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CHEMISTRY
HIGHER LEVEL
PAPER 2

Candidate session number

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Thursday 16 May 2013 (afternoon)

2 hours 15 minutes

Examination code

2	2	1	3	–	6	1	1	4

INSTRUCTIONS TO CANDIDATES

- Write your session number in the boxes above.
- Do not open this examination paper until instructed to do so.
- Section A: answer all questions.
- Section B: answer two questions.
- Write your answers in the boxes provided.
- A calculator is required for this paper.
- A clean copy of the ***Chemistry*** *Data Booklet* is required for this paper.
- The maximum mark for this examination paper is *[90 marks]*.

36 pages

SECTION A

*Answer **all** questions. Write your answers in the boxes provided.*

1. Iron tablets are often prescribed to patients. The iron in the tablets is commonly present as iron(II) sulfate, $FeSO_4$.

(a) State the function of iron in the human body. *[1]*

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Two students carried out an experiment to determine the percentage by mass of iron in a brand of tablets marketed in Cyprus.

Experimental Procedure:

- The students took five iron tablets and found that the **total mass** was 1.65 g.
- The five tablets were ground and dissolved in 100 cm^3 dilute sulfuric acid, $H_2SO_4(aq)$. The solution and washings were transferred to a 250 cm^3 volumetric flask and made up to the mark with deionized (distilled) water.
- 25.0 cm^3 of this $Fe^{2+}(aq)$ solution was transferred using a pipette into a conical flask. Some dilute sulfuric acid was added.
- A titration was then carried out using a $5.00 \times 10^{-3}\ mol\ dm^{-3}$ standard solution of potassium permanganate, $KMnO_4(aq)$. The end-point of the titration was indicated by a slight pink colour.

The following results were recorded.

	Rough titre	**First accurate titre**	**Second accurate titre**
Initial burette reading / $cm^3 \pm 0.05$	1.05	1.20	0.00
Final burette reading / $cm^3 \pm 0.05$	20.05	18.00	16.80

(This question continues on the following page)

(Question 1 continued)

(b) When the Fe^{2+}(aq) solution was made up in the 250 cm^3 volumetric flask, deionized (distilled) water was added until the bottom of its meniscus corresponded to the graduation mark on the flask. It was noticed that one of the two students measured the volume of the solution from the top of the meniscus instead of from the bottom. State the name of this type of error. *[1]*

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(c) State what is meant by the term *precision*. *[1]*

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(d) When the students recorded the burette readings, following the titration with $KMnO_4$(aq), the top of the meniscus was used and not the bottom. Suggest why the students read the top of the meniscus and not the bottom. *[1]*

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(This question continues on the following page)

(Question 1 continued)

(e) This experiment involves the following redox reaction.

$$5Fe^{2+}(aq) + MnO_4^{-}(aq) + 8H^{+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

(i) Define the term *reduction* in terms of electrons. *[1]*

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(ii) Deduce the oxidation number of manganese in the $MnO_4^{-}(aq)$ ion. *[1]*

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(This question continues on the following page)

(Question 1 continued)

(f) (i) Determine the amount, in mol, of MnO_4^-(aq), used in each accurate titre. *[2]*

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(ii) Calculate the amount, in mol, of Fe^{2+}(aq) ions in 250 cm^3 of the solution. *[1]*

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(iii) Determine the total mass of iron, in g, in the 250 cm^3 solution. *[1]*

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(iv) Determine the percentage by mass of iron in the tablets. *[1]*

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(This question continues on the following page)

(Question 1 continued)

(g) During the rough titration, the students found that a brown precipitate, **X**, formed.

(i) When the students discussed the nature of the precipitate with their teacher, they were told that **X** is the same compound as that used as a catalyst in the decomposition of hydrogen peroxide, $H_2O_2(aq)$, to prepare oxygen, $O_2(g)$. Suggest the chemical formula and name of **X**. *[2]*

Chemical formula:

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Name:

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(ii) State the balanced chemical equation for the decomposition of hydrogen peroxide. *[1]*

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(iii) Suggest how the formation of the brown precipitate might be prevented. *[1]*

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(This question continues on the following page)

(Question 1 continued)

(h) (i) Following the experiment, the students proposed the following hypothesis:

"Since sulfuric acid is a strong acid, two other strong acids such as nitric acid, HNO_3(aq) or hydrochloric acid, HCl(aq), could also be used in this experiment".

Suggest **one** problem with this hypothesis. *[1]*

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(ii) The students also explored the role of sulfuric acid in everyday processes and found that sulfuric acid present in acid rain can damage buildings made of limestone. Predict the balanced chemical equation for the reaction between limestone and sulfuric acid, including state symbols. *[2]*

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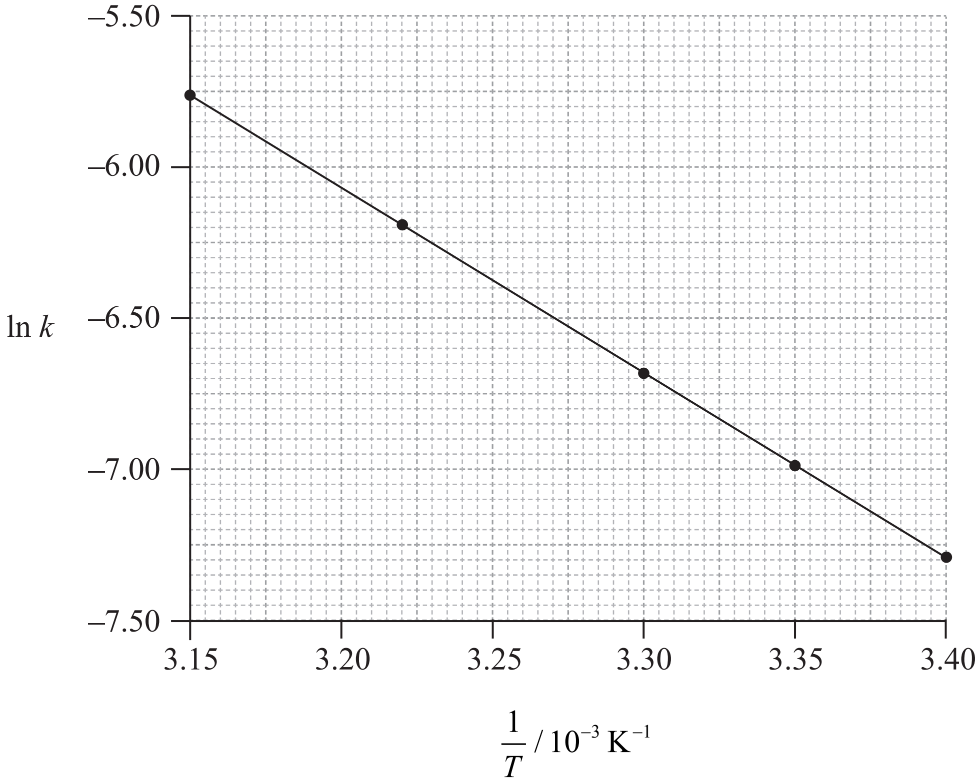
2. Consider the following graph of ln k against $\frac{1}{T}$.



(a) A catalyst provides an alternative pathway for a reaction, lowering the activation energy, E_a. Define the term *activation energy*, E_a. *[1]*

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(b) State how the rate constant, k, varies with temperature, T. *[1]*

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(This question continues on the following page)

(Question 2 continued)

(c) Determine the activation energy, E_a, correct to **three** significant figures and state its units. *[3]*

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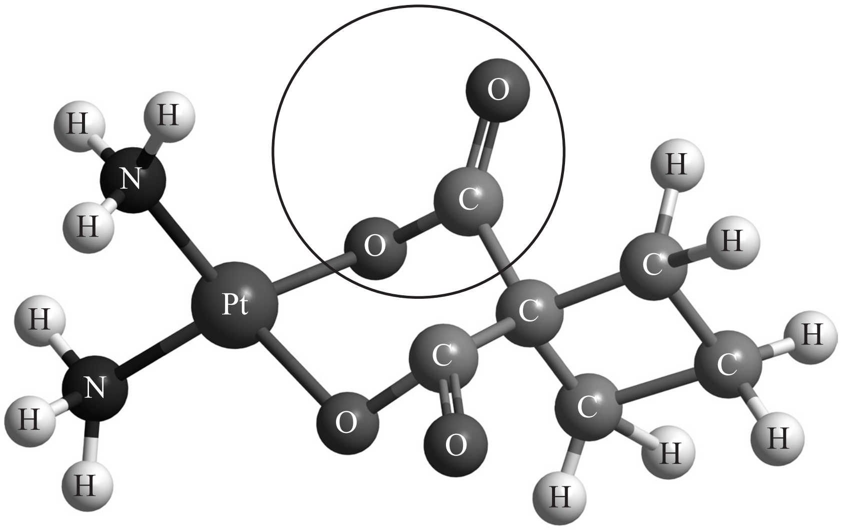
3. Carboplatin used in the treatment of lung cancer has the following three-dimensional structure.



(a) Identify the name of the functional group circled in the structure of carboplatin. *[1]*

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(b) State the type of bonding between platinum and nitrogen in carboplatin. *[1]*

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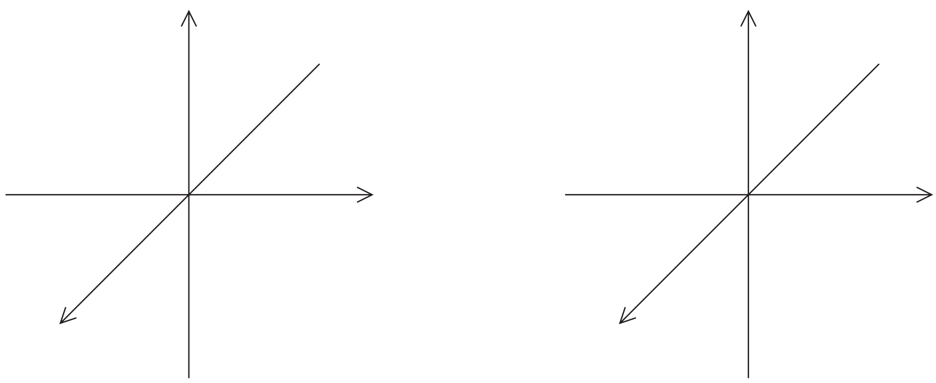
(This question continues on the following page)

(Question 3 continued)

(c) Elemental platinum has electrons occupying s, p, d and f atomic orbitals.

(i) Draw the shape of an s orbital and a p_x orbital. Label the x, y and z axes on each diagram. *[2]*



s orbital p_x orbital

(ii) State the maximum number of orbitals in the $n = 4$ energy level. *[1]*

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(d) A number of ruthenium-based anti-cancer drugs have also been developed. State the **full** electron configuration of the ruthenium(II) ion, Ru^{2+}. *[1]*

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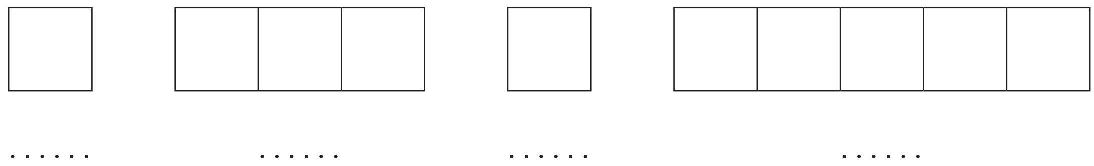
(This question continues on the following page)

(Question 3 continued)

(e) Iron is in the same group in the periodic table as ruthenium.

Construct the orbital diagram (using the arrow-in-box notation) for iron, showing the electrons in the $n = 3$ and $n = 4$ energy levels only **and** label each sub-level on the diagram. *[1]*



4. (a) Hydrogen gas reacts with iodine gas to form hydrogen iodide gas. A 2.00 dm^3 flask was filled with 1.50×10^{-2} mol of hydrogen and 1.50×10^{-2} mol of iodine at a temperature, *T*. The equilibrium constant, K_c, has a value of 53.0 at this temperature.

(i) Deduce the equilibrium constant expression, K_c, for the formation of HI(g). *[1]*

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(ii) Determine the equilibrium concentrations, in mol dm^{-3}, of hydrogen, iodine and hydrogen iodide. *[4]*

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(b) Identify the intermolecular forces present in hydrogen iodide in the liquid state, HI(l). *[1]*

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(This question continues on the following page)

(Question 4 continued)

(c) Consider the compounds $(CH_3)_2NH$ and CH_4.

(i) State and explain which compound can form hydrogen bonds **with water**. *[2]*

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(ii) Draw a diagram showing the resulting hydrogen bonds between water and the compound chosen in (i). *[1]*

(iii) Apply IUPAC rules to state the name of $(CH_3)_2NH$. *[1]*

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SECTION B

*Answer **two** questions. Write your answers in the boxes provided.*

5. Phosphoryl chloride, $POCl_3$, is a dehydrating agent.

(a) $POCl_3(g)$ decomposes according to the following equation.

$$2POCl_3(g) \rightarrow 2PCl_3(g) + O_2(g)$$

(i) Predict and explain the sign of the entropy change, ΔS, for this reaction. *[1]*

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(ii) Calculate the standard entropy change for the reaction, $\Delta S^{\ominus}$, in $J\,K^{-1}\,mol^{-1}$, using the data below.

Substance	$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$
$POCl_3(g)$	325.0
$PCl_3(g)$	311.7
$O_2(g)$	205.0

[1]

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(iii) Define the term *standard enthalpy change of formation*, $\Delta H_f^{\ominus}$. *[1]*

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(This question continues on the following page)

(Question 5 continued)

(iv) Calculate the standard enthalpy change for the reaction, $\Delta H^{\ominus}$, in $kJ\,mol^{-1}$, using the data below.

Substance	**$\Delta H_f^{\ominus}$ / $kJ\,mol^{-1}$**
$POCl_3$ (g)	–542.2
PCl_3 (g)	–288.1

[1]

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(v) Determine the standard free energy change for the reaction, $\Delta G^{\ominus}$, in $kJ\,mol^{-1}$, at 298 K. *[1]*

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(vi) Deduce the temperature, in K, at which the reaction becomes spontaneous. *[1]*

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(This question continues on the following page)

(Question 5 continued)

(b) (i) Deduce the Lewis (electron dot) structure of $POCl_3$ (with P as the central element) and PCl_3 and predict the shape of each molecule, using the valence shell electron pair repulsion theory (VSEPR). *[4]*

	$POCl_3$	PCl_3
Lewis (electron dot) structure		
Shape	. . . .	. . . .

(ii) State and explain the Cl–P–Cl bond angle in PCl_3. *[3]*

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(iii) State the balanced chemical equation for the reaction of $PCl_3(l)$ with water. *[1]*

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(This question continues on the following page)

(Question 5 continued)

(c) $POCl_3$ can be prepared by the reaction of phosphorus pentachloride, PCl_5, with tetraphosphorus decaoxide, P_4O_{10}.

(i) Deduce the Lewis (electron dot) structure of PCl_5. *[1]*

(ii) Predict the shape of this molecule, using the valence shell electron pair repulsion theory (VSEPR). *[1]*

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(iii) Identify all the different bond angles in PCl_5. *[1]*

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(This question continues on the following page)

(Question 5 continued)

(iv) PCl_3Br_2 has the same molecular shape as PCl_5. Draw the three isomers of PCl_3Br_2 and deduce whether each isomer is polar or non-polar. *[3]*

	Isomer 1	Isomer 2	Isomer 3
Structure			
Molecular polarity	. . . .	. . . .	. . . .

(d) PCl_3 and Cl^- can act as ligands in transition metal complexes such as $Ni(PCl_3)_4$ and $[Cr(H_2O)_3Cl_3]$.

(i) Define the term *ligand*. *[2]*

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(ii) Explain why the complex $[Cr(H_2O)_3Cl_3]$ is coloured. *[3]*

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6. Acid–base chemistry can play a major role in chemical and biological processes.

(a) Ammonia, NH_3, can be used to clean ovens. The concentration of hydroxide ions, $OH^-(aq)$, in a solution of ammonia is $3.98 \times 10^{-3}\ mol\ dm^{-3}$. Calculate its pH, correct to **one** decimal place, at 298 K. *[2]*

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(b) White vinegar, which contains ethanoic acid, CH_3COOH, can be used as a cleaning agent to dissolve mineral deposits from coffee machines.

(i) Define an *acid* according to the Brønsted–Lowry theory and the Lewis theory. *[2]*

Brønsted–Lowry theory:

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Lewis theory:

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(ii) Ethanoic acid is an example of a weak acid. Distinguish between a *strong acid* and a *weak acid* in terms of the extent of dissociation. *[1]*

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(Question 6 continued)

(c) Buffer solutions play a pivotal role in solution chemistry.

(i) State whether the following mixtures, in the appropriate molar ratios, can be classified as buffer solutions. Show your answer by stating **yes** or **no** in the table below. *[1]*

Mixture	**Buffer**
$HCOOH$ and $HCOO^{-}K^{+}$	
HCl and excess NH_3	

(ii) A buffer solution contains lactic acid, $CH_3CH(OH)COOH(aq)$, with a concentration of 1.55×10^{-1} mol dm^{-3} and sodium lactate, $NaCH_3CH(OH)COO(aq)$, with a concentration of 1.05×10^{-1} mol dm^{-3}. Determine the pH of this buffer solution, correct to **two** decimal places.
(K_a for lactic acid $= 1.40 \times 10^{-4}$ at 298 K.) *[4]*

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(Question 6 continued)

(d) Acid–base indicators are often organic dyes.

(i) Describe qualitatively the action of an acid–base indicator. *[3]*

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(ii) Using Table 16 of the Data Booklet, identify the most appropriate indicator for the titration of ethanoic acid with sodium hydroxide. Explain your choice. *[2]*

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(iii) $150\,cm^3$ of $5.00 \times 10^{-1}\,mol\,dm^{-3}$ $HCl(aq)$ is mixed with $300\,cm^3$ of $2.03 \times 10^{-1}\,mol\,dm^{-3}$ $NaOH(aq)$. Determine the pH of the solution, correct to **two** decimal places. *[4]*

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(This question continues on the following page)

(Question 6 continued)

(e) (i) State and explain whether the following solutions will be acidic, basic or neutral. *[4]*

$FeCl_3$:

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$CH_3CH_2NH_3NO_3$:

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(ii) The K_a value for HF is 6.80×10^{-4} at 298 K. Using this information and any additional information from Tables 2 and 15 of the Data Booklet, deduce whether a solution of NH_4F would be acidic, basic or neutral. *[2]*

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7. (a) Define *oxidation* in terms of oxidation number. *[1]*

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(b) (i) Deduce the balanced chemical equation for the redox reaction of copper, Cu(s), with nitrate ions, NO_3^-(aq), **in acid**, to produce copper(II) ions, Cu^{2+}(aq), and nitrogen(IV) oxide, NO_2(g). *[2]*

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(ii) Deduce the oxidizing and reducing agents in this reaction. *[1]*

Oxidizing agent:

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Reducing agent:

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(This question continues on the following page)

(Question 7 continued)

(c) A voltaic cell was set up, using the standard hydrogen electrode as a reference electrode and a standard $Cu^{2+}(aq)/Cu(s)$ electrode.

(i) Describe the standard hydrogen electrode including a fully labelled diagram. *[3]*

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(ii) Define the term *standard electrode potential*, $E^{\ominus}$. *[1]*

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(iii) Deduce a balanced chemical equation, including state symbols, for the overall reaction which will occur spontaneously when the two half-cells are connected. *[2]*

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(This question continues on the following page)

(Question 7 continued)

(d) Another voltaic cell was set up, using a $Sn^{2+}(aq)/Sn(s)$ half-cell and a $Cu^{2+}(aq)/Cu(s)$ half-cell under standard conditions.

(i) Draw a fully labelled diagram of the voltaic cell, showing the positive electrode (cathode), the negative electrode (anode) and the direction of electron movement through the external circuit. *[3]*

(ii) Using Table 14 of the Data Booklet, calculate the cell potential, $E^{\ominus}_{cell}$, in V, when the two half-cells are connected. *[1]*

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(This question continues on the following page)

(Question 7 continued)

(e) Water in a beaker at a pressure of 1.01×10^5 Pa and a temperature of 298 K will not spontaneously decompose. However, decomposition of water can be induced by means of electrolysis.

(i) Deduce the sign of the standard free energy change, $\Delta G^{\ominus}$, for any non-spontaneous reaction. *[1]*

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(ii) State why dilute sulfuric acid needs to be added in order for the current to flow in the electrolytic cell. *[1]*

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(iii) State why copper electrodes cannot be used in the electrolysis of water. Suggest instead suitable **metallic** electrodes for this electrolysis process. *[1]*

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(This question continues on the following page)

(Question 7 continued)

(iv) Deduce the half-equations for the reactions occurring at the positive electrode (anode) and the negative electrode (cathode). *[2]*

Positive electrode (anode):

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Negative electrode (cathode):

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(v) Deduce the overall cell reaction, including state symbols. *[1]*

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(This question continues on the following page)

(Question 7 continued)

(vi) Draw a fully labelled diagram of the electrolytic cell, showing the positive electrode (anode) and the negative electrode (cathode). *[2]*

(vii) Comment on what is observed at both electrodes. *[1]*

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(f) Two electrolytic cells are connected in series (the same current passes through each cell). One cell for the electrolysis of water produces $100\,cm^3$ of oxygen, measured at $273\,K$ and $1.01 \times 10^5\,Pa$. The second cell contains molten lead(II) bromide, $PbBr_2$. Determine the mass, in g, of lead produced. *[2]*

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8. Geometrical isomerism and optical isomerism are two sub-groups of stereoisomerism in organic chemistry.

(a) Describe what is meant by the term *stereoisomers*. *[1]*

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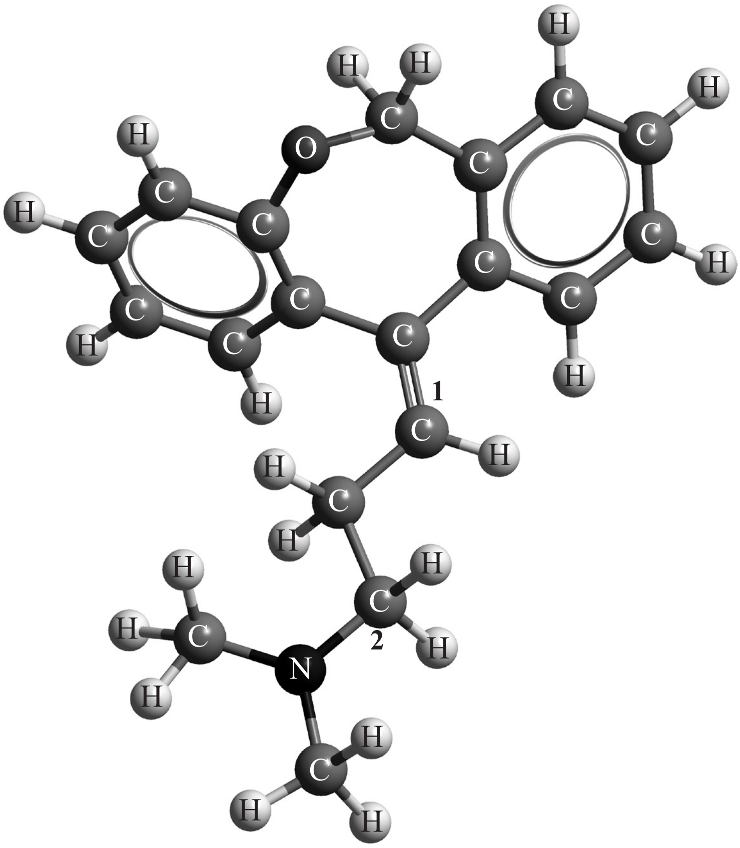
(b) Geometrical isomers have different physical properties and many drugs, such as doxepin (which has antidepressant properties), have geometrical isomers.



Example of a geometrical isomer of doxepin

For each of the carbon atoms labelled **1** and **2** in doxepin, deduce the type of hybridization involved (sp, sp^2 or sp^3). *[1]*

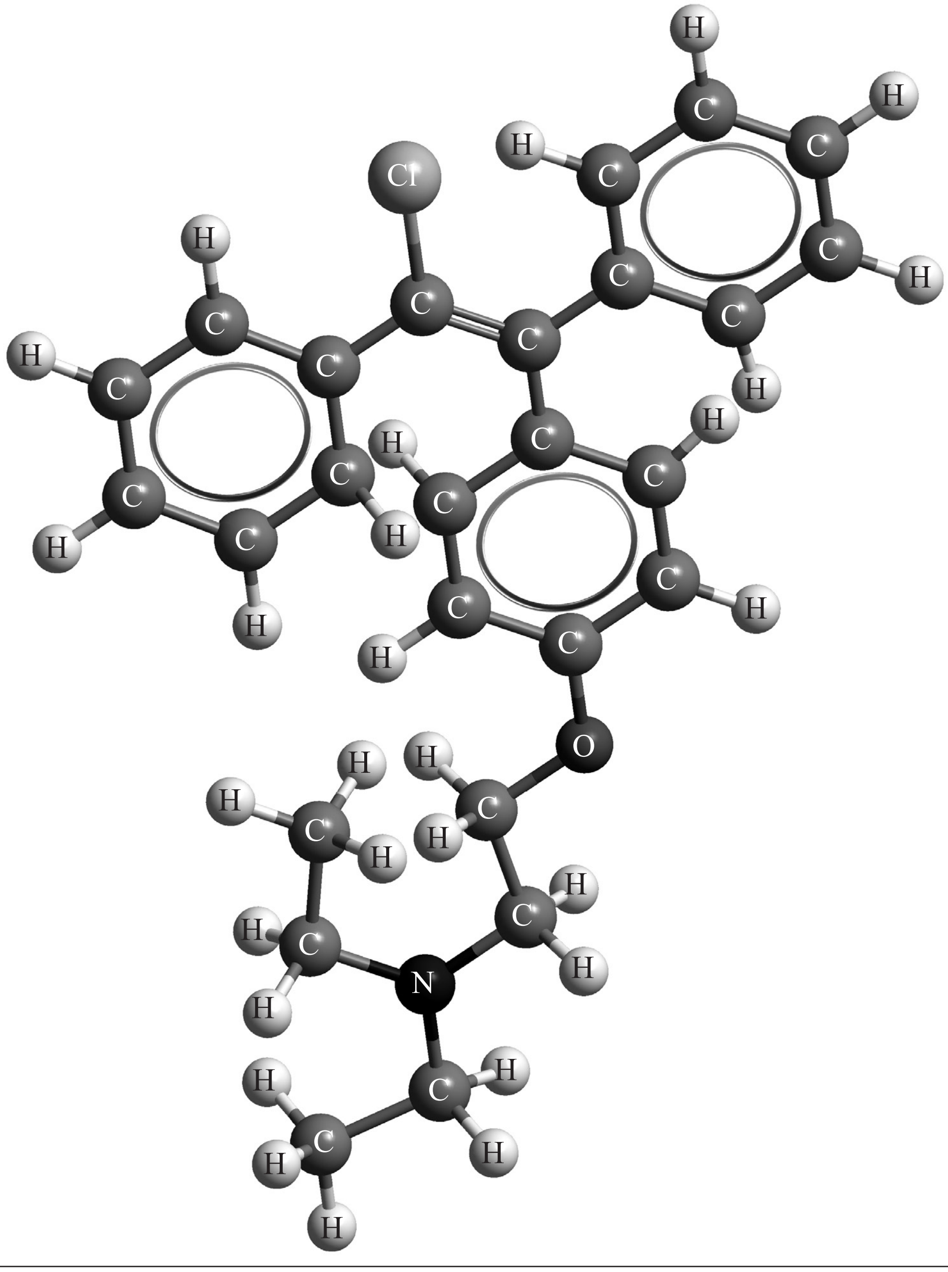
1: . . . .

2: . . . .

(This question continues on the following page)

(Question 8 continued)

(c) Clomifene, a fertility drug, whose three-dimensional structure is represented below, also has geometrical isomers.



Identify the name of **one** functional group present in clomifene. *[1]*

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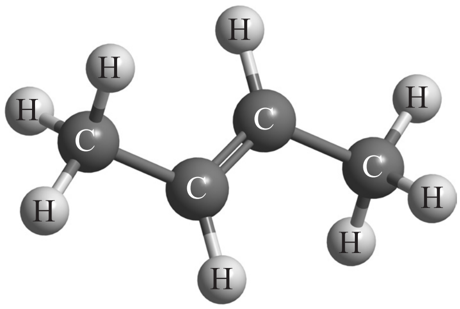
(Question 8 continued)

(d) Compound **P** has the following three-dimensional structure. **P** also has geometrical isomers.



P

(i) Draw any **two** other isomers of **P**. *[2]*

(ii) Apply IUPAC rules to state the names of all the straight-chain isomers of compounds of molecular formula C_4H_8 (including **P**). *[2]*

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(This question continues on the following page)

(Question 8 continued)

(iii) State the structural formula of the organic products, **Q**, **R**, **S** and **T**, formed in the following reactions. *[4]*

$CH_3CH{=}CHCH_3 + HBr(g) \longrightarrow$ **Q**

Q:

$CH_3CH{=}CHCH_3 \xrightarrow[\text{(2) } H_2O(l)]{\text{(1) concentrated } H_2SO_4(aq)}$ **R**

R:

$CH_3CH{=}CHCH_3 + Br_2(aq) \longrightarrow$ **S**

S:

Q + $OH^-(aq) \longrightarrow$ **T**

T:

(This question continues on the following page)

(Question 8 continued)

(iv) Suggest **one** suitable mechanism for the reaction of **Q** with aqueous sodium hydroxide to form **T**, using curly arrows to represent the movement of electron pairs. *[4]*

(v) State the structural formula of the organic product formed, **U**, when **R** is heated under reflux with acidified potassium dichromate(VI). *[1]*

(vi) Apply IUPAC rules to state the name of this product, **U**. *[1]*

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(This question continues on the following page)

(Question 8 continued)

(e) Menthol can be used in cough medicines. The compound contains C, H and O only.

(i) When a 6.234×10^{-2} g of the compound was combusted, 1.755×10^{-1} g of carbon dioxide and 7.187×10^{-2} g of water were produced. Determine the molecular formula of the compound showing your working, given that its molar mass is $M = 156.30\,\text{g mol}^{-1}$. *[4]*

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(ii) Menthol occurs naturally and has several isomers. State the structural feature of menthol which is responsible for it having enantiomers. *[1]*

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(This question continues on the following page)

(Question 8 continued)

(iii) State the instrument used to distinguish between each of the two enantiomers, and how they could be distinguished using this instrument. *[1]*

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(iv) Compare the physical and chemical properties of enantiomers. *[2]*

Physical properties:

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Chemical properties:

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