

CHEMISTRY

Paper 3 Free Response

9647/03

Thursday 27 August 2015
2 hours

Additional Materials: Data Booklet
Answer Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen on both sides of the paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions. Write your answers on the answer paper provided.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

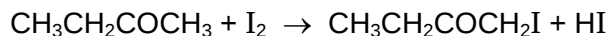
This document consists of **14** printed pages and **0** blank page.

[Turn over

Answer any **four** questions.

- 1** Butanone is an industrial organic solvent used in the manufacture of plastics, lacquers and varnishes.

(a) Butanone reacts with iodine in the presence of an acid according to the equation:



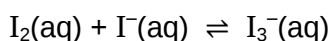
In a series of experiments, the reaction was carried out with different concentrations of reagents, and the following initial rates were obtained:

Expt.	$[\text{CH}_3\text{CH}_2\text{COCH}_3]$ / mol dm ⁻³	$[\text{I}_2]$ / mol dm ⁻³	$[\text{H}^+]$ / mol dm ⁻³	Initial rate / mol dm ⁻³ min ⁻¹
1	0.010	0.010	0.010	8.31×10^{-8}
2	0.010	0.010	0.013	10.8×10^{-8}
3	0.013	0.010	0.013	14.0×10^{-8}
4	0.018	0.013	0.018	26.9×10^{-8}

- (i)** Using the data given, deduce the order of reaction with respect to each of the three reagents, clearly showing how you arrive at your answers. Hence, write a rate equation for the reaction.
- (ii)** Explain how the rate of reaction would change if the solution was diluted with an equal volume of inert solvent, using r to represent the original rate before dilution.
- (iii)** The reaction can also be carried out in the presence of a strong base instead of an acid. State what would be observed when a strong base is used and write an equation for the reaction that occurs.

[7]

- (b)** Elemental iodine, I_2 , has limited solubility in water. Its solubility is greatly increased in a solution containing iodide ion, I^- , due to the formation of triiodide ion, I_3^- , as shown:



- (i)** Write an expression for the equilibrium constant, K_c , of this reaction, stating its units.
- (ii)** Experiments have shown that when $[\text{I}^-] = 1.4 \times 10^{-3}$ mol dm⁻³, the concentrations of I_2 and I_3^- are equal. Use this information to calculate a value for K_c .
- (iii)** Using your answer from **(b)(ii)**, calculate the concentration of iodide ions necessary for 99 % of the iodine to be dissolved.

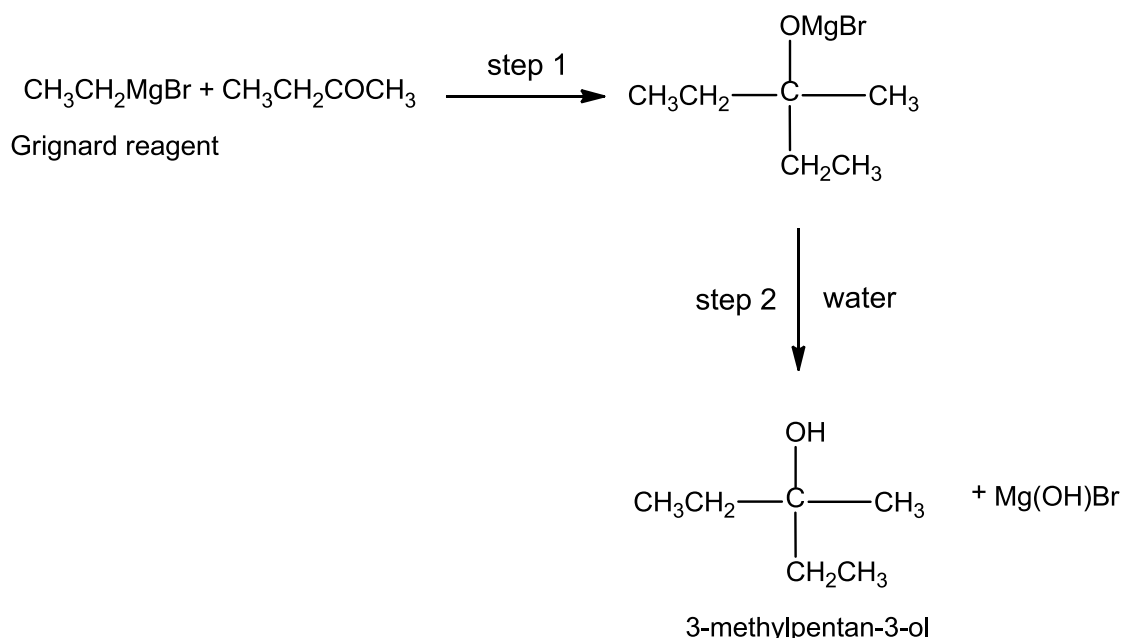
[4]

- (c) Explain, using Maxwell-Boltzmann distribution curves, how the rate of a reaction would change if the temperature was increased.

[3]

- (d) Grignard reagents are organo-magnesium halides, commonly used in synthesis to prepare a variety of organic compounds.

The carbon-magnesium bonds in Grignard reagents are highly polar and this makes it extremely useful in organic synthesis as it is able to react with other polar organic molecules to form carbon-carbon bonds. An example of the use of a Grignard reagent is the two-step reaction of $\text{CH}_3\text{CH}_2\text{MgBr}$ with butanone, $\text{CH}_3\text{CH}_2\text{COCH}_3$, to form 3-methylpentan-3-ol.



- (i) Suggest the type of reaction that has taken place in step 1.
- (ii) Suggest the structural formula of the organic compound to be used with $\text{CH}_3\text{CH}_2\text{MgBr}$ to form propan-1-ol, if the reaction undergoes a similar two-step process.
- (iii) Suggest a suitable Grignard reagent and another organic compound to be used if propan-2-ol is to be prepared using a similar two-step process.

[4]

- (e) There are certain practical issues with the use of Grignard reagent, notably slow formation of the Grignard reagent and its susceptibility to reaction with water in air.

The slow formation of the Grignard reagent may be offset by cutting the precursor magnesium into smaller pieces or scraping the sides of the metal before use. Using a balanced equation, explain why magnesium, which has been stored in dry ambient conditions, may not react as quickly as expected.

[2]

[Total: 20]

[Turn over]

- 2 The direct oxidation of alcohols in a fuel cell represents potentially the most efficient method of obtaining useful energy from renewable fuel.

The diagram below illustrates the functional parts of a direct-ethanol fuel cell (DEFC). The anode and cathode compartments are separated by the proton exchange membrane. The protons are transported across the proton exchange membrane to the cathode where they react with oxygen to produce water.

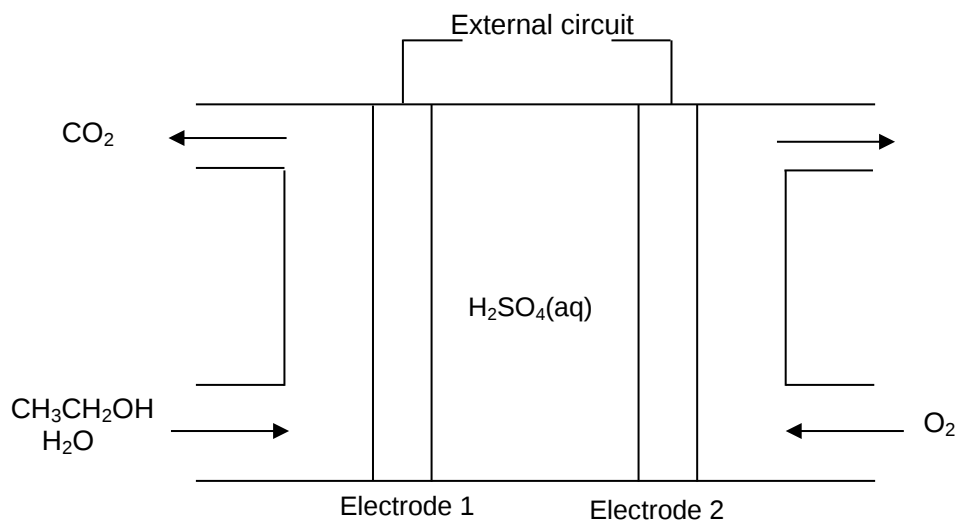


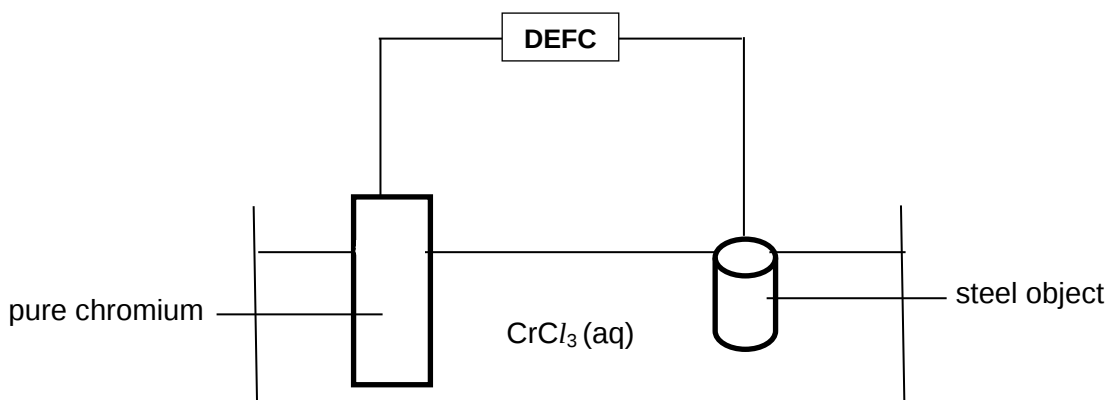
Diagram of a DEFC

- (a) (i) Explain, in terms of the change in **average** oxidation number of the carbon atoms, whether electrode 1 or 2 acts as the anode.
- (ii) Write the half-equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.
- (iii) The cell is capable of producing an e.m.f. of 1.47 V. By using suitable data from the *Data Booklet*, calculate a value for the $E^{\ominus}$ of the $\text{CO}_2/\text{CH}_3\text{CH}_2\text{OH}$ electrode reaction.
- (iv) By quoting relevant $E^{\ominus}$ values from the *Data Booklet*, explain why an acidic electrolyte is preferred to an alkaline electrolyte in the DEFC.
- (v) Describe and explain the effect on the cell potential when the concentration of ethanol is increased.

[9]

- (b) Chromium plating is an important industrial application of electrolysis, where a steel object is plated with a thin layer of chromium to make it resistant to rusting and scratches.

In an electroplating experiment, a researcher connected the DEFC to an electrolytic cell as shown below. The aqueous solution containing chromium(III) chloride was electrolysed using a piece of pure chromium and the steel object to be electroplated as the electrodes.



- (i) The total time taken for 10 g of chromium to be plated was 4 hours. Calculate the current produced by the DEFC.
- (ii) Calculate the volume of ethanol used when 10 g of chromium metal was plated onto the steel object under room conditions, given that the density of ethanol is 0.789 g cm^{-3} .

[3]

- (c) Chromium is a *transition element*.

- (i) Explain what is meant by the term *transition element*.
- (ii) Chromium(III) chloride, CrCl_3 , reacts with water to form a violet hydrate $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$. This violet hydrate is isomeric to the dark green $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ and the pale green $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$

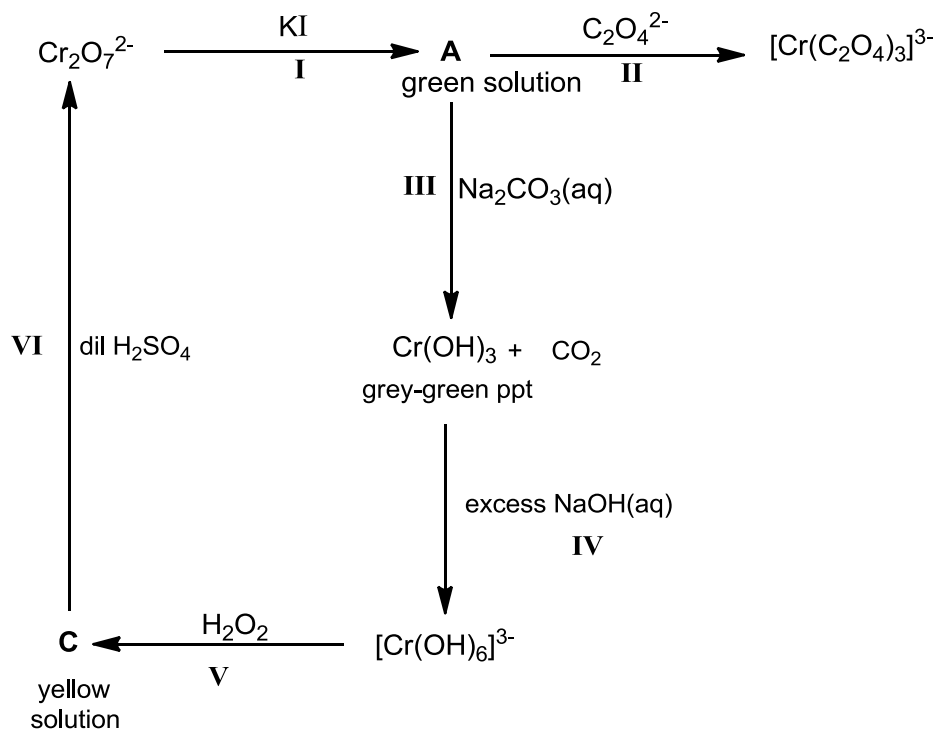
Based on the above information, give one property of transition elements or their compounds that is **not** shown by s-block elements.

- (iii) When 0.03 mol of aqueous silver nitrate was added to 0.01 mol of one of the chromium-containing compounds in (c)(ii), a white precipitate weighing 1.44 g was formed. Deduce the formula of the compound to which the silver nitrate was added.

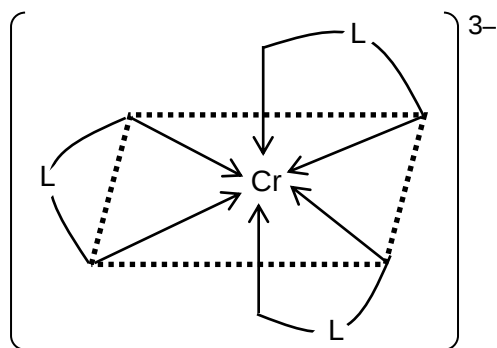
[3]

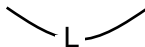
[Turn over]

- (d) The following reaction scheme shows the chemistry of some chromium-containing species in aqueous solution.



- (i) Identify the chromium-containing species present in **A**. Describe how this species accounts for the formation of carbon dioxide in Step **III**. Include any relevant equations in your answer.
- (ii) Give a balanced equation for step **VI**.
- (iii) Similar to some organic molecules, the complex $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ formed in step **II** can exist as a pair of optical isomers. One of the isomers is as shown below:



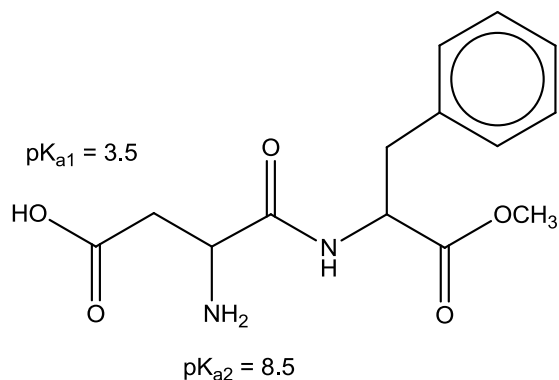
where  is used to represent the $\text{C}_2\text{O}_4^{2-}$ ion.

Draw the structure of the other optical isomer.

[5]

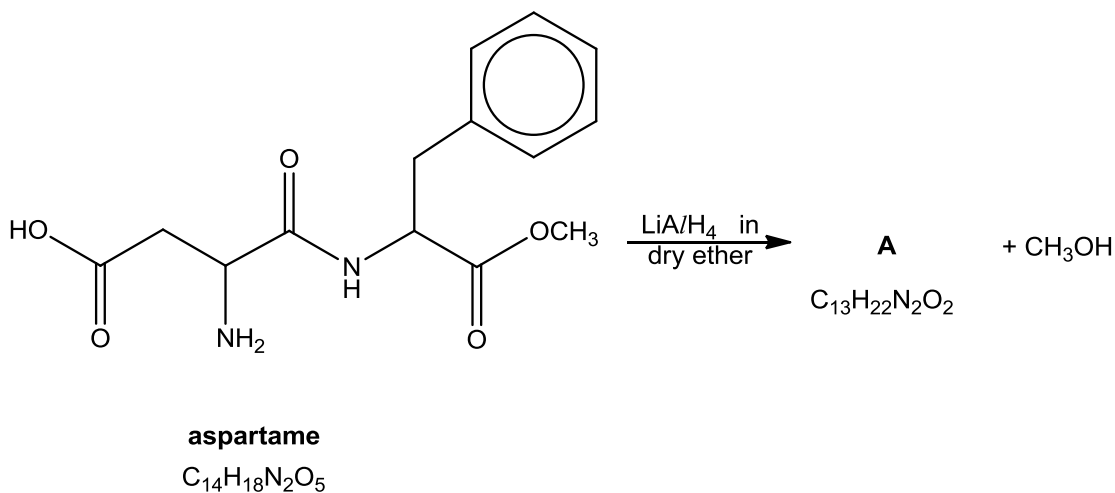
[Total: 20]

- 3 (a) Aspartame is made from the amino acids aspartic acid and phenylalanine. It is one of the most commonly used artificial sweeteners as it is about 200 times sweeter than sugar so lesser amount is required to achieve the same level of sweetness. The structure of aspartame is shown below:



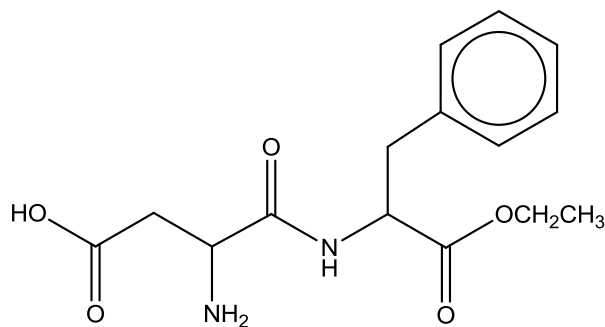
aspartame

- (i) Aspartame can exist as a zwitterion. Using the information given above, draw the structure of the zwitterion and suggest one possible pH value at which aspartame exists predominantly as a zwitterion.
- (ii) Draw the structural formulae of the organic products formed when aspartame reacts with
- I an excess of hot NaOH(aq)
 - II cold HCl(aq)
- (iii) Draw the structure of compound **A** in the following reaction.



[Turn over

- (iv) Describe a simple chemical test to distinguish between aspartame and compound **B**, clearly stating the reagents, conditions and observations for each compound.



Compound **B**

[9]

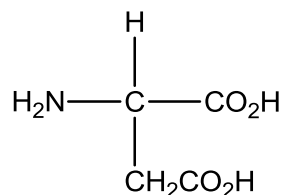
- (b) Aspartic acid and phenylalanine can be found in insulin, which consists of two polypeptide chains. Insulin is responsible for the regulation of blood glucose level in the human body. The following table shows some amino acid residues that can be found in insulin:

Amino acid	Abbreviation	R group
aspartic acid	asp	$-\text{CH}_2\text{CO}_2\text{H}$
phenylalanine	phe	$-\text{CH}_2-\text{C}_6\text{H}_5$
lysine	lys	$-(\text{CH}_2)_4\text{NH}_2$
cysteine	cys	$-\text{CH}_2\text{SH}$
glycine	gly	$-\text{H}$

- (i) When mercury ions, Hg^{2+} , are added to a sample of insulin, the protein is found to be denatured. State which aspects of the protein structure are affected during this denaturation.
- (ii) By considering all the interactions formed by the above amino acid residues, explain clearly how Hg^{2+} can interact with the insulin protein to bring about denaturation.
- (iii) Upon partial hydrolysis of insulin, the polypeptide chain is broken down into several fragments. One of the fragments formed is **cys-gly-asp**. Draw the displayed structure of this tripeptide.

[4]

(c)

**aspartic acid**

Aspartic acid, $\text{C}_4\text{H}_7\text{NO}_4$, is heated gently to produce a cyclic compound **C**, $\text{C}_4\text{H}_5\text{NO}_3$, and H_2O as by-product. **C** does not react with PCl_5 and does not give any orange precipitate with 2,4-dinitrophenylhydrazine. The addition of water to **C** re-forms aspartic acid. In a similar reaction, **C** reacts with methanol in the presence of an organic solvent to give compound **D**, $\text{C}_5\text{H}_9\text{NO}_4$. 2 mol of **D** reacts completely with 1 mol of Na_2CO_3 to produce effervescence of CO_2 .

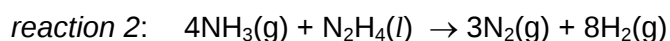
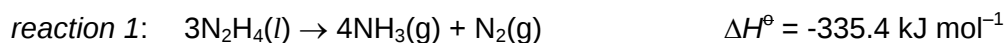
- (i) Deduce structures of **C** and **D**. Give your reasoning.
- (ii) Write a balanced equation for the reaction of **D** with sodium carbonate.

[7]

[Total: 20]**[Turn over]**

- 4 Hydrazine is a hydride of nitrogen with the formula N_2H_4 . It is a colourless, flammable liquid with an ammonia-like odour. It behaves as a weak monoacidic base, forming salts with common mineral acids.

- (a) Draw the structure of hydrazine molecule to show the shape of the molecule and indicate the bond angle. [2]
- (b) Write a balanced equation for the reaction between hydrazine and sulfuric acid. [1]
- (c) One of the industrial uses of hydrazine is as a low-power monopropellant in spacecraft. In all hydrazine monopropellant engines, the hydrazine is passed over a catalyst which causes it to decompose into ammonia, nitrogen and hydrogen according to the following reactions:



Given that ΔH°_f of $\text{NH}_3(g) = -45.9 \text{ kJ mol}^{-1}$, calculate

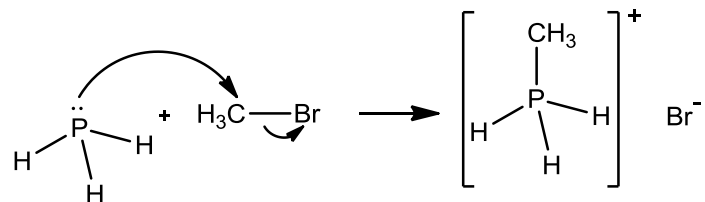
- (i) ΔH°_f of $\text{N}_2\text{H}_4(l)$
- (ii) ΔH° for reaction 2 [3]
- (d) By considering the entropy and enthalpy changes in reaction 1 and reaction 2, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude.
- Hence predict which reaction will be more spontaneous. Give your reasoning. [3]
- (e) Diphosphine, P_2H_4 , is the phosphorus analogue of hydrazine. Unlike hydrazine, diphosphine is not basic. It disproportionates into phosphine, PH_3 , and phosphorus, P_4 , in UV light. Both phosphine and diphosphine have lower boiling points than their nitrogen analogues.

Compound	b.p./ °C	compound	b.p./ °C
NH_3	-33	PH_3	-87
N_2H_4	113	P_2H_4	(decompose at 30)

- (i) Suggest, with a reason, the bond angle in diphosphine.
- (ii) Estimate what the boiling point of diphosphine would be if it did not decompose. Explain your answer.

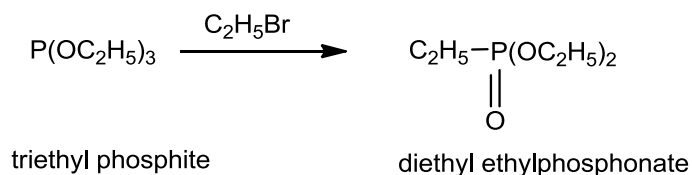
[3]

- (f) In a similar reaction to that of ammonia, phosphine can react with bromoethane as follows.



Use this information to help explain the following reaction.

When heated with a catalytic quantity of bromoethane, triethyl phosphite isomerises to diethyl ethylphosphonate:



The isomerisation of triethylphosphite in the presence of bromoethane is thought to proceed in two steps.

- The first step involves the formation of an intermediate upon reaction with bromoethane.
- The second step involves the cleavage of a C–O bond in the intermediate to form the final product, diethylethylphosphonate. Bromoethane is also regenerated.

Use the information given above to draw out the full mechanism for the isomerisation of triethylphosphite. You are advised to use the structural formulae for all species so that it is clear which bonds are broken and which are formed. Include all charges and use curly arrows to show the movement of electron pairs.

[3]

- (g) Bromoethane is formed when ethane and bromine are irradiated with light at room temperature.

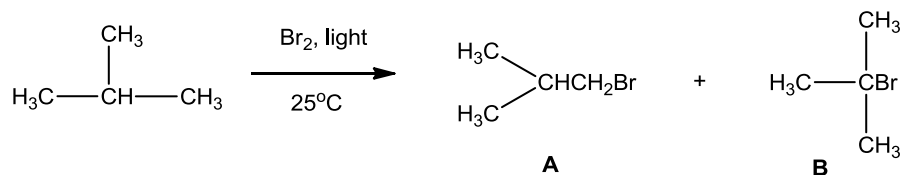
Outline the mechanism of this reaction.

[3]

[Turn over

- (h) The reaction described in (g) is seldom used for synthesis of halogenoalkanes as it results in the formation of several isomeric products.

It was observed that methylpropane reacts with bromine to form a mixture of two monobrominated alkanes, **A** and **B**, as shown below.



- (i) State the expected ratio of products **A** and **B** in the mixture, assuming equal rate of substitution of H atom.

The ratio of the isomeric products is more accurately determined if the relative rates of substitution of H atoms are taken into account. The types of hydrogen atoms in alkanes, together with their relative rates of substitution, are shown in the following table.

Types of H atoms	Structure	Relative rate of substitution
primary	$ \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{H} \end{array} $	1
secondary	$ \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{R}' \end{array} $	4
tertiary	$ \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{R}'' \\ \\ \text{R}' \end{array} $	6

- (ii) By taking into account the relative rates of substitution of H atoms given above, show that products **A** and **B** are formed in the ratio of 3:2.

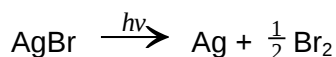
[2]

[Total: 20]

- 5 (a) Explain the following observation and give balanced equations, where appropriate, to support your answers.

When chlorine is bubbled through cold sodium hydroxide and acidified silver nitrate solution is added, only half of the chlorine which has dissolved is precipitated as silver chloride. When the sodium hydroxide is hot, up to five-sixth of the chlorine can be precipitated. [3]

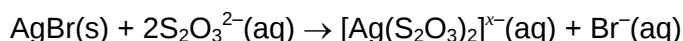
- (b) In film photography, light strikes an emulsion containing silver bromide grains. The grains which are exposed turn partially into silver.



A **developer** is then added to turn all the silver bromide in the affected grains to silver.

- (i) Name the type of reaction taking place in the action of light on AgBr.

The remaining silver bromide in the unaffected grains is then removed by a **fixer**, containing thiosulfate ions, which is a monodentate ligand.



- (ii) State the value of x in $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{x-}(\text{aq})$ and suggest the shape of this ion.
- (iii) A student suggests adding concentrated sulfuric acid to the photographic emulsion to test for the presence of bromide ions. Describe and explain, with the aid of balanced equations, what the student would observe as a result of a successful test.
- (iv) If a photographic film is over-exposed, a **reducer** is used to diminish the intensity of the image. One such reducer is 'Farmer's reducer' which contains aqueous hexacyanoferrate(III), $[\text{Fe}(\text{CN})_6]^{3-}$. This dissolves some of the silver metal and hexacyanoferrate(II) ions, $[\text{Fe}(\text{CN})_6]^{4-}$, are formed.

Write an **ionic** equation to represent the action of 'Farmer's reducer'. Hence explain why, to a chemist, 'reducer' is a wrong word in view of what happens to the silver.

[7]

- (c) An organic compound **A**, $\text{C}_9\text{H}_{11}\text{Br}$, on treatment with hot aqueous potassium hydroxide gave compound **B**, $\text{C}_9\text{H}_{12}\text{O}$.

B responded to oxidation in three different ways. With acidified potassium dichromate(VI), it yielded **C**, $\text{C}_9\text{H}_{10}\text{O}$. With sodium hydroxide and iodine, it yielded **D**, $\text{C}_8\text{H}_7\text{O}_2\text{Na}$, and a yellow precipitate. With hot, acidic potassium manganate(VII), it yielded **E**, $\text{C}_7\text{H}_6\text{O}_2$.

- (i) Identify compounds **A** to **E**.
- (ii) Suggest a possible mechanism for the formation of compound **B** from compound **A**, include all charges and curly arrows to show movement of electrons.

[8]

[Turn over

- (d) Bromoethane and bromomethane, present in 1:1 molar ratio, can both react with ethylamine to form three different tertiary amines.

Suggest the structures of these three tertiary amines and hence state the ratio in which they are formed. [2]

[Total: 20]