2011 Year 6 H2 Chemistry Preliminary Exams – Paper 2 Answers

1 Planning

When aqueous sodium chloride, NaC*l*, is added to aqueous lead(II) nitrate, $Pb(NO_3)_2$, a white precipitate of lead chloride, $PbCl_2$, is produced. A suggested stoichiometric equation is

$$Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$$

In separate experiments, different volumes of 0.20 mol dm^{-3} aqueous sodium chloride are added to a fixed volume of 0.10 mol dm^{-3} aqueous lead(II) nitrate. In each case, the precipitate, $PbCl_2$ will be formed. This precipitate is then filtered, washed with distilled water and thoroughly dried. The mass of the precipitate is recorded.

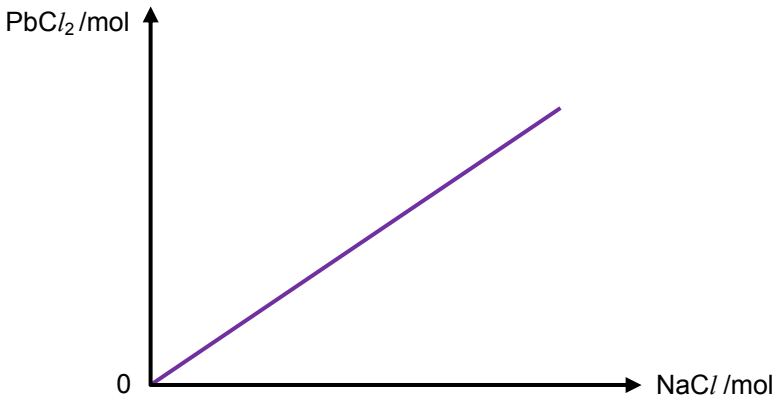
You are to plan an experiment to investigate this reaction in order to confirm or reject the stoichiometry of the equation.

(a) (i) By considering the suggested stoichiometric equation, predict how the number of moles of the precipitate, $PbCl_2$, will change as the number of moles of NaC*l* added increases.

Prediction: No. of moles of $PbCl_2$, **increases** as no. of moles of NaC*l* added

Increases.

(ii) Sketch the graph which would result if NaC*l* is the *limiting reagent*. Start your graph with no NaC*l* added.



(b) You are provided with 250 cm^3 of 0.20 mol dm^{-3} aqueous sodium chloride and some solid lead(II) nitrate.

(i) Outline how you would prepare 250 cm^3 of 0.10 mol dm^{-3} aqueous lead(II) nitrate.
[A_r: N, 14.0; O, 16.0; Pb, 207.0]

- **Weigh 8.275 g** of solid **$Pb(NO_3)_2$** into an empty weighing bottle / beaker.
- Transfer and **dissolve** it in some **distilled/deionised water in a beaker**.
- **Rinse** weighing bottle with distilled water and **transfer** the **washings** to the beaker.
- Ensure **all solid has dissolved**.

- **Transfer to a 250 cm^3 standard/volumetric/graduated flask** using a funnel and glass rod.
- Rinse beaker with distilled water and transfer the washings to the flask
- **Add** distilled **water to** the standard/volumetric/graduated flask to the 250 cm^3 **mark**
- **Shake thoroughly** to ensure a homogenous mixing.

(ii) You will be carrying out five sets of experiments to obtain different masses of precipitate. Give a step by step description of how you would carry out **one** such experiment.

You need to state only the following:

- the volumes of each solution to be used,
- how the volumes will be measured, and
- how you would dry the precipitate.

- Measure **40 cm^3 of $Pb(NO_3)_2$** into an beaker using a **measuring cylinder/burette/pipette**
- Measure **5 cm^3 of NaC*l*** using a **measuring cylinder/burette/pipette** and
- Dry the precipitate by:
  - allowing water to evaporate
  - pressing between filter papers
  - warming in oven
  - adding propanone

(c) In the table below

- enter appropriate headings to show recorded and calculated data. The headings should include appropriate units,
- enter the volumes from your plan in **(b)**,
- enter suitable volumes for four further experiments.

experiment	**volume of $Pb(NO_3)_2$ / cm^3**	**volume of NaC*l* / cm^3**	**mass of $PbCl_2$ / g**	**no. of moles of $PbCl_2$**	**no. of moles of NaC*l***
1	**40**	**5**			
2	**40**	**10**			
3	**40**	**20**			
4	**40**	**30**			
5	**40**	**35**			

(d) How would you ensure that at the end of each experiment the precipitate is thoroughly dried?

Repeat drying/heating process until a **constant mass** is obtained.

2 Iodine forms an intense blue complex with starch and many chemical reactions make use of this property.

(a) In the iodine clock reaction, the following set of reactions take place and a colour change involving the iodine–starch complex happens after a fixed time delay, allowing the kinetics of the reaction to be determined.

Step I: $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$

Step II: $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

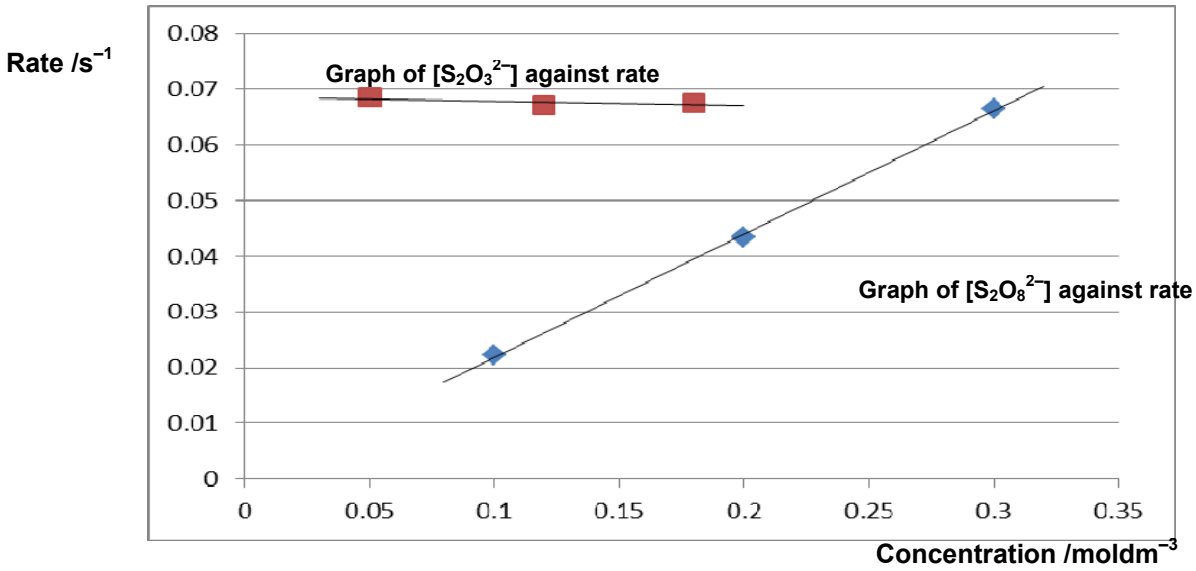
During an experiment to determine the rate equation for these reactions, different concentrations of KI, $Na_2S_2O_8$ and $Na_2S_2O_3$ are mixed according to the following table. The rates of colour change in each solution are shown below.

Flask	$[I^-]$/ mol dm^{-3}	$[S_2O_8^{2-}]$ / mol dm^{-3}	$[S_2O_3^{2-}]$ / mol dm^{-3}	rate /s^{-1}
1	0.10	0.10	0.06	0.0222
2	0.10	0.20	0.06	0.0434
3	0.10	0.30	0.06	0.0665
4	0.20	0.15	0.05	0.0685
5	0.20	0.15	0.12	0.0675
6	0.20	0.15	0.18	0.0672

(i) Deduce two sets of variables whose values can be plotted to obtain the order of reaction with respect to either $S_2O_8^{2-}$ or $S_2O_3^{2-}$.

Plot	**rate (or relative rate) / s^{-1}**
against	**concentration / moldm^{-3}**

(ii) On the grids provided, plot a graph using the variables in **(i)** and determine the order of reaction with respect to $S_2O_8^{2-}$. Label the axes and the graph.



Order of reaction with respect to $S_2O_8^{2-}$ **1**

(iii) Plot another line on the axes above to determine the order of reaction with respect to $S_2O_3^{2-}$.

Order of reaction with respect to $S_2O_3^{2-}$ **0**

(iv) Using a non–graphical method, deduce the order of reaction with respect to I^-.

Let order w.r.t. I^- be x. Rate = k $[S_2O_8^{2-}][I^-]^x$

Comparing experiments 2 and 4,

$$\frac{\text{Rate}_2}{\text{Rate}_4} = \frac{k(0.20)(0.10)^x}{k(0.15)(0.20)^x}$$

$$\frac{0.0434}{0.0685} = \frac{(0.20)(0.10)^x}{(0.15)(0.20)^x}$$

$0.47518 = 0.5^x$

$x = 1.07 \approx \mathbf{1}$

Order of reaction with respect to I^- = 1

or *(Reasoning method)*

Comparing experiments 1 and 4,
When **$[I^-]$ doubles / increases by 2 times and $[S_2O_8^{2-}]$ increases by 1.5 times,**
while the **other concentrations remain constant**,
rate **increases by about** $\frac{0.0685}{0.0222} \approx$ **3 times**
Since order wrt $S_2O_8^{2-}$ is one, **order of reaction with respect to I^- must be 1** to increase rate by 3 times.

(v) Hence or otherwise, write the rate equation and decide if step I could be the rate determining step for the iodine clock reaction.

Rate = k $[S_2O_8^{2-}][I^-]$

No, step I is not the rate determining step.

(b) In the determination of the mass percentage of ascorbic acid ($C_6H_8O_6$) present in vitamin C tablets, the following reaction involving iodine takes place.

$$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2I^- + 2H^+$$

Due to the low solubility of iodine in water, it is generated *in situ* using potassium

iodate (V), potassium iodide and sulfuric acid. In this reaction, iodine is the only product.

(i) Write a balanced equation for the reaction between IO_3^- and I^- to obtain I_2.

$5I^- + 6H^+ + IO_3^- \rightarrow 3I_2 + 3H_2O$

Or **$5KI + 3H_2SO_4 + KIO_3 \rightarrow 3I_2 + 3H_2O + 3K_2SO_4$**

A 3.0 g sample of the tablet is crushed and dissolved in 100.0 cm^3 of dilute sulfuric acid. To this solution, 1.08 g of potassium iodate(V) and 4.32 g of potassium iodide is added. A 25.0 cm^3 aliquot is withdrawn and 21.60 cm^3 of 0.1 mol dm^{-3} thiosulfate is required to titrate with the excess iodine, using starch as an indicator.

(ii) Calculate the total amount of iodine produced from reacting potassium iodate (V) with potassium iodide.

No. of mol of KIO_3 = 0.005044 mol
No. of mol of KI = 0.02600 mol
Since $5I^- \equiv IO_3^-$, **IO_3^- is the limiting reagent**

Since $IO_3^- \equiv 3I_2$,
Total amount of iodine produced = 0.005044 x 3
=0.015133 mol = **0.0151 mol**

(iii) Determine the total amount of *excess* iodine in the 100 cm^3 solution.

No. of mol of $S_2O_3^{2-}$ = $\frac{21.60}{1000}(0.1)$ = **0.00216 mol** in 25 cm^3

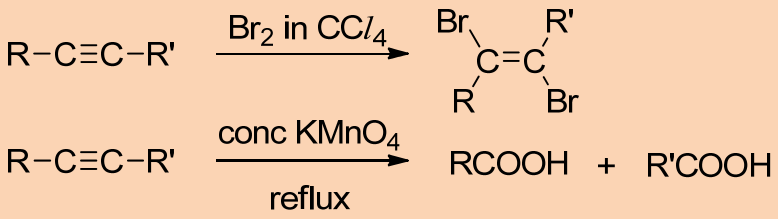
$I_2 \equiv 2S_2O_3^{2-}$

No. of mol of excess I_2 in 100 cm^3 = $\frac{0.00216}{2}(4)$ = **0.00432 mol**

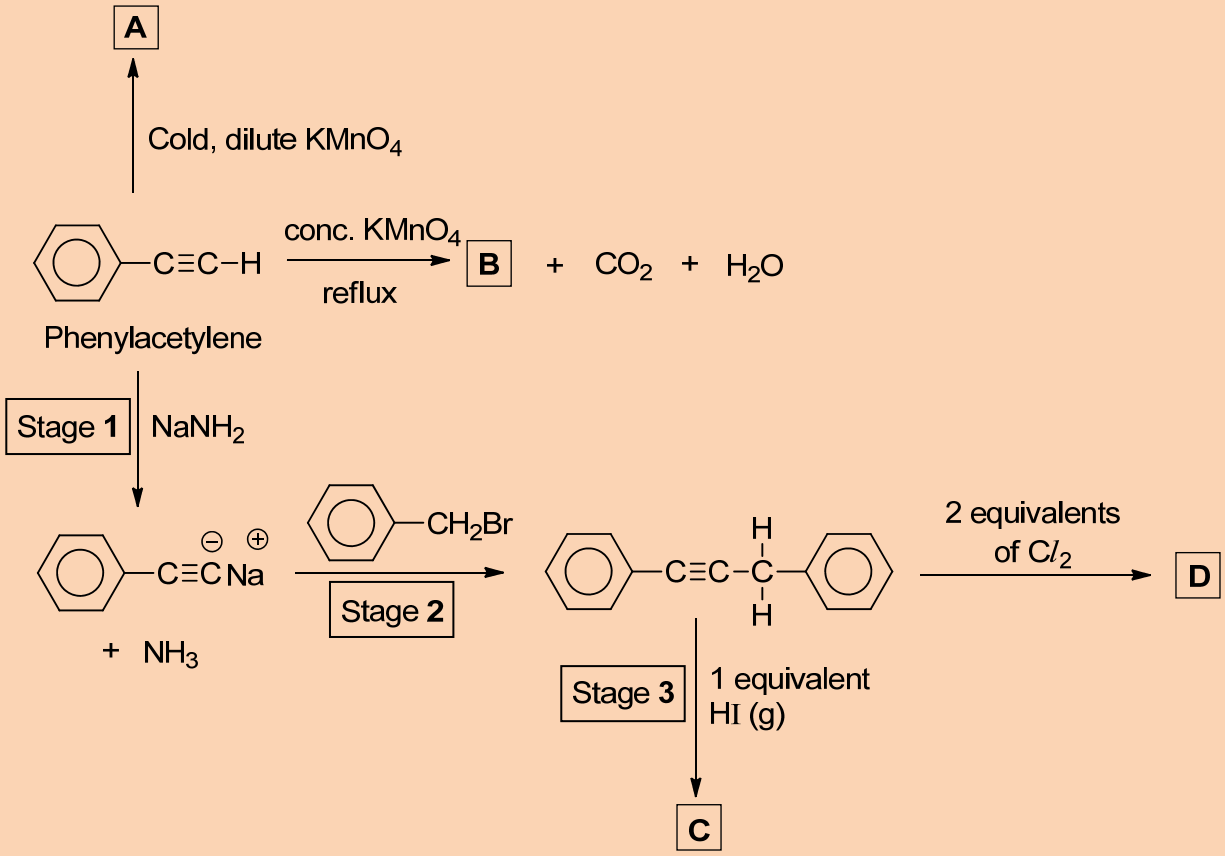
(iv) Hence or otherwise, obtain the mass percentage of ascorbic acid in the sample.

No. of mol of iodine reacted with ascorbic acid = 0.015133 – 0.00432
= **0.010813 mol**
Mass of ascorbic acid = 0.010813 x 176.0 = 1.9030 g
Mass percentage of ascorbic acid = $\frac{1.9030}{3}(100\%)$ = **63.4%**

3 Alkynes are hydrocarbons containing a C≡C triple bond. Reactions involving alkynes resemble that of corresponding alkenes. For example, alkynes react with bromine in tetrachloromethane to give dibromoalkenes. In the mild oxidation of alkynes, the π bonds are broken and a dicarbonyl compound is formed, while oxidation with powerful oxidising agents such as potassium manganate(VII) cleaves the C≡C triple bond.



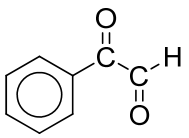
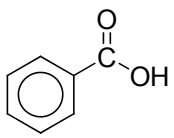
(a) The following reaction scheme shows some reactions involving phenylacetylene (C_6H_5CCH), an alkyne that is useful in organic synthesis.

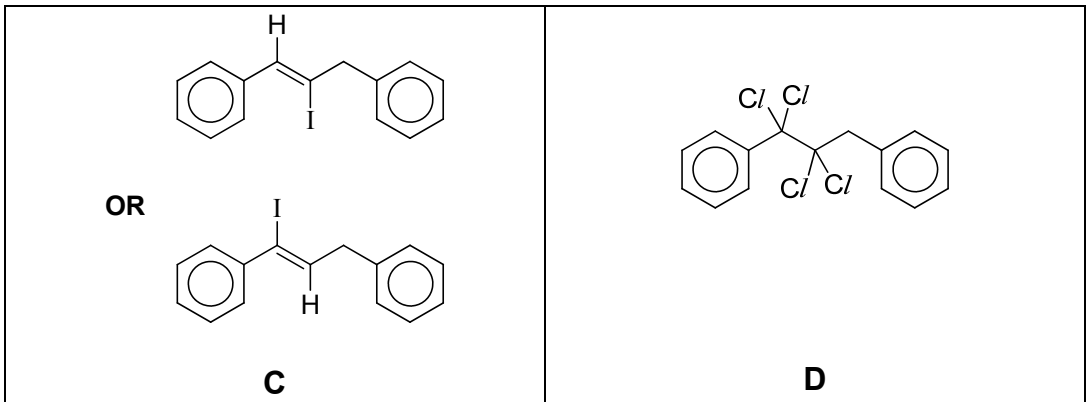


(i) State the types of reaction for stages **1** and **2**.

Stage **1**:	**Neutralisation / acid base**
Stage **2**:	**Nucleophilic Substitution**

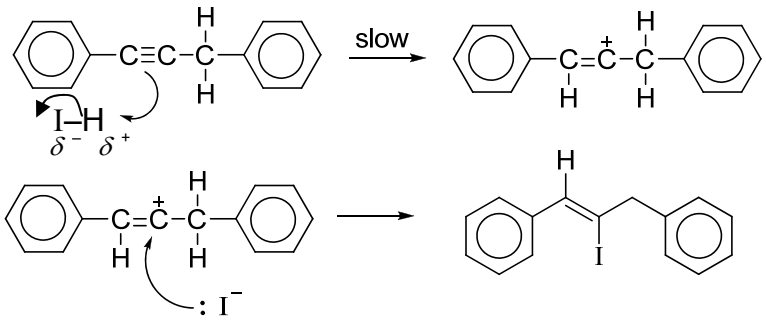
(ii) Draw the structures for the organic products **A** to **D** from the reaction scheme.

 **A**	 **B**

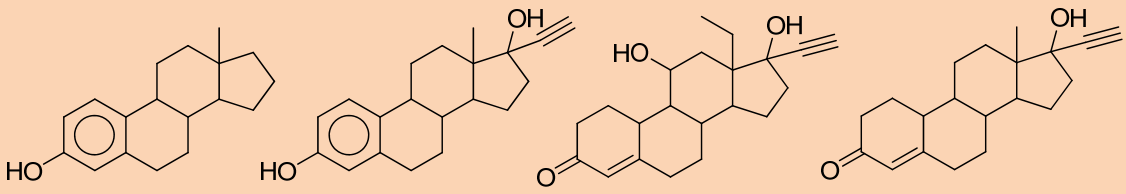


(iii) Name and outline the mechanism for stage **3**, using only equations. Clearly indicate the arrows and the intermediate.

Electrophilic Addition



(b) Alkynes are also found in many naturally occurring organic molecules, such as the hormone molecules shown below.



E **F** **G** **H**

Complete the following sequence of chemical tests by stating suitable reagents, conditions and observations at each step, to identify the stated hormone molecules

Step	reagents, conditions and observations	molecule
1	Reagent and conditions: **Acidified $K_2Cr_2O_7$, reflux** Observation: **Orange solution turns green**	**G**
2	Reagent and conditions: **2,4–dinitrophenylhydrazine, warm** Observation: **Orange ppt formed**	**H**
3	Reagent and conditions: **PCl_5 / Cold** dilute **$KMnO_4$** Observation: **White fumes produced / Decolourisation** of **purple** $KMnO_4$	**F**

4	Reagent and conditions: **Aqueous bromine / liquid bromine in the dark / Neutral $FeCl_3$** Observation: **Decolourisation of reddish–brown aqueous / liquid bromine** and white ppt formed / Formation of **purple** complex	**E**

4 Group IV elements progress towards metallic behavior down the group. The table below shows selected data for the dioxides from carbon to germanium.

Compound	Formula	Melting point /^oC	acid–base nature
Carbon dioxide	CO_2	–78	acidic
Silicon dioxide	SiO_2	1600	weakly acidic
Germanium dioxide	GeO_2	1200	**amphoteric**

(a) State the valence shell electronic configuration of these elements, and their oxidation state in the above dioxides.

Valance shell electronic configuration: **ns^2np^2**
In the dioxides, the oxidation state is **+4**.

(b) Explain the difference in melting points between carbon dioxide and silicon dioxide, with respect to chemical bonding and structure.

CO_2 has **simple molecular structure with <u>weak</u> intermolecular van der Waals' forces (between molecules)**. SiO_2 has **giant molecular structure with <u>strong</u> covalent bonds**. Thus **a greater amount of energy** is required to break the strong covalent bonds in SiO_2

(c) Using the concept of diagonal relationship as well as information from the trend above, suggest the acid–base nature of germanium dioxide by completing the table above.

(d) Tin(II) chloride can react with water according to the following equilibrium.

$$SnCl_2\,(aq) + H_2O\,(l) \rightleftharpoons Sn(OH)Cl\,(s) + HCl\,(aq)$$

Qualitatively explain the effect when sodium carbonate is added into the mixture at equilibrium.

Sodium carbonate reacts with / neutralises hydrochloric acid. Thus, **concentration of hydrochloric acid decreases**. By **Le Chatelier's Principle**, equilibrium **shifts right** to **increase concentration** of hydrochloric acid.

(e) Different lead compounds can be reduced to the elemental form. One example is the reaction between lead(II) oxide and lead(II) sulfide.

$$2PbO\,(s) + PbS\,(s) \rightarrow 3Pb\,(s) + SO_2\,(g) \qquad (\Delta H = +180\ kJ\ mol^{-1})$$

(i) State how the entropy of the reaction will most likely change.

The entropy of the reaction will **increase** as gaseous molecules are produced.

(ii) Hence or otherwise, explain why heating is required for the reaction to occur.

$\Delta G = \Delta H - T\Delta S$

Since $\Delta H > 0$, $\Delta S > 0$

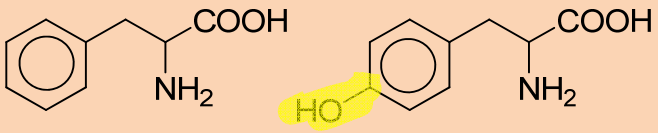
At high temperatures, $|\Delta H| < |T\Delta S|$**, thus ΔG < 0**

The reaction is **feasible at high temperatures**.

or

Since the reaction is endothermic, **products are less stable than reactants** and there is **high activation energy**, thus heat is required for the reaction to take place.

5 The natural occurring amino acids phenylalanine and tyrosine are important building blocks for many molecules in plants and animals.

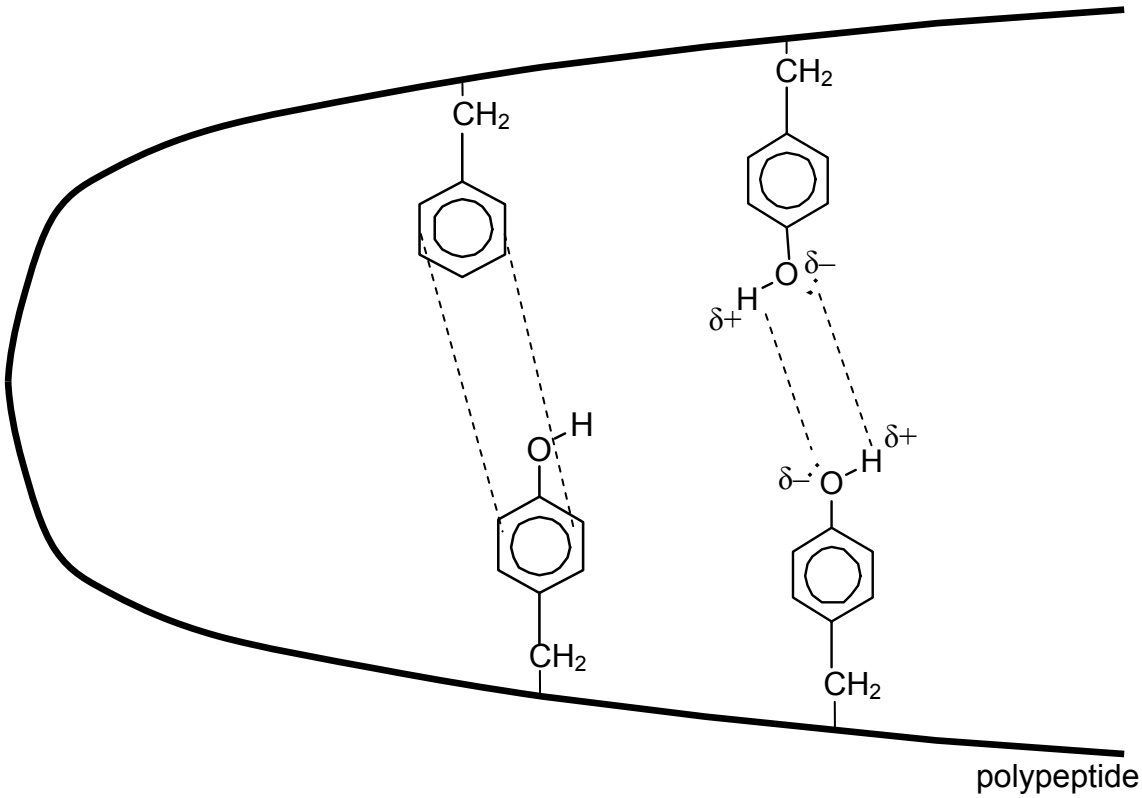


phenylalanine tyrosine

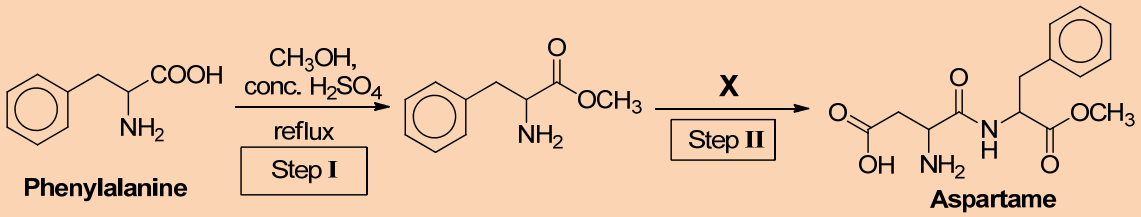
(a) Draw and label on the polypeptide below, different side chain interactions for each pair of amino acid residues.

(i) two tyrosine residues

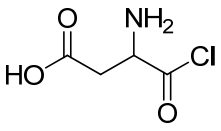
(ii) a phenylalanine and a tyrosine residue



(b) Phenylalanine, together with aspartic acid and methanol, is also used to make aspartame, an artificial sweetener. The main synthetic steps are shown below.



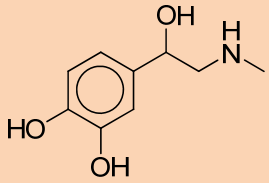
(i) Draw a possible structure for **X** used in Step **II**.



(ii) Suggest a reason for **not** mixing **X**, phenylalanine and methanol together in a one–step synthesis of aspartame.

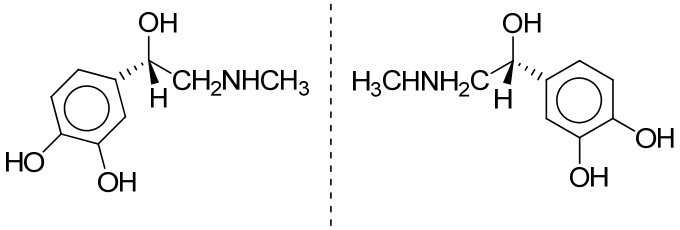
X contains **two functional groups / two carboxylic acids which can react with methanol or phenylalanine**, forming **unwanted side products**.

(c) In mammals, tyrosine forms adrenaline, a 'fight or flight' hormone.



adrenaline

(i) Draw a pair of enantiomers for adrenaline in the space below.



(ii) Tyrosine and adrenaline are separately reacted with aqueous bromine in a cold, dark room. State and explain which molecule would decolourise bromine at a faster rate.

Adrenaline contains **two electron donating hydroxyl groups**, while tyrosine only has **one**. The benzene ring in adrenaline is **more activated / reactive**. Thus, **adrenaline** would react at a faster rate.

or

The presence of **more electron donating hydroxyl groups in adrenaline** compared to tyrosine makes the ring **more electron–rich**. Thus, **adrenaline** would react at a faster rate.

(iii) Tyrosine is soluble in water, while adrenaline is not. Explain this difference in their solubilities.

Tyrosine exists as a **zwitterion / ionic compound**, thus can form **favourable ion–dipole interactions with water**. Adrenaline can **form hydrogen bonds with water molecules** but the **energy released is insufficient to overcome the hydrogen bonds between water molecules / adrenaline molecules.**

6 Rhodium is a second row transition element with a melting point of 1964 ^{o}C.

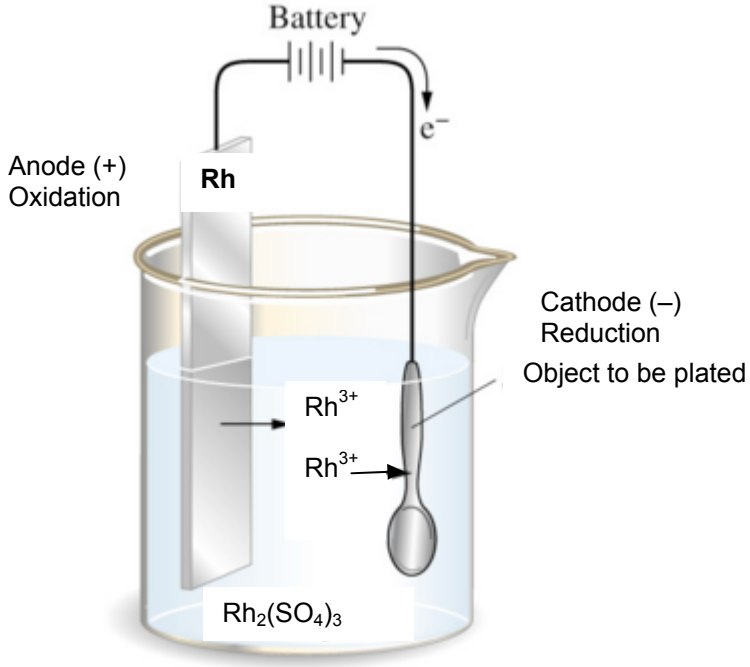
(a) Explain why rhodium has a much higher melting point than strontium, which is also found in the same period.

Rhodium has **valence electrons from both 5s and 4d orbitals / subshells available for delocalisation**, while strontium only has 2 **valence electrons from 5s orbital**. **or** Rhodium has **more valence electrons** than strontium. Rhodium also has a **smaller cationic radius** than strontium. Thus, rhodium has **stronger metallic bonding** between its cations and delocalised electrons, which **requires more energy to overcome**.

(b) Although the rhodium atom has more electrons than the strontium atom, the atomic radius of rhodium is smaller than that of strontium.
Provide an explanation for this.

Although rhodium has more electrons than strontium, the **electrons are added to the inner 4d orbitals** and thus provide **poor shielding** of the 5s electrons. Thus, **effective nuclear charge of rhodium increases** relative to strontium and the atomic radius is smaller.

(c) Rhodium is often plated onto white gold jewellery to make it look brighter. Jewellers use a "bath solution" containing aqueous rhodium(III) sulfate in the process. Draw a labeled diagram for the electroplating of rhodium, including appropriate labels, polarity and the direction of electron flow.



(d) Some rare metals are extracted from their chlorides using magnesium as the reducing agent. Using the standard electrode potential of rhodium(III) and any other relevant data from the *Data Booklet*, suggest and explain if the same method can be applied to rhodium(III) chloride.

$$Rh^{3+} + 3e \rightleftharpoons Rh \qquad E^{\theta} = +0.76\ V$$

From Data Booklet,

$Mg^{2+} + 2e \rightleftharpoons Mg$ $\quad E^{\theta} = -2.38$ V

In the extraction of rhodium, rhodium(III) is reduced while magnesium is oxidised.

$E^{\theta}_{cell} = +0.76 - (-2.38) = +3.14$ V > 0, reaction is **feasible**.

Yes, the same method can be applied.