PART 1 (60 marks = 30% of paper)

Answer ALL questions in Part 1 on the separate Multiple Choice Answer Sheet provided. Each question in this part is worth 2 marks.

each

PART 2 (70 marks = 35% of paper)

Answer ALL questions in Part 2 in the spaces provided below.

1. Write equations for any reactions that occur in the following procedures. If no reaction occurs write 'no reaction'.

 \mathcal{L}_max and \mathcal{L}_max and \mathcal{L}_max and \mathcal{L}_max and \mathcal{L}_max and \mathcal{L}_max

In each case describe in full what you would observe, including any colours, odours, precipitates (give the colour) and gases evolved (give the colour or describe as colourless). If no change is observed you should state this.

a) Dilute nitric acid is added to magnesium carbonate.

Equation $(3\mathbf{q})$ **+ MgCO**_{3(s)} \rightarrow **Mg²⁺**(aq)</sub> **+ H₂O**(l)</sub> **+ CO_{2(g)}** \bullet **//**

Observation **A white solid dissolves into a colorless solution and an odourless and colourless gas evolves.**

[3 marks]

- b) An excess of 2 mol L^{-1} potassium hydroxide solution is gradually added to a zinc chloride solution.
- Equation cap **+ 2OH** cap \rightarrow **Zn(OH)**_{2(s)}

 $\mathsf{Zn}(\mathsf{OH})_{2(\mathsf{s})} + 2\mathsf{OH}^{\cdot}_{(\mathsf{aq})} \rightarrow [\mathsf{Zn}(\mathsf{OH})_{4}]^{2-\mathsf{q}}$

Observation **A white precipitate forms which redissolves, forming a colorless solution.**

[3 marks]

(aq)

c) A piece of sodium is added to 2-propanol.

Observation **A grey metallic solid dissolves and an odourless and colourless gas evolves.**

[3 marks]

d) Hydrochloric acid is added to potassium permanganate solution.

Equation $\mathbf{C}_{(aq)}$ + 16H⁺_(aq) + 10Cl⁻_(aq) \rightarrow 2Mn²⁺_(aq) + 8H₂O_(l) + 5Cl_{2(g)} \checkmark \checkmark Observation **A purple solution becomes discoloured and a pungent yellow-green gas evolves.**

[3 marks]

- 2. For each of the species listed in the table below:
	- a) draw the structural formula, representing all valence shell electron pairs as either : or –
	- b) indicate the shape of each species by either a sketch or a name

3. a) On the following set of axes, sketch a graph that depicts the trend in first ionisation energy of the alkali metals.

b) Briefly account for the trend depicted in a).

Moving down the group, the nuclear charge increases.

However, the valence electron is located in the next principal energy level and experiences a greater degree of shielding.

Thus the attraction of the valence electron to the nucleus is decreased, resulting in a decease in the energy required to remove one mole of electrons from one mole of atoms in the gas phase (ionization energy).

[3 marks]

[1 mark]

4. a) Complete the following table by matching the boiling points with the following compounds: butanal, pentane, 2,2-dimethylpropane and propanoic acid.

[2 marks]

b) Explain your choices in a).

2,2-dimethylpropane and pentane are both nonpolar molecules with only dispersion forces between molecules.

The more compact shape of 2,2-dimethylpropane reduces the strength of dispersion forces between molecules so it has the lowest boiling point.

Butanal, of similar molar mass, has the polar -CHO group, which provides for dipole-dipole forces between molecules. This increases the strength of intermolecular attractions above that of the hydrocarbons of similar size.

Propanoic acid, also of similar molar mass, has the -COOH group, which provides for hydrogen bonding between molecules. This particularly strong form of dipole-dipole interaction increases the strength of intermolecular attractions above that of the other compounds.

[4 marks]

5. Hydrogen gas for use in the Haber Process can be produced by the reaction of methane and water, according to the following equation:

 $CH_{4(a)} + H_2O_{(a)} \rightleftarrows CO_{(a)} + 3H_{2(a)}$ $\Delta H = -ve$

The usual conditions for this reaction are a temperature of 750°C in the presence of a nickel catalyst.

Consider an equilibrium mixture of these gases. Comment upon how each of the changes described in the table below will affect:

- the **initial** rate of the forward reaction; and
- the yield of hydrogen gas.

[10 marks]

each

6. a) Write an equation for the ionisation of water.

$$
2H_2O_{(I)} \rightleftarrows H_3O^{\dagger}_{(aq)} + OH^{\dagger}_{(aq)} \text{ or } H_2O_{(I)} \rightleftarrows H^{\dagger}_{(aq)} + OH^{\dagger}_{(aq)} \qquad \checkmark
$$

[1 mark]

b) The pH of pure water decreases with increasing temperature. Using Le Chatelier's Principle, explain whether the ionisation of water is an endothermic or exothermic process.

 $pH = -log[H^+]$ **] By LCP,** ↑ **temp causes shift in endothermic direction** ↓ **pH =** ↑**[H+], therefore forward reaction is endothermic**

[3 marks]

- 7. Lactic acid $(CH_3CH(OH)COOH)$ is a weak monoprotic acid. The pH of a 0.100 mol L^{-1} solution of lactic acid is 2.43.
	- a) Write an equation representing the ionisation of lactic acid in aqueous solution.

 $CH_3CH(OH)COOH$ _(aq) + $H_2O_{(l)} \rightarrow CH_3CH(OH)COO^-(aq)$ + H_3O^+ **(aq)** [2 marks]

b) Determine the $[H^+]$ in the 0.100 mol L^{-1} lactic acid solution.

 $[H^+] = 10^{-pH} = 10^{-2.43} = 3.72 \times 10^{-3} \text{ mol}$

[1 mark]

c) What percentage of lactic acid molecules have ionised in solution?

% ionisation =
$$
3.72 \times 10^{-3} / 0.100 \times 100 = 3.72\%
$$

[1 mark]

d) Compare the electrical conductivity of a 0.100 mol L^{-1} lactic acid solution with pH 2.43 and a 0.100 mol L^{-1} hypochlorous acid (HOCI) solution with pH 4.23. Explain your answer.

Both are weak monoprotic acids.

The lower pH of lactic acid indicates that it has ionized to a greater extent, therefore 0.100 molL-1 lactic acid will contain a greater concentration of ions.

As the concentration of ions increases, so does electrical conductivity of the solution.

[3 marks]

8. Describe a chemical test could be performed to distinguish between the following two compounds. State your expected observations for each compound.

[3 marks]

9. Consider the following unbalanced equation:

$$
As_2O_{3(s)}\;+\;NO_3{}^-{}_{(aq)}\;\longrightarrow\;H_3AsO_{4(aq)}\;+\;NO_{(g)}
$$

b) Write the oxidation and reduction half equations.

Oxidation $\mathsf{As}_2\mathsf{O}_{3(s)}$ + $5\mathsf{H}_2\mathsf{O}_{(l)} \rightarrow 2\mathsf{H}_3\mathsf{AsO}_{4(aq)}$ + $4\mathsf{H}^+_{(aq)}$ + $4\mathsf{e}^ \checkmark$ [2 marks] Reduction NO_3^- _(aq) + 4H⁺_(aq) + 3e⁻ → $NO_{(g)}$ + 2H₂O_(l) \checkmark [1 mark]

c) Write the balanced overall equation for the reaction. $3As_2O_{3(s)}$ + $4NO_3^-$ _(aq) + $4H^+$ _(aq) + $7H_2O_{(l)}$ → $6H_3AsO_{4(aq)}$ + $4NO_{(g)}$ ✓ ✓ [2 marks]

- 10. a) In the space below, sketch an electrolytic cell that could be used to plate an iron spoon with nickel. Clearly identify the following:
	- the materials that you would use at each electrode and as the electrolyte
		- the anode and cathode
		- the direction of flow of electrons

b) Write equations for the reactions that would occur at each electrode

[1 mark]

11. The structure salicylic acid is depicted below.

Note that salicylic acid has an alcohol functional group and a carboxylic acid functional group.

Sketch the product of the reaction of salicylic acid, under appropriate conditions, with:

12. Polyacrylonitrile (PAN) is a polymer that is widely used in carpets. A section of its structure is depicted in the following diagram:

a) In the space below sketch the monomer, acrylonitrile.

b) What class of polymer, addition or condensation, is polyacrylonitrile?

End of Part 2

PART 3 (50 marks = 25% of paper)

Answer ALL questions in Part 3. The calculations are to be set out in detail in this Question/Answer booklet. Marks will be allocated for correct equations and clear setting out, even if you cannot complete the problem. When questions are divided into sections, clearly distinguish each section using (a), (b), and so on. Express your final numerical answers to three (3) significant figures where appropriate, and provide units where applicable. Information which may be necessary for solving the problems is located on the separate Chemistry Data Sheet. Show clear reasoning: if you don't, you will lose marks.

1. A common ore of manganese is hausmannite, which contains Mn_3O_4 . A particular sample of hausmannite is known to contain 29.2% $Mn₃O₄$.

 $Mn₃O₄$ can be reduced to manganese metal by reduction with aluminium as follows

 $3 \text{ Mn}_3\text{O}_4$ + 8 Al \rightarrow 9 Mn + 4 Al₂O₃

In a particular process, 5.00 kg of the sample of hausmannite is reacted with 500.0 g of aluminium.

a) Assuming that the reaction is 100% efficient, what mass of manganese metal can be obtained?

(7 marks)

b) What mass of the excess reactant will remain?

(3 marks)

- 2. When England win the Rugby World Cup (again!), they will be presented with a trophy that is an alloy of several metals, including chromium. The chromium content of a trophy can be determined by oxidising the chromium to sodium dichromate by reacting with an excess of persulfate (S₂O₈²⁻) ions, boiling to destroy any excess oxidant and then titrating the acidified solution with standardised iron (II) sulfate solution. Using this method, a 8.405 g sample of the same alloy used to make the trophy was converted into an acidified solution of sodium dichromate and diluted to 250 mL. A 25.0 mL sample was then titrated against 0.415 mol L^{-1} iron (II) sulfate and required 24.80 mL to reach the endpoint.
	- a) Write a balanced equation for the reaction between $\mathsf{Cr_2O_7}^{2-}$ and Fe^{2+}

(2 marks)

b) Calculate the percentage by mass of chromium in the trophy.

(6 marks)

3. A D.C. electric current was passed through three cells connected in series for 30.0 minutes. The first cell contained silver nitrate solution with silver electrodes, the second cell contained nickel(II) sulfate solution with nickel electrodes and the third cell contained potassium iodide solution with graphite electrodes. In the first cell, 0.6389 g of silver was deposited.

(4 marks)

b) If the nickel anode had a mass of 2.00 g before the electrolysis, what would be its mass at the end?

(3 marks)

c) What volume of gas would be given off at the cathode of the third cell, measured at 103 kPa and 24.0 $^{\circ}$ C?

(2 marks)

4. Putrescine $(C_4H_{12}N_2)$ is an organic chemical that is responsible for the foul odour of decaying flesh. By determining the putrescine content of body tissue of corpses, forensic scientists can estimate how long a body has been dead. Putrescine contains two amine $(-NH₂)$ groups and reacts with hydrochloric acid as follows;

$$
H_2N-(CH_2)_4-NH_2(aq) + 2H^+(aq) \rightarrow H_3N-(CH_2)_4-NH_3^+(aq)
$$

During a murder investigation, a 500.0 g sample of dead tissue was boiled up in 3.00 L of 0.200 mol L^{-1} hydrochloric acid to react all the putrescine.

The organic product was removed from the reaction mixture by precipitation and then 20.00 mL samples of the remaining solution were extracted and titrated against 0.200 mol L^{-1} sodium hydroxide solution with a phenolphthalein indicator. The following results were obtained.

a) Calculate the average titre of sodium hydroxide

(1 mark)

b) Calculate the percentage by mass of putrescine in the dead tissue.

(8 marks)

a) V(NaOH)ave = (18.30 + 18.25) / 2 = 18.275 mL

a)

5. Desflurane is a commonly used general anaesthetic, and is known to contain carbon, hydrogen, oxygen and fluorine only. The following experiments were performed to determine the molecular formula of desflurane.

Firstly, 2.00 g of desflurane was completely combusted in excess oxygen to form 1.57 g of carbon dioxide and 0.214 g of water.

In a second experiment, the fluorine in 1.20 g of desflurane was completely converted into hydrofluoric acid, HF(aq), and made up to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of this solution required 21.43 mL of 0.200 mol L^{-1} sodium hydroxide solution for neutralisation.

Finally, a 1.00 g sample of desflurane was vapourised at 250 $^{\circ}$ C and 101.3 kPa and was found to occupy a volume of 256.0 mL.

a) Calculate the empirical and molecular formula of desflurane.

(13 marks)

b) Given that it does not contain an –OH (alcohol) group, suggest a *possible* structural formula of desflurane.

(1 mark)

$$
C \qquad n(C) = n(CO_2) = m/M = 1.570 / 44.01 = 0.03567 \text{ mol}
$$

m(C) = n.M = 0.03567 x 12.01 = 0.4784 g

%(C) = 0.4784 / 2.00 x 100 = 21.42%

H
$$
n(H) = 2 \times n(H_2O) = 1 \times 0.214 / 18.016 = 0.02376
$$
 mol

m(H) = n.M = 0.02376 x 1.008 = 0.02395 g

%(H) = 0.02395 / 2.00 x 100 = 1.197%

$$
F \tH^+ + OH^- \rightarrow H_2O
$$

n(OH-) = c.V = 0.200 x 0.2143 = 0.004286 mol

$$
n(H^{\dagger})_{25mL} = n(OH^{\dagger}) = 0.004286 \text{ mol}
$$

$$
n(F) = n(H+)250mL = n(H+)25mL x 250 / 25 = 0.04286 mol
$$

$$
m(F) = n.M = 0.04286 \times 19.00 = 0.8143 g
$$

$$
\%(\mathrm{F}) = 0.8143 / 2.00 \times 100 = 67.86\%
$$

$$
0 \qquad \% (O) = 100 - (\% (C) + \% (H) + \% (F)) = 9.523\%
$$

b)

(Note: Full structural formula required)

PART 4 (20 marks = 10% of paper)

Answer the following extended answer question. Where applicable use equations, diagrams and illustrative examples of the chemistry you are describing.

Marks are awarded for the relevant chemical content of your answer, but you will lose marks if what you write is unclear or lacks coherence.

Many metals are extracted from their ores by chemical processing. The following methods have been used commercially.

- Sodium is obtained by electrolysis of NaCl $_{(1)}$
- Magnesium is obtained by electrolysis of MgCl_{2 (l)}
- Aluminium can be obtained by the reaction of sodium with $AICI_3$:

$$
AICI_{3 (g)} + 3 Na_{(l)} \rightarrow Al_{(l)} + 3 NaCl_{(l)}
$$

- Silicon can be obtained by treatment of $SiCl₄$ with Zn :

 $SiCl_{4 (a)} + 2 Zn_{(1)} \rightarrow Si_{(s)} + 2 ZnCl_{2 (1)}$

- Lead can be obtained by roasting PbS in air then heating the PbO product with C :

2 PbS_(s) + 3 O_{2 (g)} \rightarrow 2 PbO_(s) + 2 SO_{2 (g)} then

2 PbO_(s) + C_(s) \rightarrow 2 Pb_(l) + CO_{2(g)}

- Copper can be obtained by roasting CuS in air and then reducing the resultant CuO with further CuS :

> $2 \text{ CuS}_{\text{(s)}} + 3 \text{ O}_{2 \text{(q)}} \rightarrow 2 \text{ CuO}_{\text{(s)}} + 2 \text{ SO}_{2 \text{(q)}}$ $CuS_{(s)}$ + 2 $CuO_{(s)} \rightarrow 3 Cu_{(l)}$ + 2 $SO_{(q)}$

- Silver can be found in nature in the elemental state or it can be extracted from ore by a cyanide-complex method. It is also a by-product of gold production.

Discuss the chemical basis and condition of these processes comparing them with what you know about the extraction of metals such as Al, Au and Fe.

Use your E^o table as a quide to the relative ease of reduction of the metal compounds.

There is no single correct solution to this question, as it could be responded to in a variety of ways.

In order to achieve high marks, responses would need to:

- *- be relevant to the topic/s referred to in the question*
- *- make specific reference to the material/information presented*
- *- provide equations where appropriate*
- *- link evidence to theory*
- *- contain no errors*

Responses that were largely comprised of 'regurgitated' notes on the extraction of Fe, Al, Au from a calculator scored poorly.

The best responses grouped together elements or similar reactivity and linked the method of extraction to the relative ease of reduction, as determined by values in the table of standard reduction potentials

Listed below are some points that could have been addressed.

Metals are usually found in nature chemically combined with other elements (commonly oxygen and sulfur). Only very unreactive metals such as gold, and in rare cases silver and copper, occur in an uncombined state. Therefore, the extraction of metals from these compounds involves reduction. The method of extraction is closely linked to the ease of reduction. For unreactive metals, there needs to be an initial oxidation process in order to take the metal into solution so as to remove the unwanted rock/soil.

For the elements discussed, as well as Au, Fe, Al, based on table of standard reduction potentials, the ease of reduction of metal ions is:

Although industrial processes for metal extraction do not occur under standard conditions, the ranking still provides an indication as to the metals' reactivity.

Unreactive metals (e.g. Au, Ag) must first be oxidised. They are too inert to be oxidised by oxygen alone. For example, gold:

However they can be oxidised in the presence of cyanide ions (CN⁻) to form a stable complex ion.

$$
Au_{(S)} + 2CN^{(aq)} \rightarrow Au(CN)_{2\ (aq)} + e^{+} \qquad E^{0} = + 0.60V
$$

\n
$$
O_{2(g)} + 2 H_{2}O_{(l)} + 4 e^{-} \rightarrow 4OH^{(aq)} \qquad E^{0} = + 0.40V
$$

\n(+ 1.00V)

Presumably, silver reacts in a similar manner to gold in cyanide solution:

 $Ag_{(S)} + 2CN_{(aq)} \rightarrow Ag(CN)_{2\ (aq)} + e^-$ (E⁰ = +0.31V)

The concentration of the gold/silver-bearing solution is increased via carbon adsorption, with the gold/silver recovered by electrolytic reduction of the concentrated solution and purified by smelting.

Ions of less reactive metals (e.g. Cu) can be reduced by simply heating strongly in air. In the roasting of CuS, the sulfide ion itself acts as the reductant:

$$
2 CuS_{(s)} + 3 O_{2(g)} \rightarrow 2 CuO_{(s)} + 2 SO_{2(g)}
$$
 then

$$
CuS_{(s)} + 2 CuO_{(s)} \rightarrow 3 Cu_{(l)} + 2 SO_{2(g)}
$$

Ions of metals of intermediate reactivity (e.g. Pb, Fe) can be reduced by heating strongly in air with a reductant such as carbon (coke).

2 PbS_(s) + 3 O_{2(g)} \rightarrow 2 PbO_(s) + 2 SO_{2(g)} then 2 PbO_(s) + C_(s) \rightarrow 2 Pb_(l) + CO_{2(g)}

The reduction of PbO in the second stage of the process described above is similar to the reduction of iron in the blast furnace:

In the blast furnace, carbon is initially oxidised to carbon dioxide, which is subsequently reduced by carbon forming carbon monoxide:

$$
\begin{array}{l}C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \\ CO_{2(g)} + C_{(s)} \rightarrow 2 CO_{(g)}\end{array}
$$

Iron is reduced by carbon monoxide forming molten iron:

 $Fe₂O_{3(s)} + 3 CO_(a) \rightarrow 2 Fe_(l) + 3 CO_{2(a)}$

Ions of the most reactive metals (e.g. Na, Mg, Al) must be reduced by electrolysis of a molten salt and not from aqueous solution since the reduction of water is more likely, as indicated by their standard redution potential values:

Aluminium is extracted via the electrolysis of molten aluminium oxide with carbon electrodes in the Hall-Heroult process. Alumina (AI_2O_3) , purified from bauxite via the Bayer process, is mixed into molten cryolite (AlNa₃F₆) in order to decrease the temperature at which the electrolysis can occur (from 2000°C to 900°C). Aluminium is reduced at the cathode while the carbon anodes are oxidised to CO and $CO₂$

Anode (ox): ${Al}^{3+}_{(l)} + 3 e^- \rightarrow Al_{(l)}$ Cathode (red): $C_{(s)} + O^2_{(l)} \rightarrow CO_{(g)}$ and $C_{(s)} + 2O^2_{(l)} \rightarrow CO_{2(g)}$

Alternatively, metals can be reduced by treatment with a more reactive metal. For example, gold used to be reduced from the aurocyanide ion by reaction with powdered zinc:

$$
2 \text{ Au}(CN)_2^-_{(aq)} + Zn_{(s)} \rightarrow Zn(CN)_4^2^-_{(aq)} + 2 \text{ Au}_{(s)}
$$

Similarly, aluminium can be reduced by treatment with the more reactive sodium and silicon with the (presumably) more reactive zinc:

 $AICI_{3(q)} + 3 Na_{(l)} \rightarrow Al_{(l)} + 3 NaCl_{(l)}$ $\text{SiCl}_{4(q)} + 2 \text{ Zn}_{(l)} \rightarrow \text{Si}_{(s)} + 2 \text{ ZnCl}_{2(l)}$