinder for measuring.*
i) Place about 50 mL of distilled water into a graduated cylinder.
ii) Measure 1 mL of 10 M HCl using a clean, dry, graduated cylinder or graduated pipette.
iii) Add the acid to the water in the graduated cylinder, stir and make up volume up to 100.0 mL.

22.

(a) *methyl orange* (b) *phenolphthalein*
(c) *any indicator* (d) *phenolphthalein*

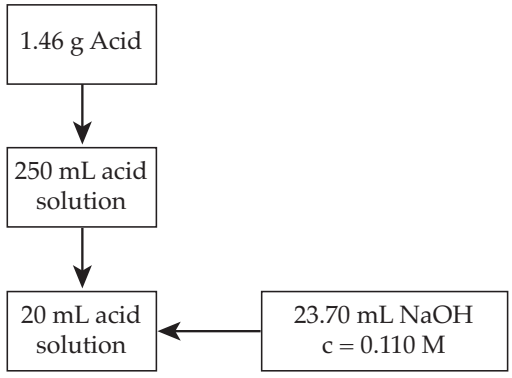
23.

(a) $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$

(b) *Since H_2CO_3 is a very weak acid, it can be analysed volumetrically using NaOH and a phenolphthalein indicator following the usual volumetric analysis procedure – or use a pH meter.*

24. *(i) Loss of mass of hydrated acid*
= 0.808 – 0.576 = 0.232 g of H_2O
% water = (0.232/0.808) × 100 = 28.71%
% Anhydrous acid = 71.29%
(ii) 2.05 g of hydrated acid will contain 0.7129 × 2.05 g of anhydrous acid = 1.46 g

Flow chart:



$n(NaOH) = 0.110 \times 0.02370$
$= 2.607 \times 10^{-3}$ mol
Ratio of acid to NaOH = 2 : 1
$n(Acid) = ½ \times n(NaOH)$
$= 1.3035 \times 10^{-3}$ mol in 20 mL

$$\text{In 250 mL } n(Acid) = 1.3035 \times 10^{-3} \times \frac{250}{20}$$
$= 0.01629$ mol

$$M_r = \frac{m}{n} = \frac{1.46}{0.01629} = 89.6 \text{ g mol}^{-1}$$

(iii) Empirical mass of CHO_2 = 45.01 which is ½ of 89.6 approx, so molecular = 2 × empirical mass
Molecular formula is $C_2H_2O_4$ possible isomer is HOOCCOOH (oxalic acid).
(iv) Mass of water in 2.05 g sample
= 2.05 × 0.2871 = 0.588 g

$n(H_2O) = 0.588/18.016 = 0.03267$ mol
Ratio of H_2O to $C_2H_2O_4$ is 0.03267: 0.01629 = 2.005:1
So hydrated acid formula is $C_2H_2O_4.2H_2O$.

25. $n(NaOH) = 0.698 \times 0.0107$
$= 7.469 \times 10^{-3}$ mol = total $n(H^+)$ in the solution.
$n(BaSO_4) = 0.541/233.37 = 2.318 \times 10^{-3}$ mol which must equal $n(H_2SO_4)$ in 25 mL
$n(H_2SO_4)$ in 20 mL is which would contribute double the H^+
$2 \times 1.855 \times 10^{-3}$ mol of $H^+ = 3.71 \times 10^{-3}$ mol.
$\therefore$ n(HCl) in solution X
$= 7.469 \times 10^{-3} - 3.710 \times 10^{-3}$ mol
$= 3.759 \times 10^{-3}$ mol.
[HCl] in solution X = $\dfrac{3.759 \times 10^{-3}}{0.020}$
$= 0.188$ mol L^{-1}

26. (i) Mass of NaOH = $4000 \times 0.2 = 800$ g
$n(NaOH) = 800/39.998 = 20.0$ mol
$m(CuSO_4.5H_2O) = 45000 \times 0.05 = 2250$ g
$n(CuSO_4.5H_2O) = 2250/ 249.7 = 9.01$ mol

Reaction: $CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$
So 9.01 mol of $CuSO_4$ would need 18.02 mol of NaOH to be completely used up.
20.0 mol of NaOH is available so all the $CuSO_4$ is used up = Limiting Reagent
Hence NaOH and OH^- ion is in excess.
Amount of excess NaOH is 20 – 18.02
= 1.978 mol
(ii) HCl could be used to neutralise the OH^- ions. The farmer would need to add 1.978 mol
m(HCl) needed = $1.978 \times 36.458 = 72.1$ g.

27.

(a) $2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$

(b) $HCl + NaOH \rightarrow NaCl + H_2O$

(c) $n(NaOH) = c \times V$
$= 0.150$ mol $L^{-1} \times 0.01966 = 2.94 \times 10^{-3}$ mol
Therefore, $n(HCl) = 2.94 \times 10^{-3}$ mol

(d) Initial moles of HCl that was added to washing soda = cV
$= 1.00 \times 0.0200 = 0.0200$ mole

(e) Therefore, n(HCl) that actually reacted = Initial moles of HCl – Excess moles of HCl Left over
$= 0.02$ mol $- 2.94 \times 10^{-3}$ mol $= 0.01706$ mol
Therefore, $n(Na_2CO_3) = n(HCl/2) = 0.01706/2 = 0.00853$ mol
Therefore, $m(Na_2CO_3) = n \times M$
$= 0.00853 \times 105.99 = 0.904$ g

(f) % of Na_2CO_3 in the sample
$= [(0.904/1.682) \times 100] = 53.7$ %

(g) Sodium hydroxide absorbs both H_2O and CO_2 from air when exposed and this alters its concentration. Therefore, NaOH should be used as soon as it is standardised.

(h) There won't be any effect since HCl (a strong acid) is titrated with NaOH (a strong base).

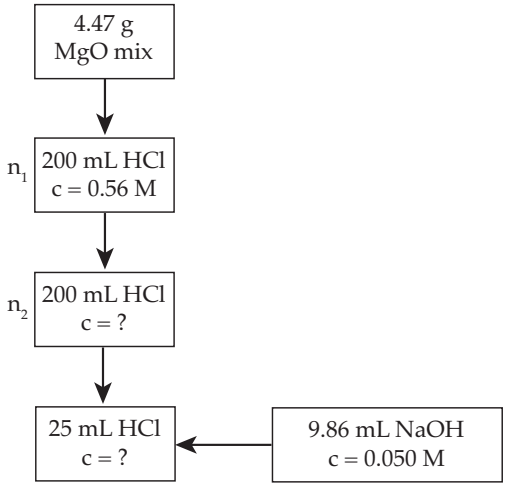
28.

(a) The mass of aspirin tablet = 0.4376 g
(The tablet contains acetylsalicylic acid, $[C_6H_4(OCOCH_3)COOH)]$
The number of moles of HCl added = cV
$= 0.298 \times 0.01864$ L $= 5.555 \times 10^{-3}$ mol
Since, $HCl + NaOH \rightarrow NaCl + H_2O$
The number of moles of NaOH reacted
$= 5.555 \times 10^{-3}$ mol

(b) Initial amount of NaOH added to aspirin
= n (NaOH)
$= c \times V = 0.196$ mol $L^{-1} \times 0.050$ L
$= 9.800 \times 10^{-3}$ mol

(c) Therefore, n(NaOH) that actually reacted with the acetylsalicylic acid in the tablet,
= [initial moles of NaOH – left over excess moles of NaOH]
$= (9.800 \times 10^{-3} - 5.555 \times 10^{-3})$
$= 4.245 \times 10^{-3}$ mol
$C_6H_4(OCOCH_3)COOH + 2NaOH \rightarrow C_6H_4(OH)COONa + CH_3COONa + H_2O$
$nC_6H_4(OCOCH_3)COOH = ½ \times n(NaOH)$
$= 2.123 \times 10^{-3}$ mol
Therefore, $m[C_6H_4(OCOCH_3)COOH]$
$= n \times M = 2.123 \times 10^{-3} \times 180.164$
$= 0.3825$ g
Therefore % mass of the acid in the tablet
$= [(0.3825/ 0.4376) \times 100]$
$= 87.4\%$

29.



$n(NaOH) = 0.05 \times 0.00986$
$= 4.93 \times 10^{-4}$ mol
1:1 ratio $\therefore$ n(HCl)
$= 4.93 \times 10^{-4}$ mol in
25 mL
$\therefore$ in 200 mL n(HCl)
$= 4.93 \times 10^{-4} \times \dfrac{200}{25} = 3.944 \times 10^{-3}$ mol

$n_2 = 3.944 \times 10^{-3}$ mol
$n_1 = 0.56 \times 0.2 = 0.112$ mol

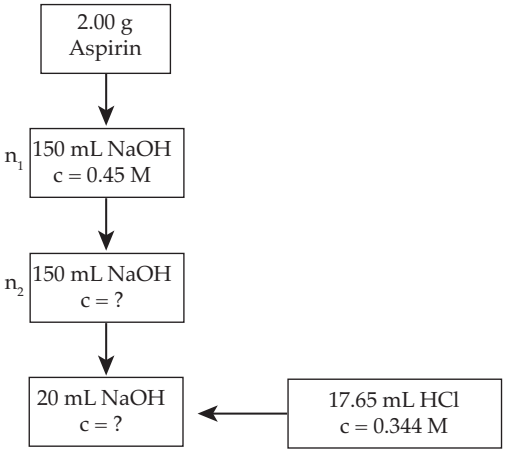
Amount of HCl used $= n_1 - n_2$
$= 0.112 - 3.944 \times 10^{-3}$
$= 0.1081$ mol

Ratio MgO : HCl is 2:1 so
$n(MgO) = ½ \times 0.1081 = 0.05403$ mol

$m(MgO) = 0.05403 \times (24.31 + 16)$
$= 2.18$ g
$\%$ of $MgO = \frac{2.18}{4.47} = \times 100\%$

$\%$ Purity $= 48.7\%$

30.
(i)



$n(HCl) = 0.344 \times 0.01765$
$= 6.072 \times 10^{-3}$ mol
Ratio NaOH to HCl is 1:1 so
$n(NaOH) = 6.072 \times 10^{-3}$ mol in 20 mL
$\therefore$ in 150 mL $n(NaOH) =$
$6.072 \times 10^{-3} \times \frac{150}{20} = 0.0455$ mol
$n_2 = 0.0445$ mol
$n_1 = 0.45 \times 0.15 = 0.0675$ mol

Amount of HCl used $= n_1 - n_2$
$= 0.0675 - 0.0455$
$= 0.0220$ mol

Ratio Aspirin to NaOH is 1:2
So $n(Aspirin) = ½\ n(NaOH)$
$= 0.0110$ mol
$m(Aspirin) = 0.0110 \times 168.144 = 1.85$ g
$\%$ of Aspirin $= \frac{1.85}{2.00} \times 100\%$

$\%$ Purity $= 92.5\%$

(ii) This value exceeds the 90% set value and so conforms to the law.

Chapter 3.
Redox Reactions

Set 1 Oxidation and Reduction

1. Species Oxidised Na
   Species reduced O_2
   Oxidant O_2
   Reductant Na
2. Species Oxidised Zn
   Species reduced Cr^{3+}
   Oxidant Cr^{3+}
   Reductant Zn
3. Species Oxidised H_2
   Species reduced O_2
   Oxidant O_2
   Reductant H_2
4. Species Oxidised H_2S
   Species reduced $Cr_2O_7^{2-}$
   Oxidant $Cr_2O_7^{2-}$
   Reductant H_2S
5. Species Oxidised Cl^-
   Species reduced H_2O_2
   (ON of Cl is $^+1$ in HClO)
   Oxidant H_2O_2
   Reductant Cl^-
6. 4+ 7. 5+ 8. 4+ 9. 2+ 10. 7+
7. Species Oxidised HBr
   Species reduced H_2SO_4
8. Species Oxidised $SnCl_2$
   Species reduced O_2
9. Species Oxidised Fe^{2+}
   Species reduced $Cr_2O_7^{2-}$
10. Species Oxidised None
    Species reduced None
11. Species Oxidised I^-
    Species reduced Cl_2

Set 2 Oxidation

Multiple Choice Answers

1. d, 2. b, 3. d, 4. b, 5. c, 6. c, 7.a, 8. b, 9. a, 10. a, 11. e, 12. b

Written Answers

1.
(a) S = +6
(b) Mn = +7
(c) N = +5
(d) C = +4,
(e) N = +4
(f) S = +6
(g) S = +6
(h) S = -2

2.
(a) H = +1, S = -2
(b) P = +5, O = -2
(c) Na = +1, P = -3

(d) Cr = +3, O = -2, H = +1
(e) S = +6, O = -2
(f) Ba = +2, Mn = +7, O = -2
(g) S = +4, O = -2
(h) H = +1, O = -2
(i) Al = +3, Cl = -1
(j) K = +1, N = +5, O = -2

3.

a) (i) $Ni + I_2$ YES
(ii) $Ag + Au^{3+}$ YES
(iii) $Al + Cd^{2+}$ YES
(iv) $Cl^- + Br_2$ YES

b) Order is C^{2+}, B^{3+} A. Redox table would be:

A^+	A
B^{3+}	B^{2+}
C^{2+}	C

4.

(a) S in SO_2 is reduced from +4 to 0.
(b) Cl in HCl is oxidised from –1 to 0.
(c) Cl in Cl_2 is reduced from 0 to –1.
(d) Cu in CuO is reduced from +2 to 0.

5.

Oxidising agent	Reducing agent	Redox reaction?
a) MnO_4^-	H_2O_2	Redox
b)		***Not a redox***
c) I_2	$S_2O_3^{2-}$	Redox
d) N_2	H_2	Redox
e) H_2O	C	Redox
f) NO_3^-	Fe^{2+}	Redox
g)		***Not a redox***
h)		***Not a redox***
i)		***Not a redox***
j) NaClO	Na_2SO_3	Redox
k) CH_3OH	Na	Redox
l)		***Not a redox***
m) H_2SO_4	Zn	Redox
n)		***Not a redox***
o) MnO_2	NaCl	Redox
p) H_2SO_4	HBr	Redox
q) HNO_3	HCl	Redox
r) HNO_3	CuS	Redox

6.

(a) $I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$
(b) $HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O$
(c) $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$
(d) $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$
(e) $H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H^+ + 2e^-$
(f) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
(g) $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$
(h) $C_2O_4^{2-} + 2H_2O \rightarrow 2CO_3^{2-} + 4H^+ + 2e^-$
(i) $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$
(j) $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

7.

(a) Oxygen
(b) Nitrogen
(c) Gold
(d) Chlorine
(e) Bromine

8.

(a) $4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$
(b) $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$

9. ZnO; ZnH_2; ZnI_2

10.

(a) PCl_3 or PCl_5
(b) PCl_5
(c) $CuCl_2$
(d) $I_2 + Cl^-$

11.

(a) $Cu_2SO_4 \rightarrow CuSO_4 + Cu$
(b) $Hg_2Cl_2 \rightarrow HgCl_2 + Hg$
(c) $2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$
(d) $Cl_2 + H_2O \rightarrow HCl + HOCl$

Set 3 Redox Reactions

Multiple Choice Answers

1. d, 2. c, 3. a, 4. c, 5. e, 6. c, 7. e, 8. c, 9. e, 10. d.

Calculations

1.

(i) $(Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 5$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow$
$5Fe^{3+} + Mn^{2+} + 4H_2O$ (Redox)

(ii) $\therefore n(MnO_4^-) = c \times V = 0.10 \times 0.0250$
$= 0.00250$ mol
$\therefore n(Fe^{2+}) = 5 \therefore n(MnO_4^-) = 5 \times 0.00250$
$= 0.0125$ mol
$\therefore [Fe^{2+}] = n/V = (0.0125/0.020)$
$= 0.625$ mol L^{-1}

2. Initial volume (commercial H_2O_2) = 10.0 mL
The 10.0 mL is made up to 100.0 mL
Volume of the diluted H_2O_2 used for titration = 10.0 mL
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
$(H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-) \times 3$
$Cr_2O_7^{2-} + 8H^+ + 3H_2O_2 \rightarrow 2Cr^{3+} + 7H_2O +$

$3O_2$ — Redox
$n\ (Cr_2O_7^{2-}) = c \times V = 0.0030$ mol
$\therefore\ n\ (H_2O_2) = 3 \times 0.0030 = 0.0090$ mol
20.0 mL of diluted solution is equal to 0.0090 mol
The original volume of commercial H_2O_2 = 10.0 mL
Volume of water added = 100.0 mL and so the final volume is 110.0 mL = 0.110 L
Volume of diluted H_2O_2 used for titration = 20.0 mL = 0.020 L
Based on the reacting mol ratio, the mols of diluted H_2O_2 used in titration is equal to Number mols of $K_2Cr_2O_7$ used in each titration × 3 = 0.0090 mol.
$\therefore$ concentration of H_2O_2 in the original solution = $[(0.0090 \times 0.110)/0.02]$
$= 4.95\ mol\ L^{-1}$

3. $(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$
$(H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-) \times 5$
$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow$
$2Mn^{2+} + 8H_2O + 10CO_2$ — Redox
$n\ (MnO_4^-) = c \times V = 0.11 \times 0.010$
$= 0.0011$ mol
$\therefore\ n\ (H_2C_2O_4) = [(0.0011 \times 5)/2]$
$= 2.75 \times 10^{-3}$ mol
$\therefore\ c\ (H_2C_2O_4) = (n/V)$
$= (2.75 \times 10^{-3}/0.020) = 1.375 \times 10^{-1}\ mol\ L^{-1}$

4. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
$(Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 6$
$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$ — Redox
$n(Fe^{2+}) = cV = 0.01$ mol
$\therefore\ n\ (Cr_2O_7^{2-}) = 1.67 \times 10^{-3}$ mol
$\therefore\ n\ (Cr) = 2 \times 1.67 \times 10^{-3}$ mol
$\therefore\ m\ (Cr) = 2 \times 1.67 \times 10^{-3} \times 52.0 = 0.173\ g$
% Cr = $[(0.173/1.70) \times 100] = 10.2\%$

5. $c(H_2C_2O_4) = (n/V) = [(12.6/42.036)/1.0]$
$= 0.14\ mol\ L^{-1}$
$(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$
$(H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-) \times 5$
$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow$
$2Mn^{2+} + 8H_2O + 10CO_2$ – Redox
$n\ (H_2C_2O_4$ in each titration) $= c \times V$
$= 0.14 \times 0.020 = 2.8 \times 10^{-3}$ mol
$\therefore\ n\ (MnO_4^-) = [(2.8 \times 10^{-3} \times 2)/5]$
$= 1.12 \times 10^{-3}$ mol
$\therefore\ c\ [MnO_4^-] = (n/V) = (1.12 \times 10^{-3}/0.025)$
$= 4.48 \times 10^{-2}\ mol\ L^{-1}$

6. $(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$
$(H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-) \times 5$
$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow$
$2Mn^{2+} + 8H_2O + 5O_2$ – Redox
$n\ (MnO_4^-) = c \times V = 0.02 \times 0.04$
$= 8.00 \times 10^{-4}$ mol
$\therefore\ [H_2O_2] = [(8.00 \times 10^{-4} \times 5)/2]$
$= 2.0 \times 10^{-3}$ mol
$\therefore\ c\ [H_2O_2] = (2.0 \times 10^{-3}/0.002) = 1.0\ mol\ L^{-1}$
Pressure of 755 mm Hg = 100 × 755/760 = 99.34 kPa
$V = (nRT/P) = (0.002 \times 8.314 \times 308)/99.34$
Volume of oxygen = (5.122/100.633)
= 0.0516 L = 51.6 mL

7. $(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$
$(H_2C_2O_4 \rightarrow 2H^+ + 2CO_2 + 2e^-) \times 5$
$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow$
$2Mn^{2+} + 8H_2O + 10CO_2$ — Redox
$n\ (H_2C_2O_4) = c\ V = 0.0022$ mol
$\therefore n\ (KMnO_4) = [(0.0022 \times 2)/5]$
$= 0.00088$ mol
$\therefore c\ (KMnO_4) = (n/V) = (0.00088/0.009)$
$= 0.098\ mol\ L^{-1}$

8. The redox equation is
$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$
$n\ (Fe^{2+}) = cV = 0.05 \times 0.02 = 0.001$ mol
$\therefore n\ (Cr_2O_7^{2-}) = [(0.001 \times 1)/6] = 1.67 \times 10^{-4}$ mol
$\therefore\ c\ (Cr_2O_7^{2-}) = (1.67 \times 10^{-4}/7.5 \times 10^{-3})$
$= 0.021\ mol\ L^{-1}$

9. The redox equation is $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
$\therefore\ n\ (MnO_4^-) = 0.0010 \times 0.0015$
$= 0.0000015\ mol = 1.5 \times 10^{-6}$ mol
$\therefore\ n\ (FeSO_4) = (1.5 \times 10^{-6}\ mol) \times 5$
$= 7.5 \times 10^{-6}$ mol
$\therefore\ c\ (FeSO_4) = (n/V) = (7.5 \times 10^{-6}/0.05)$
$= 0.00015\ M = 1.5 \times 10^{-4}\ mol\ L^{-1}$

10. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
$(H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-) \times 3$
$Cr_2O_7^{2-} + 8H^+ + 3H_2O_2 \rightarrow$
$2Cr^{3+} + 7H_2O + 3O_2$ – Redox

(a) $n\ (H_2O_2) = (1.0/34.016) = 0.0294$ mol
$\therefore\ n\ (Cr_2O_7^{2-}) = (0.0294/3) = 0.0098$ mol
$m\ (K_2Cr_2O_7) = 0.0098 \times 294.2 = 2.88\ g$

(b) $n\ (O_2) = n\ (H_2O_2) = 0.0294$ mol
$V(O_2$ @STP) $= 0.0294 \times 22.71 = 0.659$ L

11. $(C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-) \times 5$
$(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$
$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow$
$10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

(a) Titre values of $KMnO_4$ = 24.48 mL, 24.54 mL, 24.48 mL = Average = 24.50 mL

(b) $n\ (KMnO_4) = cV = 0.020 \times 0.02450$
$= 4.90 \times 10^{-4}$ mol
$\therefore\ n\ (C_2O_4^{2-}) = [(4.9 \times 10^{-4} \times 5)/2]$
$= 1.225 \times 10^{-3}$ mol
$\therefore\ [C_2O_4^{2-}] = (n/V) = (1.225 \times 10^{-3}/0.0250)$
$= 0.049\ mol\ L^{-1}$

(c) $n\ (CO_2) = n\ (KMnO_4 \times 5) = 4.9 \times 10^{-4} \times 5$
$= 2.45 \times 10^{-3}$ mol
$V(CO_2$ @ STP) $= 2.45 \times 10^{-3} \times 22.71$
$= 0.056$ L = 55.6 mL

12. The redox equation is $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
$n\ (KMnO_4) = cV = 0.020 \times 0.020$
$= 4.0 \times 10^{-4}$ mol
$n\ (Fe^{2+}) = 5 \times n\ (MnO^{4-}) = 5 \times 0.0004$
$= 0.002$ mol
$[Fe^{2+}] = (n/V) = (0.002/0.025)$
$= 0.080$ mol L^{-1}
$n\ (Fe^{2+}$ in 0.50 L) $= 0.08 \times 0.500$
$= 0.040$ mol
$m\ (Fe^{2+}) = m(Fe) = 0.040 \times 55.85 = 2.234$ g
$\therefore$ % of Fe in the ore $= [(2.234/4) \times 100]$
$= 55.9\%$

13. The redox equation is
$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

(a) $n\ (MnO_4^-$ used in the titration) $= cV$
$= 0.016 \times 0.02020 = 3.232 \times 10^{-4}$ mol
$\therefore\ n\ (H_2O_2) = [(3.232 \times 10^{-4} \times 5)/\ 2]$
$= 8.08 \times 10^{-4}$ mol
$n\ (H_2O_2)$ in 0.020 L $= 8.08 \times 10^{-4}$ mol
$\therefore\ n\ (H_2O_2)$ in the stock solution of 1.0 L)
$= [(8.08 \times 10^{-4} \times 1000)/20] = 0.0404$ mol
$\therefore\ n\ (H_2O_2)$ in the 40.0 mL of commercial solution $= 0.0404$ mol
$\therefore\ c\ [H_2O_2]$ in the commercial solution
$= (n/V) = (0.0404/\ 0.040) = 1.01$ mol L^{-1}

(b) % H_2O_2 by mass in 40.0 mL of the commercial solution (40.0 g of the solution)
= (mass of H_2O_2 present in 40.0 mL/mass of 40.0 mL of the solution) $\times 100$
$= [(1.01 \times 34.016)/\ 40] \times 100$
$= (34.36/40) \times 100$
$= 85.9\%$

(c) Since 1 mol of H_2O_2 releases 1 mol of oxygen gas according to this equation,
1.01 mol in 1.0 L will release 1.01mol of oxygen gas which is $1.01 \times 22.71 = 22.94$ L
$\therefore$ Volume strength of the solution = 22.9.

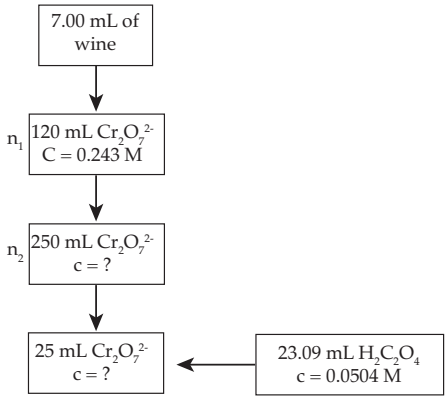
Redox Back-Titrations

14.

(a) $3C_2O_4^{2-} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6CO_2 + 2Cr^{3+} + 7H_2O$

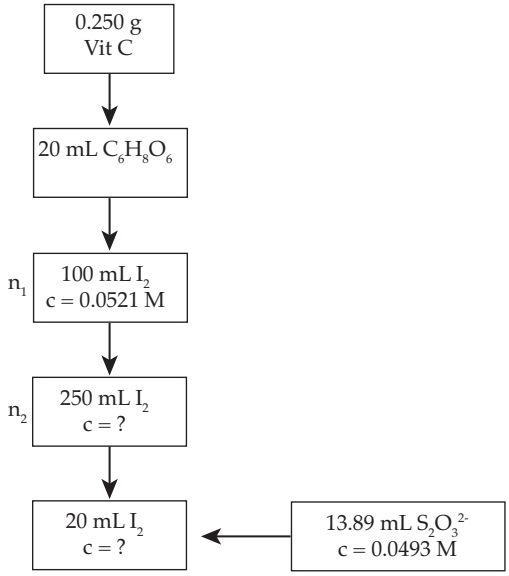
(b) Average titre = 23.09 mL

(c) Flow-chart:



$n(Cr_2O_7^{2-})$ added $= 0.120 \times 0.243$
$= 0.02916$ mol
$n_1 = 0.02916$ mol
$n(H_2C_2O_4)$ in titre $= 0.0504 \times 0.02309$
$= 1.165 \times 10^{-3}$ mol
From above: $n(Cr_2O_7^{2-}) = 1/3 \times n(H_2C_2O_4)$
$= 3.879 \times 10^{-4}$ mol in 25 mL
Hence in 250 mL $n(Cr_2O_7^{2-})$
$= 3.879 \times 10^{-4} \times \frac{250}{25}$
$= 3.879 \times 10^{-3}$ mol
$n_2 = 3.879 \times 10^{-3}$ mol
$n(Cr_2O_7^{2-})$ reacted $= n_1 - n_2$
$= 0.02916 - 3.879 \times 10^{-3} = 0.0253$ mol.
Reaction with alcohol: $n(CH_3CH_2OH)$
$= 3/2 \times n(Cr_2O_7^{2-}) = 3/2 \times 0.0253$
i.e. 0.0379 mol alcohol is in 7 mL of solution.
$c(CH_3CH_2OH) = n/V = 0.0379/\ 0.007$
$= 5.41$ mol L^{-1}.

15.



(a) $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

(b) $C_6H_8O_6(aq) + I_2(aq) \rightarrow C_6H_6O_6(aq) + 2I(aq) + 2H^+(aq)$

(c) Titres: 15.05; 13.96; 13.78; 13.92. Average 13.89 mL.
$n(S_2O_3^{2-})$ added $= 0.0493 \times 0.01389$
$= 6.848 \times 10^{-4}$ mol
Ratio $S_2O_3^{2-}$: I_2 is 2 : 1 so:
$n(I_2)$ in aliquot $= ½ \times 6.848 \times 10^{-4}$
$= 3.423 \times 10^{-4}$ mol. In 20 mL
$\therefore$ in 250 mL $n(I_2) =$
$= 4.280 \times 10^{-3}$ mol
$n_2 = 4.280 \times 10^{-3}$ mol
$n_1 = 0.0521 \times 0.1 = 0.00521$ mol
$n(I_2)$ reacted $= n_1 - n_2 = 0.00521 - 0.004280$
$= 9.301 \times 10^{-4}$ mol
$n(C_6H_8O_6) = n(I_2) = 9.301 \times 10^{-4}$ mol in tablet
$Mr(C_6H_8O_6) = 176.124$ g mol^{-1}
$m(C_6H_8O_6) = 9.301 \times 10^{-4} \times 176.124$
$= 0.164$ g

$$\%\,composition = \frac{0.164}{0.25} \times 100 = 65.5\%$$

16.

(a) $2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

(b) $MnO_4^-(aq) + 8\,H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

(c) $n(Fe^{2+})$ *in titre* $= 0.0081 \times 0.01267$
$= 1.102 \times 10^{-4}$ *mol*
From tables $n(MnO_4^-) = 5 \times (Fe^{2+})$ *so:*
$n(MnO_4^-)$ *in aliquot* $= 1/5 \times 1.102 \times 10^{-4}$ *mol*
$= 2.205 \times 10^{-5}$ *mol in 20 mL*
Total volume of MnO_4^- *solution* $= 100 + 50$
$= 150$ *mL*

$$n(MnO_4^-) \text{ in 250 mL} = 2.205 \times 10^{-5} \times \frac{150}{20}$$
$= 1.654 \times 10^{-4}$ *mol* $= n_2$.

$n_1 = 0.0052 \times 0.050 = 2.60 \times 10^{-4}$ *mol.*
$n(MnO_4^-)$ *reacted* $= n_1 - n_2$
$= 2.60 \times 10^{-4} - 1.654 \times 10^{-4} = 9.463 \times 10^{-5}$ *mol.*
From tables: $n(C_2O_4^{2-}) = 5/2 \times n(MnO_4^-)$
$= 9.463 \times 10^{-5} \times \frac{5}{2} = 2.366 \times 10^{-4}$ *mol*
$n(C_2O_4^{2-}) = n(Ca^{2+})$
$\therefore\ n(Ca^{2+}) = 2.366 \times 10^{-4}$ *mol*
So: $m(Ca) = 2.366 \times 10^{-4} \times 40.08$
$= 0.00948$ *g (9.48 mg) in 100 mL of blood.*

(d) $[Ca^{2+}] = \frac{2.366 \times 10^{-4}}{0.1} = 2.366 \times 10^{-3}$ *mol* L^{-1}

Set 4 Exercises and Problems

Multiple Choice Answers

1. e, 2. e, 3. a, 4. a, 5. d, 6. d, 7.e, 8. b, 9. b, 10. b, 11. e, 12. b, 13. e

Long Questions Answers

1.

(a) $F_2(g)$ (b) $K(s)$ (c) $F_2(g)$ (d) $K(s)$

(e) $Zn \rightarrow Zn^{2+} + 2e^-$ +0.76 V
$Fe^{2+} + 2e^- \rightarrow Fe$ -0.44 V
$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$ +0.32 V

(f) i) $3 \times (O_2 + 2H_2O + 4e^- \rightarrow 4OH^-)$ +0.40 V
$1 \times (Cr \rightarrow Cr^{3+} + 3e^-)$ +0.74 V
$3O_2 + 6H_2O + 4Cr \rightarrow 12OH^- + 4Cr^{3+}$ +1.14 V

ii) $I_2 + 2e^- \rightarrow 2I^-$ +0.54 V
$2 \times (Au + 2CN^- \rightarrow Au(CN)_2^- + e^-)$ +0.60 V
$I_2 + 2Au + 4\,CN^- \rightarrow 2I^- + 2Au(CN)_2^-$ +1.14 V

(g) $2 \times (Fe \rightarrow Fe^{2+} + 2e^-)$ +0.44 V
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ +0.40 V
$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$ +0.84 V

2.

(a) $Ca \rightarrow Ca^{2+} + 2e$- +2.87 V
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ -0.41 V
$Ca + 2H_2O \rightarrow Ca^{2+} + H_2 + 2OH^-$
+2.46 V *Reaction will occur.*

(b) $2 \times (MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$ +1.51 V
$5 \times (Sn^{2+} \rightarrow Sn^{4+} + 2e^-)$ -0.15 V
$2MnO_4^- + 16H^+ + 5Sn^{2+} \rightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$
$E^0 = +1.36$ V *Reaction will occur.*

(c) $Na^+ + e^- \rightarrow Na$ -2.71 V
$K \rightarrow K^+ + e^-$ +2.93 V
$Na^+ + K \rightarrow Na + K^+$
+0.22 V *Reaction will occur.*

3.

(a) $Ni \rightarrow Ni^{2+} + 2e^-$ +0.26 V
$2 \times (Ag^+ + e^- \rightarrow Ag)$ +0.80 V
$Ni + 2Ag^+ \rightarrow Ni^{2+} + 2Ag$ +1.06 V

(b) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$ -1.23 V
$3 \times (H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O)$ +1.78 V
$2Cr^{3+} + 7H_2O + 3H_2O_2 \rightarrow Cr_2O_7^{2-} + 8H^+ + 6H_2O$ +0.55 V

(c) $Zn \rightarrow Zn^{2+} + 2e^-$ +0.76 V
$Ni^{2+} + 2e^- \rightarrow Ni$ -0.26 V
$Zn + Ni^{2+} \rightarrow Zn^{2+} + Ni$ +0.50 V

4.

(a) *Copper ions are receiving the negative charges which flow towards the positive electrode.*

(b) *Zinc gives away the negative charges so it must be charged negative.*

(c) *1.10 V (0.76 + 0.34 = 1.10 V).*

(d) *Copper oxidises zinc.*

(e) *1.10 V.*

(f) *The same as before (1.10 V).*

5. *The assigned* E^0 *value for each will increase by 2.93 V.*

6.

(a) $2Au(s) + 8Br^-(aq) + 3IO^-(aq) + 3H_2O(l) \rightarrow 2AuBr_4^-(aq) + 3I^-(aq) + 6OH^-(aq)$
$E^0 = 0.858 + 0.49 = 1.35$ V

(b) $2Eu^{2+}(aq) + Sn^{2+}(aq) \rightarrow 2Eu^{3+}(aq) + Sn(s)$
$E^0 = 0.43 - 0.14 = 0.29$ V

7.

(a) *Standard conditions are:*
one mol L^{-1} *concentration of electrolytes, one atmospheric pressure, and a temperature of* 25^oC.

(b) $Fe^{2+} + 2e^- \rightarrow Fe$ -0.44V
$Mg^{2+} + 2e^- \rightarrow Mg$ -2.37V (reduction)
$Mg \rightarrow Mg^{2+} + 2\,e^-$ +2.37V (oxidation)

8.

(a) *In order of increasing strength as oxidising agents:*

$Cu^{2+}(aq) < O_2(g) < Cr_2O_7^{2-}(aq) < Cl_2(g) < H_2O_2(aq)$

(b) *In order of increasing strength as reducing agents:*

$Al < Zn < Sn < I^- < H_2O_2$

9. *The critical variable for spontaneous reactivity is E^o.*

(a) *E^o Positive, spontaneous*

(b) *E^o Positive, spontaneous*

(c) *E^o Negative, not spontaneous*

(d) *E^o Negative, not spontaneous*

10. *Applying Le Châtelier's principle, any change that shifts the equilibrium to the left will make the reaction less spontaneous, and so will decrease E^o.*

(a) *No effect* (b) *No effect*

(c) *Decreases E^o* (d) *Decreases E^o*

11.

(a) *Physical contact between the two different phases*

(b) *An inert electrode*

(c) *A salt bridge or a porous separator*

12.

(a) $Cr_2O_7^{2-}$

(b) Ni^{2+}

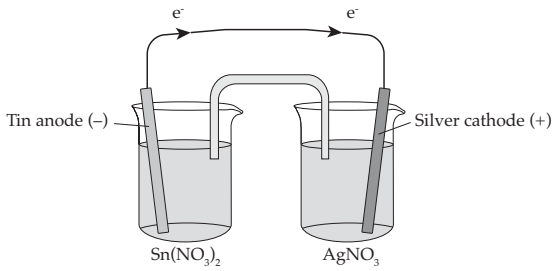
(c) Cr^{3+}

13.

(a) $Sn \rightarrow Sn^{2+} + 2e^-$ +0.14 V

$2Ag^+ + 2e^- \rightarrow 2Ag$ +0.80 V

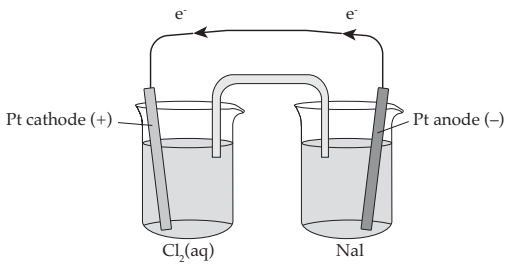
$Sn + 2Ag^+ \rightarrow Sn^{2+} + 2Ag$ +0.94 V



(b) $Cl_2 + 2e^- \rightarrow 2Cl^-$ +1.36 V

$2I^- \rightarrow I_2 + 2e^-$ -0.54 V

$Cl_2 + 2I \rightarrow 2Cl^- + I_2$ +0.82 V



(c) $Fe/Fe^{2+}// Sn^{4+}/Sn^{2+}$ -0.44 V +0.15 V

$Fe \rightarrow Fe^{2+} + 2e^-$ +0.44 V

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ +0.15 V

$Fe + Sn^{4+} \rightarrow Fe^{2+} + Sn^{2+}$

+0.59 V

14.

(a) *Anode* $Cd(s) \rightarrow Cd^{2+} + 2e^-$

Cathode $Ni^{3+} + e^- \rightarrow Ni^{2+}$

(b) *Anode* $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Cathode $Ag^+ + e^- \rightarrow Ag$

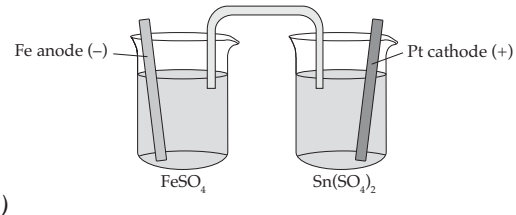
15.

(a) *Anode: $Fe \rightarrow Fe^{2+} + 2e$-*

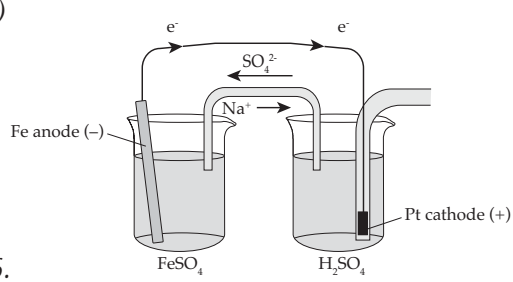
Iron rod will be the anode.

(b) $2H^+ + 2e^- \rightarrow H_2$

Platinum provides the reacting surface and is the cathode.



(c)



16.

(a) *Anode reaction: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$*

- 0.77 V

(b) *Cathode reaction: $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$*

+1.07 V

Cell potential: +0.30 V

(c) *Platinum cathode is labelled positive as it receives negative charges.*

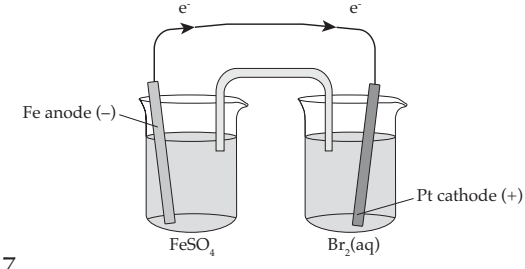
(d) *Iron anode is labelled negative as it releases negative charges.*

(e) *Bromide ions migrate towards the iron anode.*

(f) *Electrons flow from Fe anode to Platinum cathode.*

(g) *0.30 V.*

(h) *A reaction is obvious as the colour of bromine in the cathode half-cell fades, as bromine is reduced to bromide ions.*



17.

(a) *Looking at the electrode potentials, HCl does not react with copper. HCl does react with zinc.*

$Cu \rightarrow Cu^{2+} + 2e^-$ -0.34 V

$Zn \rightarrow Zn^{2+} + 2e^-$ +0.76 V

$2H^+ + 2e^- \rightarrow H_2$ 0.00 V

$Cu + 2H^+ \rightarrow Cu^{2+} + H_2$ -0.34 V
$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ +0.76 V
Reaction does not occur – E^0 negative.
Reaction does occur – E^0 positive.

(b) *The fall in concentration of sulfuric acid means the battery is not recharging adequately to restore the sulfuric acid. This is indicated by the hydrometer that is used to measure the density of the electrolyte. Recharging using the mains current with a battery charger, or replenishing the battery with fresh sulfuric acid should restore the higher concentration of the electrolyte.*

18.

(a) *The NO_3^- species does not react with other chemicals in the cell but Cl^- can be oxidised to Cl_2.*

(b) *Being spectator species in the salt bridge, they are better able to maintain ionic equilibrium between the anode and the cathode half cells, i.e. can transfer charge.*

(c) *The chloride ions tend to get preferentially oxidised and will interfere with the reactions for which the cell is designed. With silver, a precipitate would be formed.*

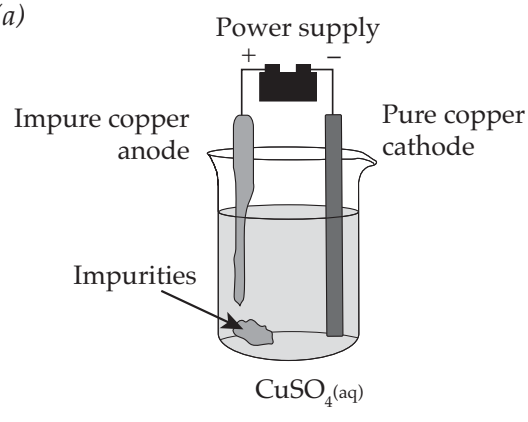
19.

(a) *For an ethanol fuel cell:*
The reactions in an acid environment are as follows:
Anode reaction:
$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$
Cathode reaction:
$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$

(b) *The reactions in an acid environment are as follows:*
Anode reaction:
$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$
The reactions in an acid environment are as follows:
Cathode reaction:
$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O$

20.

(a)



(b) *Anode: $Cu_{(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2e^-$*
Cathode: $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$

(c) *$Cu_{(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2e^-$ $E^o = -0.34$ V*
$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$ $E^o = -0.44$ V
Overall voltage required would be 0.34 + 0.44 = 0.78V
The voltage required to deposit iron on the cathode is only 0.78 V so the voltage must be kept below this.

(d) *Impurities like gold, silver and platinum will not be oxidised and as such will fall to the bottom of the cell as the anode slime to be recovered.*

Chapter 4. Organic Chemistry

Set 1 Nomenclature

1.

(a) butane, saturated
(b) but-1-ene, unsaturated
(c) 3-methylpentane, saturated
(d) 3,4-dimethylhept-3-ene, unsaturated

2.

(a) $CH_3CH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_3$
2,4-dimethylheptane

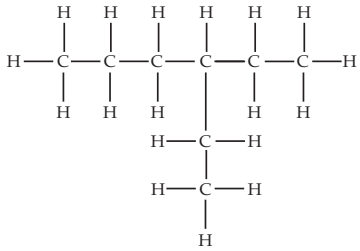
(b) $CH_3CH_2C(CH_3)_2CH_2CH_2CH_3$
3,3-dimethylhexane

(c) $CH_2CHC(CH_3)_2CH_3$
3,3-dimethylbut-1-ene

(d) $CH_3CH(CH_3)CH_2CH_2CH_2CH_2CH(CH_3)CH_3$
2,7-dimethyloctane

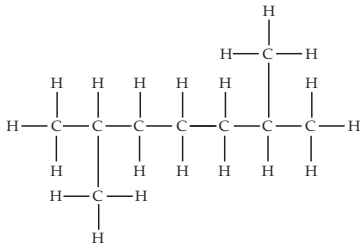
3.

(a)



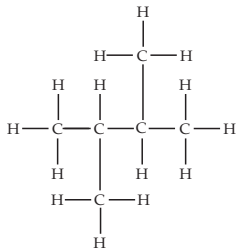
3-ethylhexane

(b)



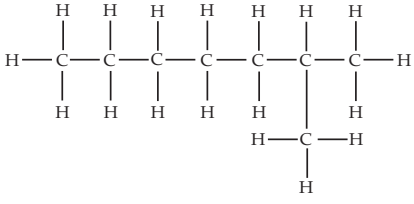
2,6-dimethylheptane

(c)



2,3-dimethylbutane

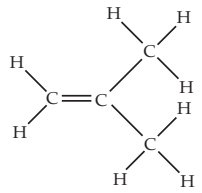
(d)



2-methylheptane

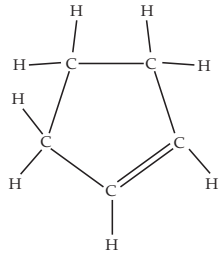
4.

(a)



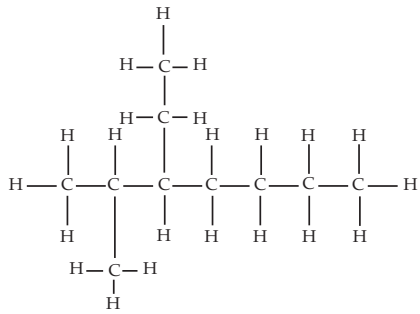
aliphatic

(b)



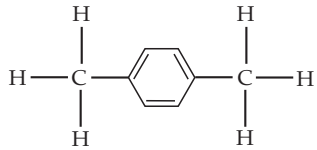
alicyclic

(c)



aliphatic

(d)



aromatic

5.

(a)	*alcohol*	*butan-1-ol*
(b)	*alkene*	*hex-3-ene*
(c)	*alkane*	*4-ethyl-2-methylheptane*
(d)	*halogenoalkane*	*5,6-dibromo-1-chlorooctane*
(e)	*aldehyde*	*pentanal*
(f)	*alcohol*	*pentan-3-ol*
(g)	*ketone*	*hexan-3-one*
(h)	*carboxylic acid*	*pentanoic acid*
(i)	*amine*	*butanamine*
(j)	*ester*	*propylpropanoate*
(k)	*amide*	*butanamide*
(l)	*amino acid*	*2-aminobutanoic acid*
(m)	*carboxylic acid*	*3,3-dimethylhexanoic acid*
(n)	*alkene*	*1-chlorohex-3-ene*
(o)	*amine*	*3-chloro-2-methylbutanamine*
(p)	*ester*	*pentylbutanoate*
(q)	*ketone (alcohol)*	*6-hydroxyhexan-3-one*
(r)	*ester*	*ethylpropanoate*

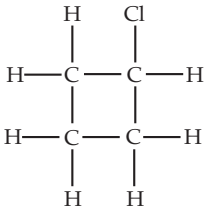
(s) *amide* *5-chloro-4-methylpentanamide*
(t) *alcohol* *octan-2,6-diol*
(u) *aldehyde* *4-bromobutanal*
(v) *amine* *3,6-octandiamine*
(w) *carboxylic acid (-ol)* *4-hydroxybutanoic acid*

6.

(a) $CH_3CH(OH)CH_2CH_3$
(b) $CH_3CHICl_2CH_2CH_3$
(c) CH_3CH_2CHO
(d) $CH_3CH(OH)C(CH_3)_2CH_2CH_2CH_3$
(e) $CH_3CH_2CH_2COOH$
(f) $CH_3(CH_2)_4NH_2$
(g) $CH_3(CH_2)_3CH(OH)CH_2COOH$
(h) $CH_3CH_2COCH_2CH_3$
(i) $CH_3CH_2CH(NH_2)CH_2CH_2COOH$
(j) $CH_3(CH_2)_2CONH_2$
(k) $CH_3CHCHCHCClCHClCH_3$
(l) $CH_3COCH_2CH_2COOH$

7.

(a)



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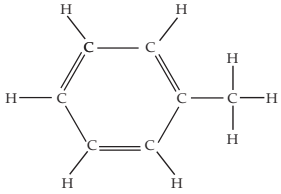

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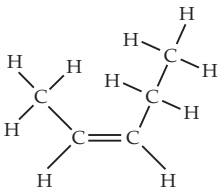

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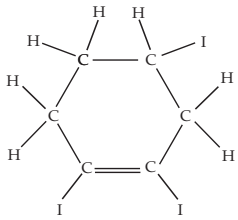

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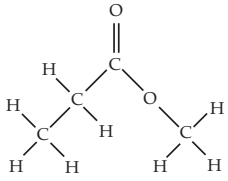

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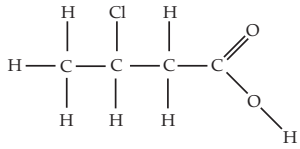

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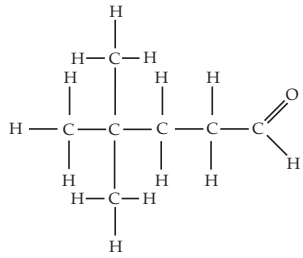

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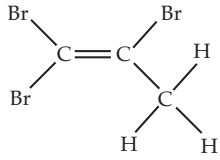

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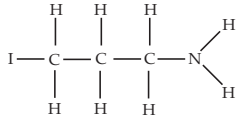

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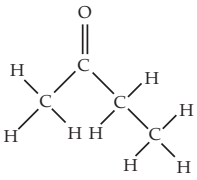

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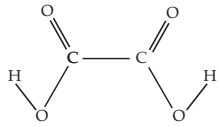

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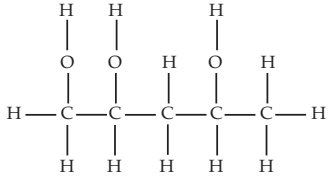

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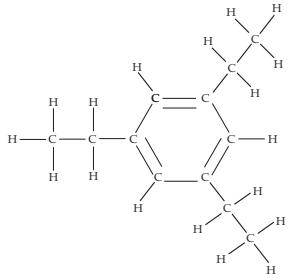

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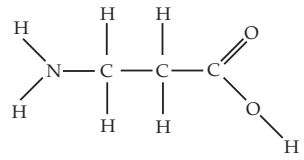

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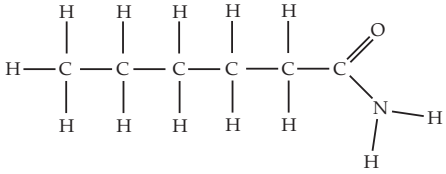
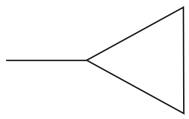


8.

(a) cyclopentane
(b) 1-bromo-3-chlorocyclopentane
(c) 4-ethyl-5-methyloctane
(d) trans hexa-1,4-diene
(e) 1,4-diethylbenzene
(f) cis-2-pentene
(g) 1,3-diiodocyclohexene

9.

(a)



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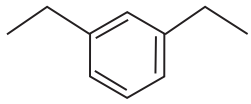

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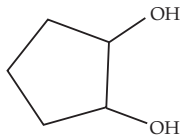
(d)



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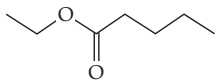

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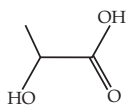

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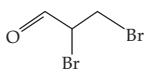

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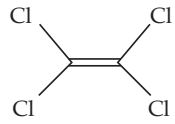

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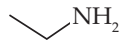

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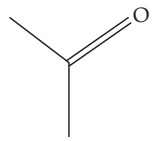

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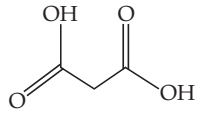

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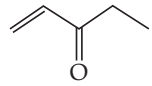

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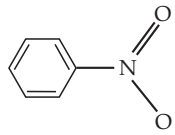

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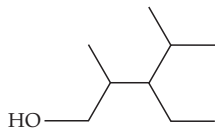

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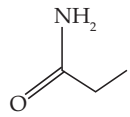

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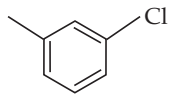

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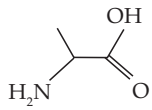

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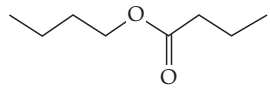
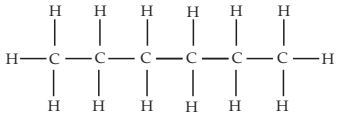
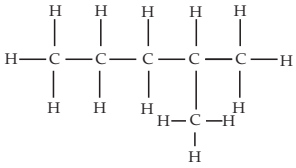
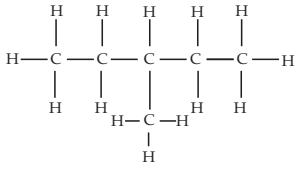


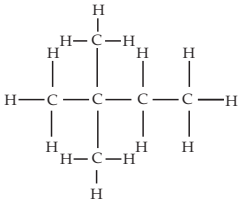
Set 2 Isomers

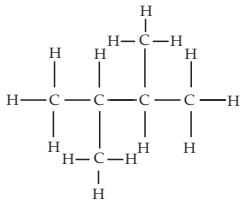
1.

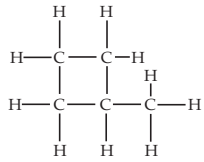




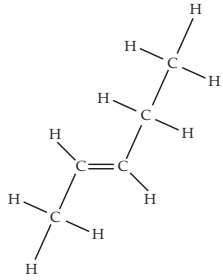




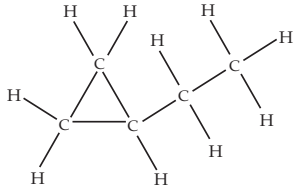




methylcyclobutane

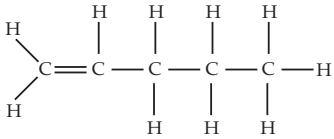


trans-pent-2-ene

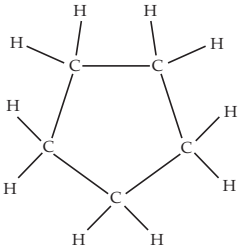


ethylcyclopropane

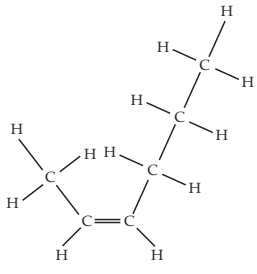
2.



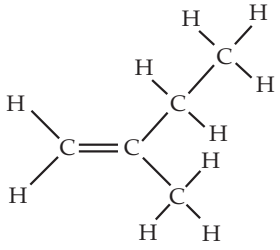
pent-1-ene



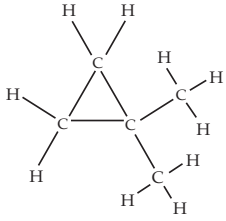
cyclopentane



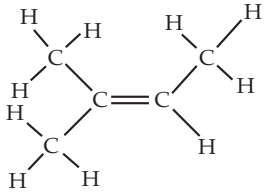
cis pent-2-ene



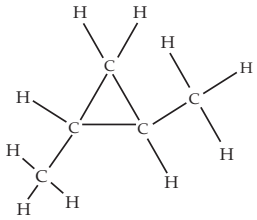
2-methylbut-1-ene



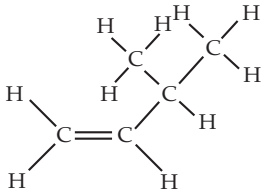
1,1-dimethylcyclopropane



2-methylbut-2-ene

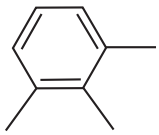


1,2-dimethylcyclopropane

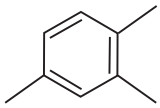


3-methylbut-1-ene

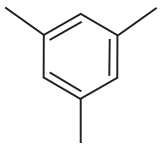
3.



1,2,3-trimethylbenzene



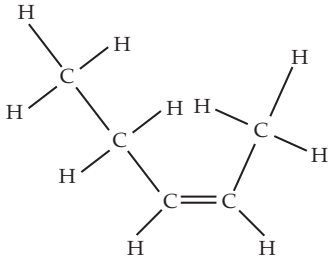
1,2,4-trimethylbenzene



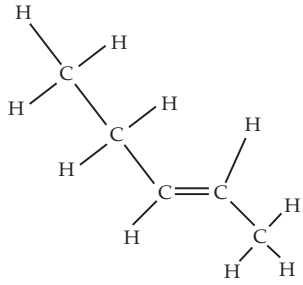
1,3,5-trimethylbenzene

4.

(a) pent-2-ene

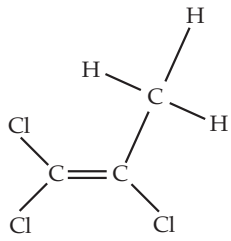


cis



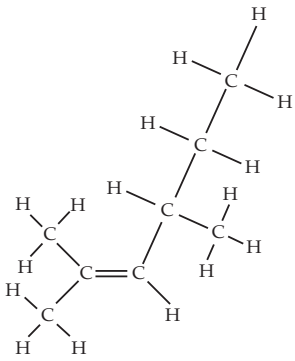
trans

(b) 1,1,2-trichlorobut-1-ene



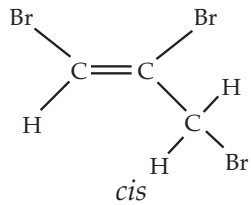
No cis or trans

(c) 2,4-dimethylhex-2-ene

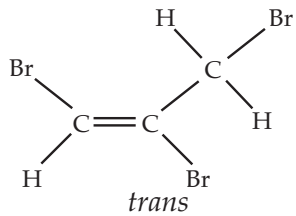


No cis or trans

(d) 1,2,3-tribromopropene

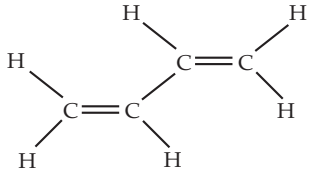


cis



trans

(e) 1,3-butadiene



No cis or trans

Set 3 Reactions and Properties of the Aliphatic Hydrocarbons

1.

(a)

i) $CH_2CHCH_2CH_3 + 6O_2 \rightarrow 4CO_2 + 4H_2O$

ii) $2CH_3CH(CH_3)CH_3 + 13O_2 \rightarrow 8CO_2 + 10H_2O$

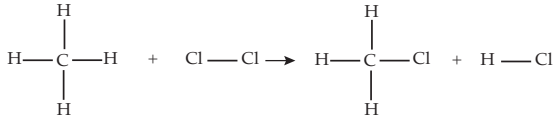
(b)

i) $2CH_3(CH_2)_3CH_3 + 11O_2 \rightarrow 10CO + 12H_2O$

ii) $C_6H_{12} + 6O_2 \rightarrow 6CO + 6H_2O$

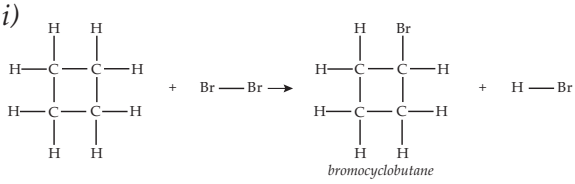
2.

(a)



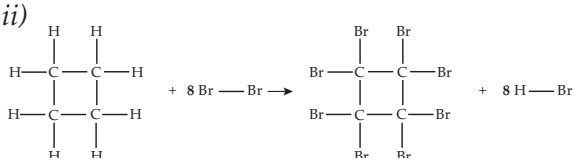
(b)

i)

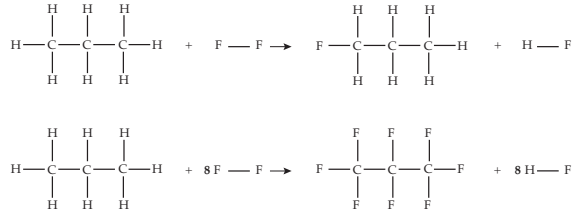


bromocyclobutane

ii)

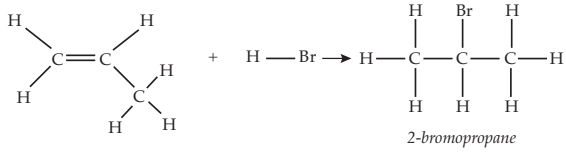


(c)



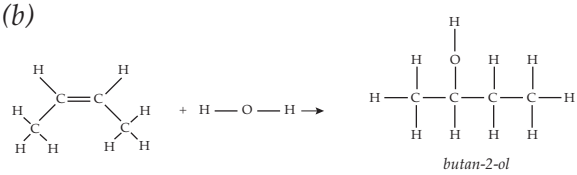
3.

(a)



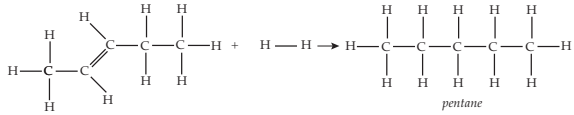
2-bromopropane

(b)



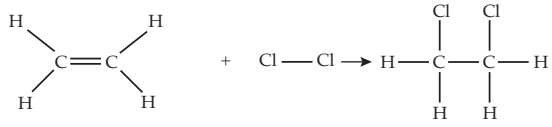
butan-2-ol

(c)



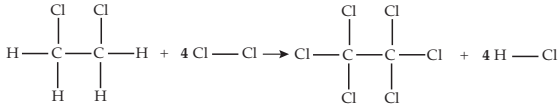
pentane

(d)



1,2-dichloroethane

and then…



hexachloroethane

4.

(a) 2-chloropropane

(b) 2-chloro-2-methylbutane

(c) 2,2-dichloropropane

Properties

5. To boil each of these alkanes requires dispersion forces only to be broken. As more branching occurs there is less surface area over which dispersion forces can act. Branching prevents molecules from getting close together, so the dispersion forces are less effective.

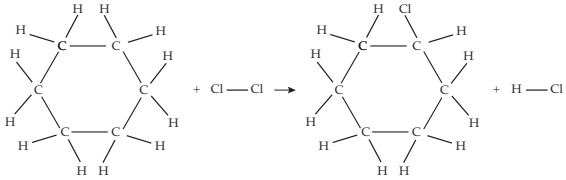
6. Tetrachloroethene is a non-polar molecule with dispersion forces between molecules. For it to be readily soluble in water, the intermolecular forces that form between it and water would have to be equal to or

stronger than the intermolecular forces of both it and water. Since the strongest bonds that can form between tetrachloroethene and water are dispersion forces these aren't strong enough to overcome the hydrogen bonding between water molecules to any reasonable extent. Trichloroethene is a polar molecule with dipole-dipole interactions between molecules. It can form dipole-dipole interactions with water and as such can overcome the bonding between water molecules to a much larger extent.

Set 4 Reactions of the Alicyclic and Aromatic Hydrocarbons

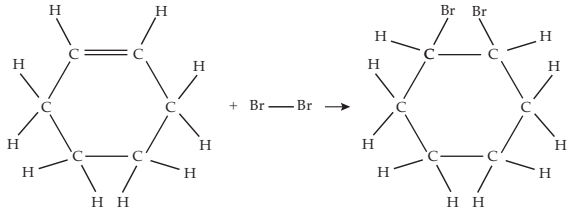
1.

(a)



chlorocyclopentane

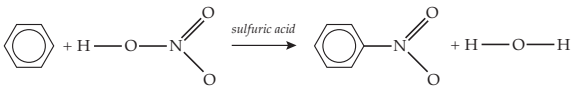
(b)



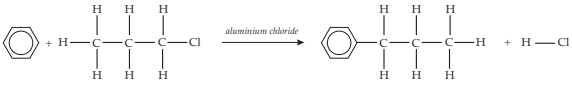
1,2-dibromocyclohexane

2.

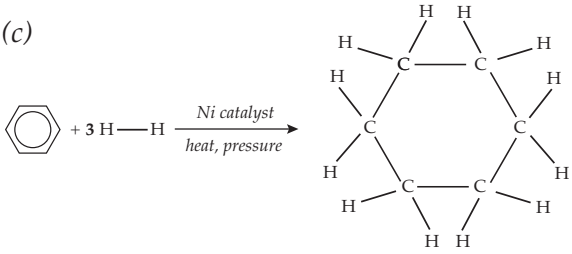
(a)



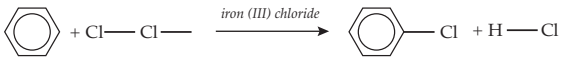
(b)



(c)



(d)



Set 5 Reactions and Properties of Alcohols

1.

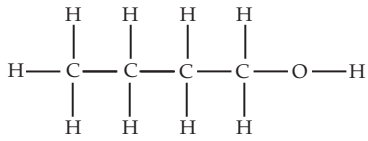
(a) 1,1-dimethylpropan-1-ol; a tertiary alcohol

(b) butan-1-ol; a primary alcohol

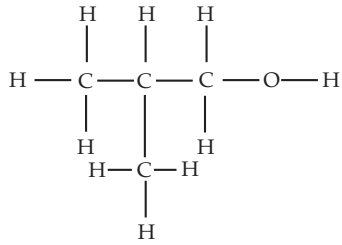
(c) 1,5-dimethylhexan-1-ol; a secondary alcohol

(d) pentan-3-ol; a secondary alcohol

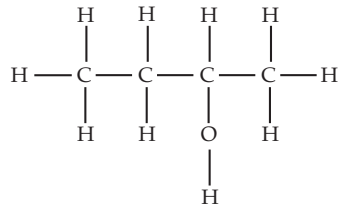
2.



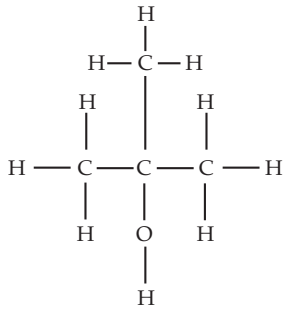
butan-1-ol



2-methylpropan-1-ol



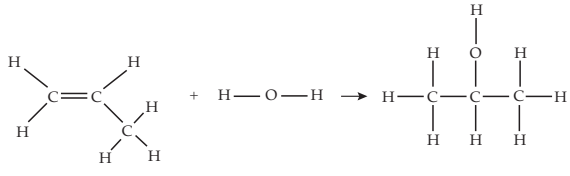
butan-2-ol



2-methylpropan-2-ol

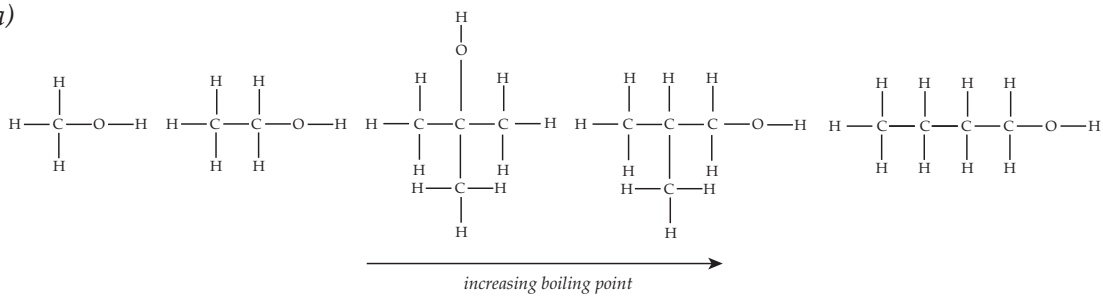
3. $2CH_3CHOHCH_3 + 9O_2 \rightarrow 6CO_2 + 8H_2O$

4.



propane *water* *propan-2-ol*

7. (a)



5.

Reduction half equation	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Oxidation half equation	$CH_3CHOHCH_2CH_3 \rightarrow CH_3COCH_2CH_3 + 2H^+ + 2e^-$ (x3)
Overall equation	$Cr_2O_7^{2-} + 8H^+ + 3CH_3CHOHCH_2CH_3 \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3COCH_2CH_3$
Names	chromium ions, water and butan-2-one

6.

Reduction half equation	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (x 4)
Oxidation half equation	$CH_3(CH_2)_4OH + H_2O \rightarrow CH_3(CH_2)_3COOH + 4H^+ + 4e^-$ (x 5)
Overall equation	$4MnO_4^- + 5CH_3(CH_2)_4OH + 12H^+ \rightarrow 4Mn^{2+} + 5CH_3(CH_2)_3COOH + 11H_2O$
Names	manganese ions, water and pentanoic acid

7.

(a) (see above).

(b) All of these substances have hydrogen bonding so you cannot use this directly to rank them in boiling point order. They will all have dispersion forces, which increase with increasing molar mass so methanol and ethanol are easy to place in order. Methylpropan-1-ol, methylpropan-2-ol and butanol all have the same molar mass. We must therefore look at how the branching affects dispersion forces and also the accessibility of the -OH for hydrogen bonding. Methylpropan-1-ol and methylpropan-2-ol are branched so butanol can be placed above these due to increased surface area for dispersion forces. The –OH on methylpropan-1-ol is more accessible for hydrogen bonding so it can be placed above methlypropan-2-ol.

8. $2Na + 2CH_3CH_2CH_2OH \rightarrow 2CH_3CH_2CH_2ONa + H_2$

9. Add orange acidified potassium permanganate to the alcohol. If it is a secondary alcohol it will be oxidised to a ketone and the solution will become green. If it is a tertiary alcohol it will remain orange as no oxidation takes place.

10.

(a) 3-methylbutan-2-ol

(b) 4,4-dimethylhexan-2-ol

(c) 2-methylpentan-3-ol

(d) cyclohexanol

Set 6 Aldehydes, Ketones, Carboxylic Acids and Esters

1.

(a) ketone

(b) ester

(c) aldehyde

(d) carboxylic acid

(e) ketone

(f) ester

(g) oxocarboxylic acid

2.

(a) butanone

(b) propylbutanoate

(c) butanal

(d) hexanoic acid

(e) octan-2-one

(f) ethylpropanoate

(g) 5-oxohexanoic acid

3. $2CH_3COCH_3 + 8O_2 \rightarrow 6CO_2 + 6H_2O$

4. $CH_3CH_2CH_2COOH + 3O_2 \rightarrow 4CO + 4H_2O$

5.

Reduction half equation	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (x 2)
Oxidation half equation	$CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CHO + 2H^+ + 2e^-$ (x 5)
Overall equation	$2MnO_4^- + 6H^+ + 5CH_3CH_2CH_2CH_2OH \rightarrow 2Mn^{2+} + 8H_2O + 5CH_3CH_2CH_2CHO$
Names of all species	permanganate ions, hydrogen ions, butan-1-ol, manganese ions, water, butanal

6.

Reduction half equation	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Oxidation half equation	$CH_3CH_2CHOHCH_2CH_3 \rightarrow CH_3CH_2COCH_2CH_3 + 2H^+ + 2e^-$ (x 3)
Overall equation	$Cr_2O_7^{2-} + 8H^+ + 3CH_3CH_2CHOHCH_2CH_3 \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CH_2COCH_2CH_3$
Names of all species	dichromate ions, hydrogen ions, pentan-3-ol, chromium ions, water, pentan-3-one

7. *1-butanol and an oxidising agent like $KMnO_4$ or $K_2Cr_2O_7$*
8. *$CH_3CH_2CH_2OH + CH_3CH_2CH_2COOH \rightarrow CH_3CH_2CH_2OOCCH_2CH_2CH_3 + H_2O$*
9.

(a) *$2CH_3CH_2COOH_{(aq)} + MgCO_{3(s)} \rightarrow Mg^{2+}_{(aq)} + 2CH_3CH_2COO^-_{(aq)} + H_2O_{(l)} + CO_{2(g)}$*
White solid added to clear, colourless solution. Solid dissolves to produce a clear colourless solution with effervescence of a colourless, odourless gas.

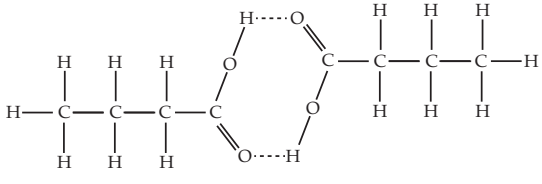
(b) *$2CH_3CH_2COOH_{(aq)} + 2Na_{(s)} \rightarrow 2Na^+_{(s)} + 2CH_3CH_2COO^-_{(aq)} + H_{2(g)}$*
Dull grey metallic solid added to clear, colourless solution. Solid dissolves to produce a clear, colourless solution with vigorous effervescence of a colourless, odourless gas.

(c) *$CH_3CH_2COOH_{(aq)} + KOH_{(aq)} \rightarrow K^+_{(aq)} + CH_3CH_2COO^-_{(aq)} + H_2O_{(l)}$*
or ionic equation
$CH_3CH_2COOH_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CH_2COO^-_{(aq)} + H_2O_{(l)}$
Clear, colourless solution added to clear, colourless solution. No visible reaction.

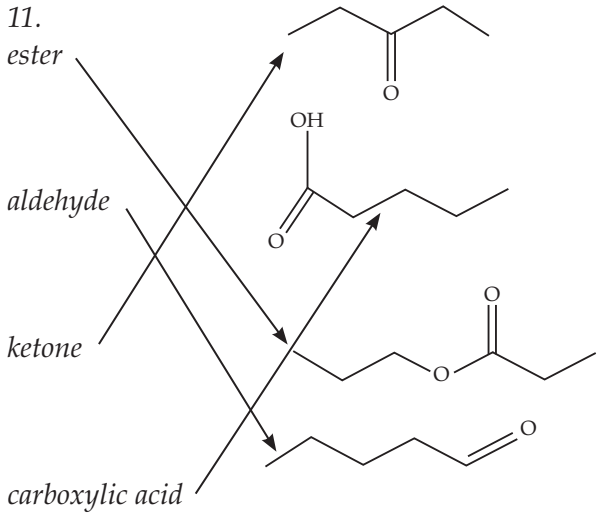
(d) *$CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$*
Clear, colourless solution added to a clear, colourless liquid. Two clear colourless immiscible layers are produced. The top layer has a fruity, sweet odour.

(e) *$CH_3CH_2COOH_{(aq)} + 2K^+_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} \rightarrow$ NR*
An orange solution is added to a clear, colourless solution. The resulting solution remains orange.

10. *butane, butanal, butan-1-ol, butanoic acid. Butane is non-polar and has weak dispersion forces. Butanal is a polar molecule and has stronger dipole-dipole intermolecular forces. 1-butanol and butanoic acid are polar and both have the strongest intermolecular forces, hydrogen bonding, between their molecules. Butanoic acid has the ability to form more hydrogen bonds per molecule (and also a dimer shown below where two molecules hydrogen bond with each other giving greater dispersion forces).*



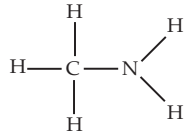
11.



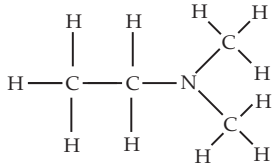
Set 7 Amines, Amides and Amino Acids

1.
(a) *amide; 3-methylbutanamide*
(b) *amine; butan-2-amine*
(c) *amine; octan-1-amine*
(d) *amino acid; 2-aminopropanoic acid*
(e) *amide; pentanamide*
(f) *amino acid; 3-aminopropanoic acid*

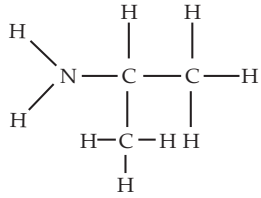
2.
(a) *primary*



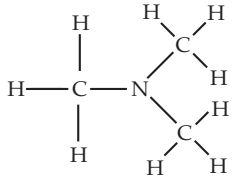
(b) *tertiary*



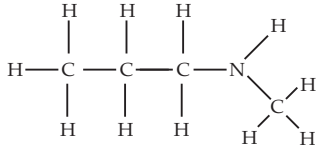
(c) *primary*



(d) *tertiary*



(e) *secondary*

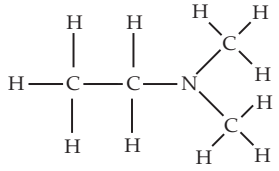


3.

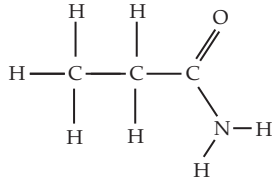
(a) butanamide
(b) 4-aminobutan-2-ol
(c) 2-aminoheptanoic acid
(d) pentanamide
(e) 1-hexanamine
(f) 2-aminobenzoic acid

4.

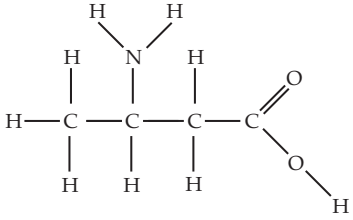
(a)



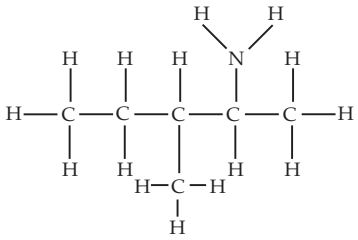
(b)



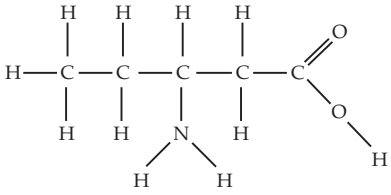
(c)



(d)



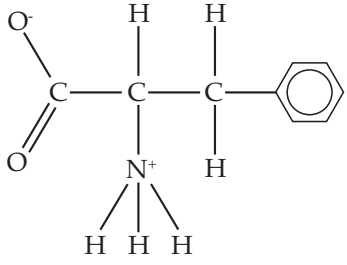
(e)



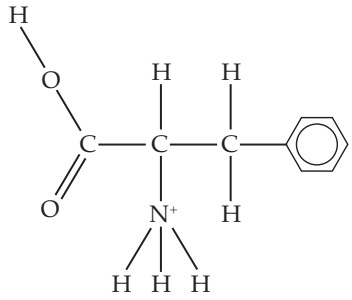
5. a, b and e are α-amino acids.

6.

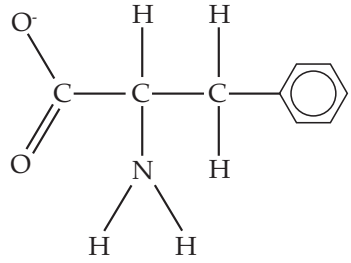
(a)



(b)



(c)

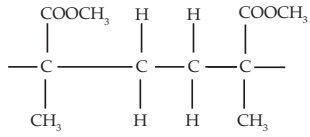


Set 8 Polymers and Amino Acids

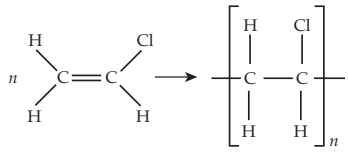
1.

(a) Perspex is an addition polymer.

(b)



2.



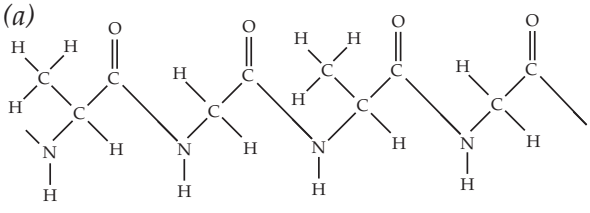
3. The PVC chain contains polar carbon to chlorine bonds which can form dipole-dipole interactions with neighbouring chains. These relatively strong intermolecular forces give PVC its strength.

4.

(a) (ii)
(b) (i)
(c) (iii)

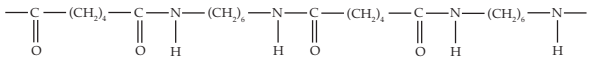
5. Silks produced by insects are natural protein fibres or polypeptides. They consist of amino acid residues. One such silk was found to consist mainly of alternating glycine and alanine residues.

(a)

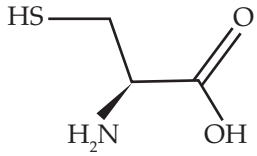


(b) Condensation polymerisation.
(c) A peptide link.
(d) The α-helix structure of the silk is determined by hydrogen bonding between amide and carbonyl functional groups within a peptide chain.

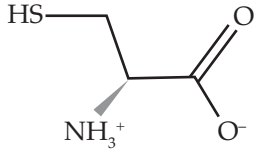
6. The monomers below are used to produce Nylon 6,6.
(a) hexanedioic acid and 1,6-hexanediamine
(b)



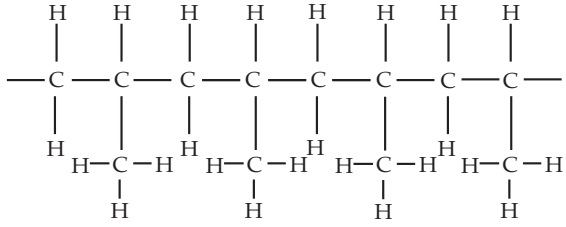
7.
(a)



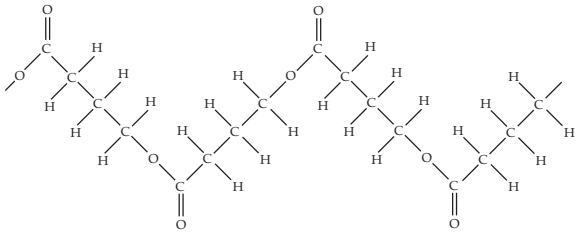
(b)



8.

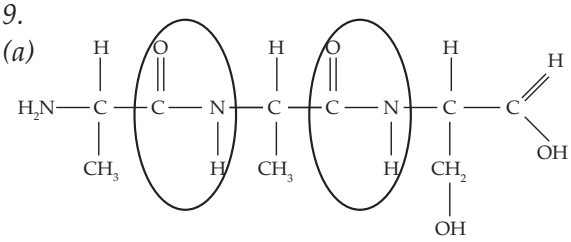


(a) Addition polymer

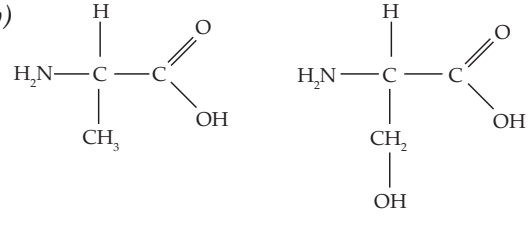


(b) Condensation polymer

9.
(a)



(b)



(c) The sequence of amino acids in the polypeptide determines the primary structure of a tripeptide. Two of the first amino acids form a peptide bond and then the second amino acid forms a peptide bond with them.
(d) The –NH amide functional group, the C=O carbonyl group and the -OH in CH_2OH can all hydrogen bond with one another and so could contribute to α-helix structures or β-pleating secondary structures in a protein.
*(e) α-helix structures form where hydrogen bonding between amide and carbonyl functional groups occur **within** a peptide chain. β-pleated sheets occur when hydrogen bonding happens **between** functional groups on adjacent polypeptide chains.*
(f) Disulphide bridges are covalent bonds between two sulphur containing side groups.
Hydrogen bonding occurs between groups like –OH and $–NH_2$.
Dipole-dipole interactions occur between polar side groups.
Dispersion forces are weak interactions between non-polar side groups like methyl, CH_3.
Ionic interactions are between charged side groups like CO_2^- and NH_3^+.

10.
(a) It is important that the reaction system shown can move easily and quickly in either direction as it is the blood buffer system and needs to be able to maintain the pH balance in blood efficiently as any changes in pH occur.
(b) Carbonic anhydrases are catalysts and so provide an alternative reaction pathway with a lower activation energy.

Set 9 Empirical and Molecular Formulae

1. %N = 100 - 40.67 - 8.54 - 27.09
= 23.7%

	C	H	O	N
%	40.67	8.54	27.09	23.70
Mass in 100 g	40.67	8.54	27.09	23.70
Moles	40.67/12.01 = 3.3863	8.54/1.008 = 8.4722	27.09/16.00 = 1.6931	23.70/14.01 = 1.6916
Simplest Ratio	3.3863/1.6916 = 2.001	8.4722/1.6916 = 5.008	1.6931/1.6916 = 1.001	1.6916/1.6916 = 1
	2	5	1	1

E.F. = C_2H_5NO

2. $m(AgCl) = 0.861\ g$
$n(AgCl) = 0.861/143.35$
$= 6.006 \times 10^{-3}\ mol$
$n(Cl^-) = 6.006 \times 10^{-3}\ mol$
$m(Cl^-) = 6.006 \times 10^{-3} \times 35.45$
$= 0.2129\ g$
$\%Cl = 0.2129/0.295 \times 100$
$= 72.18\%$
$\%O = 100 - 16.30 - 0.68 - 72.18$
$= 10.84\ \%$

	C	H	O	Cl
%	16.30	0.68	10.84	72.18
Mass in 100 g	16.30	0.68	10.84	72.18
Moles	40.67/12.01 = 1.3572	0.68/1.008 = 0.6746	10.84/16.00 = 0.6777	72.18/35.45 = 2.036
Simplest Ratio	1.3572/0.6746 = 2.012	0.6746/0.6746 = 1	0.6777/0.6746 = 1.005	2.036/0.6746 = 3.018
	2	1	1	3

$E.F = C_2Cl_3OH$

$n(MF) = PV/RT$
$= (101.3 \times 0.0492) / (8.314 \times 300.15)$
$= 1.997 \times 10^{-3}\ mol$
$M(MF) = 0.295/1.997 \times 10^{-3}$
$= 147.705\ g\ mol^{-1}$
$M(EF) = (2 \times 12.01) + (3 \times 35.45) + 16.00 + 1.008$
$= 147.378\ g\ mol^{-1}$
Since M(MF) ≈ M(EF) the molecular formula is C_2Cl_3OH

3.

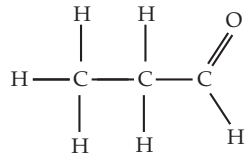
(a) $m(CO_2) = 5.281\ g$
$n(CO_2) = 5.281/44.01$
$= 0.1200\ mol$
$n(C) = 0.1200\ mol$
$m(C) = 0.1200 \times 12.01$
$= 1.441\ g$
$m(H_2O) = 2.162\ g$
$n(H_2O) = 2.162/18.016$
$= 0.1200\ mol$
$n(H) = 2 \times 0.1200$
$= 0.2400\ mol$
$m(H) = 0.2400 \times 1.008$
$= 0.2419\ g$
$m(O) = 2.323 - 1.441 - 0.2419$
$= 0.6399\ g$
$n(O) = 0.6399/16.00$
$= 0.0400\ mol$

	C	H	O
Moles	0.1200	0.2400	0.0400
Simplest ratio	0.1200/0.0400 = 3	0.2400/0.0400 = 6	0.0400/0.0400 = 1

$E.F. = C_3H_6O$

(b) $n(MF) = 0.5797/22.71$
$= 0.02553\ mol$
$M(MF) = 1.503/0.02553$
$= 58.88\ g\ mol^{-1}$
$M(EF) = (3 \times 12.01) + (6 \times 1.008) + 16.00$
$= 58.078\ g\ mol^{-1}$
Since M(MF) ≈ M(EF) the molecular formula is C_3H_6O

(c)



4.

(a) $m(CO_2) = 1.320\ g$
$n(CO_2) = 1.320/44.01$
$= 0.0300\ mol$
$n(C) = 0.0300\ mol$
$m(C) = 0.0300 \times 12.01$
$= 0.3602\ g$
$n(NH_3) = 1.050 \times 0.08570$
$= 0.0900\ mol$
$n(HCl) = 0.0900\ mol$
$n(Cl^-) = 0.0900\ mol$
$m(Cl) = 0.0900 \times 35.45$
$= 3.190\ g$
$m(F) = 4.121 - 03602 - 3.190$
$= 0.5708\ g$
$n(F) = 0.5708/19.00$
$= 0.03004\ mol$

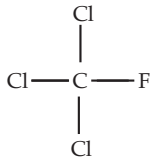
	C	F	Cl
Moles	0.0300	0.03004	0.0900
Simplest ratio	0.0300/0.0300 = 1	0.03004/0.0300 = 1.002	0.0900/0.0300 = 3.000
	1	1	3

$E.F. = CFCl_3$

(b) $n(MF) = V/22.71$
$= 0.6068/22.71$
$= 0.02672\ mol$
$M(MF) = 3.661/0.02672$
$= 137.016\ g\ mol^{-1}$
$M(EF) = 12.01 + 19.00 + (3 \times 35.45)$
$= 137.36\ g\ mol^{-1}$

Since M(MF) ≈ M(EF) the molecular formula is $CFCl_3$

(c) trichlorofluoromethane



5.

(a) Sample 1

$m(CO_2) = 10.50\ g$

$n(CO_2) = 10.50/44.01$

$= 0.2386\ mol$

$n(C) = 0.2386\ mol$

$m(C) = 0.2386 \times 12.01$

$= 2.865\ g$

$m(H_2O) = 6.421\ g$

$n(H_2O) = 6.421/18.016$

$= 0.3564\ mol$

$n(H) = 2 \times 0.3564$

$= 0.7128\ mol$

$m(H) = 0.7128 \times 1.008$

$= 0.7185\ g$

Sample 2

$m(Na_2SO_3) = 9.980\ g$

$M(Na_2SO_3) = (2 \times Na) + (1 \times S) + (3 \times O)$

$= 126.05\ g\ mol^{-1}$

$n(Na_2SO_3) = 9.980/126.05$

$= 0.07917\ mol$

$n(S) = 0.07917\ mol$

$m(S) = 0.07917 \times 32.07$

$= 2.5391\ g$

$m(S)_{Sample\ 1} = 2.5391 \times 15.00/10.00$

$= 3.809\ g$

$m(O) = 15.00 - 2.8654 - 0.7185 - 3.809$

$= 7.607\ g$

$n(O) = 7.607/16.00$

$= 0.4755\ mol$

$n(S) = 3.809/32.07$

$= 0.1188\ mol$

	C	H	O	S
Moles	0.2386	0.7128	0.4755	0.1188
Simplest ratio	0.2386/0.1188 = 2.009	0.7128/0.1188 = 6.002	0.4755/0.1188 = 4.003	0.1188/0.1188 = 1
	2	6	4	1

$E.F. = C_2H_6O_4S$

(b) $n(MF) = PV/RT$

$= (100.0 \times 0.651) / (8.314 \times 493.15)$

$= 0.015877858\ mol$

$M(MF) = 2.000/0.015877858$

$= 125.962\ g\ mol^{-1}$

$M(EF) = (2 \times 12.01) + (6 \times 1.008) + (4 \times 16.00) + 32.07$

$= 126.138\ g\ mol^{-1}$

Since M(MF) ≈ M(EF) the molecular formula is $C_2H_6O_4S$

(c) $CH_3CH_2HSO_4$

6.

(a) $m(CO_2) = 0.9267\ g$

$n(CO_2) = 0.9267/44.01$

$= 0.02106\ mol$

$n(C) = 0.02106\ mol$

$m(C) = 0.02106 \times 12.01$

$= 0.2529\ g$

$n(NH_3) = 3.062 \times 0.01720$

$= 0.05267\ mol$

$n(HCl) = 0.05267\ mol$

$n(Cl^-) = 0.05267\ mol$

$m(Cl) = 0.05267 \times 35.45$

$= 1.8670\ g$

$m(F) = 2.320 - 0.2529 - 1.8670$

$= 0.2001\ g$

$n(F) = 0.2001/19.00$

$= 0.01053\ mol$

	C	F	Cl
Moles	0.02106	0.01053	0.05267
Simplest ratio	0.02106/0.01053 = 1.999	0.01053/0.01053 = 1	0.05267/0.01053 = 5.001
	2	1	5

$E.F. = C_2FCl_5$

(b) $n(MF) = V/22.71$

$= 0.1528/22.71$

$= 0.006728313\ mol$

$M(MF) = 1.503/0.006728313$

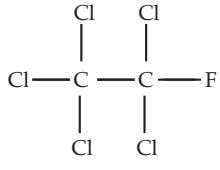
$= 223.384\ g\ mol^{-1}$

$M(EF) = (2 \times 12.01) + 19.00 + (5 \times 35.45)$

$= 220.27\ g\ mol^{-1}$

Since M(MF) ≈ M(EF) the molecular formula is C_2FCl_5

(c)



7. Sample 1

$m(CO_2) = 0.792\ g$

$n(CO_2) = 0.792/44.01$

$= 0.01800\ mol$

$n(C) = 0.01800\ mol$

$m(C) = 0.01800 \times 12.01$

$= 0.2161\ g$

$m(H_2O) = 0.324\ g$

$n(H_2O) = 0.324/18.016$

$= 0.01798\ mol$

$n(H) = 2 \times 0.01798$

$= 0.03597\ mol$

$m(H) = 0.03597 \times 1.008$

$= 0.03626\ g$

Sample 2

$n(NaOH) = 0.100 \times 0.0765$

$= 7.65 \times 10^{-3}\ mol$

$n(H_2SO_4) = 0.100 \times 0.0500$

$= 5.00 \times 10^{-3}\ mol$

$n(H^+) = 2 \times 5.00 \times 10^{-3}$

$= 0.0100\ mol$

$n(NH_3) = 0.0100 - 7.65 \times 10^{-3}$

$= 2.35 \times 10^{-3}\ mol$

$n(N) = 2.35 \times 10^{-3}\ mol$

$m(N) = 2.35 \times 10^{-3} \times 14.01$

$= 0.03292\ g$

$m(N)_{Sample\ 1} = 0.03292 \times 0.450/0.240$

$= 0.06173\ g$

$m(O) = 0.450 - 0.2161 - 0.03626 - 0.06173$

$= 0.1359\ g$

	C	H	N	O
Mass	0.2161	0.03626	0.06173	0.1359
Moles	0.2161/12.01 = 0.01800	0.03626/1.008 = 0.03597	0.06173/14.01 = 4.406×10^{-3}	0.1359/16.00 = 8.493×10^{-3}
Simplest ratio	$\frac{0.01800}{4.406 \times 10^{-3}}$ = 4.08	$\frac{0.03597}{4.406 \times 10^{-3}}$ = 8.16	$\frac{4.406 \times 10^{-3}}{4.406 \times 10^{-3}}$ = 1	$\frac{8.493 \times 10^{-3}}{4.406 \times 10^{-3}}$ = 1.92
	4	8	1	2

$E.F. = C_4H_8NO_2$

8.

(a) $m(CO_2) = 8.802\ g$

$n(CO_2) = 8.802/44.01$

$= 0.2000\ mol$

$n(C) = 0.2000\ mol$

$m(C) = 0.2000 \times 12.01$

$= 2.402\ g$

$m(H_2O) = 3.603\ g$

$n(H_2O) = 3.603/18.016$

$= 0.2000\ mol$

$n(H) = 2 \times 0.2000$

$= 0.4000\ mol$

$m(H) = 0.4000 \times 1.008$

$= 0.4032\ g$

$m(O) = 3.605 - 2.402 - 0.4032$

$= 0.7998\ g$

$n(O) = 0.7998/16.00$

$= 0.04999\ mol$

	C	H	O
Moles	0.2000	0.4000	0.04999
Simplest ratio	0.2000/0.04999 = 4.0009	0.4000/0.04999 = 8.0013	0.04999/0.04999 = 1
	4	8	1

$E.F. = C_4H_8O$

(b) $n(MF) = PV/RT$

$= (95.0 \times 0.4418)/(8.314 \times 295.15)$

$= 0.017103953\ mol$

$M(MF) = 2.466/0.017103953$

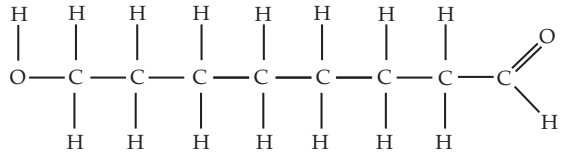
$= 144.1772\ g\ mol^{-1}$

$M(EF) = (4 \times 12.01) + (8 \times 1.008) + 16.00$

$= 72.104\ g\ mol^{-1}$

Since $M(MF) \approx 2 \times M(EF)$ *the molecular formula is* $C_8H_{16}O_2$

(c) hydroxy group can be on any but the terminal C.



9.

(a) $m(CO_2) = 1.759\ g$

$n(CO_2) = 1.759/44.01$

$= 0.03997\ mol$

$n(C) = 0.03997\ mol$

$m(C) = 0.03997 \times 12.01$

$= 0.4800\ g$

$m(H_2O) = 0.8436\ g$

$n(H_2O) = 0.8436/18.016$

$= 0.04683\ mol$

$n(H) = 2 \times 0.04683$

$= 0.09365\ mol$

$m(H) = 0.09365 \times 1.008$

$= 0.09440\ g$

$m(O) = 0.7870 - 0.4800 - 0.09440$

$= 0.2126\ g$

$n(O) = 0.2126/16.00$

$= 0.01329\ mol$

	C	H	O
Moles	0.039997	0.09365	0.01329
Simplest ratio	0.03997/0.01329 = 3.00	0.09365/0.01329 = 7.05	0.01329/0.01329 = 1
	3	7	1

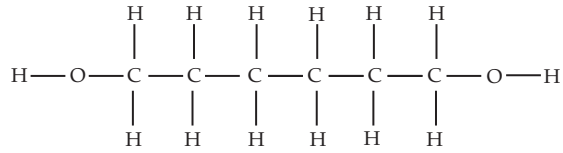
$E.F. = C_3H_7O$

(b) $n(MF) = PV/RT$

$= (101.3 \times 0.198) / (8.314 \times 318.15)$

$= 0.007582853$ mol
$M(MF) = 0.8980/0.007582853$
$= 118.425$ g mol^{-1}
$M(EF) = (3 \times 12.01) + (7 \times 1.008) + 16.00$
$= 59.086$ g mol^{-1}
Since $M(MF) \approx 2 \times M(EF)$ the molecular formula is $C_6H_{14}O_2$

(c) OH's can be on any carbon



(d) hexane-1,6-diol

Chapter 5. Chemical Synthesis

Set 1 Chemical Synthesis

1. $M(Mn_3O_4) = (3 \times 54.94) + (4 \times 16.00) = 228.82$ gmol^{-1}
$n(Mn_3O_4) = 2.62 \times 10^3 \times 10^3/228.82$ g mol^{-1}
$= 11450$ mol
$n(CO) = 100 \times 871 \times 10^3/8.314 \times 873.15$
$= 11998$ mol
$\therefore Mn_3O_4$ is L.R.
$n(MnO) = 3 \times n(Mn_3O_4)$
$= 34350$ mol
$M(MnO) = 54.94 + 16.00 = 70.94$ g mol^{-1}
$m(MnO) = 34350 \times 70.94$
$= 2.44$ tonnes
2. $M(Cu_2S) = (2 \times 63.55) + 32.07$
$= 159.17$ g mol^{-1}
$n(Cu_2S) = 5.10 \times 10^3 \times 10^6/159.17$
$= 3.204 \times 10^7$ mol
$n(CuFeS_2) = 2 \times 3.204 \times 10^7$
$= 6.408 \times 10^7$ mol
$M(CuFeS_2) = 63.55 + 55.85 + (2 \times 32.07)$
$= 183.54$ g mol^{-1}
$m(CuFeS_2) = 6.408 \times 10^7 \times 183.54$
$= 1.176 \times 10^{10}$ g
% purity $= 1.176 \times 10^{10}/1.25 \times 10^{10} \times 100$
$= 94.1$ %
3. $M(Al_2O_3) = (2 \times 26.98) + (3 \times 16.00)$
$= 101.96$ g mol^{-1}
$n(Al_2O_3) = 7.50 \times 10^3 \times 10^6/101.96$
$= 7.356 \times 10^7$ mol
$n(Al(OH)_3) = 2 \times 7.356 \times 10^7$
$= 1.471 \times 10^8$ mol
$n(NaAl(OH)_4) = 1.471 \times 10^8 \times 100/83$
$= 1.772 \times 10^8$ mol
$n(Al_2O_3) = ½ \times 1.772 \times 10^8 \times 100/97$
$= 9.137 \times 10^7$ mol
$m(Al_2O_3) = 9.137 \times 10^7 \times 101.96$
$= 9.316 \times 10^9$ g
% efficiency $= 9.316 \times 10^9/1.1 \times 10^{10} \times 100$
$= 84.7\%$
4. $n(Ti) = 5.076 \times 10^3/47.88$
$= 106.0$ mol
$n(TiCl_4) = n(Ti)$
$= 106.0$ mol
$n(TiO_2) = n(TiCl_4)$
$= 106.0 \times 100/95$
$= 111.6$ mol
$M(TiO_2) = 47.88 + 2 \times 16.00 = 79.88$ g mol^{-1}
$m(TiO_2) = 111.6 \times 79.88$
$= 8914$ g
% purity $= 8914/10000 \times 100$
$= 89.1$ %
5.

(a) $M(Na_2CO_3) = (2 \times 22.99) + 12.01 + (3 \times 16.00)$
$= 105.99$ g mol^{-1}
$n(Na_2CO_3) = 325000 \times 10^6/105.99$
$= 3.066 \times 10^9$ mol
$n(NaHCO_3) = 2 \times n(Na_2CO_3)$
$= 6.133 \times 10^9$ mol
$n(CO_2)$
$= n(NaHCO_3) = 6.133 \times 10^9$ mol
$n(CaCO_3) = n(CO_2)$
$= 6.133 \times 10^9$ mol
$M(CaCO_3) = 40.08 + 12.01 + (3 \times 16.00)$
$= 100.09$ g mol^{-1}
$m(CaCO_3) = 6.133 \times 10^9 \times 100.09$
$= 6.138 \times 10^{11}$ g
$= 6.14 \times 10^5$ tonnes

(b) $n(NaCl) = n(CO_2)$
$= 6.133 \times 10^9$ mol
$M(NaCl) = 22.99 + 35.45 = 58.44$ g mol^{-1}
$m(NaCl) = 6.133 \times 10^9 \times 58.44$
$= 3.584 \times 10^{11}$ g
$m(\text{mined salt}) = 3.584 \times 10^{11} \times 100/60$
$= 5.97 \times 10^5$ tonnes

(c) $n(NH_3) = n(NaCl)$
$= 6.133 \times 10^9$ mol
$M(NH_3) = 14.01 + (3 \times 1.008)$
$= 17.034$ g mol^{-1}
$m(NH_3) = 6.133 \times 10^9 \times 17.034$
$= 1.04 \times 10^5$ tonnes

(d) $n(CaO) = n(CaCO_3)$
$= 6.133 \times 10^9$ mol
$n(Ca(OH)_2) = n(CaO)$
$= 6.133 \times 10^9$ mol

$n(NH_4Cl) = 6.133 \times 10^9$ mol

	$n(NH_4Cl)$	$n(Ca(OH)_2)$
Stoichiometric ratio	2	1
Actual ratio	6.133×10^9	6.133×10^9
	1	1

$\therefore$ L.R. is NH_4Cl
$n(CaCl_2) = ½ \times n(NH_4Cl)$
$= ½ \times 6.133 \times 10^9 \times 85/100$
$= 2.606 \times 10^9$ mol
$M(CaCl_2) = 40.08 + (2 \times 35.45)$
$= 110.98$ g mol^{-1}
$m(CaCl_2) = 2.606 \times 10^9 \times 110.98$
$= 2.89 \times 10^{11}$ g
$= 2.89 \times 10^5$ tonnes

6.

(a) $M(CH_3CH_2OOCCH_3) = (8 \times H) + (2 \times O) + (4 \times C)$
$= 88.104$ g mol^{-1}
$n(CH_3CH_2OOCCH_3) = 35.76/88.104$
$= 0.4059$ mol
$n(CH_3CH_2OH) = n(CH_3CH_2OOCCH_3)$
$= 0.4059$ mol
$M(CH_3CH_2OH) = (2 \times C) + (6 \times H) + O$
$= 46.068$ g mol^{-1}
$m(CH_3CH_2OH) = 0.4059 \times 46.068$
$= 18.7$ g
$m(CH_3OH) = 20.0 - 18.7$
$= 1.302$ g
% $CH_3OH = 1.302/20.0 \times 100$
$= 6.51$ %

(b) $n(H_2O)eth = 0.4059$ mol
$m(H_2O)eth = 0.4059 \times 18.016$
$= 7.312$ g
$M(CH_3OH) = (1 \times C) + (4 \times H) + O$
$= 32.042$ g mol^{-1}
$n(CH_3OH) = 1.302/32.042$
$= 0.04063$ mol
$n(H_2O) = 0.04063$ mol
$m(H_2O)meth = 0.04063 \times 18.016$
$= 0.7319$ g
$m(H_2O)total = m(H_2O)eth + m(H_2O)meth$
$= 8.04$ g

7. $n(H_2SO_4) = 1.500 \times 15.00$
$= 22.50$ mol
$n(SO_3) = 100/67 \times 22.50$
$= 33.58$ mol
$n(SO_2) = 100/85 \times n(SO_3)$
$= 100/85 \times 33.58$
$= 39.51$ mol
$n(FeS_2) = 4/8 \times 100/95 \times n(SO_2)$
$= 4/8 \times 100/95 \times 39.51$
$= 20.79$ mol
$M(FeS_2) = Fe + (2 \times S)$
$= 119.99$ g mol^{-1}
$m(FeS_2) = 20.79 \times 119.99$
$= 2495$ g
% purity $= 2495/2550 \times 100$
$= 97.8$ %

8.

(a) $M(oil) = (57 \times C) + (110 \times H) + (6 \times O)$
$= 891.45$ g mol^{-1}
$N(oil) = 50.0/891.45 = 0.05609$ mol
$n(NaOH) = 3 \times 0.05609 = 0.1683$ mol
$M(NaOH) = 22.99 + 16.00 + 1.008$
$= 39.998$ g mol^{-1}
$m(NaOH) = 0.1683 \times 39.998$
$= 6.73$ g

(b) $n(glycerol) = 0.05609$ mol
$M(glycerol) = (3 \times C) + (3 \times O) + (8 \times H)$
$= 92.094$ g mol^{-1}
$m(glycerol) = 0.05609 \times 92.094$
$= 5.17$ g

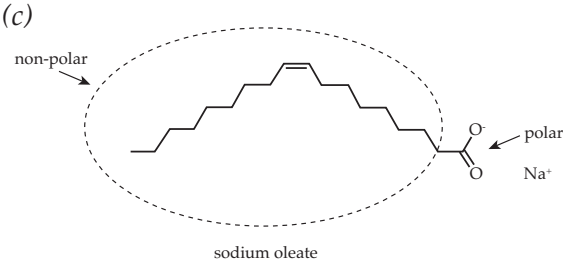
(c) $2CH_3(CH_2)_{16}COONa + Ca^{2+} \rightarrow (CH_3(CH_2)_{16}COO)_2Ca + 2Na^+$
$M(soap) = (18 \times C) + (2 \times O) + (35 \times H) + Na$
$= 306.45$ g mol^{-1}
$n(soap) = 10.0/306.45$
$= 0.03263$ mol
$n(scum)$
$= ½ \times 0.03263$
$= 0.01632$ mol
$M(scum) = (36 \times C) + (4 \times O) + (70 \times H) + Ca$
$= 607$ g mol^{-1}
$m(scum) = 0.01632 \times 607$
$= 9.90$ g

9.

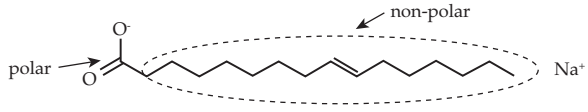
(a) none.

(b) $CH_3(CH_2)_7CHCH(CH_2)_7COOCH_3$

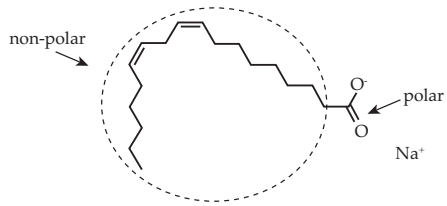
(c)



sodium oleate



sodium palmitate



sodium linoleate

(d) *On agitation in water the soap molecules can surround small droplets of oil and grease forming micelles. The hydrophobic end dissolves in the oil and the hydrophilic end in water. These small droplets can now be washed away as they are effectively dissolved in water.*

(e) *With soaps the non-polar end is a hydrocarbon chain and with anionic detergents the non-polar end is a hydrocarbon chain containing a benzene ring. With soaps the polar end is the carboxylate group -COO^- and with detergents it is the sulfonate group –SO_2O-.*
Soaps are not effective in hard water as they form scum with calcium and magnesium ions. Detergents do not form scum with calcium or magnesium ions and so can be used in hard water.

10. *The first step is the hydration of ethene to produce ethanol.*

$$CH_2CH_2 + H_2O \xrightarrow[\text{heat and pressure}]{\text{phosphoric acid catalyst}} CH_3CH_2OH$$

The second step is the oxidation of 1-propanol to propanoic acid using an oxidising agent like potassium permanganate (shown) or potassium dichromate.

$$5CH_3CH_2CH_2OH + 4MnO_4^- + 12H^+ \rightarrow 5CH_3CH_2COOH + 4Mn^{2+} + 11H_2O$$

The final step is to react the ethanol from step one with the propanoic acid from step two to produce ethylpropanoate.

$$CH_3CH_2COOH + CH_3CH_2OH \xrightarrow{\text{conc. sulfuric acid}} CH_3CH_3COOCH_2CH_3 + H_2O$$

11.

(a) *Using nitrogen from the air is an example of using local and renewable resources. Natural gas is a fossil fuel and is non-renewable. As hydrogen is used further as a fuel production should become more sustainable and storage methods improved.*

(b) *Unreacted gases N_2 and H_2 are separated from the ammonia product when it is liquefied and returned to the converter, shifting the equilibrium in the forward direction.*

(c) *When the ammonia is cooled and liquefied a heat exchanger could be used to recover the heat and then that energy used to heat the converter.*

(d) *Continuous input of N_2 and H_2 and removal of ammonia favours forward direction. High pressures would favour the forward direction but safety and cost must be considered so a compromise is made and a moderate pressure is chosen.*
High temperatures would improve the rate of the reaction, but since the reaction is exothermic in the forward direction this would shift the equilibrium in the reverse direction decreasing yield. A compromise is made and a moderate temperature is chosen.
To offset the effect of lower pressure and temperature a catalyst is used to increase rate.

12.

(a) $S(l) + O_2(g) \rightarrow SO_2(g)$
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$
$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$

(b) *Raw materials: Most sulfur is produced by removing contaminants from natural gas and petroleum. It is a sustainable use of the by-product of another process, which is favourable, although natural gas and petroleum are fossil fuels and non-renewable. There are natural sources of sulfur but it mostly occurs as sulfides and sulphates and would require processing. The oxygen for the process is obtained from air and so is local and renewable. Water is used in step 4, and whilst pure, clean water is in short supply in some locations, it is considered a local resource.*
Energy and energy cycling: In step 1 energy is required to melt the sulfur and also to burn it in oxygen. Step 2 is carried out at 400-450°C and so energy is required. Heat can be recovered from step 1 for use in step 2.
Recycling unused reactants: In step 1 an excess of oxygen is used so it is already available for step 2. Sulfur trioxide is the only product of step 2 and it is passed directly into step 3. Sulfuric acid is a reactant in in step 3 and this can be obtained from the final product.
Toxic products/by products: The products of all steps are toxic and as such it is important that none escapes into the environment. Sulfurous oxides contribute to acid rain if released into the atmosphere.
Rate and equilibrium considerations: Step 1 utilises molten sulfur which is sprayed into excess oxygen (surface area) at high temperatures (increased collisions and collisions with greater energy) to maximise the rate of this step.
Step 2 is the equilibrium step. Ideally high pressures would be used to shift the equilibrium in the forward direction since

there are less gaseous molecules on the right hand side of the equation. A compromise is used, since high pressures increase costs. This reaction is exothermic in the forward direction. High temperatures increase rate but decrease yield so a compromise is used. A catalyst V_2O_5 is used in order to improve the rate. Without a catalyst this reaction occurs very slowly.
Steps 3 and 4 are rate controlling steps. If sulfur trioxide is reacted directly with water to produce sulfuric acid it is uncontrollable, and produces lots of heat. Instead it is reacted with sulfuric acid to make oleum and then this is added to water to produce sulfuric acid in a controllable way.

13. *Atom economy can be used in green chemistry as an alternative to yield. It is given as a percentage and represents the proportion of reactant atoms that make their way into the final product.*

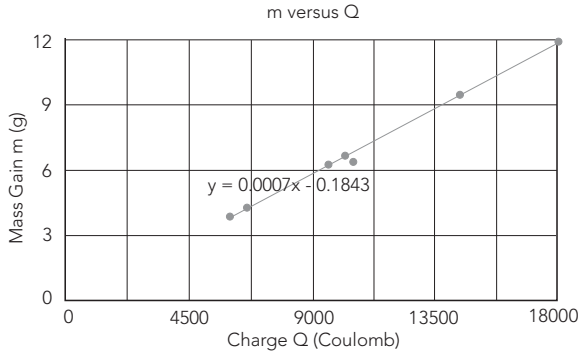
$$\text{Atom economy \%} = \frac{\text{Relative molecular/formula mass of desired product} \times 100}{\text{Relative molecular/formula mass of all reactants}}$$

(a) $CH_2CH_{2(g)} + HCl_{(g)} \rightarrow CH_3CH_2Cl_{(g)}$
$M(CH_2CH_2) = 28.052\ g\ mol^{-1}$
$M(HCl) = 36.458\ g\ mol^{-1}$
$M(CH_3CH_2Cl) = 64.51\ g\ mol^{-1}$
Atom economy $= 64.51/(28.052 + 36.458) \times 100 = 100\%$

(b) $CH_3CH_{3(g)} + Cl_{2(g)} \rightarrow CH_3CH_2Cl_{(g)} + HCl_{(g)}$
$M(CH_3CH_3) = 30.068\ g\ mol^{-1}$
$M(Cl_2) = 70.90\ g\ mol^{-1}$
$M(CH_3CH_2Cl) = 64.51\ g\ mol^{-1}$
$M(HCl) = 36.458\ g\ mol^{-1}$
Atom economy $= 64.51/(30.068 + 70.90) \times 100 = 63.9\ \%$

(c) *The addition reaction has the best atom economy at 100% since the substitution reaction has the by-product of HCl.*

Chapter 6.
Science Inquiry Skills

1. *There seems to be no underlying trend in the results as, when the concentration increases the mass decreases in a non-linear manner*
2. *Student #1 hypothesis is not accepted as there seems to be no link in the two variables.*
3. *Student #2 hypothesis: Comparing the results of Students #6 and #7, as the current rises the gain in mass reduces. Comparing the results of Students #1 and #2, as the current goes from 1.7 to 2.2 A the mass gain reduces hence there is no link between I and m.*
4. *Comparing the results of students #6 and #4 The current rises by 5 times but the mass only increases by 1.9 time (6.3 to 11.9). This is not in the same ratio.*
Mass gain is not proportional to current increase.
5. *Student #3 hypothesis: Students #4 and #7 have the same time = 9000 s.*
Mass gains are not identical (11.9 vs 9.5 – a 20% difference)
Hypothesis #3 is rejected.
6. *Using the results of students #1, #2 and #3.*
$Q = 10200 \quad m = 6.7 \quad m/Q = 6.56 \times 10^{-4}$
$Q = 6600 \quad m = 4.3 \quad m/Q = 6.51 \times 10^{-4}$
$Q = 10500 \quad m = 6.4 \quad m/Q = 6.10 \times 10^{-4}$
7. *(i) and (ii) are very close values but (iii) has a 6% error – this could be an outlier.*
8. 

9. *The data points seem to be very close to the Line of Best Fit.*
10. *± 0.5 s*
11. *Relative Error = 0.008%, (negligible)*
12. *± 0.05 g*
13. *(Very small!)*
14. *Point #3 from Student #3 - the datum is the line and seems to be an Outlier.*
15. *The students may not have washed and dried the electrode or may not have recorded the average current effectively throughout the experiment.*
16. *The gradient is $7.0 \times 10^{-4} g\ C^{-1}$.*
17. *$I = 1.7$, $t = 6000$, $m = 6.7$ so*
Total RE = (3.0 + 0.008 + 0.7)% = 3.71%
Value of $k = 6.6 \times 10^{-4} \pm 3.71\%$ or
$(6.6 \pm 0.2) \times 10^{-4}\ g\ C^{-1}$

Solutions to Exam Questions

Unit 3 Examination Questions

CHEMICAL EQUILIBRIUM, ACIDS & BASES AND REDOX REACTIONS

Multiple-choice Questions

1	C	Sulfuric acid >2 $molL^{-1}$ ions, NaCl 2 $molL^{-1}$ ions, weak acid so <2 $molL^{-1}$ ions, ethanol no charged particles
2	C	↑CrO_4^{2-} equilibrium will shift to the left to partially counteract the imposed change. CrO_4^{2-} higher than original conc, Ag^+ decreases
3	B	No changes imposed, so no equilibrium shift. K remains const.
4	B	A catalyst changes the E_a but not the enthalpy of reactants or products, so no change in ΔH. Catalyst doesn't affect yield, only rate.
5	C	I $MgCO_3$ ppt, II PbS and $PbCl_2$ ppt, III $BaSO_4$ ppt. IV no ppt.
6	D	Catalyst ↓E_a but has no effect on E_k nor the velocity of particles.
7	C	A, B and C are valid, but the Q emphasizes small ↑T, so C is the main reason.
8	C	C is a typical rate curve. As reactants are used up the gradient decreases uniformly.
9	C	Becomes cold so +ive ΔH. Energy in from the surroundings. Dissolves readily, so low E_a.
10	A	K = [products]/[reactants], and solid species aren't included.
11	D	K = $[CO_2]$ so for any change other than a change in temperature the system will return to original K, and so also returns to original $[CO_2]$.
12	C	Very small E_a indicates very low conc of products.
13	B	Adding HCl increases $[Cl^-]$ so equilibrium shifts right, so more blue.
14	B	10 mins is first time that partial pressures of gases become constant.
15	C	Graph indicates that the equilibrium shifts right. Since the reaction is exothermic, a decrease in temperature would do this. Removing NO will also result in a shift right.
16	B	Adding a catalyst (I) will not affect yield, only rate. Increasing temperature (II) of exothermic reaction will shift left so reduce N_2. Increasing pressure (III) and removing H_2O (IV) will shift right and increase N_2.
17	C	Cooling (IV) will decrease rate, all the others will increase rate as per collision theory.
18	D	All answers except D quote 'half the original value'. Quantity of catalyst is not directly proportional to temperature or rate, and catalysts don't affect yield.
19	A	Curves show constant concentrations of both species at approx. 35min.
20	B	Nitric acid would neutralize ammonia, equilibrium would shift left and so the solution would turn paler blue.

21	C	NaCl won't affect pH, but the added volume of solution will dilute the $[OH^-]$ so pH will be below 12 but won't decrease to neutral 7 and certainly won't become acidic. Or perform calculation: $n(OH^-) = cV = 0.01 \times 0.02 = 0.0002$mol $c(OH^-) = n/V = 0.0002/0.04 = 0.005$ molL^{-1} $[H^+] = 1.0 \times 10^{-14}/0.005 = 2.0 \times 10^{-12}$ molL^{-1} $pH = -\log(2.0 \times 10^{-12}) = 11.70$
22	A	A is a redox ½ equation. Electrons are transferred but no protons donated or accepted.
23	C	The sodium ethanoate dissolves and the ethanoate ions hydrolyse with water to produce an alkaline solution. So pH increases. $CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$
24	D	Weak electrolytes only partially ionise in aqueous solution.
25	B	In A CO_2 will produce an acidic solution and NaCl is a neutral salt. In C the NH_4^+ ions hydrolyse to produce an acidic solution. In D the Al_2O_3 is insoluble and KCl is a neutral salt. In B, all produce basic solutions.
26	A	$[H^+] = 10^{-pH}$, so $[H^+]$ would change from 10^{-3} to 10^{-6}. $10^{-3}/10^{-6} = 1000$ so will decrease by 1000 times.
27	C	The strength of an acid is determined by the extent to which it ionises in solution.
28	B	Ethanoic acid is a weak acid, but glacial ethanoic acid is said to be nearly pure, hence concentrated.
29	D	1 M HCl and 1M HNO_3 are strong acids have a pH of 0, so both would be yellow. So A and D possible. CH_3COOH is a weak acid so won't be yellow, therefore answer D.
30	C	KCl and $NaNO_3$ are neutral salts, so C.
31	D	NaOH unsuitable as it is hygroscopic and so its mass can't be determined accurately. HCl can't be obtained in pure form for weighing as it is a gas at room temp. Oxalic acid can be used in both redox and acid base titrations, but the most suitable is Na_2CO_3 as it easily obtainable in pure form, has a relatively high molar mass and doesn't react with moisture in the air.
32	C	$n(OH^-) = 0.01 \times 0.02 = 0.0002$ mol $n(H^+) = 0.03 \times 0.02 = 0.0006$ mol $n(H^+)$ after addition $= 0.0006 - 0.0002 = 0.0004$ mol $[H^+] = n/V = 0.0004/0.04 = 0.01$ M $pH = -\log(0.01) = 2.00$
33	B	$c(Ba(OH)_2) = 5 \times 10^{-5}$ M, $[OH^-] = 2 \times 5 \times 10^{-5}$, $[H^+] = 1.0 \times 10^{-14}/10^{-4} = 10^{-10}$ $pH = -\log(10^{-10}) = 10$
34	B	OH^- is the conjugate base of H_2O after it has donated a proton
35	B	Burettes and pipettes should be rinsed with distilled water and then the solution going in them, so II would contribute to error. Conical flasks should be washed with distilled water only before an accurate aliquot is added via pipette, so III would also contribute to error. I, IV and V are procedurally correct.
36	D	$[OH^-] = 2 \times 0.15 = 0.30$ M, $[H^+] = 1.0 \times 10^{-14}/0.30 = 3.33 \times 10^{-14}$ M $pH = -\log(3.33 \times 10^{-14}) = 13.48$
37	B	$n(OH^-) = 2 \times 0.15 \times 0.02 = 0.006$ mol $n(H^+) = 0.223 \times 0.03 = 0.00669$ mol excess $n(H^+) = 0.00669 - 0.006 = 0.00069$ mol $[H^+] = 0.00069/0.050 = 0.0138$ M $pH = -\log(0.0138) = 1.86$
38	D	Weak electrolytes only partially ionise in aqueous solution.
39	C	Water accepts a proton in C. Brønsted Lowry base.

40	C	$n(H^+) = cV = 2.00 \times 0.02 = 0.04$ mol $[H^+] = n/V = 0.04/0.220 = 0.182$ M pH = -log(0.182) = 0.74
41	A	Na_2CO_3 is alkaline so with methyl orange will begin yellow. 2:1 mole ratio of Na_2CO_3:HC*l*, so 40mL will have to be added to reach equivalence point and end point orange.
42	B	The conjugate base (Cl^-) of a strong acid (HC*l*) is weak, and the conjugate base (NH_3) of a weak acid (NH_4^+) is strong, so Cl^- is a weaker base than NH_3.
43	D	HC*l* and H_2SO_4 are strong acids and so don't form buffers. NH_4^+ and NH_2^- aren't an acid/conjugate base pair so won't form a buffer. $NaHCO_3$ and Na_2CO_3 are a weak acid/conjugate base pair and so do form a buffer solution if equimolar and both of adequate concentration.
44	B	Since NaOH (a strong base) is in the conical flask and ethanoic acid (a weak acid) is in the burette, the equivalence point occurs earlier in the titration where the mixture has a pH of between 9 and 11. To reach the end point where the colour change occurs (pH = 3.0 – 4.6) more acid needs to be added from the burette. The end point occurs after the equivalence point.
45	B	CH_3COCH_3 cannot accept nor donate protons.
46	C	HS^- is donating a proton, and so is acting as an acid.
47	C	PO_4^{3-} and S^{2-} can both accept protons from water to produce alkaline solutions. $Ba(OH)_2$ dissociates to produce OH^- ions in solution and is therefore a basic solution. KNO_3 and $Ca(NO_3)_2$ are neutral salts. Fe_2O_3 is insoluble. Al^{3+} is an acidic ion in solution.
48	A	$CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$ Adding nitric acid will cause the equilibrium to shift to the left producing more ethanoic acid molecules.
49	D	$CuSO_4$: anode: $2H_2O \leftrightarrows O_2 + 4H^+ + 4e^-$ cathode: $Cu^{2+} + 2e^- \leftrightarrows Cu$ H_2SO_4: anode: $2H_2O \leftrightarrows O_2 + 4H^+ + 4e^-$ cathode: $2H^+ + 2e^- \leftrightarrows H_2$ NaOH: anode: $4OH^- \leftrightarrows O_2 + 2H_2O + 4e^-$ cathode: $2H_2O + 2e^- \leftrightarrows H_2 + 2OH^-$ NaC*l*: anode: $2H_2O \leftrightarrows O_2 + 4H^+ + 4e^-$ cathode: $2H_2O + 2e^- \leftrightarrows H_2 + 2OH^-$ Apart from the $CuSO_4$ cell, all the rest will produce oxygen and hydrogen gases.
50	C	-2 = (1 x Mn) + (4 x -2), Mn = -2 – (-8) = +6
51	C	BrO_3^- (+5) to Br_2 (0)
52	D	A*l*, Zn and F only exhibit one oxidation state. Cr, Fe and N are variable.
53	B	Copper ions will be reduced at the cathode more readily than water and zinc. Water is oxidized to produce oxygen at the anode.
54	D	The key words in the alternatives 'a, b and c' are 'must have'. This makes the statements for these alternatives incorrect. Both half cells may have negative half-cell potentials and can still produce a positive E_{cell} when the half equation with the lower reduction potential is reversed.
55	A	Oxidation takes place at the anode, where copper is oxidised. Reduction takes place at the cathode, where hydrogen gas is produced.
56	C	In a dry cell, zinc is the anode and undergoes oxidation. $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ The MnO_2 paste that surrounds the carbon cathode undergoes reduction. $2MnO_2(s) + 2H^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + H_2O(l)$

57	B	NaI solution will not give O_2 at the anode, since the half reaction $2I^- \rightarrow I_2 + 2e^-$ has a more positive half-cell potential compared to water. Hence iodine will be produced at the anode.
58	B	Magnesium will be oxidised in preference to iron.
59	D	H_2O_2 is both oxidised and reduced in this reaction. Since it is oxidised this also makes it a reducing agent.
60	B	$Fe^{2+}(aq) + 2e^- \leftrightarrows Fe(s)$ $E^o = -0.44$ V $Zn^{2+}(aq) + 2e^- \leftrightarrows Zn(s)$ $E^o = -0.76$ V Fe will be reduced and Zn will be oxidised. Since Zn is oxidised electrons will flow from the zinc electrode to the iron electrode.
61	A	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^o = +0.76$ V $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^o = -0.44$ V $Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$ $E^o = +0.32$ V.
62	C	$Au^{3+}(aq) + 3e^- \leftrightarrows Au(s)$ $E^o = +1.50$ V $Ag^+(aq) + e^- \leftrightarrows Ag(s)$ $E^o = +0.80$ V Gold has a higher standard reduction potential than silver, so silver will be oxidised and displace gold from solution.
63	C	$H_3PO_2 + 2H_2O \rightarrow H_3PO_4 + 4H^+ + 4e^-$
64	D	Nickel resists corrosion so the best answer is that a thin coating prevents the iron from reacting. It excludes water and oxygen from the surface. Nickel also has a standard reduction potential higher than iron, so answer C is a correct statement, but doesn't provide a suitable answer.
65	B	The oxidant, or oxidising agent, is itself reduced. The species reduced in the equation is Cr_2O_3.
66	C	MnO_4^- has a high standard reduction potential and so is used as an oxidising agent in many situations.
67	C	The E_{cell} for equation C is +0.58V and so will occur spontaneously.
68	A	Using the E° values from the Standard Reduction Potentials at 25°C, you can calculate the E_{cell} potentials for each pair of reactants. A negative net cell potential indicates no reaction. MnO_4^- and I^- $E_{cell} = +0.97$ V Cl_2 and H_2S $E_{cell} = +1.19$ V $Cr_2O_7^{2-}$ and F^- $E_{cell} = -1.53$ V Fe^{2+} and Ni $E_{cell} = -0.20$ V Cu and HCl $E_{cell} = -0.34$ V Therefore, only the first two reactions (I and II) will occur.
69	C	Gases become less soluble at increased temperature.

Solutions to Short Answer, Written and Calculation Questions

1. (a) $2I^-(aq) + Cl_2(g) \rightarrow I_2(aq) + 2Cl^-(aq)$

   Greenish yellow gas dissolves into a clear colourless solution to produce a clear, brown solution.

   (b) $2Fe^{3+}(aq) + 3S^{2-}(aq) \rightarrow Fe_2S_3(s)$

   A pale brown solution reacts with a clear, colourless solution to produce a brown solid.

   (c) $Na_2CO_3(s) + 2CH_3COOH(aq) \rightarrow 2Na^+(aq) + 2CH_3COO^-(aq) + CO_2(g) + H_2O(l)$

   A white solid slowly dissolves in a clear, colourless, vinegar-smelling solution. A colourless, odourless gas evolves leaving a clear, colourless solution.

   (d) $Fe(s) + Pb^{2+}(aq) \rightarrow Fe^{2+}(aq) + Pb(s)$

   A grey metallic solid is added to a clear, colourless solution. A black solid forms on the surface of the solid and a clear, pale green solution is produced.

2. (a) 20 minutes

   (b) Hydrogen gas added to the system.

   (c) Temperature increase.

   (d) None, since carbon is a solid and isn't in the equilibrium constant expression.

   (e) If you halved the volume of the container the pressure of all gaseous species would increase. LCP predicts that the equilibrium will shift in the direction that decreases pressure so towards the side of the equation that has the least number of gaseous molecules. The equilibrium will shift in the forward direction.

3. (a) $K = [[Ag(NH_3)_2]^+].[Cl^-] \ / \ [NH_3]^2$

   (b)

	At new equilibrium		
Imposed change	**Effect on forward reaction rate**	**Effect on $[Ag(NH_3)_2]^+(aq)$**	**Observation**
$NH_3(g)$ is bubbled through the solution.	increase	increase	The bubbles of ammonia will dissolve into solution and the amount of white solid AgCl will decrease.
NaCl(s) is added to the solution.	increase	decrease	The sodium chloride will dissolve and the amount of white solid AgCl will increase.
A few drops of concentrated HNO_3 (aq) are added to the solution.	decrease	decrease	The amount of white solid AgCl will increase

4. (a) At equilibrium the rate of dissolution of magnesium hydroxide (the forward reaction) is the same as the rate of crystallisation (the reverse reaction) so as the magnesium hydroxide dissolves, more crystallises out of solution.

(b)

Imposed change	**Effect on solid $Mg(OH)_2$ (write 'increase', 'decrease' or 'no change')**	**Explanation**
A little concentrated sodium hydroxide solution is added to the beaker	increase	Adding hydroxide ions increases the collisions between product species so the rate of the reverse reaction increases relative to the forward reaction, the equilibrium shifts to the left and more magnesium hydroxide is produced.
Some sodium phosphate solution is added to the beaker	decrease	Magnesium ions will produce a precipitate with the phosphate ions, decreasing the collisions between product species, so the rate of the reverse reaction decreases relative to the forward reaction, the equilibrium shifts to the right and some magnesium hydroxide dissolves.
More water is added to the beaker	decrease	Adding water will decrease the concentration of the product species. This means that the rate of the reverse reaction will decrease relative to the rate of the forward reaction, the equilibrium shifts to the right and some magnesium hydroxide dissolves.

5. (a)

Change	Effect
Decreasing the temperature	Decrease
Increasing the pressure of hydrogen	Increase
Adding a catalyst	Increase

(b)

Change	Effect
Increasing the temperature	Decrease
Increasing the pressure of the system	Increase
Adding a catalyst	No change

6. (a) $K = [[Al(OH)(H_2O)_5]^{2+}].[H_3O^+] / [[Al(H_2O)_6]^{3+}]$

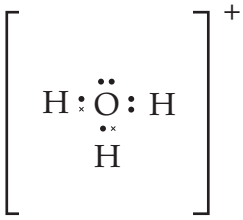
(b) (i) The pH would decrease. Adding aluminium nitrate would increase the concentration of $[Al(H_2O)_6]^{3+}$ which would increase the rate of the forward reaction relative to the rate of the reverse reaction as there will be more collisions between reactant species. The equilibrium will shift to the right, increasing the concentration of H_3O^+ and decreasing the pH.

(ii) Adding water would decrease the concentrations of all aqueous species, and if the H_3O^+ ion concentration decreases the pH goes up. This

dilution would have a greater effect on the rate of the reverse reaction, as there are more aqueous species on the product side of the equation. The rate of the reverse reaction will decrease relative to the rate of the forward reaction and the equilibrium would shift to the right. This would increase the H_3O^+ concentration, but not to its initial value as the change is only partially counteracted, so the pH will decrease to below 6 but above 5.6.

(c) Endothermic in the forward direction. A decrease in pH suggests that increasing temperature favoured the forward reaction, or an equilibrium shift to the right. Equilibrium will shift to favour the endothermic direction if the temperature is increased, as this is the direction with the larger activation energy so an increase in temperature will have a more pronounced effect. So the rate of the forward reaction will increase relative to the rate of the reverse reaction.

(d)



(e) +3, since the water is 0, the hydroxide is -1 and the complex is overall +2

Or

+2 = A*l* + (6 x O) + (11 x H)

+2 = A*l* + (-12) + (+11)

+2 = A*l* -1

A*l* = +3

7. (a) $K = [Ba^{2+}].[SO_4^{2-}]$

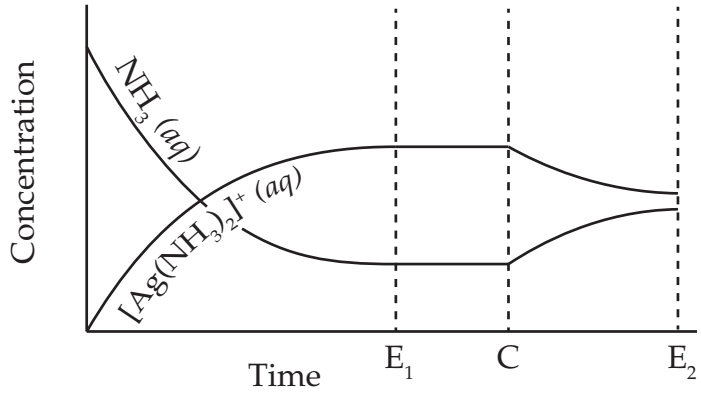
(b) $K = [Cr_2O_7^{2-}] / [CrO_4^{2-}]^2.[H^+]^2$

8.

Test tube	Change	Direction	Reason
A	3 mL water added	No change	Adding water would decrease the concentrations of all aqueous species but since there are the same number of aqueous species on both sides of the equation K remains the same so there is no shift in equilibrium
B	A few drops of concentrated nitric acid are added	right	Adding nitric acid increases the H^+ ion concentration so there will be more collisions between reactant species. The rate of the forward reaction will increase relative to the rate of the reverse reaction and the equilibrium will shift to the right to partially counteract the imposed change.
C	A few drops of concentrated silver nitrate solution are added	right	Adding Ag^+ ions will form an $AgCl$ precipitate with the Cl^- ions. This will decrease collisions between product species. The rate of the reverse reaction will decrease relative to the rate of the forward reaction and the equilibrium will shift to the right to partially counteract the imposed change.

9.

$$AgCl(s) + 2NH_3(aq) \leftrightarrows [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$



10.

Change	Change in concentration of $NH_3(g)$	Brief explanation
The volume of the reaction vessel is doubled	decrease	Increasing volume decreases the pressure of all gaseous species. Since there are a greater number of species on the product side (10 vs 9) the decrease in pressure will have a greater effect on the reverse reaction. The rate of the reverse reaction will decrease relative to the rate of the forward reaction and the equilibrium will shift to the right, decreasing the concentration of $NH_3(g)$.
The temperature of the reaction system is doubled	increase	An increase in temperature of the system favours the endothermic reverse reaction so the equilibrium will shift to the left, increasing the concentration of $NH_3(g)$.
$N_2(g)$ is injected into the reaction system while keeping the volume constant	no change	Nitrogen does not take part in the reaction and is not in the K expression. It will increase the total pressure of the system but not the partial pressures of reacting species so there is no shift in equilibrium position and no change in the concentration of $NH_3(g)$.
Water vapour is injected into the reaction system while keeping the volume constant	increase	Adding water vapour will increase collisions between product species, so the rate of the reverse reaction will increase relative to the rate of the forward reaction and the equilibrium will shift to the left, increasing the concentration of $NH_3(g)$

11 (a) Anhydrous sodium carbonate has a high molar mass, is highly soluble in water and does not absorb moisture from nor react with any gases in the air.

Sodium hydroxide is hygroscopic, which means that it absorbs moisture from the air. It also absorbs carbon dioxide from air. This makes it difficult to determine its mass and therefore calculate an accurate concentration for use as a primary standard.

(b) Sodium hydrogencarbonate dissolves to produce sodium ions and hydrogencarbonate ions. Hydrogencarbonate ions can hydrolyse with water, accepting a proton, to produce carbonic acid and hydroxide ions. The hydroxide ions increase the pH of water.

$NaHCO_3(s) \rightarrow Na^+(aq) + HCO_3^-(aq)$

$HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$

(c) The titration between sodium hydroxide (strong base) and ethanoic acid (weak acid) has an alkaline equivalence point due to the production of the alkaline salt, sodium ethanoate. This means that the equivalence point of the titration will be between pH 7 – 11. Methyl orange has a colour change between pH 3 – 5 and so is unsuitable. The ideal indicator would be phenolphthalein, whose colour change/end point would be close to the equivalence point.

12. The pH of the 0.200 mol L^{-1} HC*l* was found to be lower than the pH of the 0.100 mol L^{-1} H_2SO_4 solution. This suggests that 0.200 mol L^{-1} HC*l* has a higher concentration of H_3O^+ ions compared to the 0.100 mol L^{-1} H_2SO_4 solution.
HC*l* is monoprotic and is a strong acid, and its ionisation is complete.
$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
So a 0.200 mol L^{-1} solution of HC*l* produces 0.200 mol L^{-1} concentration of H_3O^+ ions.
H_2SO_4 is a diprotic acid and it ionises in two stages. Its first stage of ionisation is complete.
$H_2SO_4(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$
So a 0.100 mol L^{-1} solution of H_2SO_4 produces 0.100 mol L^{-1} H_3O^+ ions.
The second stage the ionisation does not go to completion.
$HSO_4^-(aq) + H_2O(l) \leftrightarrows SO_4^{2-}(aq) + H_3O^+(aq)$
So 0.100 mol L^{-1} HSO_4^- produces less than 0.100 mol L^{-1} H_3O^+ ions in solution.
Therefore, 0.100 mol L^{-1} H_2SO_4 solution produces less than 0.200 mol L^{-1} H_3O^+ ions and has a higher pH compared to a 0.200 mol L^{-1} solution of HC*l*.

13.

	Mistake 1	**Mistake 2**	**Mistake 3**
Description of mistake	Burette was rinsed with water.	Phenolphthalein was used as the indicator.	Pipette was not rinsed with the correct solution.
Effect on volume of HCl	More HCl would have been added to reach the equivalence point.	Less HCl would have been added as the end point appears early at a pH of around 9.	Less HCl would have been added.
Reason HCl volume is affected as stated above	The water in the burette has diluted the HCl and more of the HCl would be required to neutralise Na_2CO_3.	The colour change that shows the end point occurs earlier than the equivalence point.	Because less Na_2CO_3 is added to the conical flask, an equivalent, but lesser, amount of HCl would have been added.
Correct technique	Burette should have been rinsed with HCl.	Methyl orange should have been used for this strong acid – weak base titration.	The pipette should have been rinsed with Na_2CO_3 solution.

14. Like water, ammonia is able to react with itself, in the process known as 'self-ionisation'. The equation for the self-ionisation of ammonia is below.

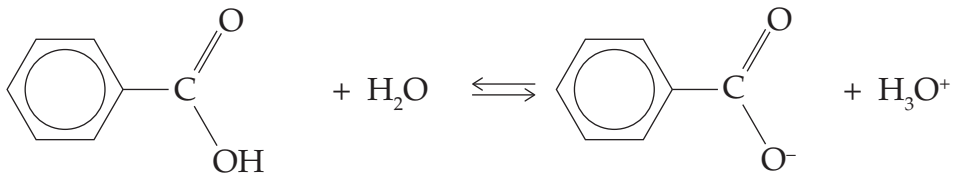
$NH_3(aq) + NH_3(aq) \leftrightarrows NH_4^+(aq) + NH_2^-(aq)$

(a) Identify the conjugate acid and base pairs in the reaction.

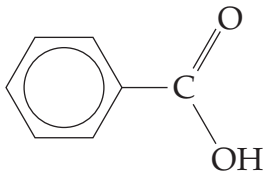
$NH_3(aq)$	+	$NH_3(aq)$	$\leftrightarrows$	$NH_4^+(aq)$	+	$NH_2^-(aq)$
base		acid		conjugate acid		conjugate base

(b) Since the reaction is endothermic an increase in temperature will cause the equilibrium to shift in the forward direction, so the K value will increase. So greater than 1×10^{-30}.

15. (a)



(b) In an acidic environment in the stomach the H_3O^+ ions will shift the equilibrium in the reverse direction, so the predominant species would be the benzoic acid molecule:



(c) Benzoic acid and benzoate ion can exist as a buffer system as they are a weak acid-conjugate base pair. The buffer can resist a change in pH by reacting with both OH^- ions and H_3O^+ ions as shown in the equations below:

Reaction with H_3O^+ ions: $H_3O^+ + C_6H_5COO^- \leftrightarrows H_2O + C_6H_5COOH$

Reaction with OH^- ions: $OH^- + C_6H_5COOH \leftrightarrows H_2O + C_6H_5COO^-$

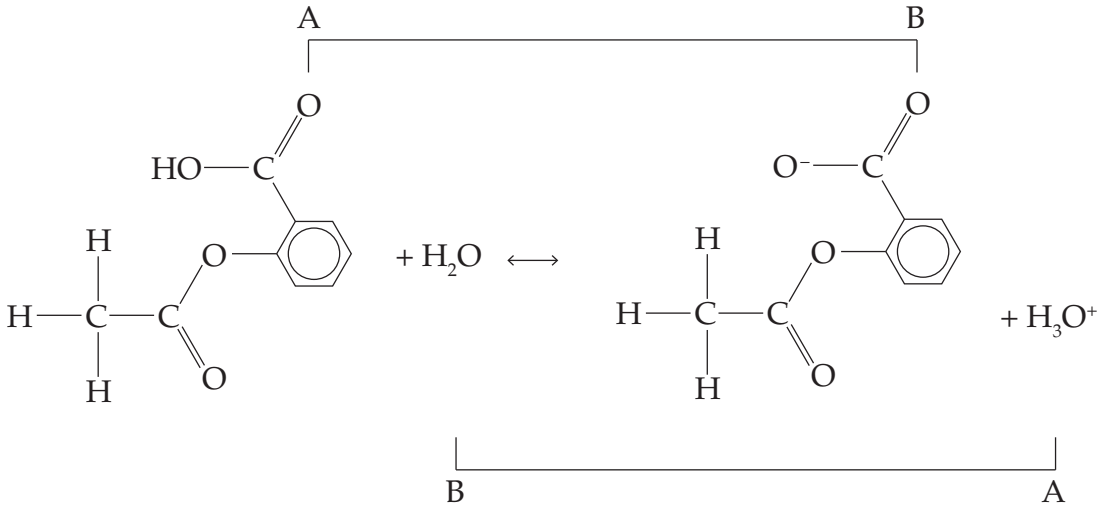
(d) Acetic acid, CH_3COOH has a small non-polar end ($–CH_3$) and a polar end (–COOH.) Though the $–CH_3$ end repels water, the dominant –COOH end readily dissolves in water as it can form hydrogen bonds with water molecules. This makes acetic acid more miscible with water and excreted from the body via water.

Benzoic acid is a larger molecule than acetic acid and whilst it has a –COOH at one end which could form hydrogen bonds with water it has a dominant large non-polar benzene ring which resists miscibility with water. This prevents it from being excreted with water from the body as easily as acetic acid.

16. Write a relevant equation or equations to explain each of the observations shown in the table below.

Observation	Explanatory equation(s)
The pH of a $NaHSO_4$ solution is 5	$HSO_4^- + H_2O \leftrightarrows SO_4^{2-} + H_3O^+$
$Mg(OH)_2$ is basic	$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$
A solution of Na_2HPO_4 is basic, while a solution of KH_2PO_4 is acidic	$HPO_4^{2-} + H_2O \leftrightarrows H_2PO_4^- + OH^-$ $H_2PO_4^- + H_2O \leftrightarrows HPO_4^{2-} + H_3O^+$

17. (a)



(b) Acetylsalicylic acid has a long non-polar part which reduces its solubility in water to some extent even though it has a hydrogen-bonding site. CH_3COOH on the other hand is polar and, has a hydrogen bonding site with a small non-polar chain and dipole-dipole bonding capacity. It is more soluble in water because the solute-solvent interactions are stronger than the interaction between the solute particles and the interaction between the solvent particles. Acetylsalicylic acid also has a high molar mass increasing the dispersion forces with non-polar solvents compared to polar solvents.

18. (a) The reactions for the self-ionisation of water can be represented by this equation:

$2H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$

b) at 25°C: $[H^+] = 1.0 \times 10^{-7}$ mol L^{-1} ; $[OH^-] = 1.0 \times 10^{-7}$ mol L^{-1}

Therefore, $[H^+] = [OH^-]$
at 10°C: $[H^+] = 5.39 \times 10^{-8}$ mol L^{-1} ; $[OH^-] = 5.39 \times 10^{-8}$ mol L^{-1}
Therefore, $[H^+] = [OH^-]$

c) At 10°C, the concentrations of H^+ and OH^- are 5.39×10^{-8} mol L^{-1} each whereas as 25°C, the concentrations are 1.0×10^{-7} mol L^{-1} each. This indicates that water ionises more at a higher temperature. So as temperature increases, the extent of ionisation increases favouring the products. Therefore, the self-ionisation of water is an endothermic process.

19. (a)

i) It has a relatively high molar mass enabling a greater accuracy in determining concentrations.

ii) It is highly soluble and is obtained with a high degree of purity.

iii) It does not absorb moisture and does not react with any gases in the air when exposed and therefore maintains a stable concentration.

(b)

i) Calculate the mass required to prepare a 500.0 mL solution of Oxalic acid ($H_2C_2O_4.2H_2O$)
n (acid) = c × v = 0.05 × 0.500 = 0.0250 mol
m (acid) = n × M = 0.0250 × 126.048 = 3.1512 g

ii) Weigh out accurately, approximately 3.15 g of oxalic acid powder in a filter paper. Record the accurate mass.

iii) Recalculate the concentration to be prepared using the accurate mass.
n = (3.15 / 126.048) = 0.0250 mol
c (Acid) = (0.0250 mol / 0.500 L) = 0.050 mol L^{-1}

iv) Transfer the powder into a 50.0 mL beaker, washing the paper a few times to remove all the solid particles of the acid into the beaker. Stir the mixture in the beaker.

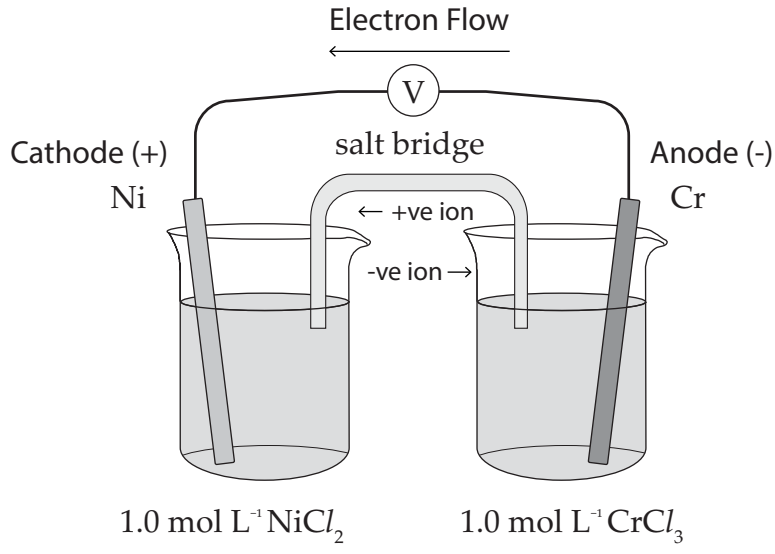
v) Transfer the solution into a 500.0 mL volumetric flask which is clean and dry. Wash the beaker with some distilled water a few times and transfer all the washings into the flask.

vi) Nearly half-fill the volumetric flask with distilled water. Close the lid tightly and invert the flask a few times to make sure that all the solid dissolves.

vii) After the bubbles disappear, fill the flask up to the mark in the neck of the flask with a dropping pipette until the lower level of the concave meniscus is level with the mark on the neck.

viii) Transfer the standard oxalic acid solution into a reagent bottle and label the bottle with the concentration and the date prepared.

20. (a)



(b) The half reactions and the overall equation in the cell

Anode reaction: $2Cr(s) \rightarrow 2Cr^{3+}(aq) + 6e^-$ $E^o = +0.74$ V

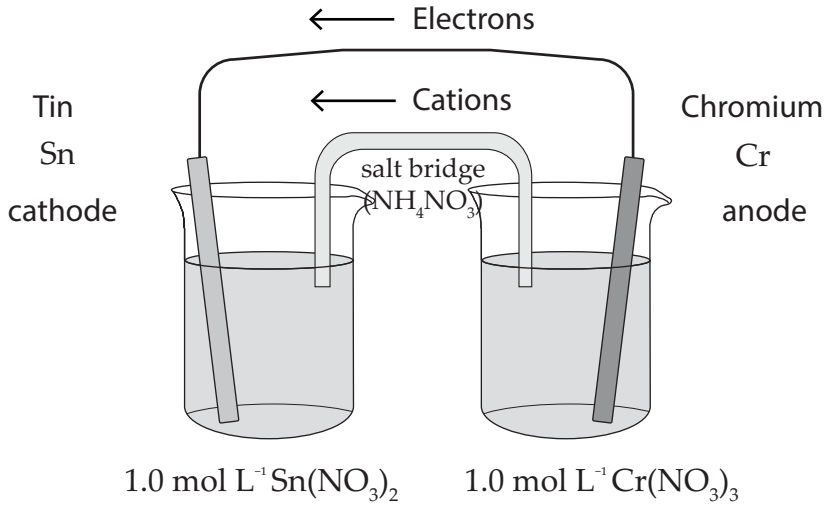
Cathode reaction: $3Ni^{2+}(aq) + 6e^- \rightarrow 3Ni(s)$ $E^o = -0.24$ V

Redox reaction: $2Cr(s) + 3Ni^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Ni(s)$

(c) EMF = 0.74 + (-0.24) = 0.50 V

(d) Potassium carbonate is unsuitable as a salt in the salt bridge, as carbonate ions will form precipitates with Cr^{3+} ions and Ni^{2+} ions. Ionic concentrations will substantially decrease, the salt bridge will be clogged and the migration of ions will be blocked.

21. (a)



(b) Anode and cathode reactions:

Anode: $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$

Cathode: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

(c) As the reaction proceeds, the ions are used up and their concentrations fall which decreases the cell voltage. The cell emf is a function of the electrolyte concentrations.

(d) If the anode and the cathode come into contact, electrons will transfer directly from the anode to cathode rather than flowing through the external circuit.

22. (a)

Anode half-equation: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$
Cathode half-equation: $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$
Overall equation: $Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

(b) The potassium hydroxide electrolyte allows for the migration of ions and thus completes the circuit through the electrolyte.

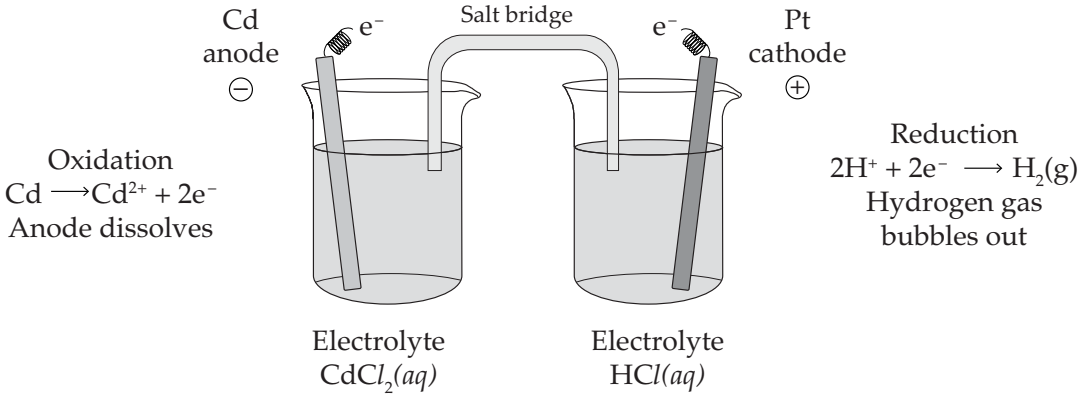
(c) The voltage of an electrochemical cell is the difference in the reduction potentials for the two half-cells making up the cell. A measure of the reduction potential for a half-cell can only be obtained by joining it with a common reference couple. The selected reference is the H^+/H_2 couple. For this reference half-cell, a E° value of 0.00 V is assigned. The standard reduction potentials for other half cells are obtained by measuring the total cell voltage when attached to a standard hydrogen half-cell. Compared to

hydrogen, cadmium has a greater tendency to oxidise, indicated by its half-cell potential, –0.40 V. When a cadmium half-cell is connected to a hydrogen half-cell, cadmium is oxidised and hydrogen is reduced and the voltmeter reading (at standard conditions of 25°C, 1molL^{-1} concentrations and 1 atmosphere pressure) will be 0.40 V. This cell voltage is due to the following half reactions.

Oxidation of cadmium:	$Cd \leftrightarrows Cd^{2+} + 2e^-$	$E^o = 0.40$ V
Reduction of hydrogen:	$2H^+ + 2e^- \leftrightarrows H_2$	$E^o = 0.00$ V
Redox reaction:	$Cd + 2H^+ \leftrightarrows Cd^{2+} + H_2$	$E_{cell} = 0.40$ V

While the half-cell or reduction potential for cadmium is –0.40 V, the cell potential when coupled with a hydrogen half-cell is +0.40 V.

A cadmium-hydrogen cell



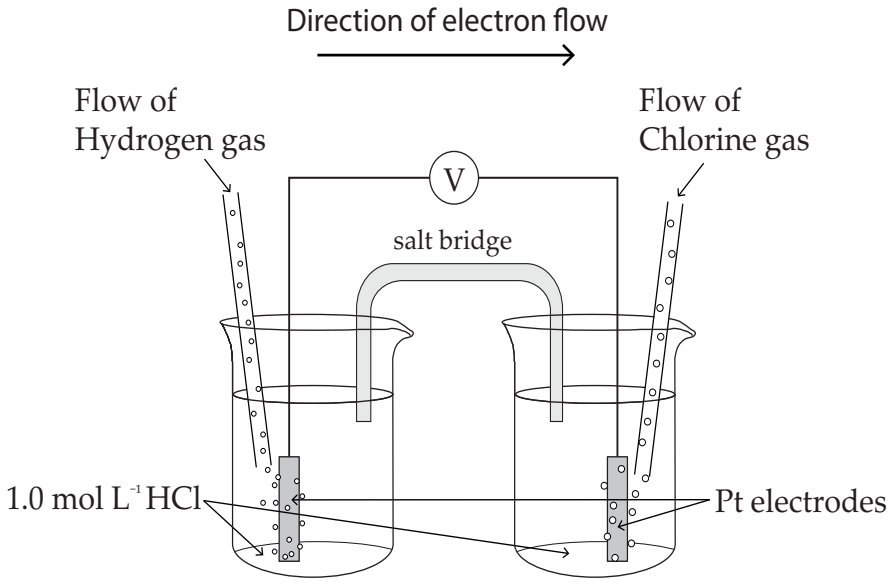
23. (a)

Anode half-equation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$
Cathode half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
Overall equation: $H_2(g) + Cl_2(g) \rightarrow 2H^+(aq) + 2Cl^-(aq)$

(b)

$H_2(g) \leftrightarrows 2H^+(aq) + 2e^-$	$E^o = 0.00V$
$Cl_2(g) + 2e^- \leftrightarrows 2Cl^-(aq)$	$E^o = 1.36V$
$H_2(g) + Cl_2(g) \leftrightarrows 2H^+(aq) + 2Cl^-(aq)$	$E_{cell} = 1.36V$

(c)



(d) Platinum is chosen for the electrode material as it is inert and will not take part in the reaction.

24. (a) Oxidation half-equation: $Mn^{2+}(aq) + 4H_2O(l) \leftrightarrows MnO_4^-(aq) + 8H^+(aq) + 5e^-$

Reduction half-equation: $BiO_3^-(aq) + 6H^+(aq) + 2e^- \leftrightarrows Bi^{3+}(aq) + 3H_2O(l)$

Redox equation:

$2Mn^{2+}(aq) + 14H^+(aq) + 5BiO_3^-(aq) \leftrightarrows 2MnO_4^-(aq) + 5Bi^{3+}(aq) + 7H_2O(l)$

(b) Concentrated HC*l* is not used to acidify permanganate or dichromate as the chloride ion will be oxidised in preference to the intended species. Sulfuric acid is used instead, as the sulfate ion is not able to be oxidised further.

25. (a)

$$[H^+] = 1.00 \times 10^{-14} / [OH^-]$$
$$= 1.00 \times 10^{-14} / 0.4161$$
$$= 2.4032 \times 10^{-14}$$

$$pH = -\log[H^+]$$
$$= -\log(2.4032 \times 10^{-14})$$
$$= 13.6$$

(b)

$$n(H^+)_{\text{bottle A}} = cV$$
$$= 0.010 \times 0.0465$$
$$= 0.000465 \text{ mol}$$

$$n(H^+)_{\text{bottle B}} = cV$$
$$= 0.0555 \times 0.0657$$
$$= 0.00364635 \text{ mol}$$

$$n(H^+)_{\text{total}} = 0.000465 + 0.00364635$$
$$= 0.00411135 \text{ mol}$$

$$n(OH^-)_{\text{bottle C}} = cV$$

$= 0.4161 \times 0.0209$

$= 0.00869649$ mol

$n(OH^-)_{final} = n(OH^-)_{initial} - n(OH^-)_{reacted\ with\ H+}$

$= 0.00458299$ mol

$[OH^-] = n(OH^-) / \text{total volume}$

$= 0.00458299 / (0.0465 + 0.0657 + 0.0209)$

$= 0.034432682\ molL^{-1}$

$[H^+] = 1.00 \times 10^{-14} / 0.034432682$

$= 2.904217552 \times 10^{-13}\ molL^{-1}$

$pH = -\log[H^+]$

$= -\log(2.904217552 \times 10^{-13})$

$= 12.5$

26.

(a) $H_2C_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$

(b)

Titration Results	Trials (mL)			
	1	2	3	4
Final volume	32.05	32.10	31.11	33.25
Initial volume	0.50	2.45	1.40	3.65
Titre	31.55	29.65	29.71	29.60

(c)

average titre $= (29.65 + 29.71 + 29.60) / 3$

$= 29.65$ mL

$n(NaOH) = cV$

$= 0.115 \times 0.02965$

$= 0.003410133$ mol

$n(H_2C_2O_4) = ½ \times n(NaOH)$

$= 0.001705066$ mol

$c(H_2C_2O_4) = n / V$

$= 0.001705066 / 0.020$

$= 0.085253333\ molL^{-1}$

(d)

$n(H_2C_2O_4)_{in\ 20mL} = 0.001705066$ mol

$n(H_2C_2O_4)_{in\ 250mL} = 250/20 \times 0.001705066$ mol

$= 0.021313325$ mol

$m(H_2C_2O_4) = n \times M(H_2C_2O_4)$

$= 0.021313325 \times 90.036$

$= 1.91896653$ g

% purity $= 1.91896653 / 2.05 \times 100$

$= 93.6\ \%$

(e) Since the reaction is that of a weak acid versus a strong base and the salt produced, $Na_2C_2O_4$, is a basic salt the equivalence point of the reaction will have an alkaline pH. An indicator must be chosen so that the end point coincides with the alkaline equivalence point. Phenolphthalein is a suitable indicator as it changes colour in the region pH 8 – 10.

27. (a)

Burette readings (mL)	Titrations			
	1	2	3	4
Final volume	32.50	37.25	43.15	38.40
Initial volume	0.00	5.50	11.30	6.60
Titre	32.50	31.75	31.85	31.80

average titre = (31.75 + 31.85 + 31.80) / 3
= 31.80 mL

(b) This is a back titration. We can determine the moles of HC*l* that reacted with the calamine by titrating to find the moles of HC*l* remaining after the sample was added to the excess initial HC*l*, then subtracting that from the initial HC*l*.

$n(NaOH) = cV$
$= 0.105 \times 0.03180$
$= 0.003339$ mol

$n(HCl)_{\text{in 25mL aliquots}} = n(NaOH)$
$= 0.003339$ mol

$n(HCl)_{\text{in 250m L}} = 250/25 \times 0.003339$ mol
$= 0.03339$ mol

$n(HCl)_{\text{initial}} = cV$
$= 2.00 \times 0.050$
$= 0.100$ mol

$n(HCl)_{\text{reacted}} = n(HCl)_{\text{initial}} - n(HCl)_{\text{in 250mL}}$
$= 0.100 - 0.03339$
$= 0.06661$ mol

(c) $ZnCO_3 + 2HCl \rightarrow ZnCl_2 + H_2O + CO_2$

$n(ZnCO_3) = ½ \times n(HCl)$
$= 0.033305$ mol

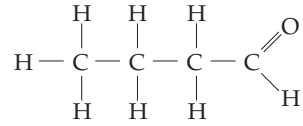
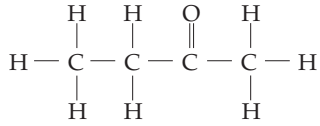
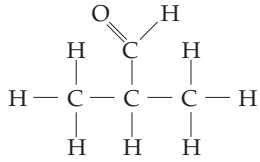
$m(ZnCO_3) = n \times M(ZnCO_3)$
$= 0.033305 \times 125.39$
$= 4.176$ g

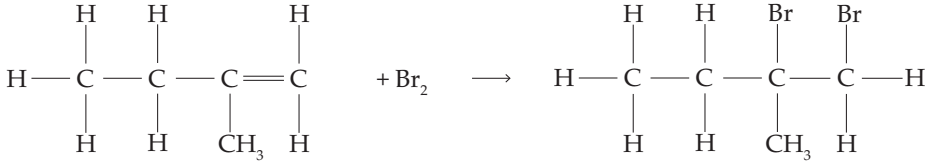
% purity $= 4.176 / 4.54 \times 100$
$= 91.98$ %
$= 92.0$ % (3sf)

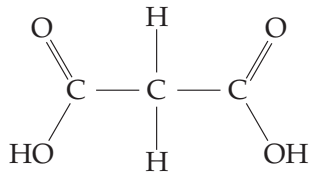
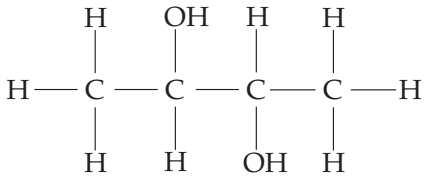
Unit 4 Examination Questions

HYDROCARBONS AND CHEMICAL SYNTHESIS

Solutions to multiple-choice questions

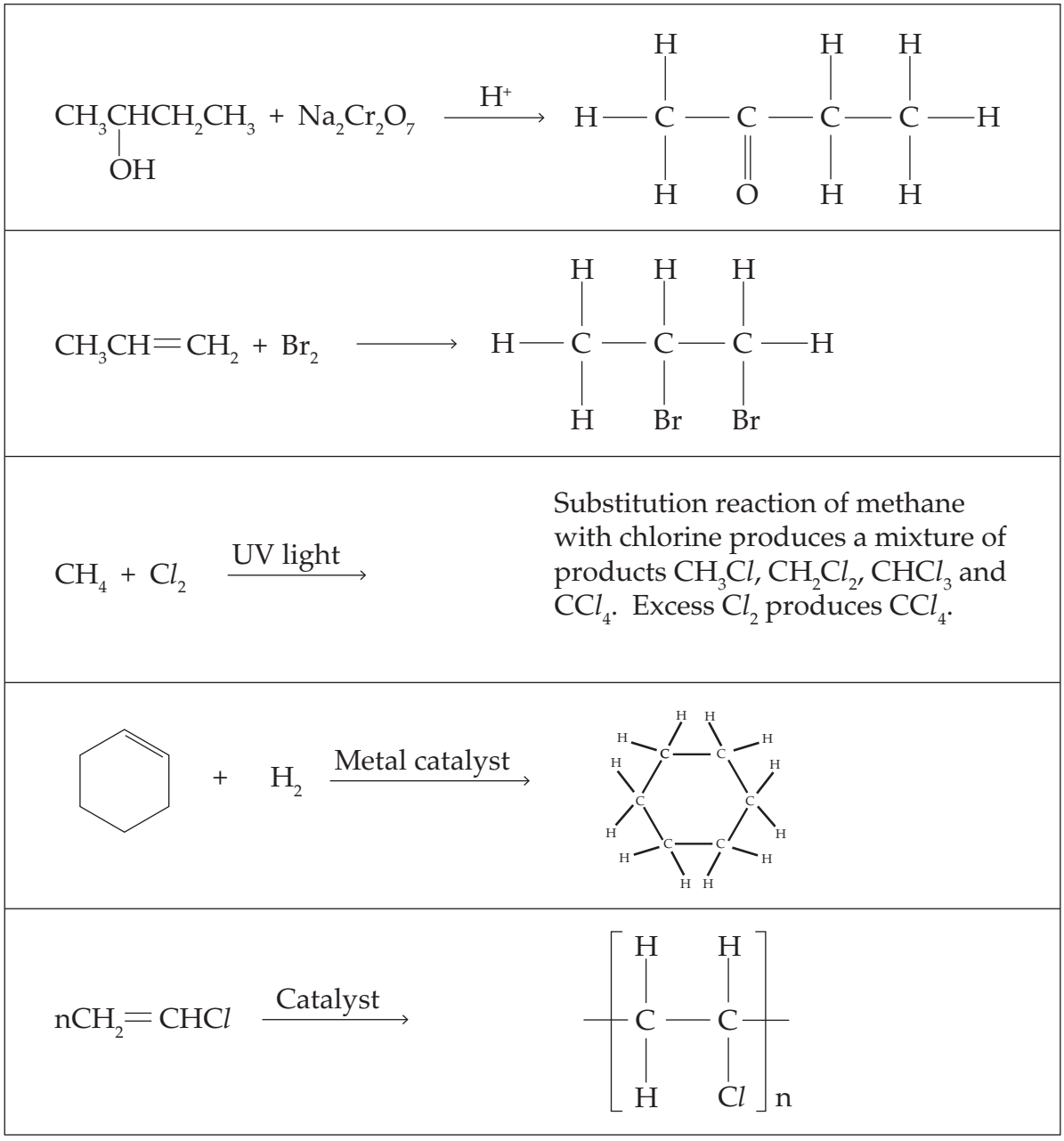
1	B	Butanoic acid is the answer. Since it is the end product of oxidation, it does not react with potassium dichromate solution. As an acid, it reacts vigorously with sodium metal liberating hydrogen gas. It also undergoes esterification with ethanol to produce a fruity smelling ethyl butanoate.
2	A	Adding a base will neutralise the hydronium ion and so the equilibrium will shift to the right, increasing the ethanoate ion concentration. Adding an acid will send the equilibrium to the left decreasing the ethanoate ion concentration. Adding water will decrease all concentrations. The equilibrium will shift but only partially counteract the imposed dilution.
3	B	Butanal  Butanone  Methylpropanal 
4	A	In addition reactions only one product is produced, so III and IV are addition reactions.
5	B	M(EF) = 12.01 + 1.008 + (2 x 16.00) = 45.018 g mol^{-1} M(MF) = m / n 9.00 / 0.100 = 90 g mol^{-1} So MF is 2x EF, or $C_2H_2O_4$
6	C	In A and D the double bonds are *trans*, and in B you can't tell as the semi structural formula doesn't show the shape. C is clearly *cis* as the carbon chain doesn't cross the double bond.
7	C	Propan-1-ol can be oxidised to propanal, and then to propanoic acid. It can also undergo combustion to produce CO_2. Combustion is also oxidation. So I, II, IV.
8	D	A is a ketone, B is an aldehyde, C is a carboxylic acid and D is an alcohol. Esters are formed from a carboxylic acid and an alcohol, so C & D.
9	A	Compound A has 4 carbon, 8 hydrogen and 1 oxygen. Compound B has 4 carbon, 8 hydrogen and 1 oxygen. Compound C has 4 carbon, 8 hydrogen and 2 oxygen. Compound D has 4 carbon, 10 hydrogen and 1 oxygen. Therefore, compounds A and B are isomers.
10	D	Both the carboxylic acid (C) and the primary alcohol (D) will react with sodium giving hydrogen gas.
11	C	The molecular formulae of each of these compounds are: ethanal (C_2H_4O); Propyl methanoate ($C_4H_8O_2$); ethanol (C_2H_5OH) and butanoic acid ($C_4H_8O_2$). The corresponding empirical formulae are C_2H_4O, C_2H_4O, C_2H_5OH and C_2H_4O. Ethanol is the odd one out.

12	D	I has dispersion forces only. II has hydrogen bonding and dispersion forces. III has dipole-dipole interactions and dispersion forces IV has hydrogen bonding and larger dispersion forces than II as it has a higher molar mass. So I < III < II < IV
13	C	The monomer must contain a carbon to carbon double bond to form an addition polymer, and it can be seen that the benzene ring is repeated for every second carbon.
14	A	$CH_3CHCHCH_3 + Br_2 \rightarrow CH_3CHBrHBrCH_3$
15	D	I and IV won't exhibit cis/trans isomerism as they have two of the same groups attached to a double bonded carbon. III isn't a valid compound as the double bonded carbons only have three bonds each. So the answer is II.
16	B	$CH_3(CH_2)_4CH_3$ is non-polar and hence has the lowest solubility in water. The remaining molecules are all polar and their polarity increases in order from $CH_3(CH_2)_3CHO$, $CH_3(CH_2)_4OH$, $CH_3(CH_2)_3COOH$. The order of increasing solubility in water is the order of increasing polarity.
17	A	The carboxylic acid (I) and the alcohol (II) could react to form an ester.
18	C	α-amino acids have both a carboxylic acid group -COOH and an amine group NH_2 attached to the same carbon atom. The α-carbon atom.
19	C	$CH_3CHCHCH_3 + HCl \rightarrow CH_3CH_2CHClCH_3$
20	B	$CH_3CHCHCH_3 + Cl_2 \rightarrow CH_3CHClCHClCH_3$
21	D	Ester, carboxylic acid, ketone, aldehyde
22	D	propan-1-ol can be oxidised to both propanal (IV) and propanoic acid (II)
23	A	B and D are addition reactions, C is an esterification. A is a substitution reaction.
24	C	(i) and (iv) are cis-trans isomers of each other.
25	D	$2C_5H_{10} + 15O_2 \rightarrow 10CO_2 + 10H_2O$ so $n(O_2) = 15/2 \times 1 = 7.5$ mol
26	A	 $CH_3CH_2C(CH_3)BrCH_2Br$
27	C	A is a primary alcohol, B is an aldehyde, C is secondary alcohol, D is a tertiary alcohol. Secondary alcohols form ketones so the answer is C.
28	D	Aldehyde, ketone, carboxylic acid, ester
29	B	Compound II, pentan-2-one has the carbonyl group on the second carbon, so we need a secondary alcohol with the hydroxy group on the second carbon, pentan-2-ol. This is B.
30	C	Carboxylic acids react with alcohols in the presence of an acid to produce esters. Compound III is a carboxylic acid.
31	D	All are correct. Iodine can undergo an addition reaction with the compound. 1 mole of Cl_2 will undergo an addition reaction with 1 mol of the compound. Following this any further Cl_2 can undergo substitution reactions with the compound. It is named correctly as cis-pent-2-ene. It is non-polar, and so will be soluble in non-polar solvents like hexane.
32	B	Ethane and ethene are non-polar and have dispersion forces only. Ethanal is polar and has dipole-dipole interactions and dispersion forces. Ethanol has an oxygen atom directly bonded to a hydrogen atom and so does show hydrogen bonding, as well as dispersion forces.

33	D	The polymer is a polyester, and so it is produced by condensation of a dicarboxylic acid and a diol. The dicarboxylic acid is $HOOCCH_2COOH$ and the diol is $CH_3CH(OH)CH(OH)CH_3$.  
34	D	Amino acids contain an amine group and a carboxylic acid group.
35	B	Step 1 is the hydration of ethene with water to form ethanol (A). It is an addition reaction. Step 2 is the oxidation of ethanol (A) to ethanoic acid (B). Step 3 is where the ethanol (A) and ethanoic acid (B) undergo esterification.
36	B	Esterase is a catalyst so decreases the E_a of both the forward and reverse reactions. It increases the rates of the forward and reverse reactions equally and has no effect on the position of equilibrium.
37	C	(a), (b) and (d) would cause the equilibrium to shift in the reverse direction decreasing the concentration of SO_3. Since it is an exothermic reaction decreasing the temperature would result in a shift in the forward direction and increase the concentration of SO_3.
38	A	Catalysts increase the rates of both the forward and reverse reaction equally. They do not affect yield and so the yield of ammonia will remain constant.
39	C	Ethanol by fermentation requires a biological catalyst and so is carried out at relatively low temperatures. Hydration of ethene with steam (100^oC) is an addition reaction and requires heat and pressure.
40	B	Bond A is hydrogen bonding between the C=O and the N-H of neighboring peptide links on a protein chain. These form alpha helices and beta pleated sheets and so contribute to the secondary structure of proteins. Bond B is a covalently bonded disulfide bridge between R groups of cysteine amino acid residues which contributes to the tertiary structure of proteins. Bond C is the amide or peptide link where amino acid residues join up to form the primary structure of proteins. So secondary, tertiary, primary.
41	D	Soaps aren't polymers and aren't naturally coloured and fragrant. The long chain is hydrophobic and the charged part is hydrophilic. So (a), (b) and (c) are incorrect. Soaps are produced by the base hydrolysis of triglyceride esters.
42	C	The stearate ion has a polar section ($-COO^-$) which can bond with water and a non-polar end ($CH_3(CH_2)_{16}$) which can bond with grease, enabling it to be washed away.

Solutions to Short Answer, Written and Calculation Questions

1.

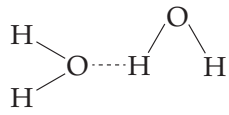


2.

Test	Observations
Add acidified $KMnO_4$ solution to both	Solution A changes colour from purple to colourless. There is no change for Solution B.
Add acidified $K_2Cr_2O_7$ solution to both.	Solution A changes colour from orange to green. There is no change for Solution B.
Add a small piece of potassium to both.	Solution A will show a very vigorous reaction producing a colourless, odourless gas. Solution B will show a much slower rate of reaction.
Add a small piece of sodium metal to both.	A will show a vigorous reaction. B will show a much slower rate of reaction.

3. (a) Intramolecular forces are the strong covalent bonds within molecules. A covalent bond is the electrostatic attraction between shared electrons and the nuclei of adjacent atoms.

Intermolecular forces are between molecules. They are responsible for their boiling and melting points. Hydrogen bonding is the strongest and exists between molecules containing a group where hydrogen is covalently bonded to an O, N or F atom. Dipole–dipole forces exist between polar covalent molecules and are about one-tenth as strong as a Hydrogen bond for substances of similar mass. Dispersion forces are the weakest intermolecular force and exist between non-polar molecules. They are about one-tenth as strong as dipole–dipole forces. However, the strength of the dispersion forces increases as the molecular mass increases.

Dispersion forces	Dipole–dipole forces	Hydrogen bonding
$H^+ — H^- - - - - H^+ — H^-$	$H^+ — Cl^- - - - - H^+ — Cl^-$	
Between hydrogen molecules	Between HC*l* molecules	Between water molecules
A Weakest	B Intermediate strength	C Strongest

(b) The boiling points of covalent molecular substances are determined by the type of intermolecular forces that exist between them. Propanone molecules are polar molecules, with the –C=O carbonyl group contributing to the dipole-dipole forces between the molecules. In propan-2-ol, which contains the hydroxy group -OH, hydrogen bonding is the predominant intermolecular force between the molecules. Hydrogen bonding intermolecular forces are about ten times as strong as the dipole–dipole forces and so propanone has a lower boiling point compared to propan-2-ol.

4.

Substances	Chemical Test	Expected observations
Cyclohexane (C_6H_{12}) and Cyclohexene (C_6H_{10})	Add acidified $KMnO_4$ solutions to each. Add bromine water to each.	No immediate change with C_6H_{12}. But, C_6H_{10} will decolourise the purple colour of $KMnO_4$ as well as the reddish-brown colour of the bromine water.
1 M H_2SO_4 solution and 1 M HC*l* solution	Add BaCl_2 or $Ba(OH)_2$ solutions to each.	With H_2SO_4, a white precipitate is produced with both the solutions. With HC*l*, there is no visible reaction with either solution.
Propanone, (CH_3COCH_3) and Propanal, (CH_3CH_2CHO)	Add a few drops of acidified $KMnO_4$ or $K_2Cr_2O_7$ solutions to each.	With Propanone, neither solution appears to have any change. With propanal, $KMnO_4$ decolourises and $K_2Cr_2O_7$ turns green.

5. C, since the methanol molecules have the hydroxy group with a hydrogen atom covalently bonded to an oxygen atom. The hydrogen bond exists between the hydrogen atom on one hydroxy group and the oxygen atom on the other.

6.

Temperature (^oC)	**Phase**				**Shift in equilibrium (right, left or no change)**
	CH_3OH	**HC*l***	**CH_3Cl**	**H_2O**	
-50	L	G	L	S	Right
40	L	G	G	L	No change
70	G	G	G	L	Right
110	G	G	G	G	No change

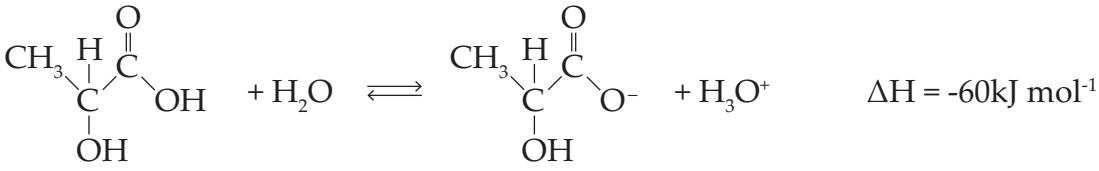
7.

Substances to be distinguished		**Description of chemical test**	**Observation with Substance 1**	**Observation with Substance 2**
Substance 1	**Substance 2**			
1. Butan-2-ol	2. 2-methylpropan-2-ol	Add acidified $KMnO_4$ or, acidified $K_2Cr_2O_7$ to each.	The purple $KMnO_4$ is decolourised. The orange $K_2Cr_2O_7$ turns green.	There is no observable colour change for either test.
1. Zinc nitrate solution	2. Zinc Sulphate solution	Add $Ba(NO_3)_2$ solution to each, or, $Pb(NO_3)_2$ solution to each, or, $AgNO_3$ solution to each.	There is no observable change	A white precipitate is formed in all cases.
1. Solid magnesium hydroxide	2. Solid lead sulfate	Add a few drops of dilute HC*l*, or H_2SO_4, or HNO_3 to each.	The solid dissolves in each of these dilute acids.	The solid does not dissolve and there is no observable change.
1. Methanol	2. Methanal	Add a few drops of acidified ethanoic acid to each, or, add a piece of sodium metal to each.	With the acid, a substance of fruity odour is produced. With sodium a vigorous evolution of a colourless gas occurs	No observable change occurs with either ethanoic acid or with the sodium metal.

8.

Conjugate base	Species X	Conjugate acid
CH_3NH^-	CH_3NH_2	$CH_3NH_3^+$ (supplied)
$C_2O_4^{2-}$ (supplied)	$HC_2O_4^-$	$H_2C_2O_4$
$^-OOCCHOHCHOHCOO^-$	$HOOCCHOHCHOHCOO^-$ (supplied)	HOOCCHOHCHOHCOOH

9.



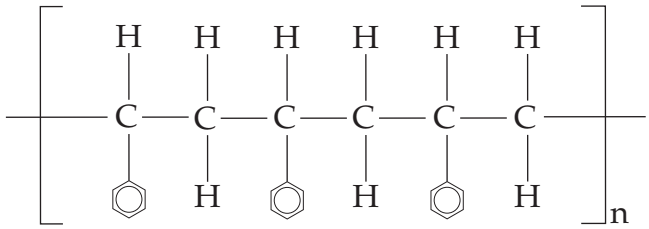
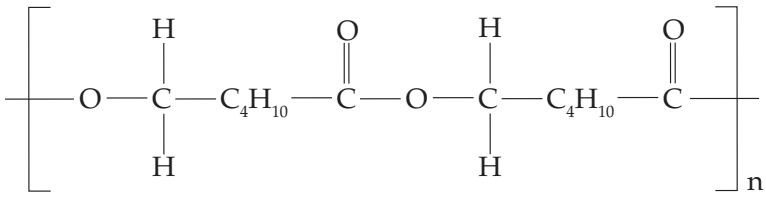
(a) Since the equilibrium constant is far less than one, the ratio of the organic products to organic reactants is less than one.

(b)

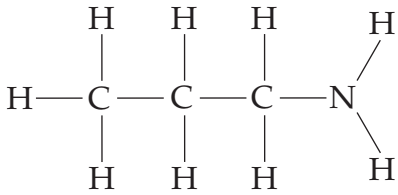
Change	Direction of initial equilibrium shift
Decreasing the temperature	To the right. (As this is an exothermic reaction, a decrease in temperature increases the yield while decreasing the rate.
Adding hydrochloric acid	To the left. (Adding H^+ ions increases the concentration of one of the products which shifts the equilibrium to the left decreasing the yield of the reaction as written).
Adding sodium hydroxide	To the right. (The added OH^- ions react with H_3O^+ ions and decrease in concentration. Hence the equilibrium shifts to the right to increase the yield of the reaction as written).

10. Menthone has dipole-dipole forces between its molecules in addition to weak dispersion forces. Menthol has hydrogen bonding between its molecules in addition to weak dispersion forces. Hydrogen bonding is considerably stronger than dipole-dipole forces. It therefore requires more energy to break the hydrogen bonds between menthol molecules and hence it has a higher melting point.

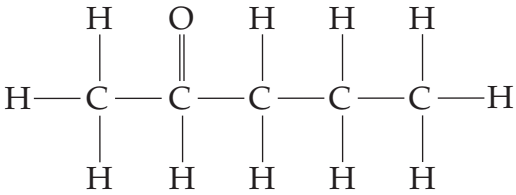
11.

Addition polymer	
Condensation polymer	

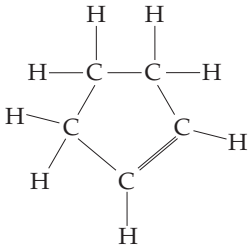
12. (a) 1-propanamine



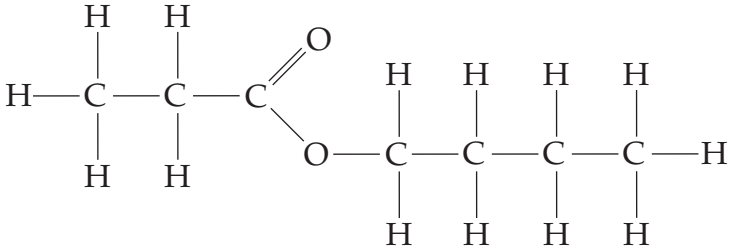
(b) pentan-2-one



(c) cyclopentene

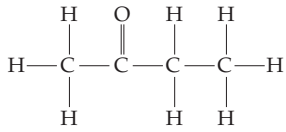


(d) butyl propanoate

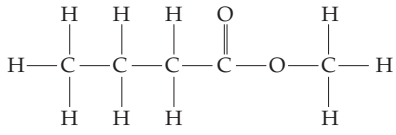


13.

(a)

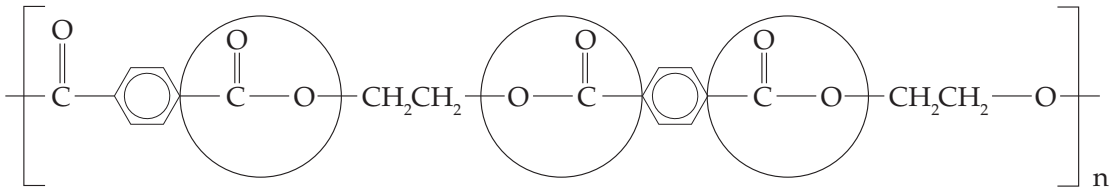
Observations	The orange colour fades and the solution turns blue
Structural formula of organic product (show all atoms)	$CH_3COCH_2CH_3$ 
Name of organic product	butanone

(b)

Observation	A fruity or sweet smell is produced
Structural formula of organic product (show all atoms)	$CH_3CH_2CH_2COOCH_3$ 
Name of organic product	methylbutanoate

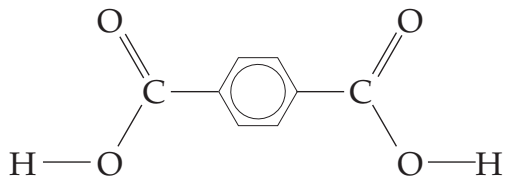
14.

(a)



(b)

Monomer A



1,4-dicarboxyl benzene

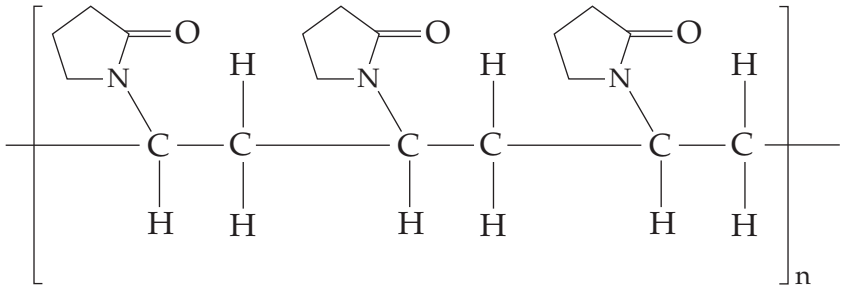
Monomer B

$HO — CH_2CH_2 — OH$

ethane-1,2-diol

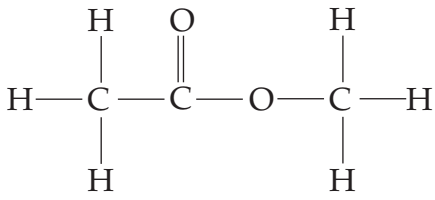
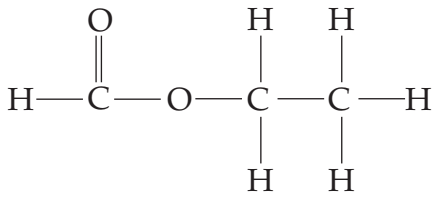
15. (a)

A polymer chain of 3 monomer units

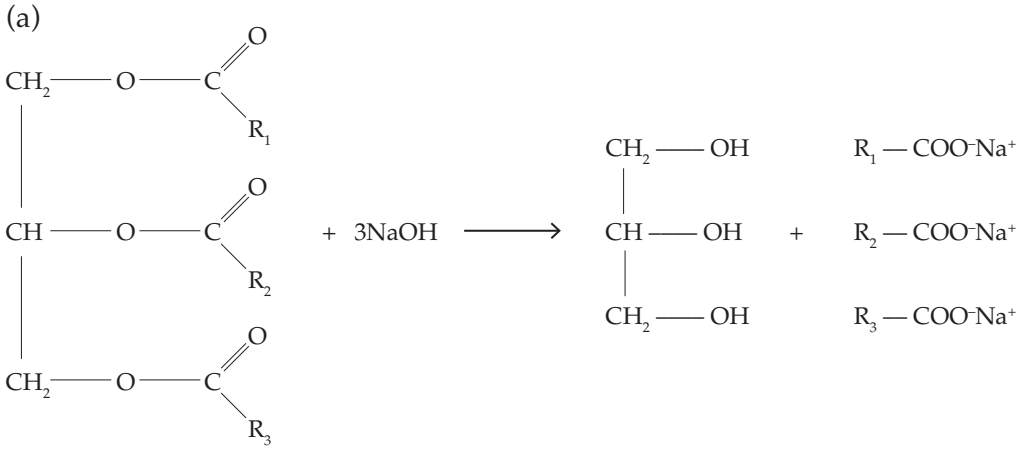


(b) The type of polymerisation reaction that occurs to form this polymer is **addition polymerisation**.

16. (a) & (b) There are two possible esters with a molar mass of 74 $gmol^{-1}$

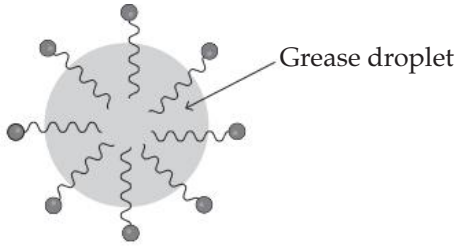
Methyl ethanoate	Ethyl methanoate
	

17. (a)



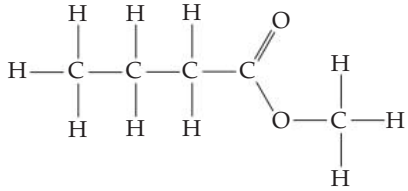
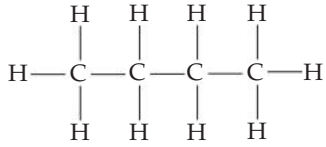
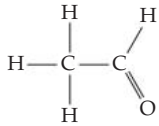
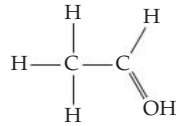
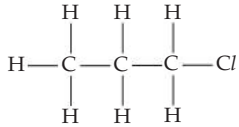
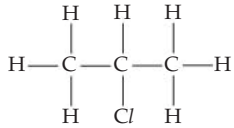
Triglyceride (fat or oil) + sodium hydroxide ⟶ glycerol + 3 soap molecules

(b) Soap is a surfactant or wetting agent. It enables water to wash away grease and dirt. Grease is non-polar and does not dissolve in water. Once soaps dissolve they have a hydrophobic non-polar, hydrocarbon end which will bond with grease through dispersion forces, and a hydrophilic, polar charged end which will bond with water through hydrogen bonding. On agitation in water, the surfactant molecules can surround small droplets of grease forming micelles. The hydrophobic end dissolves in the oil and the hydrophilic end in water. These small droplets can now be washed away as they are effectively dissolved in water.



(c) Detergents contain surfactant ions ending with a benzyl-sulfonyl group rather than the carboxylate group that soaps have. While soap ions react with the Ca^{2+} and Mg^{2+} ions in water to form scum and hence waste soap, detergent ions do not do this. Therefore, the surfactant ions of detergents are more effective in removing oil or grease stains from fabrics and are thus more useful in hard water.

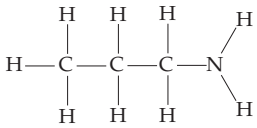
18.

Reaction	Structural formula
Acidified butanoic acid is added to methanol and heated	 Name: Methylbutanoate (Esterification) $CH_3CH_2CH_2COOCH_3$
Hydrogen gas is bubbled through but-2-ene	 Name: Butane (Hydrogenation) C_4H_{10}
Acidified potassium dichromate is added to ethanol	 Ethanal (first stage of oxidation of primary alcohol) CH_3CHO  Ethanoic acid (Complete oxidation of primary alcohol) CH_3COOH
Chlorine gas is added to excess propane and exposed to UV light	 1-chloropropane (Substitution) $CH_3CH_2CH_2Cl$  2-chloropropane (Substitution) $CH_3CHClCH_3$

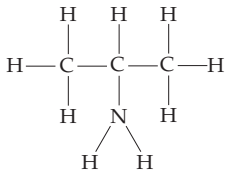
19.

(a) There are many possible answers

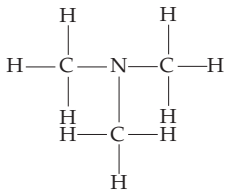
1-aminopropane



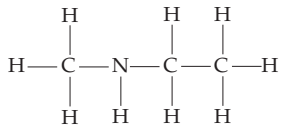
2-aminopropane



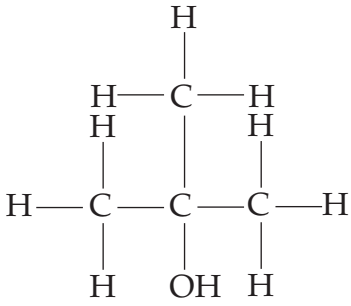
trimethylamine



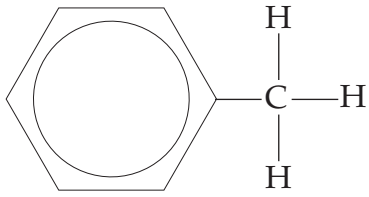
methylethylamine etc.



(b) methylpropan-2-ol



(c) methyl benzene

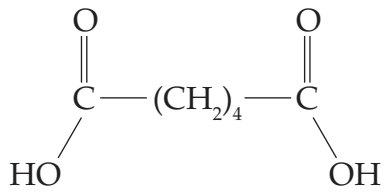


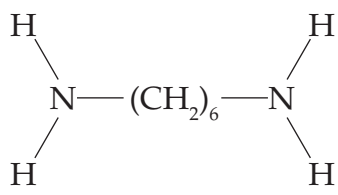
20. X = alcohols (hydroxyl group)

Y = carboxylic acids (carboxyl group)

Z = amines (amino group)

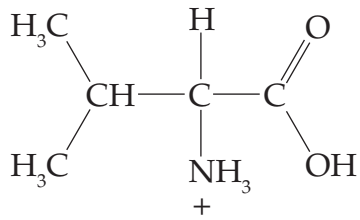
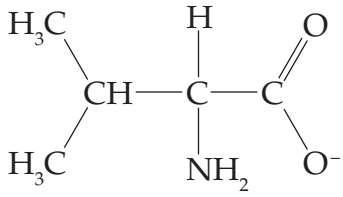
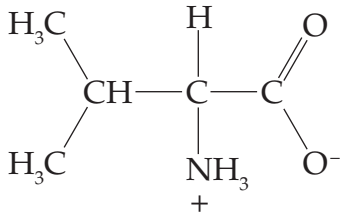
21. (a)





(b) condensation polymer, a polyamide.

22.

Valine structure	pH range
	Acidic pH <7
	Basic pH >7
	Neutral pH = 7

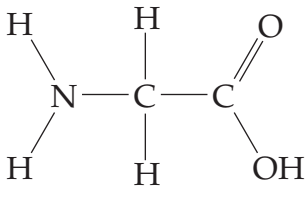
23. Butanoic acid ($CH_3CH_2CH_2COOH$) has the highest boiling point. This is due to hydrogen bonding between molecules, dipole-dipole interaction forces as well as strong dispersion forces.

    Butan-1-ol ($CH_3CH_2CH_2CH_2OH$) has a lower boiling point than butanoic acid because it has hydrogen bonding and dispersion forces only.

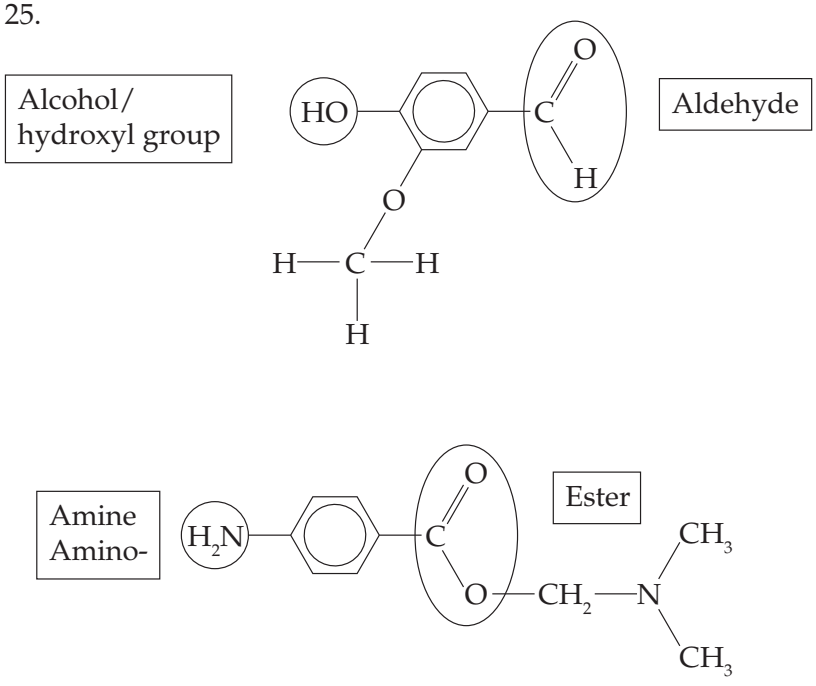
    Butanal ($CH_3CH_2CH_2CHO$) has the lowest boiling point of the three. There are no hydrogen bonding sites in the molecule. It has dipole-dipole forces and dispersion forces only.

    As the molar masses are not very much different, they do not significantly contribute to any difference in the boiling points among the three compounds.

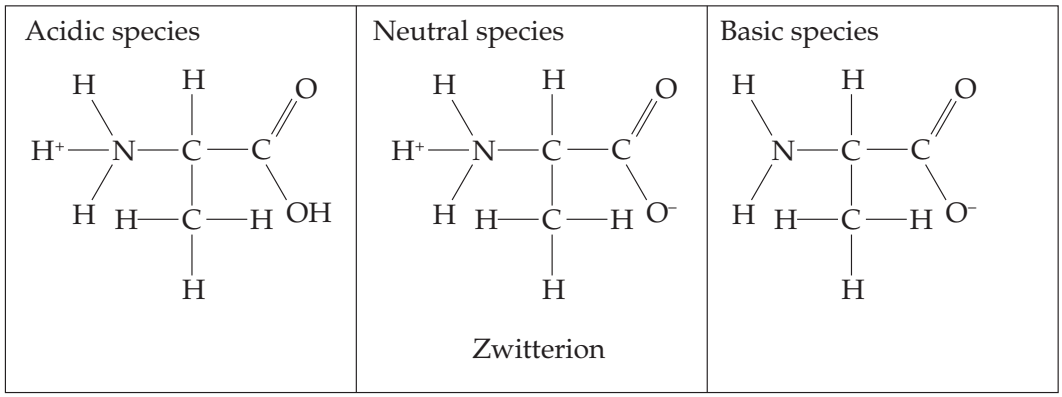
24.



25.



26. (a)



(b) In neutral conditions alanine exists as a zwitterion, or a neutral ion/molecule that contains both positive and negative ionic sites. This means that it contains strong ionic bonds which contribute to its relatively high melting point.

27. (a)

$m(CO_2) = 17.9$ g

$n(CO_2) = 17.9 / 44.01 = 0.406725744$ mol

$n(C) = 0.406725744$ mol

$m(C) = 0.406725744 \times 12.01 = 4.884776187$ g

$m(H_2O) = 4.88$ g

$n(H_2O) = 4.88 / 18.016 = 0.270870337$ mol

$n(H) = 2 \times n(H_2O) = 2 \times 0.270870337 = 0.541740675$ mol

$m(H) = 0.541740675 \times 1.008 = 0.5460746$ g

$m(O) = 9.76 - m(C) - m(H) = 9.76 - 4.884776187 - 0.5460746 = 4.329149213$ g

$n(O) = 4.329149213 / 16.00 = 0.270571825$ mol

	C	H	O
Moles (mol)	0.4067	0.5417	0.2706
Simplest ratio	0.4067/0.2706 = 1.503	0.5417/0.2706 = 2.002	0.2706/0.2706 = 1
x 2	3	4	2

Therefore, the empirical formula is $C_3H_4O_2$

(b) $n(NaOH) = cV = 0.487 \times 0.0153 = 0.0074511$ mol

Let dicarboxylic acid be H_2X

$H_2X + 2NaOH \rightarrow Na_2X + 2H_2O$

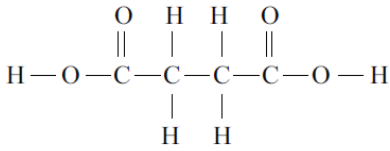
$n(H_2X)_{in\ 50mL} = ½ \times n(NaOH) = 0.00372555$ mol

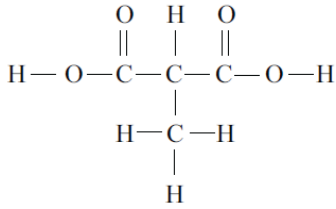
$n(H_2X)_{in\ 250mL} = 250/50 \times 0.00372555 = 0.01862775$ mol

$M(H_2X) = m/n = 2.20/0.01862775 = 118.10\ gmol^{-1}$

(c) The monomer has four oxygen atoms as it has two 'COOH' groups in it. Taking away the mass of the four oxygen atoms from the molar mass of 118, the residual mass is (118 – 64) 54 which is shared by 4 carbon atoms and 6 hydrogen atoms. This gives a molecular formula of $C_4H_6O_4$.

The following are two possible structures:





28. $m(CO_2) = 1.715$ g

$n(CO_2) = 1.715/44.01 = 0.038968416$ mol

$n(C) = 0.038968416$ mol

$m(C) = 0.038968416 \times 12.01 = 0.468010679$ g

$m(H_2O) = 0.2521$ g

$n(H_2O) = 0.2521/18.016 = 0.013993117$ mol

$n(H) = 2 \times n(H_2O) = 2 \times 0.013993117 = 0.027986234$ mol

$m(H) = 0.027986234 \times 1.008 = 0.028210124$ g

$m(NO_2) = 0.2558$ g

$n(NO_2) = 0.2558/46.01 = 0.00555966$ mol

$n(N) = 0.00555966$ mol

$m(N) = 0.00555966 \times 14.01 = 0.077890849$ g

$m(SO_2) = 0.3568$ g

$n(SO_2) = 0.3568/64.07 = 0.005568909$ mol

$n(S) = 0.005568909$ mol

m(S) = 0.005568909 x 32.07 = 0.178594911 g

m(O) = 1.021 – m(C) – m(H) – m(N) – m(S)

= 1.021 - 0.468010679 - 0.028210124 - 0.077890849 - 0.178594911

= 0.268293437 g

n(O) = 0.268293437 / 16.00 = 0.016768339 mol

	C	H	N	S	O
Moles (mol)	0.038968416	0.027986234	0.00555966	0.005568909	0.016768339
Simplest ratio	$\frac{0.038968416}{0.00555966}$ = 6.96	$\frac{0.027986234}{0.00555966}$ = 5.03	$\frac{0.00555966}{0.00555966}$ = 1	$\frac{0.005568909}{0.00555966}$ = 1.00	$\frac{0.016768339}{0.00555966}$ = 3.01
	7	5	1	1	3

Therefore, the empirical formula is $C_7H_5NSO_3$

29. m (sample) = 1.6328 g.

The volume of CO_2 produced at 50°C and 101.3 kPa = 0.866 L.

Since, PV = nRT, n = (PV / RT),

$n(CO_2)$ = [(101.3 × 0.866) / (8.315 × 323.15)] = 0.032648326 mol

n(C) = 0.032648326 mol

m(C) = n × M = 0.03266 × 12.01 = 0.3921064 g

$m(H_2O)$ = 0.220 g;

$n(H_2O)$ = (0.220 / 18.016) = 0.012211367 mol

n(H) = 2 × 0.012211367 = 0.024422735 mol

m(H) = 0.024422735 × 1.008 = 0.024618117 g

n(HF) = 0.0571 mol

n(F) = 0.0571 mol

m(F) = 0.0571 × 19.00 = 1.0849 g

m(O) = [1.6328 –(0.3921064 + 0.024618117 + 1.0849)] = 0.131175483 g

n(O) = (0.131 / 16.00) = 0.008198467 mol

	C	H	F	O
Moles (mol)	0.032648326	0.024422735	0.0571	0.008198467
Simplest ratio	$\frac{0.032648326}{0.008198467}$ = 3.98	$\frac{0.024422735}{0.008198467}$ = 2.98	$\frac{0.0571}{0.008198467}$ = 6.96	$\frac{0.008198467}{0.008198467}$ =1
	4	3	7	1

Therefore the Empirical Formula = $C_4H_3F_7O$

30. (a) m(sample) = 0.5096 g

$n(H_2O)$ = 0.4160 g

$n(H_2O) = 0.4160 \div 18.016 = 0.023090586$ mol

$n(H) = 2 \times 0.023090586 = 0.046181172$ mol

$m(H) = n \times M = 0.046181172 \times 1.008 = 0.046550621$ g

$V(CO_2) = 0.7007$ L

Using the equation, PV = nRT

$n = (PV/RT) = [(102.8 \times 0.7007) / (8.314 \times 373.15)] = 0.023218372$ mol of CO_2

$n(C) = n(CO_2) = 0.023218372$ mol

$m(C) = n \times M = 0.023218372 \times 12.01 = 0.278852648$ g

$m(O) = [0.5096 \text{ g} - (0.046550621 + 0.278852648)] = 0.184196731$ g

$n(O) = (m/M) = (0.184196731/16.00) = 0.011512295$ mol

	C	H	O
Moles (mol)	0.023218372	0.046181172	0.011512295
Simplest ratio	0.02322/0.01151 = 2.01	0.04618/0.01151 = 4.01	0.01151/0.01151 = 1
	2	4	1

Therefore the Empirical Formula is C_2H_4O

(b) m(second sample) = 0.4832 g

This sample at 261°C, has a pressure of 241 kPa in a 100.0 mL container.

Using the relationship, PV = nRT, and, n = PV/RT,

$n(\text{sample}) = [(241 \times 0.100) / (8.314 \times 534.15)] = 5.4268 \times 10^{-3}$ mol

$M(\text{sample}) = m/n = 0.4832/5.4268 \times 10^{-3} = 89.04$ g mol^{-1}

M(EF) = 44.052 g mol^{-1}

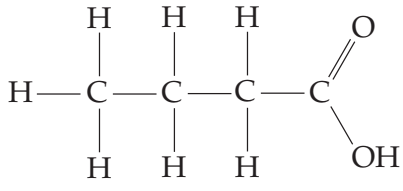
M(MF) = 89.04 g mol^{-1}

The ratio of M(MF) / M(EF) = (89.04 / 44.052) = Nearly 2.

Therefore, the molecular formula = $2 \times C_2H_4O = C_4H_8O_2$

(c) Since a fruity smell is characteristic of an ester and the ester is the product of an alcohol and a carboxylic acid, this compound is most likely to be butanoic acid with the following Lewis structure.

Structure of butanoic acid



(d) Additional chemical tests for butanoic acid:

Reaction with metallic carbonates such as $CaCO_3$ would produce a colourless, odourless gas.

$CaCO_3(s) + 2CH_3CH_2CH_2COOH(l) \rightarrow Ca(CH_3CH_2CH_2COO)_2(aq) + CO_2(g) + H_2O(l)$

Other possible tests:

Add a reactive metal such as Mg to produce a colourless, odourless gas.

Litmus test: acids turn litmus red. This confirms that the compound is an acid.

31. (a) To determine the mass of $CaCO_3$ deposited in 365 days if 1.0 L of water contains 65.0 mg of Ca^{2+} ions and a family uses 4.20 L of water a day.

1.0 L of water contains 65.0 mg of Ca^{2+} ions.

4.20 L contains = 4.20 × 65.0 mg = 273 mg of Ca^{2+} ions (0.273 g)

$n(Ca^{2+})$ ions in 4.20 L = (0.273 / 40.08) = 6.8114×10^{-3} mol

Since $n(Ca^{2+}) = n(CaCO_3)$,

$n(CaCO_3)$ in 4.20 L = 6.8114×10^{-3} mol

$m(CaCO_3) = (n \times M) = (6.8114 \times 10^{-3} \times 100.09) = 0.68175$ g per day.

$m(CaCO_3)$ produced in 365 days = 365 × 0.68175 = 248.84 g = 249 g

(b) To calculate the volume of CO_2 produced by the boiling of 1.00 L of water at standard pressure.

From the reaction,

$Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$

Since 1.0 L of water contains 65.0 mg of Ca^{2+} ions

$n(Ca^{2+}) = 0.065 / 40.08 = 0.0016218$ mol

$n(CO_2)$ in 1.0 L = $n(Ca^{2+})$

$n(CO_2) = 0.0016218$ mol

$V(CO_2) = (nRT / P) = [(1.6218 \times 10^{-3} \times 8.314 \times 373.15) / 100]$
$= 0.050312872$ L = 5.03×10^{-2} L of CO_2

(c) To calculate the pH of 1.05×10^3 L of water to which 125 mg of $Ca(OH)_2$ is added:

$n(Ca(OH)_2) = 0.125 / 74.096 = 0.001687$ mol

$c(Ca(OH)_2) = n / V = 0.001687 / 1.05 \times 10^3 = 1.606 \times 10^{-6}$ mol L^{-1}

$[OH^-] = 2 \times 1.606 \times 10^{-6} = 3.213 \times 10^{-6}$ mol

$[H^+] = 1.0 \times 10^{-14} / 3.213 \times 10^{-6} = 3.112 \times 10^{-9}$ mol L^{-1}

$pH = -\log [3.112 \times 10^{-9}] = 8.52$

(d) Buffering capacity is the ability of a solution to resist changes in pH. Quantitatively, buffering capacity is defined as the number of moles of a strong acid or strong base that are required to change the pH of a 1.0 L of the solution by 1 pH unit.

(e) Equations to show the buffering capacity of hard water containing HCO_3^- ions.

Equation 1: $HCO_3^-(aq) + H_3O^+(aq) \leftrightarrows H_2CO_3(aq) + H_2O(l)$

Addition of acid shifts the equilibrium to the right to restore balance.

Equation 2: $HCO_3^-(aq) + OH^-(aq) \leftrightarrows CO_3^{2-}(aq) + H_2O(l)$

Addition of a base shifts the equilibrium to the right to restore balance.

f) Equations to show how the addition of OH^- ions shifts the equilibria of the carbonate species in water.

Equation 1: $H_2CO_3(aq) + OH^-(aq) \leftrightarrows HCO_3^-(aq) + H_2O(l)$

Equation 2: $HCO_3^-(aq) + OH^-(aq) \leftrightarrows CO_3^{2-}(aq) + H_2O(l)$

32.

(a) Capacity of the container = 4.49×10^6 L

$V(O_2) = 4.49 \times 10^6 \times (20.9/100) = 9.3841 \times 10^5$ L

PV = nRT, and n = PV/RT

$n(O_2) = (105.3 \times 9.3841 \times 10^5) / 8.314 \times (273.15 + 175) = 2.652085844 \times 10^4$ mol

$m(NH_3) = 457.3$ kg = 457 300 g

$n(NH_3) = m/M = 457\,300/17.034 = 2.684630739 \times 10^4$ mol

	$n(NH_3)$	$n(O_2)$
stoichiometric ratio	4	5
actual ratio (divide both by smallest)	$\frac{2.684630739 \times 10^4}{2.652085844 \times 10^4}$ = 1.01	$\frac{2.652085844 \times 10^4}{2.652085844 \times 10^4}$ = 1
Therefore, O_2 is the limiting reagent		

b)

$n(NO) = 4/5 \times n(O_2) = 4/5 \times 2.652085822 \times 10^4 = 2.121668675 \times 10^4$ mol

$m(NO) = n \times M = 2.121668675 \times 10^4 \times 30.01 = 6.367217694 \times 10^5$ g = 6.37×10^5 g.

c)

$n(NH_3)$ excess = $n(NH_3)$ initial – $n(NH_3)$ reacted

$= 2.684630739 \times 10^4 - (4/5 \times 2.652085822 \times 10^4)$

$= 5.62962 \times 10^3$ mol

$m(NH_3)$ excess = $n \times M = 5.62962 \times 10^3$ mol $\times 17.034$

$= 9.59 \times 10^4$ g

33.

(a) m($CuSO_4.5H_2O$ at 95.5% purity) = 95.5/100 x 100000 = 95500 g.

n($CuSO_4.5H_2O$) = m/M = (95500 ÷ 249.70) = 382.4589507 mol

m(NH_3) = 0.880 × 15 000 mL = 13 200 g

n(NH_3) = m/M = 13 200/17.034 = 774.9207467 mol

	n($CuSO_4.5H_2O$)	n(NH_3)
stoichiometric ratio	4	6
actual ratio (divide both by smallest)	382.4589507 382.4589507 = 1	774.9207467 382.4589507 =2.02
Therefore, $CuSO_4.5H_2O$ is the limiting reagent		

(b) n($CuSO_4.3Cu(OH)_2.H_2O$) = ¼ × n($CuSO_4.5H_2O$) = ¼ × 382.4589507 = 95.61473768 mol

m($CuSO_4.3Cu(OH)_2.H_2O$) = n × M = (95.61473768 × 470. 334) = 44 971 g = 45.0 kg

(c) n(NH_3) excess = n(NH_3) initial – n(NH_3) reacted = 774.9207467 – (6/4 x 382.4589507)

= 201.2323207 mol

= 201.2 mol

34.

(a) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(b) Fe_2O_3 is the oxidant. Carbon monoxide is the reductant.

(c)

(i)

m(Fe_2O_3) impure = 1.00 tonne = 1000 kg.

Percentage purity = 96.5%.

m(Fe_2O_3) = 96.5/100 x 1000 = 965 kg = 965000 g

n(Fe_2O_3) = m/M = 965000/159.70 = 6042.58 mol

n(CO) = PV/RT = (113.46 × 2.70 × 10^6) / (8.314 × 2259.15) = 16309.90591 mol

	n(Fe_2O_3)	n(CO)
stoichiometric ratio	1	3
actual ratio (divide both by smallest)	6042.58 6042.58 = 1	16309.90591 6042.58 = 2.70
Therefore, CO is the limiting reagent		

(ii) n(Fe) = 2/3 x n(CO) = 10873.27061 mol

m(Fe) = n x M = 10873.27061 x 55.85 = 607272.1634 g = 607.3 kg

(iii)

$n(Fe_2O_3)$ initial = 6042.58 mol

$n(Fe_2O_3)$ reacted = (1/3 x 16309.90591) = 5436.635303 mol.

$n(Fe_2O_3)$ excess = (6042.58 – 5436.635) = 605.9446967 mol

$m(Fe_2O_3)$ excess = 605.9446967 × 159.70 = 96769.36806 g = 96.77 kg

To this if you add the impurities, (1000 kg × 3.5% = 35 kg), the excess reactant including impurities will be (96.77 + 35) = 131.77 kg.

(d) % yield of iron = (Actual yield / Theoretical yield) × 100 = (556 / 607.3) × 100 = 91.56%

35.

(a) Total volume of NH_3 and CO_2 together at 200.0°C and 1.50 x 10^4 kPa pressure = 5000 L

Volume of NH_3 under the same conditions = 62 / 100 x 5000 = 3100 L

Volume of CO_2 under the same conditions = 5000 – 3100 = 1900 L

Here we can apply the law of combining volumes of gases which states that under the same conditions, the reacting volume ratio is the same as the stoichiometric ratio.

	NH_3	CO_2
stoichiometric ratio (n)	2	1
actual ratio (V) (divide both by smallest)	$\frac{3100}{1900}$ = 1.63	$\frac{1900}{1900}$ = 1
Therefore, NH_3 is the limiting reagent		

(b) $n(NH_3) = PV / RT = (1.50 \times 10^4 \times 3100) / (8.314 \times (200 + 273.15)) = 11820.7243$ mol

$n(CO(NH_2)_2) = ½ \times n(NH_3) = ½ \times 11820.7243 = 5910.362151$ mol

$m(CO(NH_2)_2) = n \times M = 5910.362151 \times 60.062 = 354988.1715$ g = 3.55 x 10^5 g

(c) $n(CO_2)$ excess = $n(CO_2)$ initial – $n(CO_2)$ reacted

$n(CO_2)$ initial = PV / RT = (1.50 x 10^4 x 1900) / (8.314 x (200 + 273.15)) = 7244.960056 mol

$n(CO_2)$ reacted = ½ x $n(NH_3)$ = ½ x 11820.7243 = 5910.362151 mol

$n(CO_2)$ excess = 7244.960056 – 5910.362151 = 1334.597905 mol

$m(CO_2)$ excess = n x M = 1334.597905 x 44.01 = 58735.65381 g = 5.87 x 10^4 g

(d) PV = nRT, P = nRT / V

$P(CO_2) = (1334.596905 \times 8.314 \times (25 + 273.15)) / 5000 = 616.6$ kPa

(e) $m(CO(NH_2)_2)$ produced = (83.0 / 100) × 376000 = 312080 g

% yield of urea = (Actual yield / Theoretical yield) × 100 = (312080 / 354988.1715) × 100 = 87.9%

(f) (i) % of N in $CO(NH_2)_2$ = 2 x 14.01 / 60.062 x 100 = 46.65%

m(N) in fertiliser = 46.65/100 x 45/100 x 5 = 1.049665346 tonne = 1.05×10^6 g

(ii) n(N) in urea fertiliser = 1.049665346×10^6 / 14.01 = 74922.58 mol

$n((NH_4)_2SO_4)$ = ½ x 74922.58 = 37461.29 mol

$m((NH_4)_2SO_4)$ = n x M = 37461.29 x 132.154 = 4.950659319×10^6 g = 4.95 tonne

36. (a) m(vegetable oil) = 1.50×10^6 g

n(vegetable oil) = m/M = $1.5 \times 10^6/855.334) = 1.7537 \times 10^3$ mol

$n(CH_3OH) = 3 \times 1.7537 \times 10^3$ mol = 5.2611×10^3 mol

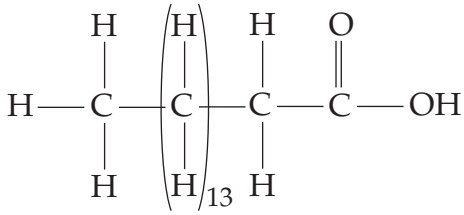
$m(CH_3OH) = n \times M = 5.2611 \times 10^3 \times 32.042 = 1.68576 \times 10^5$ g = 1.69×10^2 kg

(b) n(ester A) = n(vegetable oil) = 1753.7 mol

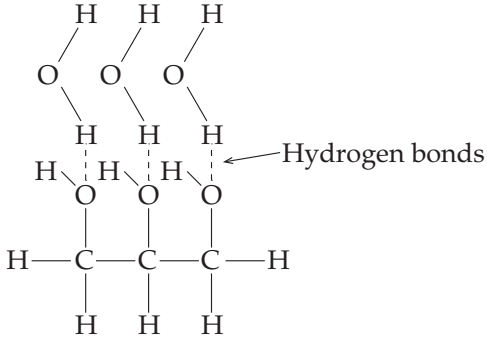
m(ester A) = n × M = 1753.7 × 270.442 = 474274.377 g = 4.74×10^5 g at 100% efficiency.

Therefore, at 78% efficiency, m(ester A) = $(0.78 \times 4.74 \times 10^5) = 3.69934 \times 10^5$ g = 3.70 kg

(c) Structure of the carboxylic acid that would be needed to produce ester A:

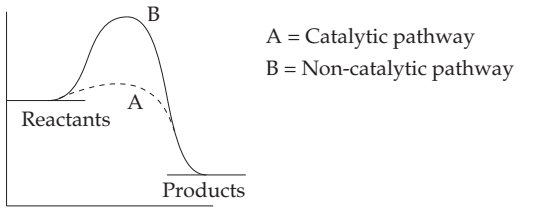


(d) The compound glycerol has three hydrogen bonding sites per molecule. Water has one hydrogen bonding site per molecule. The main reason that a substance dissolves in another is due to the intermolecular attraction between the molecules of these two different substances. The hydrogen bonding forces between water and glycerol molecules are equal to or greater than the hydrogen bonding between the glycerol molecules and between the water molecules.The similar intermolecular forces lead to a very high degree of interaction between glycerol molecules and water molecules and hence a high degree of solubility. The following sketch shows the force of attraction between a glycerol molecule and a water molecule.

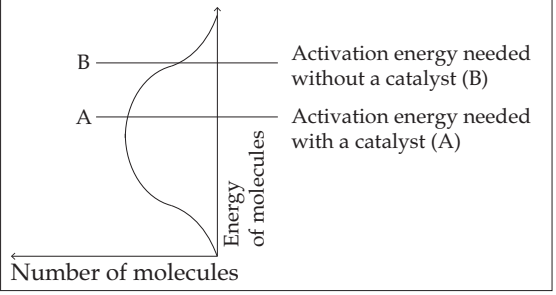


(e) As a catalyst, sodium hydroxide increases the rate of the reaction. It does this by providing an alternative reaction pathway with a lower activation energy. So, more molecules will have sufficient energy to react and to collide effectively thus increasing the number of successful collisions per unit time.

Catalytic and non-catalytic pathway



Increase in the number of reacting molecules



37. (a) $n(H_2) = 3/1 \times n(CH_4) = 3$ mol

$n(NH_3) = 2/3 \times n(H_2) = 2$ mol

$n(NO) = 4/4 \times n(NH_3) = 2$ mol

$n(NO_2) = 2/2 \times n(NO) = 2$ mol

$n(HNO_3) = 4/4 \times n(NO_2) = 2$ mol

$n(NH_4NO_3) = 1/1 \times n(HNO_3) = 2$ mol

(b) $n(NH_4NO_3) = m/M = 2.50 \times 10^5 \times 10^6 \ / \ 80.052 = 3.122970069 \times 10^9$ mol

$n(CH_4) = ½ \times 3.122970069 \times 10^9 = 1.561485035 \times 10^9$ mol

$m(CH_4) = n \times M = 1.561485035 \times 10^9 \times 16.042 = 2.504934293 \times 10^{10}$ g $= 2.50 \times 10^4$ tonne.

(c) **Using a temperature of 900°C:** 900°C is a relatively high temperature. High temperatures increase the rate of reaction since the reacting particles will have a greater average kinetic energy and average velocity. This will increase both the number of collisions and also the energy of collisions between particles. Therefore, more particles will undergo successful collisions and react. According to Le Chatelier's principle a high temperature will favour the reverse reaction and decrease the yield. This is because higher temperatures increase the kinetic energy of all particles and so more will be able to overcome the activation energy of both the forward and reverse reactions. This increased kinetic energy will have a more pronounced effect on the reverse reaction since it is endothermic and so will have a higher activation energy than the forward exothermic reaction. The temperature choice in these circumstances is often a compromise but it appears that a higher temperature has been chosen to promote rate over yield.

Using atmospheric pressure: Increasing the pressure of gaseous reactants increases the number of reacting particles in a given volume. More particles results in more collisions and therefore an increased rate of reaction. In this reaction there are more gaseous moles of particles on the product side of the reaction (10) than the reactant side (9), so a decrease in pressure will have a greater effect on the reverse reaction. Both rates will decrease at lower pressure, but the rate of the forward reaction will decrease less than the rate of the reverse reaction, and the equilibrium will shift in the forward direction, increasing the yield. So once again there needs to be a compromise between rate and yield. Atmospheric pressure is chosen for this reason, and also for economic reasons as generating high pressures requires more energy and a more robust reaction vessel.

38. (a) $n(H^+) = n(HCl) = c \times V = 0.752 \times 0.02578 = 1.938656 \times 10^{-2}$ mol
$n(NH_3) = n(B(OH)_3) = n(B(OH)_4^-) = n(H^+) = 1.938656 \times 10^{-2}$ mol (mole ratio is 1:1:1)

$n((NH_4)_2SO_4) = ½ \times n(NH_3) = 9.69328 \times 10^{-3}$ mol

$n(NH_4^+) = 2 \times n((NH_4)_2SO_4) = 1.938656 \times 10^{-2} = 1.94 \times 10^{-2}$ mol

(b) $n(N) = n(NH_4^+) = 1.938656 \times 10^{-2}$ mol

$m(N) = n \times M = 1.938656 \times 10^{-2} \times 14.01 = 0.271605705$ g = 0.272 g

(c) m(protein) = 6.38 × 0.2716 = 1.732844402 = 1.73 g

(d) Typical serving size for the product = 25 g

If 5.235 g of the sample contains 1.73 g then 25 g of the sample will contain:

= [(25 × 1.73) ÷ 5.235] = 8.275283676 g = 8.28 g

(e) Increasing the number of trials would increase the reliability.

39. (a) Overall reaction:

$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \leftrightarrows 2PbSO_4(s) + 2H_2O(l)$

Anode reaction: $Pb(s) + SO_4^{2-}(aq) \leftrightarrows PbSO_4(s) + 2e^-$

Cathode reaction: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \leftrightarrows PbSO_4(s) + 2H_2O(l)$

(b) (i) When the lead-acid battery is discharging the lead anode is oxidised in the presence of SO_4^{2-} ions to form $PbSO_4$ on its surface. The electrons move through the external circuit to the cathode and are used to do work i.e. to start the car. The electrons move to the cathode and reduce the PbO_2 cathode in the presence of H^+ and SO_4^{2-} ions to form $PbSO_4$ on its surface.

When the car is running the alternator reverses these reactions and the battery is recharged.

(ii) When two half-cells are connected there is a competition for electrons. The half-cell with the highest reduction potential is reduced and gains electrons and the other half-cell is oxidised and loses electrons. The magnitude of the electrical potential of the cell is determined by the difference between the two half-cell potentials, the temperature and the concentration of the electrolytes.

At standard conditions of 25°C, 1 atm pressure and 1 mol L^{-1} solution concentrations the E^{o} of the lead-acid battery cathode reaction is +1.69 V and the E^{o} of the anode reaction is -0.36 V.

So the overall E_{cell} is +1.69 – (-0.36) = 2.05 V.

Six of these cells in series produces a potential difference of approximately 12 V.

(c) (i) $n(H_2SO_4) = c \times V = 3.55 \times 4.50 = 15.975$ mol

$n(H^+) = 2 \times n(H_2SO_4) = 2 \times 15.975 = 31.95$ mol = 32.0 mol

(ii) $n(PbSO_4) = m/M = 138.1/303.27 = 0.455369802$ mol

$n(H^+) = 4/2 \times n(PbSO_4) = 2 \times 0.455369802 = 0.910739605$ mol = 0.911 mol

(iii) $n(H^+)$ excess = $n(H^+)$ initial – $n(H^+)$ reacted = 31.95 – 0.910739605 = 31.0392604 mol

$[H^+] = n/V = 31.0392604/4.50 = 6.897613421 = 6.90$ mol L^{-1}

(iv) $[H^+]$ initial = $2 \times c(H_2SO_4) = 2 \times 3.55 = 7.10$ mol L^{-1}

Initial pH = -log(7.10) = -0.851

$[H^+]$ final = 6.897613421 mol L^{-1}

Final pH = -log(6.897613421) = -0.839

There is a negligible difference of 0.012 pH units.

(d) Hydrogen gas is flammable, and oxygen supports combustion.

40.

m(AgCl) produced = 1.02 g

$n(AgCl) = 1.02/143.35 = 7.115451 \times 10^{-3}$ mol

$n(NaCl) = n(AgCl) = 7.115451 \times 10^{-3}$ mol

$m(NaCl) = 7.115451 \times 10^{-3} \times 58.44 = 0.415826996$ g

$\therefore m(NaHCO_3) = 12.45 - 0.415826996 = 12.034173$ g

$\therefore$ Percentage purity of $NaHCO_3 = (12.034173/12.45) \times 100 = 96.7\%$

41.

(a) $3HCO_3^-(aq) + C_6H_8O_7(aq) \rightarrow C_6H_5O_7^{3-}(aq) + 3H_2O(l) + 3CO_2(g)$

$n(NaHCO_3) = 1.998 / 84.008 = 0.023783449$ mol

$n(C_6H_8O_7) = 1.111 / 192.124 = 0.005782723$ mol

	$NaHCO_3$	$C_6H_8O_7$
stoichiometric ratio	3	1
actual ratio (divide both by smallest)	$\frac{0.023783449}{0.005782723}$ = 4.11	$\frac{0.005782723}{0.005782723}$ = 1
Therefore, $C_6H_8O_7$ is the limiting reagent		

$n(CO_2) = 3/1 \times n(C_6H_8O_7) = (3/1) \times 0.005782723 = 0.01734817$ mol

$V(CO_2) = nRT/P = (0.01734817 \times 8.314 \times (37.0 + 273.15)) / 99.2 = 0.450945235$ L = 0.451 L

(b) $n(NaHCO_3)$ reacted $= 3/1 \times n(C_6H_8O_7) = (3/1) \times 0.005782723 = 0.01734817$ mol

$n(NaHCO_3)$ excess = $n(NaHCO_3)$ initial – $n(NaHCO_3)$ reacted

$= 0.023783449 - 0.01734817 = 0.006435279$ mol

$c(NaHCO_3) = n/V = 0.006435279/0.120 = 0.053627325$ mol $L^{-1} = 5.36 \times 10^{-2}$ mol L^{-1}

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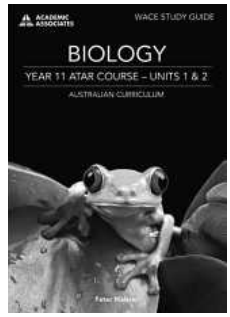

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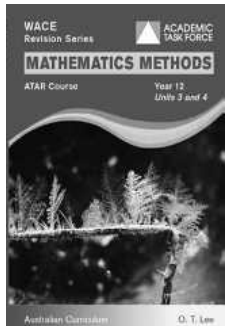

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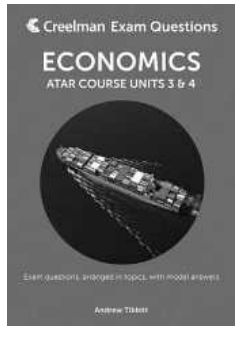

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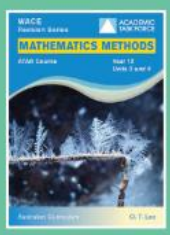

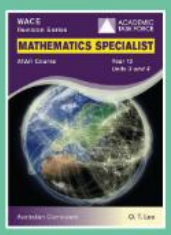

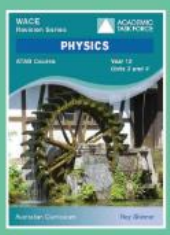

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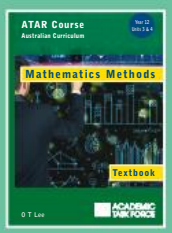

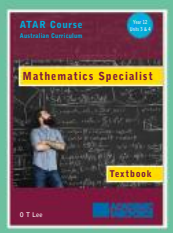

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