YEAR 12 CHEMISTRY
STAGE 3
2015

MARKING GUIDE

Section One: Multiple-choice **(50 marks)**

1	a □ b □ c ■ d □
2	a □ b □ c □ d ■
3	a □ b □ c ■ d □
4	a □ b □ c □ d ■
5	a □ b □ c □ d ■

11	a □ b □ c ■ d □
12	a □ b ■ c □ d □
13	a □ b □ c □ d ■
14	a □ b □ c □ d ■
15	a □ b ■ c □ d □

21	a ■ b □ c □ d □
22	a □ b ■ c □ d □
23	a □ b ■ c □ d □
24	a ■ b □ c □ d □
25	a ■ b □ c □ d □

6	a □ b ■ c □ d □
7	a □ b □ c ■ d □
8	a □ b ■ c □ d □
9	a ■ b □ c □ d □
10	a □ b □ c □ d ■

16	a □ b ■ c □ d □
17	a ■ b □ c □ d □
18	a □ b □ c ■ d □
19	a □ b □ c □ d ■
20	a □ b □ c ■ d □

(2 marks per question)

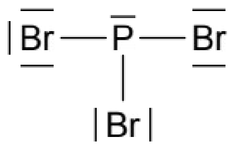
Section Two: Short answer (70 marks)

Question 26 (9 marks)

The heterogeneous equilibrium system below exists between liquid phosphorus tribromide, gaseous bromine, and solid phosphorus pentabromide.

$$\underset{\textit{colourless}}{PBr_3(l)} \quad + \quad \underset{\textit{red}}{Br_2(g)} \quad \rightleftarrows \quad \underset{\textit{yellow}}{PBr_5(s)}$$

(a) Draw the Lewis / electron dot diagram for phosphorus tribromide, representing all valence shell electron pairs either as : or –. (1 mark)



(b) Write the equilibrium constant expression for this reaction. (1 mark)

K = 1 / [Br$_2$]

(c) As the temperature of the system is increased from room temperature to 100 ˚C, it is observed that the yellow solid all but disappears and only a thick red vapour is visible. What information does this provide regarding:

(i) the enthalpy change (ΔH) of this reaction? Explain your answer. (3 marks)

- **disappearance of yellow solid and formation of red vapour indicates reverse reaction is being favoured by this temp increase**
- **the reverse direction must therefore be endothermic, as favouring the endo direction would consume some of the added heat**
- **the reaction is therefore exothermic as written, i.e. ΔH is negative**

(ii) the value of K for this reaction at 100 ˚C? Explain your answer. (2 marks)

- **increased intensity of red vapour shows increased [Br$_2$]**
- **value of K would therefore be smaller at 100 ˚C than 59 ˚C**

(d) As the temperature of the system is increased to 100 ˚C, explain the effect this would have on the rate of **both** the forward and reverse reactions. (2 marks)

- **both rates of reaction would be increased, due to an increase in average kinetic energy of the reacting particles**
- **however, the rate of the favoured direction, i.e. reverse reaction, would initially be increased more than the forward, until the system returns to equilibrium, where the rate of forward and reverse reactions will once again be equal (but still both higher than original)**

Question 27 **(6 marks)**

The following table provides information about the conductivity of two different compounds in their pure forms as a solid and liquid, and also if they were **mixed** with water.

	(s)	(l)	(aq)
HCl	✗	✗	✓
$CaCO_3$	✗	✓	✗

Explain the conductivity of each substance in its solid form, liquid form and when mixed with water. Use chemical equations to support your answer where appropriate.

- **HCl is a covalent molecular substance, therefore has no mobile charge and can not conduct electricity as (s) or (l)**
- **However, when added to water it will ionise to produce ions, which are then capable of conducting a current**
- **$HCl \rightarrow H^+ + Cl^-$ OR $HCl + H_2O \rightarrow H_3O^+ + Cl^-$**
- **$CaCO_3$ is an ionic substance therefore will not conduct as (s) because the ions are in fixed positions, but will conduct as (l) due to dissociation of ions producing mobile charge**
- **$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$**
- **$CaCO_3$ won't conduct when mixed with water because it is insoluble, therefore not enough ions dissociate in solution to conduct an electric current**

Question 28 **(6 marks)**

The two organic molecules below are alkene isomers.

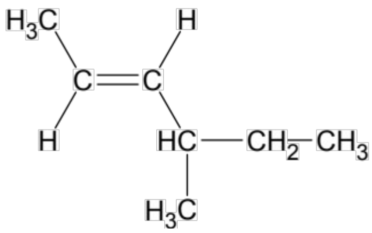
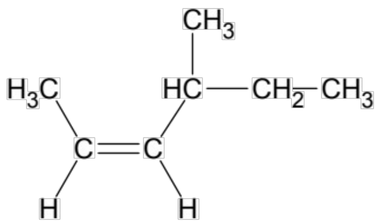
$CH_3C(CH_3)=CHCH_2CH_2CH_3$ **$CH_3CH=CHCH(CH_3)CH_2CH_3$**

Only one of these molecules exhibits geometric (*cis-trans*) isomerism.

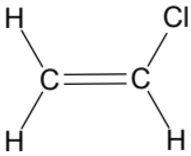
(a) Circle this molecule and explain your choice. (2 marks)

- **In the molecule on the left, one of the carbon atoms involved in the double bond has two identical methyl (CH_3-) groups attached, therefore no possibility for cis-trans conformation**

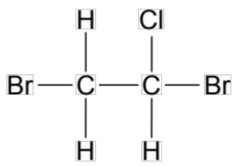
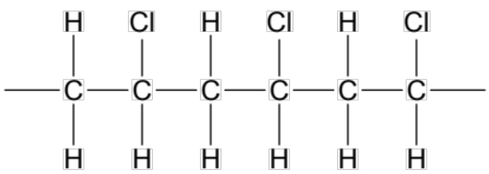
(b) Draw structural formulas for both geometric isomers and name each using the IUPAC system. (2 marks)

 Name: **trans-4-methylhex-2-ene**	 Name: **cis-4-methylhex-2-ene**

The alkene below is involved in many different chemical reactions.

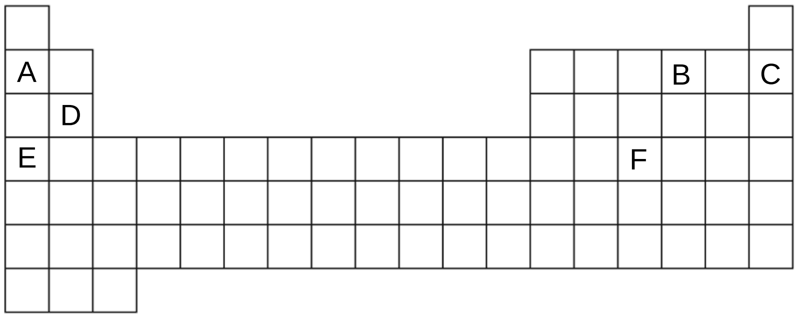


(c) Draw the structural diagram for the organic product formed when this alkene is: (2 marks)

(i) mixed with bromine water, $Br_2(aq)$	
(ii) polymerised to form PVC (show 3 repeating units)	

Question 29 **(8 marks)**

Consider elements A-E on the periodic table below.



(a) Which element has: (3 marks)

(i) the highest electronegativity? **B**

(ii) the largest atomic radius? **E**

(iii) the highest ionisation energy? **C**

(b) Write the electron configuration for element D. (1 mark)

2, 8, 2

(c) Which two elements are most likely to have the same bonding capacity? (1 mark)

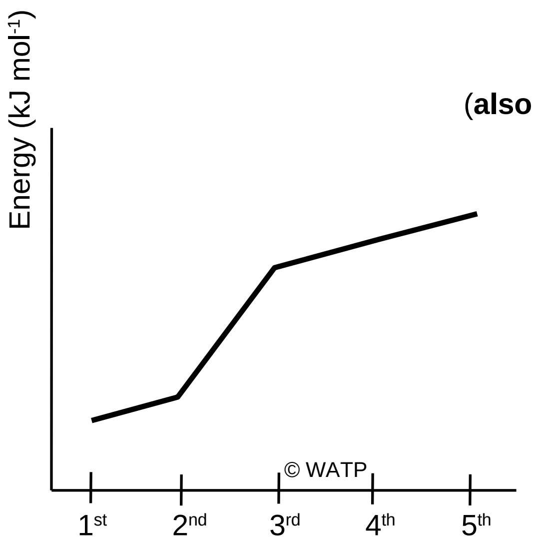
A and E

(d) What is the likely formula of the substance produced when A and B form chemical bonds? What type of bonding is likely to occur? (2 marks)

A_2B or Li_2O
Ionic bonding

(e) Sketch a rough graph showing the first 5 ionisation energies for element D. (1 mark)

(**also accept column graph**)



Question 30 **(7 marks)**

Five organic compounds and their corresponding boiling points are shown below.

	CH_4	CH_3Br	CH_2Br_2	$CHBr_3$	CBr_4
Boiling point (˚C)	-161	3.5	96	147	190

(a) Explain why all these molecules are tetrahedral in shape. (2 marks)

- **each have four bonding regions around the central atom**
- **VSEPRT states that these 4 regions will repel each other to be as far apart as possible, therefore shape is tetrahedral**

(b) Place ticks (✓) in the table to indicate the types of intermolecular forces present in each of these 5 substances. (3 marks)

	Dispersion	Dipole-dipole	Hydrogen bonds
CH_4	✓		
CH_3Br	✓	✓	
CH_2Br_2	✓	✓	
$CHBr_3$	✓	✓	
CBr_4	✓		

(c) Explain why CBr_4 has the highest boiling point. (2 marks)

- **CBr_4 has the largest molecular weight (M) / greatest number of total electrons, therefore it has the strongest dispersion forces of the 5 substances**
- **the strength of these forces must be greater than the combined dispersion and dipole-dipole forces of the other substances containing bromine, therefore CBr_4 has the highest boiling point**

Question 31 **(5 marks)**

Examine the following closed system that has reached equilibrium.

$$2\ FeS_2(s) + 7\ O_2(g) + 2\ H_2O(l) \rightleftarrows 2\ Fe^{2+}(aq) + 4\ SO_4^{2-}(aq) + 4\ H^+(aq)$$

What effect would each of these changes have on the final concentration of H^+, once equilibrium was re-established? State 'increase', 'decrease' or 'no change'.

	Effect on $[H^+]$ (increase, decrease, no change)
Several drops of $HCl(aq)$ are added	**increase**
Several drops of $Ba(NO_3)_2(aq)$ are added	**increase**
A small amount of solid FeS_2 is added	**no change**
The pressure on the system is decreased	**decrease**
Several drops of $FeCl_2(aq)$ are added	**decrease**

Question 32 **(6 marks)**

Tellurium (Te) is a rare, silver metalloid that can be used in solar panels and as a semiconducting material. It can be produced by reacting the mineral tellurite (TeO_2) with hypophosphoric acid (H_3PO_2). This produces tellurium metal and phosphorous acid (H_3PO_3).

Write the oxidation and reduction half-equations and the overall redox equation for this reaction, assuming acidic conditions.

Oxidation half-equation	$\mathbf{H_3PO_2 + H_2O \rightarrow H_3PO_3 + 2H^+ + 2e^-}$
Reduction half-equation	$\mathbf{TeO_2 + 4H^+ + 4e^- \rightarrow Te + 2H_2O}$
Overall redox equation	$\mathbf{TeO_2 + 2H_3PO_2 \rightarrow Te + 2H_3PO_3}$

Question 33 **(8 marks)**

Consider the following covalent molecules.

PH_3	HF	CO_2	F_2
CH_2O	SO_2	NF_3	HCN

(a) Complete the table below by selecting a molecule from the list above that matches the description. Each molecule may **only be used once**. (5 marks)

Description	Molecule
A molecule that is linear and polar	**HCN**
A molecule that contains only non polar bonds	**F_2**
A molecule that is trigonal (triangular) planar	**CH_2O**
A molecule that would exhibit hydrogen bonding	**HF**
A non-polar molecule with polar bonds	**CO_2**

Oxygen (O_2) is only found on Earth in the gaseous state because its boiling point is -183 ˚C (90 K). When gaseous oxygen condenses, pale blue liquid oxygen is formed. During this phase change, the dispersion forces between the oxygen molecules become stronger.

(b) Explain why dispersion forces occur. (3 marks)

- **due to the random motion of electrons (creating an asymmetrical electron distribution), an O_2 molecule can develop a temporary/instantaneous dipole**
- **this induces a temporary/instantaneous dipole in a neighbouring O_2 molecule**
- **dispersion forces then form between the slightly negative and slightly positive ends of the temporary dipoles**

Question 34 **(9 marks)**

The molecular equation below shows the chemical reaction that takes place when barium hydroxide solution is mixed with aqueous ammonium nitrate.

(1) $Ba(OH)_2(aq)$ + **2** $NH_4NO_3(aq)$ → **(1)** $Ba(NO_3)_2(aq)$ + **2** $NH_3(aq)$ + **2** $H_2O(l)$

(a) Complete the reaction above by adding coefficients to balance the equation, and write the ionic equation below, showing only those species that are reacting. (2 marks)

(see above)
$OH^-(aq) + NH_4^+(aq) \rightarrow NH_3(aq) + H_2O(l)$ (phase symbols not required)

(b) Name or give the formula for one substance present in the equation above that is basic. Write a chemical equation to support your answer. (2 marks)

$Ba(OH)_2$; $Ba(OH)_2 \rightarrow Ba^{2+} + 2\ OH^-$
OR
NH_3 ; $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

(c) Name or give the formula for one substance present in the equation above that is acidic. Write a chemical equation to support your answer. (2 marks)

NH_4NO_3 ; $NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$

(d) Which 2 substances present in the equation above could be combined to form a buffer? Explain how you could design this buffer so that it has the capacity to maintain a near constant pH when acid or base is added. (3 marks)

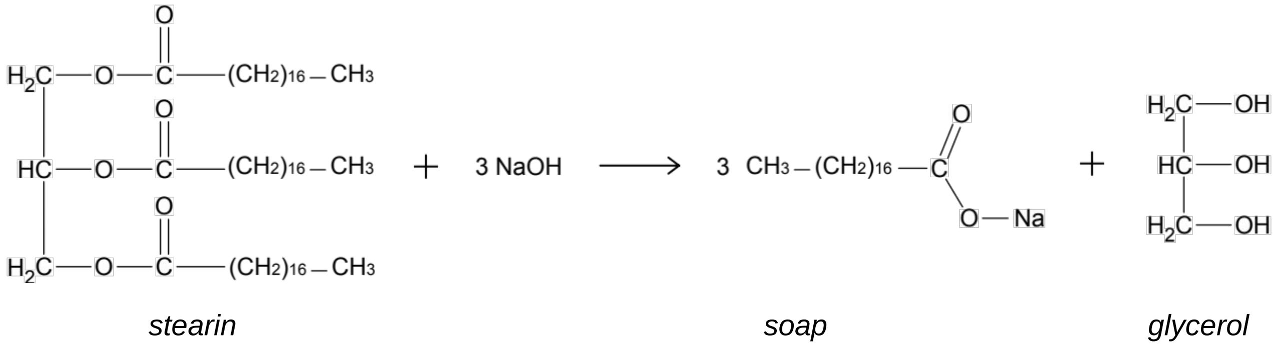
- **NH_4NO_3 and NH_3 (NH_4^+ and NH_3 would form the buffering system)**

To withstand the addition of both H^+ and OH^- you would need to ensure the solution has a high buffering capacity, which means you would mix;

- **Equal amounts of the conjugate acid/base pair**
- **Large amounts of the conjugate acid/base pair**

Question 35 **(6 marks)**

The saponification equation below shows the reaction used to produce soap from the fat ‘stearin’.



(a) Name the type of functional group present in the following substances. (2 marks)

	Functional group present
Stearin	**ester**
Glycerol	**alcohol**

(b) Describe the mechanism by which soaps clean, including the disadvantage of using soaps in hard water. (4 marks)

- **the surfactant ion in soap has a polar hydrophilic head and a non-polar hydrophobic tail**
- **the hydrophilic head dissolves in the water and the hydrophobic tail dissolves in the dirt/grease**
- **with agitation the surfactant ion can remove the dirt/grease from the object**
- **the large amounts of Ca^{2+} and Mg^{2+} found in hard water will precipitate the soap surfactant ion, therefore the soap cannot lather and clean**

End of Section Two

Section Three: Extended answer **40% (80 marks)**

Question 36 **(15 marks)**

A chemist had five bottles sitting on his laboratory bench, each containing a clear colourless liquid. The bottles contained the organic substances:

- 3-methylbutanoic acid **(MF $C_5H_{10}O_2$)**
- ethyl propanoate **(MF $C_5H_{10}O_2$)**
- pentanoic acid **(MF $C_5H_{10}O_2$)**
- 3-methylbutan-2-ol **(MF $C_5H_{12}O_1$)**
- 3-methylbutanone **(MF $C_5H_{10}O_1$)**

Unfortunately his laboratory assistant had not finished labelling the bottles before he left on vacation, so the chemist set out to determine the identity of each.

(a) What chemical test could the chemist use to quickly distinguish which substance was 3-methylbutan-2-ol? Include a chemical equation in your answer and give expected observations. (4 marks)

- **could add acidified permanganate / dichromate to all 5 substances**
- **only the 3-methylbutanol would react, either purple to pale pink/colourless (for permanganate) or orange to green (for dichromate)**

- **ox:** $CH_3CH(CH_3)CHOHCH_3 \rightarrow CH_3CH(CH_3)COCH_3 + 2H^+ + 2e^-$
  red: **either permanganate or dichromate, copy from SRPT**

- **overall:**
  $5\ CH_3CH(CH_3)CHOHCH_3 + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ CH_3CH(CH_3)COCH_3 + 2\ Mn^{2+} + 8\ H_2O$
  OR
  $3\ CH_3CH(CH_3)CHOHCH_3 + Cr_2O_7^{2-} + 8\ H^+ \rightarrow 3\ CH_3CH(CH_3)COCH_3 + 2\ Cr^{3+} + 7\ H_2O$

The chemist then took one of the remaining unknown substances and analysed it by combustion to determine its formula. A 0.368 g sample of the substance was burnt in air and produced 0.790 g of carbon dioxide and 0.325 g of water vapour.

(b) Determine the empirical formula of the substance and state which of the unknown organic substances it may be. (9 marks)

<u>OR</u>

m(C) = 12.01 / 44.01 x 0.790 **= 0.215585 g** **m(H) = 2.016 / 18.016 x 0.325** **= 0.0363677 g** **m(O) = 0.368 - 0.215585 - 0.0363677** **= 0.116047 g** **n(C) = 0.215585 / 12.01** **= 0.0179505mol** **n(H) = 0.0363677 / 1.008** **= 0.03607904 mol** **n(O) = 0.116047 / 16** **= 0.00725296 mol**	**n(C) = n(CO_2)** **= m/M** **= 0.790 / 44.01** **= 0.0179505** **m(C) = nM** **= 0.0179505 x 12.01** **= 0.215585 g** **n(H) = 2 x n(H_2O)** **= 2 x (0.325 / 18.016)** **= 0.03607904** **m(H) = 0.03607904 x 1.008** **= 0.0363677 g** **m(O) = 0.368 - 0.215585 - 0.0363677** **= 0.116047 g** **n(O) = 0.116047 / 16** **= 0.00725296 mol**

	C	H	O
ratio	**2.5**	**5**	**1**
X2	**5**	**10**	**2**

Therefore EF is $C_5H_{10}O_2$

(i.e. substance is either 3-methylbutanoic acid, ethyl propanoate or pentanoic acid, see MFs in intro to Q)

A small amount of solid sodium carbonate (Na_2CO_3) was added to a separate sample of the same unknown substance analysed in (b). However, no reaction was observed.

(c) Identify the unknown substance and state **one** characteristic physical property this substance would likely have. (2 marks)

- **must be the ester, ethyl propanoate (other two acids would have reacted)**
- **sweet / fruity odour**

Question 37 **(23 marks)**

'Drano' is a drain-cleaning product that was invented in 1923 by Harry Drackett. The active ingredient in Drano products is sodium hydroxide, which is used because of its ability to break down the grease, fat and hair that is often the cause of a blocked drain. According to the manufacturer, Drano crystals contain between 30-40% sodium hydroxide by mass. The water-soluble ingredients in the original Drano crystals are:

- sodium hydroxide, $NaOH(s)$
- sodium nitrate, $NaNO_3(s)$
- sodium chloride, $NaCl(s)$

Solid shards of aluminium are also added to this mixture before packaging to produce the final Drano product. A group of chemistry students decided to investigate some of the properties of Drano and were provided with a sample of the water-soluble components (listed above). They dissolved a spoonful of the crystals in some water and attempted to measure the resulting pH.

(a) Explain why the sodium chloride and sodium nitrate salts will not have any effect on the pH of the solution when the Drano crystals are dissolved in water. (2 marks)

- **both of these are neutral salts, meaning that their component ions do not hydrolyse with water to produce either H^+ or OH^-, therefore solutions of these salts would be pH 7 and they would not contribute to altering the pH from neutral**

The students dissolved 100 g of crystals in a beaker containing 1.00 L of water. Assuming the manufacturer is correct, and sodium hydroxide comprises between 30-40% by mass of the Drano crystals;

(b) Calculate the possible pH range of the solution formed when the crystals dissolve. (You may assume the final volume is still 1.00 L and the pH of the solution is entirely determined by the initial amount of sodium hydroxide.) (6 marks)

if NaOH comprises 30%;

$$
\begin{aligned}
\mathbf{m(NaOH)} &= \mathbf{30\ g\ in\ 1\ litre} \\
\mathbf{n(NaOH)} &= \mathbf{m/M} \\
&= \mathbf{30 / 39.998} \\
&= \mathbf{0.7500375\ mol\ in\ 1\ litre} \\
\mathbf{i.e.\ c(NaOH)} &= \mathbf{0.7500375\ mol\ L^{-1}} \\
\mathbf{[H_3O^+]} &= \mathbf{(1.0 \times 10^{-14}) / 0.7500375} \\
&= \mathbf{1.33327 \times 10^{-14}\ mol\ L^{-1}} \\
\mathbf{pH} &= \mathbf{-log\ (1.33327 \times 10^{-14})} \\
&= \mathbf{13.875}
\end{aligned}
$$

if NaOH comprises 40%;

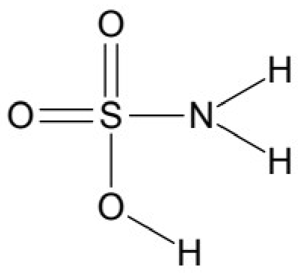
$$
\begin{aligned}
\mathbf{m(NaOH)} &= \mathbf{40\ g\ in\ 1\ litre} \\
\mathbf{n(NaOH)} &= \mathbf{m/M} \\
&= \mathbf{40 / 39.998} \\
&= \mathbf{1.00005\ mol\ in\ 1\ litre} \\
\mathbf{i.e.\ c(NaOH)} &= \mathbf{1.00005\ mol\ L^{-1}} \\
\mathbf{[H_3O^+]} &= \mathbf{(1.0 \times 10^{-14}) / 1.00005} \\
&= \mathbf{9.9995 \times 10^{-15}\ mol\ L^{-1}} \\
\mathbf{pH} &= \mathbf{-log\ (9.9995 \times 10^{-15})} \\
&= \mathbf{14.000}
\end{aligned}
$$

Therefore pH range of Drano solution is 13.9-14.0

Another group of chemistry students set out to investigate a different batch of Drano crystals (water-soluble components only) and decided to analyse them by titration, in order to determine the percent mass of NaOH present in the crystals.

They decided to titrate a solution of the Drano crystals against a standard solution of sulfamic acid (H_3NSO_3). Sulfamic acid is a weak, monoprotic acid, which appears as white crystals in solid form. Amongst its other properties, sulfamic acid is non-hygroscopic, allowing it to be used as a primary standard in volumetric analysis.

Sulfamic acid



(c) Describe the difference between a **primary standard** and a **standard solution**. (4 marks)

- **a primary standard is a substance that can be accurately weighed out and dissolved in an accurately known volume of water to produce a solution of known concentration**
- **primary standards need to have specific characteristics such as high M, not deliquescent/hydroscopic, known formula and known reactions, found with a high degree of purity etc**
- **a standard solution is any solution with an accurately known concentration**
- **these can be either primary standards (made as described above) or secondary standards, which have had their concentration determined experimentally via titration (i.e. they have been standardised)**

(d) Name an appropriate indicator for use in this titration. Explain your choice and use a chemical equation to support your answer. (3 marks)

- **phenolphthalein (or other with basic end pt around 8-10)**
- **the equivalence point of this titration will be basic due to the hydrolysis of the NaH_2NSO_3 salt produced**
- $H_2NSO_3^- + H_2O \rightleftarrows H_3NSO_3 + OH^-$

To perform the titration, 2.107 g of the water-soluble Drano crystals were dissolved in water and transferred to a volumetric flask where the volume was made up to 500 mL with distilled water. From this solution, 20.0 mL aliquots were taken and titrated against the standard sulfamic acid solution. An average titre of 24.25 mL was required for complete reaction. The reaction that took place during the titration is shown in the molecular equation below.

$$H_3NSO_3(aq) \ + \ NaOH(aq) \ \rightarrow \ NaH_2NSO_3(aq) \ + \ H_2O(l)$$

If it was determined that this batch of Drano crystals contained exactly 40.0% by mass sodium hydroxide;

(e) Calculate the concentration of the standard sulfamic acid solution that was used in this titration. (6 marks)

m(NaOH in 2.107 g Drano) = 40/100 x 2.107 g
= 0.8428 g
n(NaOH in 500 mL flask) = m/M
= 0.8428 / 39.998
= 0.021071 mol
c(NaOH) = n/V
= 0.021071 / 0.500
= 0.042142 mol L^{-1}
n(NaOH in 20 mL) = cV
= 0.042142 x 0.020
= 0.000842842 mol
n(H_3NO_3) = n(NaOH)
c(H_3NO_3) = n/V
= 0.000842842 / 0.02425
= 0.034756 mol L^{-1}
= 0.0348 mol L^{-1} (3sf)

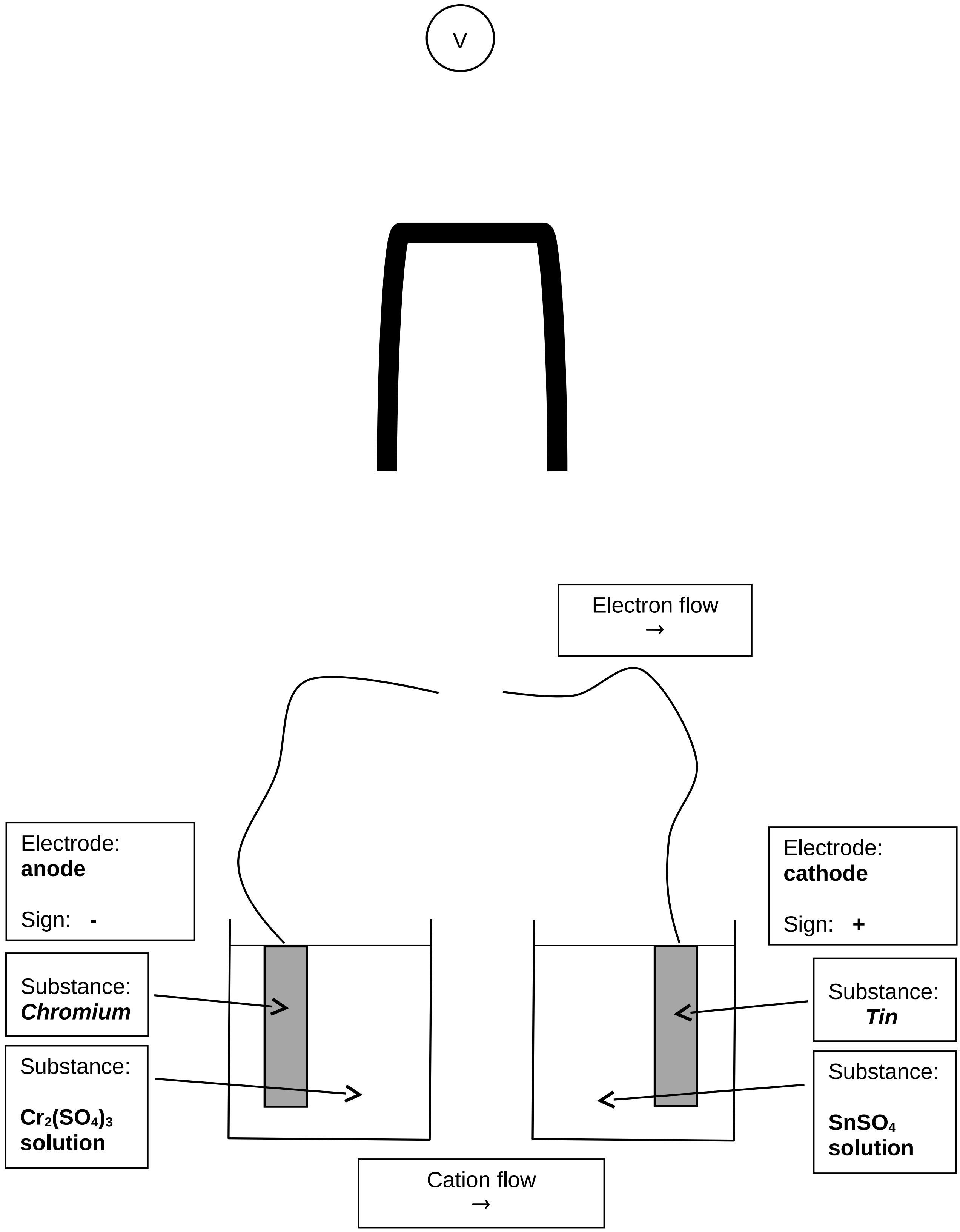
(f) Another group that was performing the same titration found that their titration volumes for sulfamic acid were consistently **lower** than expected. State an error that would account for these results. Explain your answer. (2 marks)

- **lower titration volume indicates less NaOH in flask which could be caused by:**
- **rinsing pipette with water / over filling volumetric flask / not transferring entire mass of Drano to vol flask / use of incorrect indicator (would have to be an indicator with end point at a very high pH for this to occur)**

Question 38 **(15 marks)**

The Daniell cell was invented in 1836 and was one of the earliest batteries to be designed. Essentially, the Daniell cell can be thought of as two half-cells consisting of a copper electrode submerged in copper(II) sulfate solution (Cu/Cu^{2+}) and a zinc electrode submerged in zinc sulfate solution (Zn/Zn^{2+}). In the original design, a porous clay pot was used to separate the half-cells and act as what we now call the salt bridge. The EMF produced by the Daniell cell is 1.1 V under standard conditions.

A chemistry class was studying the basic design of the Daniell cell and decided to investigate the effect of changing the metals used for each electrode/electrolyte. They decided to construct a cell using tin metal, chromium metal, tin(II) sulfate solution and chromium(III) sulfate solution. They set up their apparatus as shown in the diagram below.



(a) Label all remaining components of the cell in the diagram above, including: (6 marks)

(i) cathode and anode
(ii) sign of each electrode
(iii) substance used for each half-cell electrolyte
(iv) direction of electron and cation flow

(b) Note two observations that would be made as this electrochemical cell operates. (2 marks)

- **chromium electrode decreases in size**
- **increase in strength of green electrolyte colour in chromium half cell**
- **tin electrode increases in size**
- **drop in voltage as reaction proceeds** **(any 2)**

The overall equation for the operation of this electrochemical cell is;

$$3\ Sn^{2+}(aq) + 2\ Cr(s) \rightarrow 3\ Sn(s) + 2\ Cr^{3+}(aq)$$

Just like the Daniell cell, the cell designed by the students is a primary cell, which means it cannot be recharged. Therefore, over time the reactants will run out, as the chemicals stored within the electrochemical cell are used to produce electricity.

If the chromium electrode has a mass of 36.2 g and there was 475 mL of 2.10 mol L^{-1} tin(II) sulfate solution present;

(c) Determine the limiting reagent. (5 marks)

	Sn^{2+}	**Cr**
n(present)	**n = cV = 2.10 x 0.475 = 0.9975 mol**	**n = m/M = 36.2 / 52.00 = 0.696154 mol**
n(required)	**n = 0.696154 x 3 / 2 = 1.04423 mol**	**n = 0. 9975 x 2 / 3 = 0.665 mol**

Therefore Sn^{2+} is LR

<u>OR</u>

Stoichiometric ratio Sn^{2+} / Cr = 3 / 2 = 1.5
Actual ratio Sn^{2+} / Cr = 0.9975 / 0.696154 = 1.429

Therefore Sn^{2+} is LR

(d) If the chromium half-cell was replaced with a Cu/Cu^{2+} half-cell, would the students be able to produce a higher or lower EMF? Explain. (2 marks)

- **lower**
- **the E^0 values of the two half cells are closer in value, therefore a lower voltage (voltage produced by Cr/Sn cell is 0.6 V, whereas Sn/Cu cell is 0.48 V)**

Question 39 **(15 marks)**

The thermal reduction process, or Pidgeon Process, is one of the methods used to produce magnesium (Mg) metal. This process was developed in the early 1940s by Dr Lloyd Montgomery Pidgeon and currently dominates world magnesium production over electrolytic methods.

The Pidgeon Process makes use of the ore 'dolomite', which contains magnesium / calcium carbonate, $MgCO_3.CaCO_3$. This ore is heated at around 1100-1200 ˚C to remove the carbon from the compound as shown in Step 1.

Step 1: $MgCO_3.CaCO_3(s) \rightarrow MgO.CaO(s) + 2\ CO_2(g)$

The resulting magnesium / calcium oxide is heated with silicon and the thermal reduction process occurs as in Step 2. This reaction is highly endothermic and produces magnesium vapour, as well as a dicalcium silicate slag.

Step 2: $2\ MgO.CaO(s) + Si(s) \rightleftarrows 2\ Mg(g) + Ca_2SiO_4(l)$

A very high temperature of 1200-1250 ˚C is used for this thermal reduction step and the pressure is kept close to a vacuum, at only 65 Pa. The magnesium vapour is removed as it forms and crystallises into solid magnesium with a purity of between 99.6-99.9%.

(a) Discuss the conditions used in Step 2 of the magnesium extraction process, in terms of **both** reaction rate and yield. (6 marks)

- **the high temperature will increase the reaction rate, by increasing the average kinetic energy of the particles, therefore a greater number will have enough energy to overcome the activation energy barrier**
- **the high temperature will also increase the yield, because Step 2 is endothermic, therefore a high temperature will favour the forward reaction in an attempt to 'use up' some of this heat in accordance with LCP**
- **a low pressure will decrease the reaction rate, as particles will collide with less frequency (however only gaseous species is the Mg product, so no great impact on collision of reactants)**
- **a low pressure will increase the yield, because this will favour the forward reaction in an attempt to increase the concentration of gaseous species ($0 \rightarrow 1$) in accordance with LCP**
- **removal of Mg vapour will decrease the reverse reaction rate, as there will be fewer particles to collide, however once again, would not impact on collision of reactant particles**
- **removal of Mg vapour will increase yield, because this will favour forward reaction in an attempt to increase the concentration of Mg in accordance with LCP**

A manufacturing plant carrying out the Pidgeon process can generally produce 12.0 kg of pure magnesium vapour for every 8 hours of operation.

(b) What volume would this mass of magnesium vapour occupy at 1250 ˚C and 65.0 Pa? (Note: 1000 Pa = 1 kPa) (4 marks)

m(Mg) = 12 000 g
n(Mg) = m/M
= 12 000 / 24.31
= 493.624 mol
V(Mg) = nRT/P
= (493.624 x 8.413 x 1523) / 0.065
= 96 159 645.6 L
= 9.62 x 10^7 L OR 96.2 ML (3sf)

If 12.0 kg of pure magnesium is extracted from 128 kg of dolomite ore for every 8 hours of operation and the dolomite ore consists of 75.6% magnesium/calcium carbonate, ($MgCO_3.CaCO_3$);

(c) Calculate the efficiency of extraction of the magnesium from the dolomite ore. (5 marks)

m($MgCO_3.CaCO_3$) = 75.6/100 x 128 kg
= 96.768 kg
= 96768 g
n($MgCO_3.CaCO_3$) = m/M
= 96768 / 184.41
= 524.74378 mol
n(Mg theoretical) = n($MgCO_3.CaCO_3$)
= 524.74378 mol
m(Mg theoretical) = nM
= 524.74378 x 24.31
= 12 756.52 g
= 12.7565 kg
% efficiency/yield = m(actual) / m(theoretical) x 100
= 12 / 12.7565 x 100
= 94.0695 %
= 94.1 % (3sf)

OR use n(Mg actual) from part (b) = 493.624 mol

% efficiency/yield = n(actual) / n(theoretical) x 100
= 493.624 / 524.74378 x 100
= 94.1 % (3sf)

Question 40 **(12 marks)**

Hydrazine (N_2H_4) is a colourless, oily, flammable liquid. It is a toxic substance with an odour similar to ammonia (NH_3). Exposure to hydrazine can cause irritation of the eyes, nose and throat, as well as dizziness, headaches and nausea. High levels of exposure can damage the liver, kidneys and central nervous system. Hydrazine is corrosive and can cause burns if skin contact occurs.

Hydrazine has a boiling point of 114 ˚C, which is quite high for a substance with a molar mass of 32.05 g mol^{-1}. In contrast, ethane (C_2H_6) has a comparable molar mass of 30.07 g mol^{-1} but a boiling point of -89 ˚C. Hydrazine is miscible with (soluble in) water.

Hydrazine is quite an unstable compound unless it is dissolved in water and handled as an aqueous solution. When mixed with water it acts as a Bronsted-Lowry base and ionises in a similar way to ammonia. The value of K for this ionisation is 1.3×10^{-6}.

One method for synthesising hydrazine is by the 'peroxide process' where ammonia and hydrogen peroxide (H_2O_2) react to form hydrazine and water. There are several other ways to manufacture hydrazine, however they all generally rely on the oxidation of a nitrogen-containing compound.

Hydrazine is used in the manufacture of polymers, not directly as a monomer, but in the production of polymer catalysts and foaming agents. It is also used in the manufacture of pesticides, pharmaceuticals and to prepare the chemicals used in vehicle air bags. The volatile nature and highly exothermic combustion of hydrazine also make it a useful component in the fuel used to power rockets and other spacecraft.

(a) Discuss two physical properties of hydrazine, namely its boiling point and water solubility, in terms of the bonding present in the compound. Your answer should include a Lewis / electron dot diagram for hydrazine representing all valence shell electron pairs as : or –. (4 marks)

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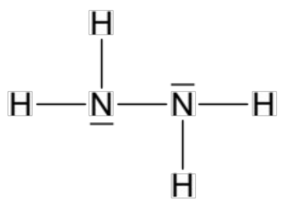

- **hydrazine has the ability to form hydrogen bonds because it has 4 very polar N-H covalent bonds and the molecule has 2 non-bonding pair of electrons, therefore hydrazine has strong intermolecular forces**
- **this accounts for the high boiling point of hydrazine, especially when compared with non-polar molecules of similar M that only have dispersion forces and therefore much lower boiling points**
- **hydrazine is soluble in water because water also forms hydrogen bonds, therefore the intermolecular forces are of similar strength, allowing the molecules to interact and dissolve in one another**

(b) Discuss the acid-base properties of hydrazine in aqueous solution. Your answer should include a chemical equation representing the ionisation of hydrazine, as well as an indication of what information the value of K provides. (4 marks)

- **hydrazine acts as a Bronsted-Lowry base, therefore has the ability to accept a proton**
- **The low K value (1.3 x 10^{-6}) indicates a greater concentration of reactants than products at equilibrium**
- **Therefore hydrazine is a weak base, ionisation does not go to completion**
- **$N_2H_4 + H_2O \rightleftarrows N_2H_5^+ + OH^-$**

(c) Hydrazine is synthesised by a redox reaction. Write a chemical equation representing the 'peroxide process' and use this equation to elaborate on redox processes. Your answer should include a definition of a redox reaction, as well as identifying which species have been oxidised or reduced in this reaction by way of oxidation numbers. (4 marks)

- **$2\,NH_3 + H_2O_2 \rightarrow N_2H_4 + 2\,H_2O$**
  (half equations are: ox $2\,NH_3 \rightarrow N_2H_4 + 2\,H^+ + 2\,e^-$
  red $H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$)
- **redox reactions are those that involve the transfer of electrons**
- **the reducing agent undergoes oxidation, which is a loss of electrons, while the oxidising agent undergoes reduction, which is a gain of electrons**
- **in this equation, oxygen atoms (in H_2O_2) have been reduced (-1) to (-2) and nitrogen atoms (in NH_3) have been oxidised (-3) to (-2)**

End of questions