2009 HSC Chemistry
Sample Answers

This document contains 'sample answers', or, in the case of some questions, 'answer may include'. These are developed by the examination committee for two purposes. The committee does this:

(a) as part of the development of the examination paper to ensure the questions will effectively assess students' knowledge and skills, and

(b) in order to provide some advice to the Supervisor of Marking about the nature and scope of the responses expected of students.

The 'sample answers' or similar advice, are not intended to be exemplary or even complete responses. They have been reproduced in their original form as part of the examination committee's 'working document'. While the handwritten notes have been typed for legibility, no further editorial change or addition has occurred.

Section I, Part B

Question 16 (a)

Sample answer:

- alkanol + alkanoic acid $\xrightleftharpoons{\text{concH}_2\text{SO}_4}$ ester + water
- Conc H_2SO_4 is catalyst
- Reflux allows reaction to occur at higher temperatures without loss of volatile reactants or products
- Since the organic chemicals are flammable, a water bath is used

Other answers may include:
- Diagram must show:
  – condenser
  – heating source
  – reaction vessel
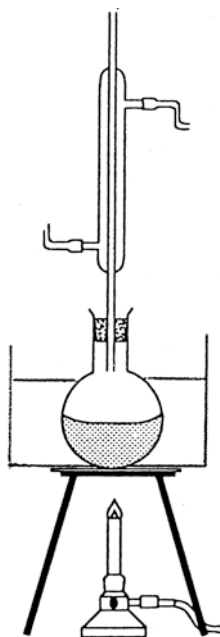

Safety precautions:
- Since the organic chemicals are flammable, a water bath is used.
- Boiling chips are added to reduce 'bumping'.
- Care taken to place water hoses away from hotplate.
- Constant water flow through condenser is monitored carefully.
- Conc H_2SO_4 handled by teacher.
- Safety glasses when in close proximity to apparatus.
- Maintain water level in water bath

Question 17

Sample answer:

Water is a small polar molecule containing only polar covalent bonds. It is attracted to other substances by strong hydrogen bonds and dipole-dipole attractions. This makes it an extremely good solvent for polar substances and some ionic compounds. 'Like dissolves like'.

Ethanol is also a small molecule but it contains both polar and non-polar bonds. It is a polar molecule and can form hydrogen bonds, dipole-dipole interactions and dispersion forces. These properties make ethanol an extremely good solvent for both polar and non-polar substances.
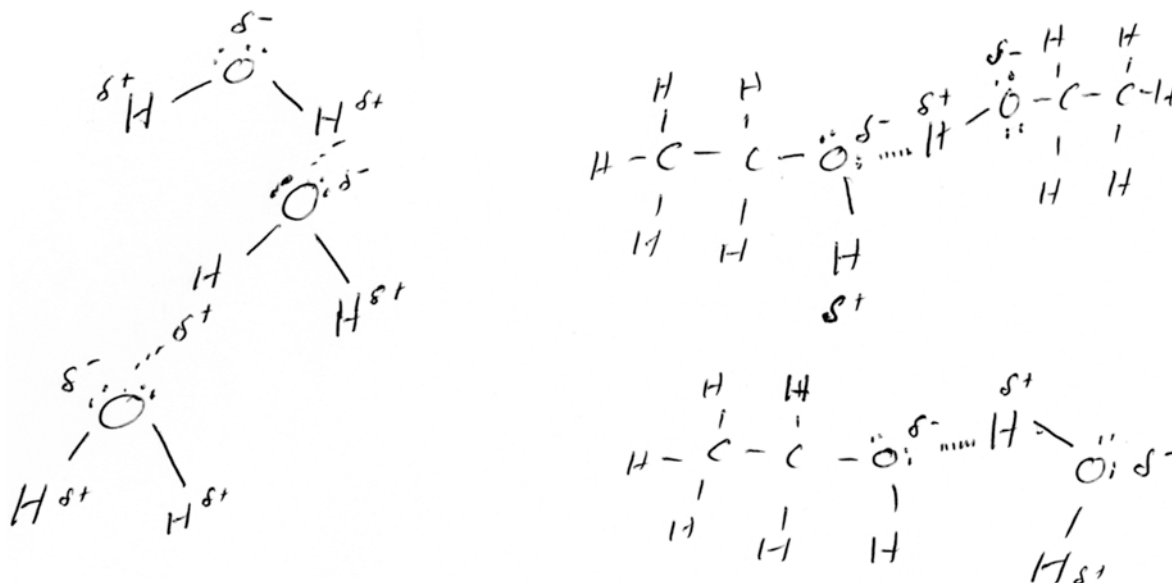
Question 18

Sample answer:

The evidence of increasing concentrations of NO and NO_2 in the atmosphere comes from direct measurement, knowledge of sources and measurement of effects. Thus there is clear factual evidence to support this statement. Monitoring is necessary due to detrimental environmental and health effects.

Combustion of fossil fuels in motor vehicles and in power stations results in the formation of NO

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
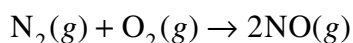
In the lower atmosphere, in the presence of sunlight NO is oxidised to NO_2

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
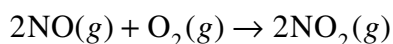
Direct measurements are made by statutory bodies, such as NSW EPA, and also by scientists researching the atmosphere. Nitrogen oxides were found to be part of pollution generated over large cities from the onset of the industrial revolution and the use of the internal combustion engine. This was essentially unrestricted till the 1950s, when concerns grew from loss of life due to smog. Some reduction of NO was achieved by the introduction of catalytic converters in motor vehicles where

$$2CO(g) + 2NO(g) \rightarrow N_2(g) + 2CO_2(g)$$
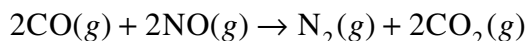
This removes NO from the exhaust gas. However the increased number and use of motor vehicles has offset further major reductions.

Measurement of effects of NO_x highlights both issues of quantities produced and detrimental effects which necessitates their monitoring.

One effect is production of photochemical smog. NO_x is part of a complex set of chemical species which have several reactions in the presence of sunlight resulting in photochemical smog.

Another effect is the direct toxicity of NO_x to people, affecting especially the respiratory tract and eyes. There is a need to monitor NO_x in cities in order to warn people most susceptible to acute effects.

Question 18 (continued)

NO_x are also contributors to acid rain:

$$2NO_2(g) + H_2O(\ell) \rightarrow HNO_2(aq) + HNO_3(aq)$$
$$2HNO_2(g) + O_2(g) \rightarrow 2HNO_3(aq)$$
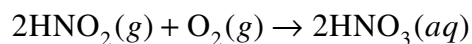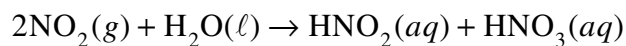
The effects of acid rain are multiple:

• Lowering pH of natural waters affecting all biota in that water body.
• Acidic precipitation affecting vegetation by acid burning or defoliating plants
• Acidic runoff from soils leaching some nutrients, specifically Ca^{2+}, Mg^{2+}
• Acidic leaching of toxic species, e.g. Al^{3+}

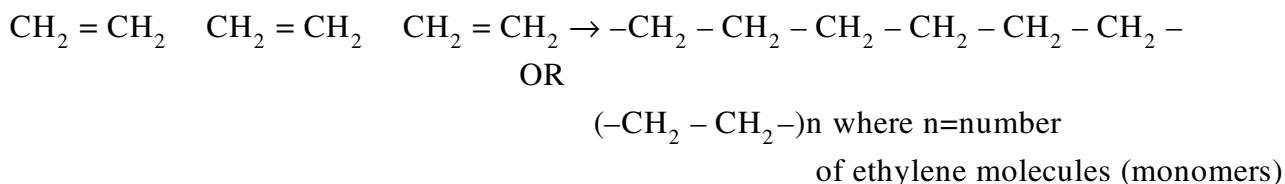Acidic attack on manmade structures, e.g. marble or limestone buildings.

Question 19

Sample answer:

Crude oil is extracted from subterranean deposits and separated into component hydrocarbon molecules using fractional distillation. A portion of the higher boiling point fractions are converted to ethylene during a chemical process called cracking, whereby these larger molecules are broken into smaller ones.

eg $C_{15}H_{32} \rightarrow C_{10}H_{22} + C_5H_{10}$

$ C_5H_{10} \rightarrow C_3H_6 + C_2H_4$ (ethylene)
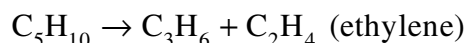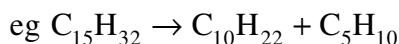
Ethylene is used by the petrochemical industry as a monomer substrate for the production of a number of different polymers (long chain molecules made up of repeating monomer units).

Many different types of plastic bottles are manufactured from one such polymer polyethylene. This molecule is formed when many ethylene monomer units chemically join by 'opening out' their double bonds to form single bonds between neighbouring units, without the loss of any atoms. Therefore polyethylene is known as an addition polymer. The following equation describes this polymerisation process.

$CH_2 = CH_2 \quad CH_2 = CH_2 \quad CH_2 = CH_2 \rightarrow -CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 -$

$$OR$$

$(-CH_2 - CH_2 -)n$ where n=number

of ethylene molecules (monomers)

The polymerisation of ethylene as an industrial process is carried out using one of two methods, both of which involve a form of chemical initiation and termination. The older gas phase results in significant chain branching between polyethylene molecules resulting in a low-density polyethylene product. It is relatively soft and is well suited for the production of soft plastic bottles like milk and personal drinking bottles. The newer Ziegler – Natta process forms unbranched polyethylene molecules resulting in a harder tougher high density polyethylene product, which can be used for plastic bottles that need to be harder and more durable.

Answers could include:
- Accept ethylene from dehydration of ethanol
- Any suitable outline involving:

    ethylene $\rightarrow$ PVC $\rightarrow$ pipe

    ethylene $\rightarrow$ polystyrene $\rightarrow$ cup

- Flow chart can also be used
- UV stabilizers added to PVC
- Polystyrene may undergo aeration to produce Styrofoam cup

Question 20 (a)

Sample answer:

$q = m \times C \times \Delta T$

$q = 210 \times 4.18 \times 65$

$q = 57057$

$q = 57.057 \text{ kJ}$

Now $\Delta H_{\text{Comb}} = \dfrac{q}{n}$

$n_{\text{C}_2\text{H}_5\text{OH}} = \dfrac{57.057}{1367}$

$n_{\text{C}_2\text{H}_5\text{OH}} = 0.04174 \text{ mol}$

$\therefore m_{\text{C}_2\text{H}_5\text{OH}} = n_{\text{C}_2\text{H}_5\text{OH}} \times MM$

$\therefore m_{\text{C}_2\text{H}_5\text{OH}} = 0.04174 \times 46.068$

$\therefore m_{\text{C}_2\text{H}_5\text{OH}} = 1.923 \text{ g}$

Now 50% of heat has been lost to surroundings.

$\therefore \text{inital } m_{\text{C}_2\text{H}_5\text{OH}} = 2 \times 1.920 \text{ g}$

$\therefore \text{inital } m_{\text{C}_2\text{H}_5\text{OH}} = 3.846 \text{ g}$

$\therefore \text{inital } m_{\text{C}_2\text{H}_5\text{OH}} = 3.8 \text{ g}$

Question 20 (b)

Answers could include:

- Insulate beaker of water
- Uses an appropriate lid covering for beaker
- Ensure a minimal appropriate distance between spirit burner, flame and beaker.

Question 21 (a)

Sample answer:

Acid 1 is a strong acid, equivalence point is at pH = 7 and initial pH is at 1. Acid 2 is a weak acid as pH at equivalence point is >7 and initial pH is >1. Acid 2 has a higher concentration than Acid 1 as it takes more KOH to neutralise it.

Answers could include:

38 mL KOH for Acid 2 and 25 mL KOH for Acid 1.

Acid 2 is more concentrated since more base is used.

Question 21 (b)

Answers could include:

Potassium acetate CH_3COOK

Potassium ethanoate.

Question 21 (c)

Sample answer:

When 20 mL KOH added, pH of mixture is 2

Since $pH = \log_{10}\left[H^+\right]$, $\left[H^+\right] = 10^{-2}$

$\left[H^+\right] = 0.01 \, mol \, L^{-1}$

Answers could include:

$\left[H^+\right] = 10^{-2} \, mol \, L^{-1}$

Question 21 (d)

Sample answer:

Phenolphthalein changes colour on the vertical section of each titration curve.

Question 22 (a)

Sample answer:

$$NH_3(g) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$
$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$
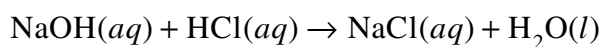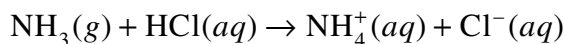
Question 22 (b)

Sample answer:

$$
\begin{aligned}
\text{Moles excess HCl} \ &= \ \text{moles NaOH used} \\
&= \ MV \\
&= \ 0.116 \times 0.02330 \\
&= \ 2.70 \times 10^{-3}
\end{aligned}
$$

Question 22 (c)

Sample answer:

$$
\begin{aligned}
\text{Moles NH}_3 \ &= \ \text{moles HCl used to trap NH}_3 \\
&= \ \text{total moles HCl – moles HCl in excess} \\
&= \ (0.125 \times .0500) - (2.70 \times 10^{-3}) \\
&= \ 6.25 \times 10^{-3} - 2.70 \times 10^{-3} \\
&= \ 3.55 \times 10^{-3}
\end{aligned}
$$

Note: Do not penalise incorrect moles HCl in excess twice.

Question 22 (d)

Sample answer:

$$
\begin{aligned}
\text{moles N} \ &= \ \text{moles NH}_3 \\
&= \ 3.55 \times 10^{-3} \\
\text{Mass N} \ &= \ 3.55 \times 10^{-3} \times 14.01 \\
&= \ 0.0497 \text{ g}
\end{aligned}
$$

$$\text{\% by mass N} \ = \ \frac{0.0497}{2.80} \times 10 \ = 1.77\%$$

Answers could include:

1.78%


Question 23

Sample answer:

Concentrations vary at 4 to 8 minutes, 10 to 12 minutes and 14-16 minutes. At 4 to 8 minutes the system is moving to the right. There is no indication that Cl_2 or CO have been initially removed or that $COCl_2$ was initially added, hence the temperature has been changed. The reaction is endothermic to the right, so this means heat has been added (temperature has been raised). The sharp drop in [CO] at 10 minutes means that CO has been removed. The system then moves to the right, seen as an increase in [CO] and [Cl_2] and a decrease in [$COCl_2$]. At 14 min all concentrations abruptly decrease, all by a 2/3 factor hence the volume of the system has increased. As the right side is proportionally more affected than the left hand side, the system moves to the right to compensate, hence [CO], [Cl_2] increases and [$COCl_2$] decreases.

Answers could include:

- Where the graph shows horizontal lines for concentrations, equilibrium has been achieved.
- Discussion on the rate of change
- Discussion on equilibrium states
- Change at 14 min may have occurred because of mechanical or chemical removal of all species, but this is very unlikely.

Question 24

Answers could include:
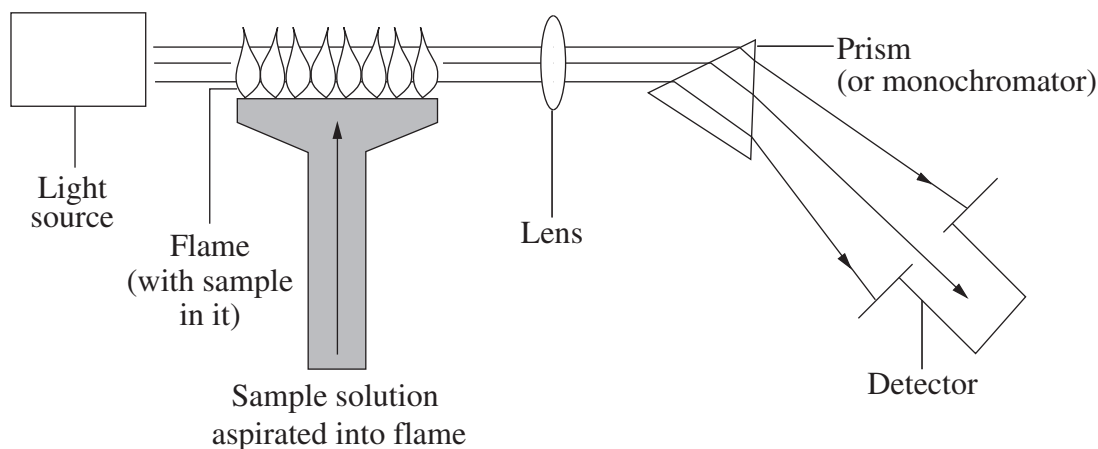
Principles – ground state (unexcited) atoms of an element irradiated by light of a particular wavelength will absorb light and become excited. By measuring the fraction of absorbed light, the concentration of the element in the sample solution can be determined.

- Light source – is a hollow cathode lamp, in which some of the element is present and is excited to emit the particular wavelength.
- Samples are digested (in acid) to produce aqueous solutions.
- Samples absorbance compared with standards of known concentration.

(Calibration curve)

Applications
  – AAS is sensitive (trace concentrations can be measured) to ppm levels
  – Suitable for heavy metals and arsenic in environment, water, soil, effluent
  – Micronutrients in agriculture
  – Pollutants/bioaccumulation in living organisms

- Because a different lamp is needed for each element, it is not as convenient when multiple elements reside in the one sample.

Question 25 (a)

Sample answer:

	Mean absorbance	*Phosphate* (mg L⁻)
1	0.090	0.030
2	0.513	0.190
3	0.235	0.088

Question 25 (b)

Answers could include:

Stream 1 with lowest phosphate levels is unimpacted relative to the other two streams. Both streams 2 and 3 are elevated, with stream 2 exceeding the recommended limit by a factor of about 2.

Possible sources of phosphate giving rise to elevated phosphate in streams 2 and 3:

<u>Natural sources</u> – soils and minerals in the catchment are leached of phosphate.

This can be elevated by

- Amount present in minerals.
- Solubility of phosphate in different minerals
- Land clearing disturbing surfaces and exposing more minerals to leaching.

<u>Man made sources:</u>

- Agricultural or horticultural runoff from land that has had fertilizer application.
- Run off or effluent from animal wastes
- Effluent from sewage treatment plants

Question 25 (c)

Sample answer:

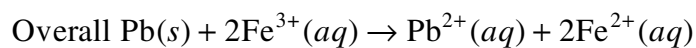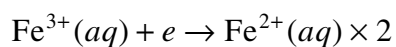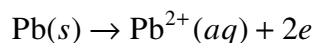Eutrophication or elevated levels of nitrogen and phosphorus.
- Algal blooms
- Mass agal decay
- Stagnant water with low dissolved oxygen
- Aerobic organisms die

This effect may be worsened by low flow in drought conditions.

Some algae (blue green/cyanophyta) are toxic, causing gastric illness or skin rashes.

Question 26 (a)

Sample answer:

$$Pb(s) \rightarrow Pb^{2+}(aq) + 2e$$

$$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq) \times 2$$

Overall $Pb(s) + 2Fe^{3+}(aq) \rightarrow Pb^{2+}(aq) + 2Fe^{2+}(aq)$
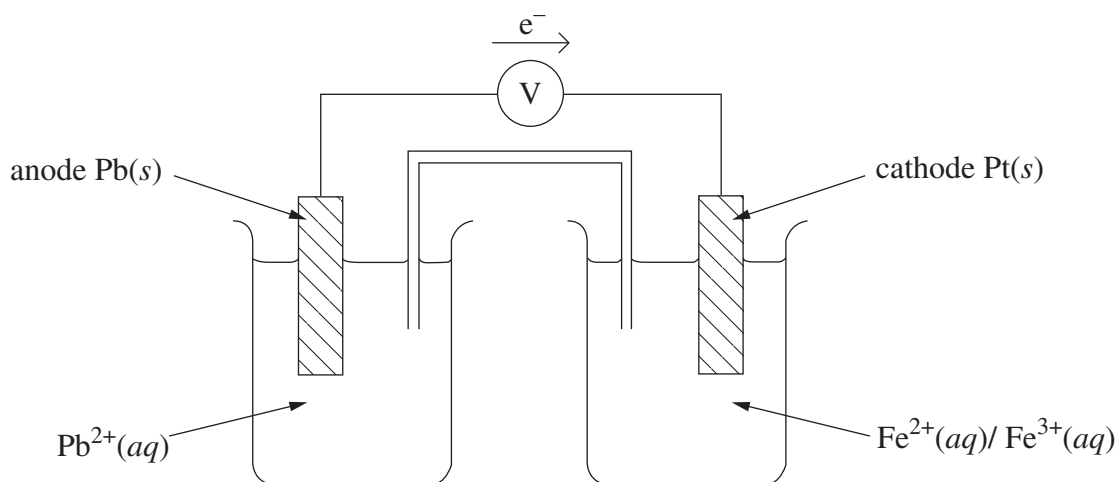
Question 26 (b)

Sample answer/Answers could include:

$$E^{\ominus} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$$
$$E^{\ominus} = 0.77 \text{ V} - (0.13 \text{ V})$$
$$E^{\ominus} = 0.90 \text{ V}$$

Question 26 (c)

Sample answer:

Question 26 (d)

Sample answer:

eg KNO_3

Potassium nitrate
Sulfate and chloride salts not correct.

Section II

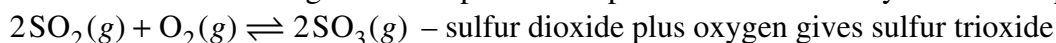**Question 27 (a) (i)**

Sample answer:

Fertilizer.

Question 27 (a) (ii)

Sample answer:

The individual production of sulfuric acid starts with elemental sulfur or metal sulfides. Firstly, sulfur can be extracted from underground deposits by the Frasch process. In this process sulfur is melted by superheated water. It is removed because it is insoluble. Next, sulfur is roasted to form sulfur dioxide in a smelter.

$S(s) + O_2(g) \rightarrow SO_2(g)$ – sulfur plus oxygen gives sulfur dioxide
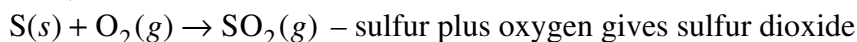
This is exothermic and goes to completion. Sulphuric acid is made by the contact process

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ – sulfur dioxide plus oxygen gives sulfur trioxide

This reaction is exothermic and occurs at 450°C using either platinum metal or vanadium pentoxide as a catalyst.

Question 27 (a) (iii)

Answers could include:

- Corrosive, therefore wear protective gloves
- Contains hydrogen ions that react with metals, so store in glass containers (dil)
- Keep away from water, hygroscopic – ionizes which is extremely exothermic

Question 27 (b) (i)

Sample answer:

$$K = \frac{\left[Cl_2\right]^3 \left[I_2\right]}{\left[ICl_3\right]^2}$$

Question 27 (b) (ii)

Sample answer:

$$K = \frac{(0.45)^3 (0.15)}{(0.05)^2}$$
$$= 5.47$$

	2 $[ICl_3]$	3 $[Cl_2]$	1 $[I_2]$
I	0.35	0	0
C	–0.30	+0.45	+0.15
E	0.05	0.45	0.15

Question 27 (b) (iii)

Sample answer:

K should increase and $[Cl_2]$ and $[I_2]$ should increase while $[ICl_3]$ should decrease.

Question 27 (c)

Sample answer:

E.g. Mayonnaise is an oil-in-water emulsion. Oil in water emulsions have a greater proportion of water than oil so they dissolve or mix better in polar solvents. They are non-greasy. Used as a healthy alternative to butter.

Answers could include:

- Water in oil emulsion
- Lipstick
  – Non-polar
  – Greasy
  – Use as lip moisturiser
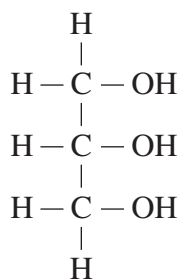

Question 27 (d) (i)

Sample answer:

Soaps dissolve in water, dissociating into an anion derived from a fatty acid or oil, and a Na^+ or K^+ cation derived from the alkali used in its manufacture. It is the anion that plays a prominent role in the cleaning action of soap. It consists of a hydrophobic tail which is non-polar. This end of the ion strongly attracts non-polar grease molecules via dispersion forces. The ion has a hydrophilic head which is polar and thus readily dissolves in water via dipole to dipole interaction. An oil in water emulsion results (micelles) and as the water is agitated the grease is carried away with it.

Answers could include:

May use labelled diagram.
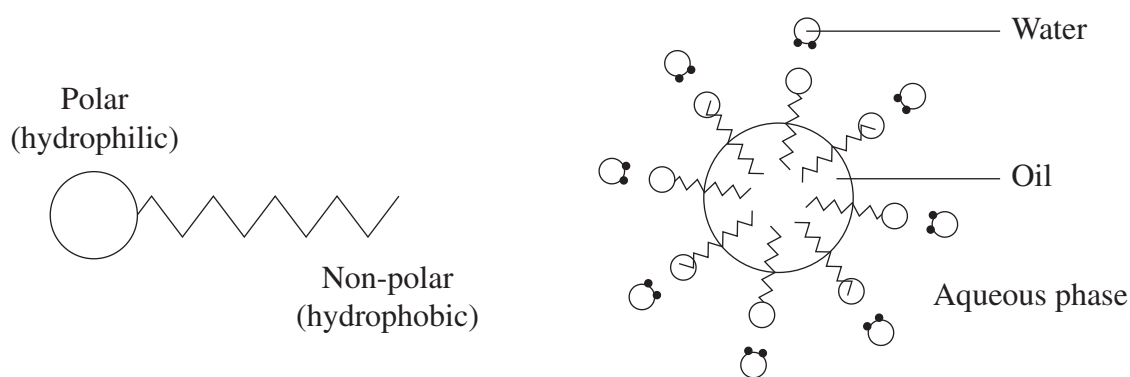
Question 27 (d) (ii)

Sample answer:

Glycerol or 1,2,3 –propanetriol

```
        H
        |
  H — C — OH
        |
  H — C — OH
        |
  H — C — OH
        |
        H
```
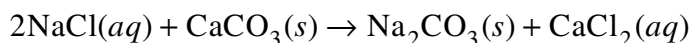
Question 27 (e)

Sample answer:

Criteria
- Proximity to raw materials
- Labour force
- Transport
- Removal of waste
- Energy and water
- Markets

Raw Materials
According to the flow chart the first requirement for the production of sodium carbonate is raw materials. Sodium carbonate is produced from salt and limestone by the Solvay Process:-

$$2NaCl(aq) + CaCO_3(s) \rightarrow Na_2CO_3(s) + CaCl_2(aq)$$

Australia only has one solvay plant, the Osborne plant in Adelaide. This plant receives its raw materials by rail. The limestone comes from the Barossa Valley and has its own rail line to transport the limestone to the plant.

The solvay plant is located on the coast so that obtaining the salt is not an issue as the seawater can be pumped directly to the plant. A concentrated brine is prepared by evaporating the seawater. Impurities also need to be removed from the seawater before use.

Therefore it is important to locate the plant either in close proximity to a raw material or directly linked to transportation ie a rail line.

As the solvay process is a relatively low energy process it is therefore more important to locate the plant nearer to raw materials than to energy supplies.

Production
The first step in the solvay process involves heating the limestone in a kiln in a process called calcination.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
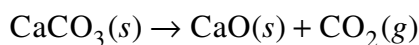
The resultant $CO_2(g)$ is compressed and cooled.

The CaO is removed to be used in a later stage.

The next step involves dissolving ammonia and the carbon dioxide in the purified brine solution in two stages according to :-

$$NaCl(aq) + NH_3(g) + H_2O(l) + CO_2(g) \rightarrow NH_4Cl(aq) + NaHCO_3(aq)$$

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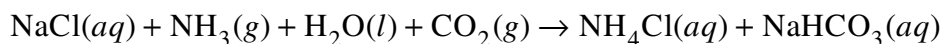
Question 27 (e) (continued)

In stage 1 the purified brine is saturated with ammonia that is derived from the Haber process. This is then partially carbonated because the acidic CO_2 is very soluble in the alkaline brine solution.

In stage 2 the CO_2 is pumped under pressure into the partially carbonated solution. Cooling increases the solubility of the CO_2 and $NaHCO_3$ precipitates out because it has a relatively low solubility at low temperatures.
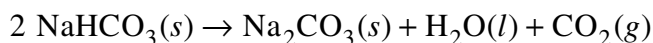
The mixture is then filtered to separate the $NaHCO_3$ crystals from the filtrate. The ammonia chloride is sent to the ammonia recovery plant so that the ammonia can be recovered and reused.

The $NaHCO_3$ crystals are washed and dried and then used to make sodium carbonate via decomposition:-

$$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

Because there are a lot of steps in this solvay process, plants need to be located near towns or cities in order to obtain the skilled workforce necessary.
Plants should also have accessible transport for their workforce.

Waste
The Solvay process has reduced the pollution that was involved in prior methods that were used to produce the sodium carbonate.

Most of the by-products (ammonia, calcium oxide and carbon dioxide) are reused. Calcium chloride is the main waste product. Some of this calcium chloride is purified and sold. Most of it, however, is discharged into the ocean.
The location of the Osborne plant near the ocean is also designed to ensure convenient and cost effective disposal of this waste product.

Another waste product is heat, as this process is exothermic. Waste water must be cooled before returning it to rivers and oceans to avoid thermal pollution. Being located near a river and ocean the Osborne plant to also dispose of this waste efficiently.

Use
The sodium carbonate that is produced from the solvay process has many uses:-
   – can be used in the manufacturing of glass and ceramics
   – can be used in petroleum refining
   – as a water softener in soaps and detergents
   – can be used in the manufacturing of paper and $NaHCO_3$.

Solvay plants must also have access to transport to remove the products, so that they can be sold and/or used. The products from the Osborne plant are transported by ship, rail and road all around Australia.

Question 28 (a) (i)

Sample answer:

Aluminium (Al) is a passivating metal used in drink cans in Australia.

Question 28 (a) (ii)

Sample answer:

Although Al is passivating, it is coated internally with lacquer to prevent attack by acidic soft drink. Protective coatings on metal tins and cans act as a barrier preventing contact between air and water with the steel. Tin is used because it is less reactive than iron. It is also non-toxic. Where the contents of the tin are acidic (beetroot/ vinegar) or when salt concentration is high, potential for corrosion is increased. In this case, a lacquer coating is used in addition inside the can. However, if the coating is scratched then the corrosion of the can will be encouraged, as iron is more active.
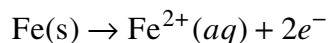
Question 28 (b)

Sample answer:

Galvanised steel is coated with zinc. Zinc provides a barrier as it is passivating. If scratched, it forms a galvanic cell supplying electrons to reduce any Fe^{2+} that forms, since Zn is more reactive than Fe. So Zn protects iron in two ways.

$Zn \rightarrow Zn^{2+} + 2e^-$ zinc is oxidised

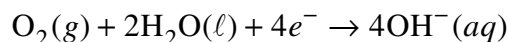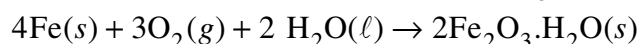to reduce the iron $Fe^{2+} + 2e^- \rightarrow Fe$

Question 28 (c) (i)

Sample answer:

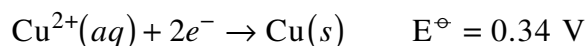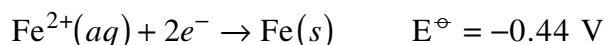Iron corrodes when oxygen and water are present:
iron is oxidised

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

while the reduction is

$$O_2(g) + 2H_2O(\ell) + 4e^- \rightarrow 4OH^-(aq)$$

The $Fe(OH)_2$ oxidises further to Fe_2O_3

$$4Fe(s) + 3O_2(g) + 2\ H_2O(\ell) \rightarrow 2Fe_2O_3.H_2O(s)$$

Question 28 (c) (ii)

Sample answer:

Standard potentials for the three metals are:

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \qquad E^\ominus = -1.68 \text{ V}$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad E^\ominus = -0.44 \text{ V}$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^\ominus = 0.34 \text{ V}$$
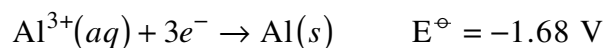
In order of reactivity, copper is least reactive, and then iron and aluminium is more reactive. When coupled (in direct contact) iron screws will corrode in the copper guttering, unless an inert barrier is used to separate the metals, eg rubber grommet/washer.

If electrode potentials alone are considered then Al would be preferentially oxidised, in this case a hole would form in the Al guttering around the screw. This is true in environments where the sea salt disrupts the passivating aluminium oxide layer. Preventing contact between different metals with inert barrier would be necessary.

However as Al is a passivating metal, with a protective inert oxide layer in normal terrestrial environments contact with steel screws shouldn't be a problem.

Answers could include:

Plastic insulator/sleeve.

Question 28 (d) (i)

Sample answer/Answers could include:

Submerged iron artefacts from the past are likely to be impregnated with chloride. This must be removed because it can lead to further corrosion. The artefact is made of the cathode; the stainless steel is the anode. Chloride (and hydroxide) ions migrate towards the anode, whilst iron ions are reduced at the cathode. (H_2 is evolved and this helps to loosen concretions)

The process is gradual; the electrolyte is monitored and changed to remove Cl^- ions. Rinsing, drying and sealing completes the conservation process.

Question 28 (d) (ii)

Sample answer:

A metal spoon (steel) was placed in a solution of silver cyanide. The metal spoon was made the cathode and a silver anode was also inserted. The cathode was connected to a power source. The Ag^+ migrate to the spoon and coat the metal spoon with $Ag(s)$.
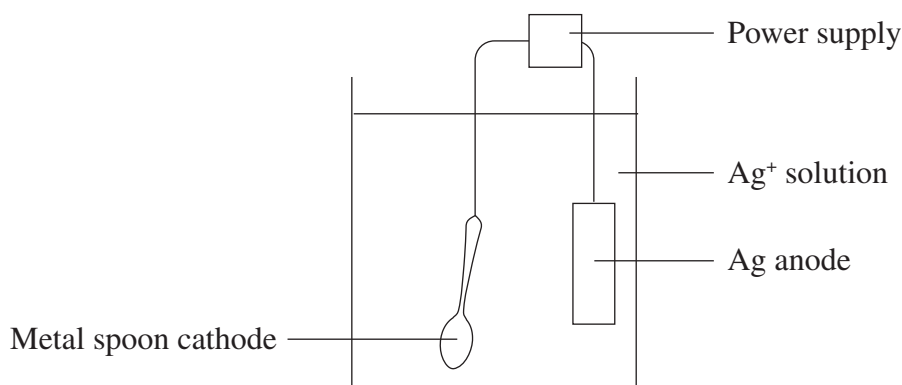
Question 28 (e)

Sample answer:

Our understanding of electrochemical reactions began when:
- Galvani observed muscle twitch (in dead frog) when touched by two dissimilar metals→electricity could pass as a current along a metal wire

- Volta experimented to provide proof of an alternative explanation; the different metals in an electrolyte rather than animal – chemical reaction generates current. Volta developed a new technology, a primitive battery (alternating discs of Cu and Zn with paper soaked in brine). Later Davy used this new source of electrical energy to decompose compounds by electrolysis, producing pure metals from their molten salts – electrical energy to produce chemical reaction. As his assistant Faraday quantitatively observed Davy's work and carried out experiments to relate amount of current to amounts of metals deposited at an electrode, eventually providing the terminology as well as the calculations of electrolysis. The work of these chemists has provided technologies, processes and understandings that impact on our everyday life in the materials and devices we use.

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Question 29 (a) (i)

Sample answer:

<u>Heating</u> the protein molecule above a particular temperature e.g. 60 degrees celsius

Answers could include:

- Shaking or stirring the protein molecule
- Significantly changing the pH of the environment
- Adding particular chemicals like organic solvents

Question 29 (a) (ii)

Sample answer:

The native shape of a protein molecule depends upon a number of levels or organisation within its structure.

Denaturation results from disruption of the intramolecular bonding forces responsible for the secondary and tertiary structure of a protein molecule. The bonding forces disrupted include hydrogen bonding, disulfide bonding, electrostatic and dispersion forces (hydrophobic).

Question 29 (b)

Sample answer:

This set of experimental results suggests through colour change that there is enzyme activity only (and to varying extents) between pH 4.0 – pH 7.0.

The dark red colour of the solution between pH 6.0 – pH 7.0 suggests that the catalysed reaction has proceeded to a greater extent than at the other pH values of 4.0 and 5.0.

The experimental results confirm that narrow pH ranges (6.0 – 7.0) are required for optimal enzyme activity.

Question 29 (c) (i)

Sample answer:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(\ell) \qquad \Delta H = -2816 \text{ kJ mol}^{-1}$$
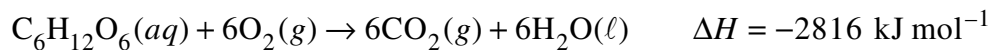
Question 29 (c) (ii)

Sample answer:

2816 kJ per mole
2816 kJ per 180 g
Formula mass = 180 glucose

$$\text{Energy released per gram } = \frac{2816}{180}$$

$$= 15.6 \text{ kJ/g}$$

Question 29 (c) (iii)

Sample answer:

$$\text{Energy from bar } = 36.7 \times \text{kJ}$$

$$= 36.7 \times 15.6$$

$$= 574.2$$

$$\text{Kilometres travelled } = \frac{\text{total kJ}}{80}$$

$$= \frac{574.2}{80}$$

$$= 7.2 \text{ km}$$

Question 29 (d) (i)

Sample answer:

Glycerol 1, 2, 3 – propanetriol is a 3 carbon chain with 3 O–H groups. This makes glycerol an extremely polar molecule and therefore very soluble in water. The 3 O–H groups also form strong hydrogen bonds between adjacent molecules resulting in an extremely viscous liquid.

Question 29 (d) (ii)

Outcomes assessed:H6, H9, H11

Sample answer:

Fatty acids contain a carboxylic acid group. The O–H group can form H bonds with water and is hydrophilic.

The R–group is hydrocarbon with dispersion forces and is hydrophobic. Therefore, small fatty acids ($C_1 – C_4$) are soluble but larger ones are insoluble.

Triacylglycerols are esters from glycerol and an alkanoic acid. There is no O–H group so they cannot H bond and are insoluble in water.

Question 29 (e)

Sample answer:

Muscle cells require energy, which is stored in the form of adenosine triphosphate (ATP), in order to contract so that locomotion can be achieved. Aerobic cellular respiration, as it commonly occurs, provides much of the energy needed in order for this to occur.

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(\ell) + 38 \text{ ATP molecules}$$
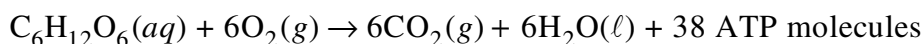
This of course is a very simplified view of a chemical process that has in excess of 100 individual steps, each catalysed by an enzyme and in some cases, requiring the action of co-enzymes.

Type 1 (slow twitch) skeletal muscle fibres obtain most of their ATP aerobically in this manner as they tend to have a rich blood supply which provides adequate amounts of <u>glucose</u> (and other fuels) <u>and oxygen</u> to their many mitochondria. These cells contract slowly and steadily and are useful in light endurance exercise.

Type 2 high intensity (fast twitch) skeletal muscle fibres, by comparison, have fewer mitochondria and a reduced blood supply. Consequently, these cells respire <u>anaerobically</u>, using <u>muscle glycogen stores</u> as a primary energy source.

GLYCOGEN $\rightarrow$ GLUCOSE-6-PHOSPHATE $\rightarrow$ GLUCOSE
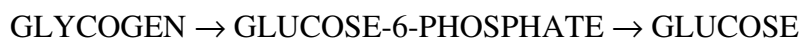
The glucose generated in this way enters the anaerobic glycolysis pathway resulting in the production of only two ATP molecules and two pyruvate ions.

$2NAD^+$ $2NADH+H^+$

Glucose $\longrightarrow$ 2 Pyruvate + 2ATP
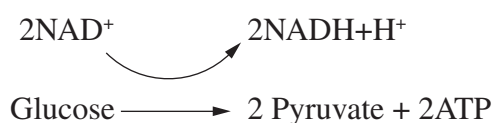
These cells are primarily used in high intensity athletic events where oxygen levels are depleted and they require maximum energy (ATP) in a relatively short period of time.

To achieve this with limited supplies of oxygen, <u>anaerobic respiration</u> takes place. Pyruvate is reduced to lactate (lactic acid), resulting in muscle fatigue and cramping due to a fall in pH. This is accompanied by a regeneration of NAD^+ which can re-enter anaerobic glycolysis to produce more ATP.

$$PYRUVATE + NADH + H^+ \rightarrow LACTATE + NAD^+$$
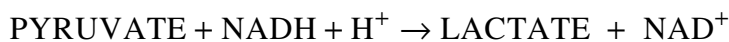
Anaerobic respiration in muscles can be summarised using the following equation.

Glucose   Lactate

$$C_6H_{12}O_6 + 2ADP + 2Pi \rightarrow 2CH_3CHOHCOO^- + 2ATP + 2H_2O + 2H^+$$
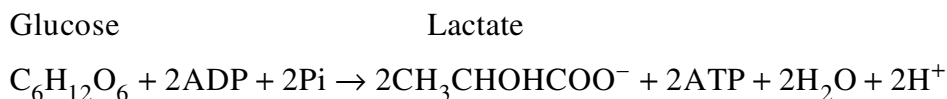
An understanding of these biochemical reactions enables improved sports performance through better and more informed training programs. An athlete will adopt a training program that will closely mimic their sport and the muscles involved. This isolates and specifically exercises the muscle cells involved, improving the efficiency and strength with which they contract, regardless of the way they respire.

Specific training programs will also incorporate aspects that will improve an athlete's ability to maximise their body's utilisation of oxygen. This minimises muscle anaerobic respiration and thus the tendency to suffer fatigue and cramping, enabling better performance.

Question 30 (a) (i)

Answers could include:

Typical monodentate ligands are:
- Water (H_2O)
- Ammonia (NH_3)
- Chloride ion (Cl^-)
- Cyanide ion (CN^-)
- Carbon monoxide (CO)
- Thiocyanate ion (NCS^-)
- Hydroxide ion (OH^-)

Question 30 (a) (ii)

Sample answer:

The term 'polydentate ligand' refers to the ligands that bond through electron pairs on more than one donor atom.

EDTA is a polydentate ligand because it has six donor atoms – two nitrogen and four oxygen atoms.

Question 30 (a) (iii)

Sample answer:

Coordinate covalent bonds form between ligands and transition metals. Electrons from the lone pairs on the donor atoms of the ligand (oxygen and nitrogen in the case of EDTA) interact with the d-orbitals of transition metals (Cu in this case). This is a Lewis acid – Lewis base interaction. EDTA is the Lewis acid and Cu^{2+} is the Lewis base.

Question 30 (b) (i)

Sample answer:

The maximum number of electrons that a p-orbital can hold is two. This is Hunds Rule.

Question 30 (b) (ii)

Sample answer:

Ca atom: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
Ca^+ ion: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$
Ca excited atom: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 4p^1$ (example)

Question 30 (c)

Sample answer:

The increase in ionisation energy from Z=2 to 10 and Z=11 to 18 relates to the increase in effective nuclear charge across periods 1 and 2 respectively. The same valence shell is being filled across a period, hence inner shell shielding and nucleus – shell distance is approximately constant while the nuclear charge increases. Hence the electron binding force increases, requiring greater energy to remove a valence shell electron.

Therefore, the ionisation energy increases across a period. When the next valence shell begins to fill, as occurs at Z=3, 11 and 19, the ionisation energy drops substantially because the electron experiences increased inner shell nuclear shielding and is further from the nucleus.

The generally lower ionisation energies for the second period elements compared to the first period elements also reflects the filling of higher valence shells.

This reflects the decrease in ionisation energy down a group in the periodic table.

Answers could include:

Variations from the general trend reflects electron-electron interactions in the valence shell.

Question 30 (d) (i)

Sample answer:

Kirchoff's observation reflects the quantum mechanical nature of atoms. The hot gas contains atoms that are in excited electronic states. Photons are emitted from these atoms as the electrons relax from a higher energy level to a lower energy level.

Kirchoff's observation was later given a basis in theory by Planck (Quantum Theory) and Bohr (electronic structure of the atom). The colour of the emission line is related to the wavelength of the emitted light. The wavelength is related to the difference in energy between the starting level and the finishing level. There are different possible higher and lower energy levels, so an element can emit light of more than one wavelength. Different elements have different sets of energy levels, so the emission lines are characteristic of the element.

Question 30 (d) (ii)

Sample answer:

There are a number of ways in which the presence of the element could be determined. The water sample could be introduced directly into the flame of the Bunsen Burner and the colour of the flame observed. This is unlikely to be definitive as the water is likely to contain other metals and compounds that will emit light and obscure the emission from the metal of interest. Salt is a common problem. Also the concentration of the metal is likely to be too low.

Question 30 (e)

Sample answer:

Early pigments were those that could be found naturally and required little or no further processing. These pigments includes those found in ochres. Many contain oxides of iron. Processing of these natural materials was typically no more than grinding to produce a fine powder, and mixing with a dispersion agent and binder, such as water (dispersion) or egg (binder). With technological development it became possible to further process mineral ores, typically through roasting, to produce new pigments. These pigments could contain Fe, Cu, Mn and other transition metals. In some cases these pigments contained quite toxic compounds of Pb, Hg and Cr. The advances in the theory and practise of chemistry that occurred from the 16th century allowed the development of many new compounds, many of which are not found in nature. Most of these new compounds still employed transition metals as the main determinant of the colour. From the 19th century, with advances in organic chemistry, many of the pigments were superseded with carbon-based compounds.

For those pigments containing transition metals the main origin of the colour is the absorption of photons of specific wavelengths by the transition metals. The energy is absorbed through d-shell electrons being raised to higher energy levels. The corresponding wavelengths of light are removed from the transmitted or reflected light, leaving a coloured substance.

The energy required to cause these d-electron transitions corresponds to photon wavelengths in the visible part of the electromagnetic spectrum. The same transition metal may give rise to compounds with different colours. This may be because the metal is in different oxidation states or because the metal is bonded to different ligands. The result is that the energy of the d-orbitals are different and hence the electron transitions between states requires different energies, ie, different wavelengths of light, and hence different colours.

Answer may include:

Direct reference to natural pigments eg,

Red ochre
Yellow ochre $\Big\}$ $Fe_2O_3.H_2O$

Chalk $CaCO_3$

Charcoal   C

Direct reference to refined mineral eg:
Malachite $CuCO_3$ $Cu(OH)_2$

Chalk   PbS

Charcoal As_2S_3

Direct reference to inorganic synthetic compounds, eg:
Prussian Blue $2CuCO_3.Cu(OH)_2$

Artificial vermilion   HgS

Direct reference to absorption or reflectance spectra. Direct reference to transition metal complexes.

Question 31 (a) (i)

Sample answer:

Peptide bond.

Question 31 (a) (ii)

Sample answer/Answers could include:

Primary structure   –   sequence of amino acids

Secondary structure –   folding of amino acid chain into α-helix or β pleated sheet

Tertiary structure   –   complete form of the chain being the combination of parts of secondary   structure held together by disulfide bonds and intramolecular bonding forces, especially hydrogen bonding.

Question 31 (a) (iii)

Sample answer:

Electrophoresis separates proteins by allowing their movement in response to an applied electric field. Their final position is revealed by staining, so bands of proteins can be visualised.
The position is protein specific. The positions of bands of known proteins can be compared to samples of possibly unknown proteins in a suspect sample.

So protein from known food, suspected adulterated food and known possible alternative sources can be compared.

Question 31 (b) (i)

Sample answer:

The oil from Ship A gives the same chromatogram as the oil spill sample. Therefore it is likely the spill originated from this vessel.

Question 31 (b) (ii)

Sample answer:

The components of the mixture separate as the mixture passes through the chromatographic system. The components then exit the system separately on a time basis and pass the detector sequentially. The chromatogram is the detector response (*y*-axis) recorded over time (*x*-axis).

Each peak occurs as the component passes the detector at a time characteristic of that component, inducing a response in the detector. The response is recorded as signal intensity on the *y*-axis.

The peak height or peak area is directly related to the amount of the component.

Question 31 (c)

Sample answer:

Chromatographic systems (GLC, HPLC) allow separation of components in a mixture as the mixture passes through the system, depending on strength of attachment of components to the stationary phase. GLC instruments have developed to allow use of small sample size by:

– Use of microsyringes to inject very small volumes

– Temperature controlled ovens to control separation conditions

– Detectors of high sensitivity eg, mass spectrometry

– Capillary columns to allow for very small samples

In HPLC a variety of stationary phases are now available, micro and capillary columns are now used. Very sensitive detectors available, eg, Mass spectrometry. In GLC variety of stationary phases available. In HPLC separation can be improved with variation of mobile phase.

Question 31 (d) (i)

Sample answer:

Materials:

– Stationary phase, paper or thin layer plates

– Mobile phase or solvent (ethanol and water to depth 5mm in chromatography jar or beaker)

– Samples of known dyes (standard)

Method:

– Spot unknown mixture on stationary phase plates about 10mm from edge

– Spot standards on same paper or plate

– Place in jar, cover jar and allow chromatography to proceed

– Allow mobile phase to ascend to close to top

– Remove and mark solvent front immediately

– Allow plates to dry

– Compare distances travelled visually or by Rf values

Question 31 (d) (ii)

Sample answer:

	Reaction with $Br_2(aq)$ in dark	Reaction with Na(s)	Reaction with Na_2CO_3
alkenes	rapid decolourise	no	no
alkanol	very slow	provides $H_2(g)$	no
alkanoic acid	no reaction	provides $H_2(g)$	produces $CO_2(g)$

Question 31 (e)

Sample answer:

The forensic chemist must consider throughout the whole process the maintenance of:
- Sample identity and security
- Sample integrity and appropriate storage for possible subsequent reanalysis

Sample collection – samples collected must be representative of the materials investigated:
- Stored so as to preserve chemical and physical properties for subsequent analysis
- Sampled and stored so as to prevent contamination, for example, human biological tissue collected for DNA analysis contaminated with skin flakes or hair from another person
- Samples need to be uniquely identified and a chain of custody initiated

Initial examination and classification:
- First step leading to further analysis
- Characterise materials as organic or inorganic e.g. by combustion
- Need to consider bulk components e.g. wood splinters, glass fragments, soil, plant matter, body tissue and trace elements which may give fingerprint
- Simple chemical tests may distinguish some groups of compounds – alkenes, alcohols, acids, bases, proteins, sugars

Instrumental analysis:
- Specific analysis of sub-samples to give identification of component compounds or fingerprint of suite of compounds. Analysis may lead to quantifying components. Specific analysis would depend on the nature of the sample, surroundings and context
- Gas chromatography with mass spectrometry can be used to identify and quantify e.g.
  – Alcohols
  – Flavours
  – Hydrocarbons
  – Pesticide residues
and allow fingerprint comparisons between standard mixtures and sample extracts.

(Other instrumentation examples: HPLC, Electrophoresis, DNA Fingerprinting, Atomic Absorption or Emission Spectroscopy). Many instrumental techniques allow use of very small samples, so the remainder can be retained for subsequent second analysis if required.
- Quality assurance via accreditation of the analytical laboratory and appropriate instrument calibration is essential

Interpretation of results:
- The analytical/ forensic chemist needs to be able to express the results and convey information precisely and unambiguously to others. This would occur in a court of law, or associated arena. The results may require defence and would need documentation of methods and quality assurance.