1 (a) $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ [1]

or $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 6H_2O$

(b) Orange [1]

$[Cu(NH_3)_4]^{2+}$ is **deep–blue** in colour. Hence, its **complementary colour** (orange) will be most strongly absorbed.

Comments:
A significant number of candidates were not able to apply their understanding of colour in transition metal compounds to predict and explain that the most strongly absorbed colour would be the complementary colour to the blue colour of the complex.

(c) *General comments:*
Candidates were expected to describe how to use the correct apparatus for a given step, rather than just outlining generally what had to be done.

Preparation of 250.0 cm^3 standard solution of 2.00 mol dm^{-3} aqueous copper(II) sulfate

No. of moles of $CuSO_4$(aq) in 250 cm^3 = 2.00 x 250/1000 = 0.500 mol
Mass of $CuSO_4.5H_2O$ to measured = 0.500 x [63.5 + 32.1 + 4(16.0) + 5(18.0)]
= 0.500 x 249.6 = **124.8 g** [1]

Procedure: [2]

1. *Weigh accurately 124.8 g* of solid $CuSO_4.5H_2O$ using a *weighing bottle*. Record the total mass of solid $CuSO_4.5H_2O$ and weighing bottle.
2. Transfer the solid into a *100 cm^3 beaker* and add 50 cm^3 *deionised water* to dissolve the solid completely. Add more deionised water to dissolve if necessary.
3. Transfer this solution carefully into a *250 cm^3 volumetric flask* using a glass rod and filter funnel. Rinse the beaker with deionised water a few times, and *transfer the washings* into the volumetric flask.
4. *Top up* the volumetric flask to the mark with deionised water. Add deionised water *drop–wise* to ensure the water level does not exceed the mark.
5. *Stopper and shake* the volumetric flask well to obtain a homogenous (standard) solution.
6. *Re–weigh* the empty weighing bottle. Record the readings in Table 1.

Mass of $CuSO_4.5H_2O$ and weighing bottle	/g	*x*
Mass of residue and weighing bottle	/g	*y*
Mass of $CuSO_4.5H_2O$ used	/g	*x* – *y* = 124.800

Table 1

Concentration of standard solution = (124.800/249.6) / 0.250 = 2.00 mol dm^{-3}

Comments:

- *It was necessary to calculate the mass of solid hydrated copper(II) sulfate needed to make up 250.0 cm^3 of 2.00 mol dm^{-3} solution of copper(II) sulfate.*
- *The water of crystallisation must be included in the calculation of M_r of hydrated copper(II) sulfate.*
- *It was necessary to describe how to weigh out the calculated mass, being specific as to how to subtract the mass of the weighing bottle.*
- *It was expected to describe that the empty bottle should be weighed and how to use the result.*
- *There was a need to recognise appropriate apparatus to be used to make up the standard solution.*
- *Sufficient practical details to the steps in making up a standard solution were required.*

Preparation of suitable range of diluted solutions (from standard solution) of accurate concentrations (between 0 and 2.00 mol dm^{-3})

Procedure: [2]

1. Using a *50 cm^3 burette*, *transfer 50 cm^3* of standard solution into a *100 cm^3 conical flask*. This is 'Reference Solution 1'.
2. Using the same *50 cm^3 burette*, *transfer 75 cm^3* of standard solution into a *100 cm^3 volumetric flask*.
3. Top up the volumetric flask to the mark with deionised water carefully.
4. Stopper and shake the flask well to obtain a homogenous solution of $CuSO_4$(aq) (of concentration 1.50 mol dm^{-3}).

   [Concentration of diluted solution = (75)(2.00)/100 = 1.50 mol dm^{-3}]

5. *Repeat steps 2 to 4* using *different volumes of the standard solution* as shown in Table 2.

Reference Solution	Volume of 2.00 mol dm^{-3} standard solution used / cm^3	[$CuSO_4$] in Reference Solution / mol dm^{-3}
1	–	2.00
2	75.00	1.50
3	50.00	1.00
4	25.00	0.50
5	12.50	0.25

Table 2

Preparation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ solutions

(Mole ratio of Cu^{2+} : NH_3 = 1 : 4)

Procedure: [2]

1. *Pipette 10.0 cm^3* of 'Reference Solution 1' (2.00 mol dm^{-3}) into a *100 cm^3 conical flask*.
2. Using a *50 cm^3 burette*, transfer *50 cm^3 of 2.0 mol dm^{-3} aqueous ammonia* into the same conical flask.
3. *Swirl* the conical flask to ensure complete reaction to obtain 'Complex Solution 1' of concentration 0.333 mol dm^{-3}.

   [Concentration of 'Complex Solution 1' = (10)(2.00)/(10 + 50) = 0.333 mol dm^{-3}]

4. *Repeat steps 1 to 3* using 'Reference Solutions 2 to 5' and Solution **X**, keeping the *total volume constant* (i.e. 60 cm^3) for all complex solutions, to obtain 'Complex Solutions 2 to 5' and 'Unknown'.

Comments:

- *It was necessary to describe a workable method to prepare at least five reference solutions of different concentrations from the 250.0 cm^3 standard solution prepared.*
- *The concentrations of the reference solutions should be well spread between 0 to 2.00 mol dm^{-3}.*
- *Any suitable combination of pipettes, burettes and/or volumetric flasks should be used.*
- *Less precise apparatus such as measuring cylinders were not acceptable.*
- *There was a need to ensure sufficient 2.0 mol dm^{-3} ammonia solution was added to each reference solution to form the $[Cu(NH_3)_4]^{2+}$ complex ion, while also keeping the total volume constant for all their solutions. Many students did not add sufficient ammonia or omitted carrying out this part with the unknown solution **X**, as well as the reference solutions.*

Obtaining calibration line and determination of concentration of copper(II) ions in solution **X**

Procedure: [1]

1. Using a dropper, place a few cm^3 of 'Complex Solution 1' inside the spectrometer.
2. Set the spectrometer to use the *wavelength of orange light*.
3. *Obtain the absorbance value* of 'Complex Solution 1'.
4. *Repeat steps 1 to 3* for 'Complex Solutions 2 to 5' and 'Unknown'.
5. *Plot a graph of absorbance against concentration* of 'Complex Solutions 1 to 5' to obtain the calibration line.
6. Using the recorded absorbance value A, obtain the $[complex]_{Unknown}$ from the graph.

Complex Solution	$[CuSO_4]$ in Reference Solution / mol dm^{-3}	Vol. of Reference Solution used / cm^3	Vol. of NH_3(aq) used / cm^3	Conc. of Complex Solution / mol dm^{-3}	Absorbance
1	2.00	10.0	50.00	0.333	
2	1.50	10.0	50.00	0.250	
3	1.00	10.0	50.00	0.167	
4	0.50	10.0	50.00	0.0833	
5	0.25	10.0	50.00	0.0417	
Unknown	$[Cu^{2+}]_{solution\ X}$	10.0	50.00	$[complex]_{Unknown}$	A

Alternative

Procedure:

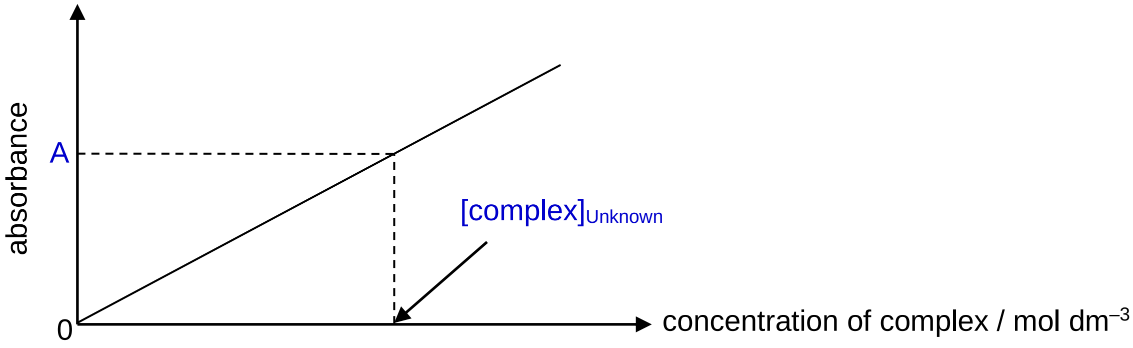
1. Using a *50 cm^3 burette*, transfer *10.0 cm^3* of 'Standard Solution' (2.00 mol dm^{-3}) into a *100 cm^3 conical flask*.
2. Using a *50 cm^3 burette*, transfer *50 cm^3 of 2.0 mol dm^{-3} aqueous ammonia* into the same conical flask.
3. *Swirl* the conical flask to ensure complete reaction to obtain 'Complex Solution 1' of concentration 0.333 mol dm^{-3}.

   [Concentration of 'Complex Solution 1' = (10)(2.00)/(10 + 50) = 0.333 mol dm^{-3}]

4. *Repeat steps 1 to 3* using a *50 cm^3 burette* to make up, with deionised water, the total volume in the same conical flask *constant* (i.e. 60 cm^3) for all complex solutions, to obtain 'Complex Solutions 2 to 5' and 'Unknown'.

Complex Solution	Vol. of Standard Solution used / cm^3	Vol. of water used / cm^3	Vol. of NH_3(aq) used / cm^3	Conc. of Complex Solution / mol dm^{-3}	Absorbance
1	10.00	0.00	50.00	0.333	
2	8.00	2.00	50.00	0.266	
3	6.00	4.00	50.00	0.200	
4	4.00	6.00	50.00	0.133	
5	2.00	8.00	50.00	0.067	
Unknown	10.00	0.00	50.00	$[\text{complex}]_{\text{Unknown}}$	A

[1]



Concentration of Cu^{2+} ions in solution **X** = $[\text{complex}]_{\text{unknown}}$ x (60/10) mol dm^{-3} [1]

Comments:
- *It was necessary to specify that each complex ion solution, including that of the unknown solution, was put into the spectrometer to measure its absorbance.*
- *A well–labelled sketch of the calibration graph showing a straight line passing through the origin, as well as a brief explanation or annotation on the sketch of how to obtain the unknown concentration was needed.*

2 **(a)** **(i)** **Reaction (1)**. It is the **most exothermic** reaction which will release the greatest amount of heat to raise the temperature of the furnace. [1]

(ii) For reactions (2) and (4), Δn (gaseous molecules) = **+1**
For reactions (1), (3) and (5), Δn (gaseous molecules) = **0**

Since **reactions (2) and (4) involve an increase in the number of moles of gaseous molecules**, the change in entropy ($\Delta S^\ominus$) of the system is much more positive. [1]

(iii) $\Delta G = \Delta H - \text{T}\Delta S$
$= (-24.8 \text{ x } 1000) - (500 \mathbf{+ 273})(+15.8)$
$= -37013.4 \text{ J mol}^{-1}$
$= \mathbf{-37.0 \text{ kJ mol}^{-1}}$ [1]

As temperature increases, the **magnitude of TΔS increases** and hence **ΔG becomes more negative**. The reaction is **more spontaneous** at temperatures above 500 °C. [1]

(iv) *Le Chatelier's Principle* states that if a change is made to a **reversible reaction in dynamic equilibrium**, the **position of equilibrium shifts so as to minimise that change** and to re–establish equilibrium. [1]

Increasing the temperature favours the **forward endothermic** reaction. The position of equilibrium will shift **right** to **reduce** the temperature by **absorbing the extra heat**. Since more CO is produced, the partial pressure of CO is **increased**. [1]

The backward reaction is accompanied by a decrease in the number of moles of gas molecules. Increasing the pressure will shift the position of equilibrium to the **left** to **decrease** the pressure by **producing fewer gas molecules**. Since less CO is produced, the partial pressure of CO is **decreased**. [1]

Comments:
Students will need to state what effect the shift in the position of equilibrium would have on the partial pressure of carbon monoxide. Although the changes in temperature and pressure would have opposite effects, students are not expected to know whether temperature or pressure would have a greater effect.

(v) Mass of SiO_2 present in 1 tonne of iron ore = $(3.5/100) \text{ x } 10^6 = 35000$ g

$n(SiO_2) = 35000 / (28.1 + 16.0 + 16.0) = 582.36$ mol [1]

From Reactions 4 and 5, $n(CaCO_3) : n(SiO_2) = 1 : 1$

$\therefore$ $n(CaCO_3)$ required = 582.36 mol

mass of $CaCO_3$ required = 582.36 x [(40.1) + 12.0 + 3(16.0)]
= **58300 g** or **58.3 kg** [1]

Comments:
Answers with any more than three significant figures were inappropriate, as the percentage of silicon dioxide was only given to two significant figures.

(b) **(i)** $2Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$ [1]

(ii) $E^\ominus (Fe^{3+}/ Fe^{2+}) = +0.77$ V
$E^\ominus (Sn^{4+}/ Sn^{2+}) = +0.15$ V

$E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$
$= +0.77 - (+0.15)$
$=$ **<u>+0.62 V</u>** [1]

(iii) From **(b)(ii)**, the reduction of Fe^{3+} to Fe^{2+} by tin(II) chloride is **<u>feasible</u>** as the $E^\ominus_{cell}$ is **<u>positive</u>**. [1]

$E^\ominus (Fe^{2+}/Fe) = -0.44$ V
$E^\ominus (Sn^{4+}/ Sn^{2+}) = +0.15$

$E^\ominus_{cell} = -0.44 - (+0.15) =$ **<u>–0.59 V</u>** < 0 (not feasible)

However, the reduction of Fe^{2+} to Fe by tin(II) chloride is **<u>not feasible</u>** under standard conditions since the $E^\ominus_{cell}$ is **<u>negative</u>**. [1]

(c) **(i)** [1]

titration number	1	2	3
initial burette reading / cm^3	0.00	21.85	0.00
final burette reading /cm^3	21.85	43.25	21.50
titre / cm^3	**21.85**	**21.40**	**21.50**

Average titre = (21.40 + 21.50) / 2 = 21.45 cm^3

$n(K_2Cr_2O_7)$ required = 21.45/1000 x 0.100
= 0.002145 mol ≈ **<u>0.00215 mol</u>** [1]

Comments:
Students are expected to apply their practical experience and know that only tires that are in close agreement (i.e. consistent to ±0.10 cm^3) should be used.

(ii) $6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \longrightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$ [1]

(iii) $n(Fe^{2+}) : n(Cr_2O_7^{2-}) = 6 : 1$

$n(Fe^{2+})$ in 25.0 cm^3 of solution = 6 x 0.002145 = 0.01287 mol
$n(Fe^{2+})$ in 250 cm^3 of solution = 0.01287/25 x 250 = 0.1287 = **<u>0.129 mol</u>** [1]

mass of Fe present = 0.1287 x 55.8 = 7.181 g

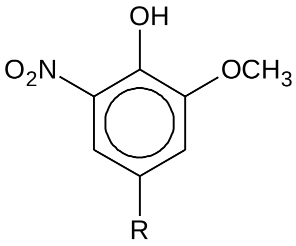
% by mass of iron in the sample of iron ore = 7.181 / 11.15 x 100 % = **<u>64.4 %</u>** [1]

Comments:
The common errors were not using the 6:1 ratio in the equation, or not multiplying the moles of iron(II) ions from the titration by ten, to give the total amount of Fe^{2+} in the 250.0 cm^3 volumetric flask.

3 **(a)** **(i)** reagent **A**: **<u>Na(s)</u>** or **<u>NaOH(aq)</u>** [1]

reagent **B**: **<u>$(CH_3)_2CHCOCl$</u>** [1]

(ii) [1]

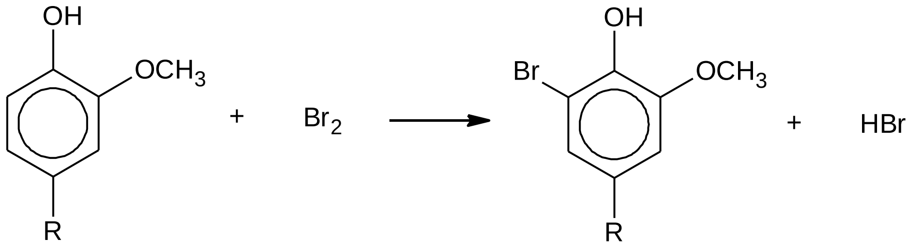


(Assume that the $–OCH_3$ group is inert)

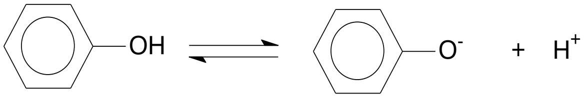
(iii) **<u>Orange</u>** bromine solution turns **<u>colourless</u>**. [1]
A **<u>white precipitate</u>** is formed.

Comments:
While HBr is also formed in this reaction, the amounts formed with a small amount of dilute aqueous bromine would not be sufficient to give a visible observation (i.e. white fumes).

(iv) [1]



(b) **(i)**



The **<u>lone pair of electrons</u>** on the oxygen atom in the phenoxide ion is **<u>delocalised</u>** into the **<u>π electron cloud</u>** of benzene ring. Thus, **<u>dispersing</u>** the **<u>negative charge</u>** and **<u>stabilising</u>** the anion. Ionisation to phenoxide ion and H^+ is more favoured. [1] [1]

$CH_3CH_2OH \rightleftharpoons CH_3CH_2O^- + H^+$

In ethanol, the ethyl group is **<u>electron donating</u>**. This **<u>intensifies</u>** the **<u>negative charge</u>** on the oxygen atom and **<u>destabilises</u>** the ethoxide ion. Ionisation to $CH_3CH_2O^-$ and H^+ is hence not favoured. [1]

Comments:
Students need to discuss the factor leading to the resulting dispersal of the negative charge in the phenoxide ion as the reason for its greater stability. This needed to be contrasted with the concentration (intensification) of negative charge on the oxygen caused by the electron donating ethyl group to give the much less stable ethoxide ion.

(ii)

$$K_a \approx \frac{[H^+]^2}{[\text{vanilloid}]_{\text{initial}}}$$

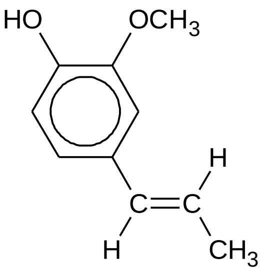
[1]

$$[H^+] = \sqrt{10^{-7.4} \times 0.001} = 6.309 \times 10^{-6}\ \text{mol dm}^{-3}$$

[1]

pH = –log[H^+] = **<u>5.20</u>**

(c) [2]



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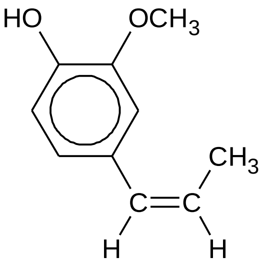


cis

4 **(a)** **(i)** *This Learning Outcome (LO) is no longer in the current syllabus.*

<u>LO in CURRENT syllabus:</u>
*Candidates should be able to contrast, qualitatively, the **melting point** and **density** of the transition elements with those of calcium as a typical s block element.*

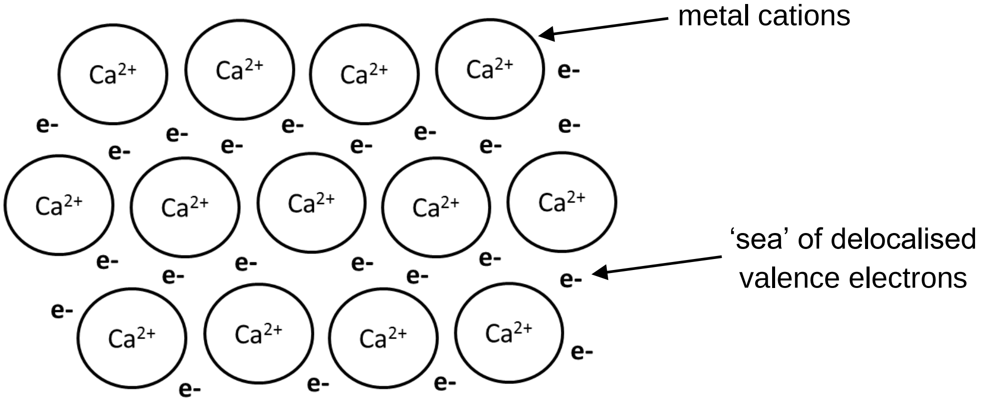
(ii) (density = mass / volume)

The **<u>larger relative atomic mass</u>** and the significantly **<u>smaller atomic radius</u>** for both iron and copper as compared to that of calcium resulted in **<u>larger mass per unit volume</u>** for both iron and copper. Densities of iron and copper are thus significantly greater than that of calcium. [1] [1]

Comments:
Students need to show an understanding that density is mass divided by volume and identify how the factors of relative atomic mass, along with the atomic radius, leads to the significantly greater density of the two transition metals.

(b) **(i)** Calcium has a **giant metallic lattice** that consists of **Ca^{2+} cations** and the **'sea' of delocalised valence electrons** held together by **strong electrostatic forces of attraction**. [1]

[1]



Comments:
The question required the structure as well as the bonding. Students should not use vague terms, describing the electrons as "free electrons' or "sea of electrons". All types of bonding involve electrostatic attraction and any description of bonding must clarify precisely what particles are being attracted.

(ii) The **greater number of delocalised electrons** and **higher charge density** of the iron cation due to its smaller ionic radius lead to **stronger metallic bonds** between the iron cations and the valence electrons and hence a higher melting point of iron. [1]

(c) **(i)** The **high density** of copper will cause the overhead electrical cable to sag. [1]

(ii) Cu $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^6 3d^{10} 4s^1}$ [1]

Cu^{2+} $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^6 3d^9}$

(iii) Copper is purified by **electrolysis**.

The impure copper is the anode while the pure copper is the cathode. The electrolyte is **$CuSO_4(aq)$**. [1]

Anode: $Cu \longrightarrow Cu^{2+} + 2e^-$

Since $E^\ominus(Cu^{2+}/Cu) = +0.34$ V, only **Cu** and impurities with $E^\ominus$ values which are less positive than +0.34 V **dissolves** at the **anode**. [1]

Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

At the **cathode**, only **Cu^{2+} is reduced to Cu** due to its more positive $E^\ominus$ value. The impurities remain in the solution. [1]

Comments:
It was necessary to state that this method uses electrolysis and identify the electrolyte as aqueous copper(II) sulfate. Lengthy descriptions of redox reactions involving other impurity metals were not required, as the question only asked for an outline of the process.

(d) **(i)** *Students are not expected to memorise the products obtained from the thermal decomposition of Group 2 nitrates.*

FYI: $Ca(NO_3)_2 \longrightarrow CaO + 2NO_2 + \frac{1}{2}O_2$ [1]

(ii) *Similar to Group 2 carbonates, explain in terms of the charge density of the cation and the polarisability of the large anion.*

Copper(II) nitrate will decompose at a **lower** temperature than calcium nitrate. [1]

Cu^{2+} has **greater polarising power** than Ca^{2+} since Cu^{2+} has a **smaller ionic radius** than Ca^{2+} and hence, **greater charge density**. [1]

Cu^{2} **distorts** the **electron cloud of NO_3^- anion** in $Cu(NO_3)_2$ **to a greater extent**.

Hence, the **N–O covalent bond in NO_3^- is weakened to a greater extent**.

5 **(a)** *This Learning Outcome (LO) is no longer in the current syllabus.*

FYI:
Any **three** of the following:
- Proteins are the major components of our body's skin, muscle, nails and hair, **providing structural support**, movement and holding cells together. [1]
- Enzymes, which are proteins, **catalyse chemical reactions** in our bodies.
- Proteins are also used as **transport** molecules.
- Protein antibodies are needed for **immune protection** to protect us from diseases.

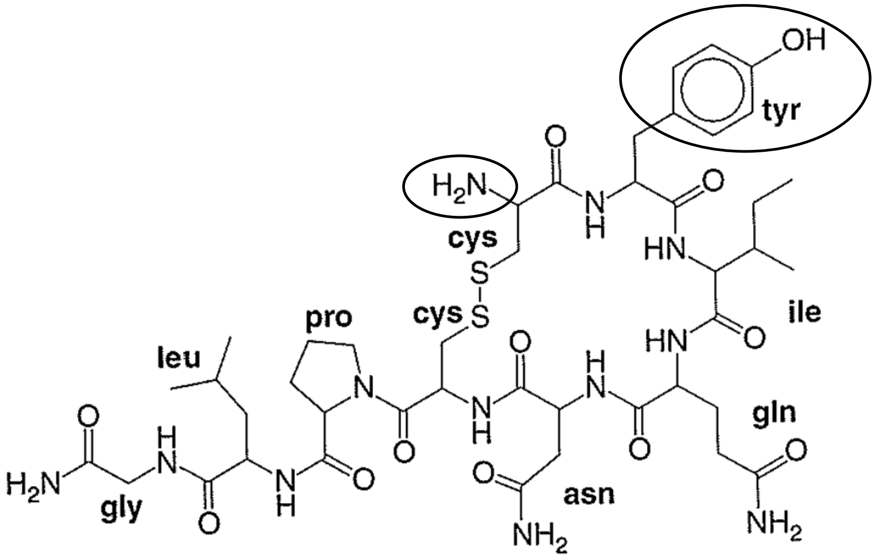
(b) **(i)** *This Learning Outcome (LO) is no longer in the current syllabus.*

FYI:
cys–tyr–ile–gln–asn–cys–pro–leu–gly–NH_2 [1]

(ii) *This Learning Outcome (LO) is no longer in the current syllabus.*

FYI:

[1]



*Either the amine **or** phenol functional group is accepted.*

(c) **(i)** *This Learning Outcome (LO) is no longer in the current syllabus.*

FYI:
The three–dimensional shape of a protein can be described by the **tertiary structure** of a protein. [1]

In oxytocin, the tertiary structure of a protein is held together by the following different types of interaction between the **R** groups, depending on the nature of the **R** group.

1) **van der Waals' forces**
exist between non–polar **R** groups (e.g. leu, pro, ile). [1]

2) **hydrogen bonds**
exist between polar **R** groups (e.g. asn, tyr, gln) with N–H, O–H, and C=O bonds [1]

3) **electrostatic forces of attraction / ionic bonds / ionic linkages** [1]
exist between charged **R** groups (the $–O^–$ of tyrosine and the $–NH_3^+$ of the N terminal amine group).

4) **disulfide bonds / disulfide bridges**
formed between two cys a.a. by the oxidation of 2 S–H groups.

Any 3 for [3m]

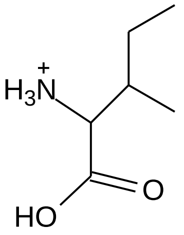
(d) *This Learning Outcome (LO) is no longer in the current syllabus.*

FYI:
Hg^{2+} ions lead to **denaturation** of the protein by: [1]

- **preventing** the **formation of disulfide bonds** by **reacting** with the **–SH** groups [1]
  OR
- breaking the **electrostatic forces of attraction / ionic bonds** between the **charged R groups**

(e) **(i)** (acid–catalysed) **complete hydrolysis** of protein [1]

(ii) [3]



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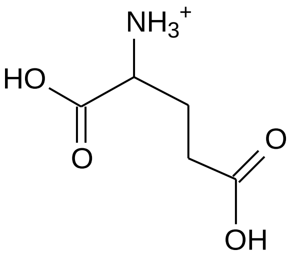

gln

[1m] will be deducted if hydrolysis of the amide side chain of glutamine is omitted.

Comments:
Some students missed out the protonation of the amine groups or the hydrolysis of the amide side chain of glutamine and some also incorrectly protonated the amide nitrogen of the glutamine. Although answers did not need to be skeletal, students should take care not to miss out hydrogen atoms if they decide to give full displayed structures instead.

(f) A *free radical* is a **reactive** atom or group of atoms that **has an unpaired electron**. [1]

The **O–O** single **bond** in hydrogen peroxide undergoes **homolytic fission** to produce •OH free radicals. [1]