

1. (a) When gaseous ammonia and gaseous hydrogen chloride are mixed, a reaction occurs to form solid ammonium chloride.

(i) Draw dot-and-cross diagrams to show the bonding present in each of the three compounds.

Ammonia Hydrogen chloride Ammonium chloride

(3)

(ii) Explain why this reaction is classified as an acid-base reaction.

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(2)

(b) (i) Draw diagrams to show the shapes of the ammonia molecule and the ammonium ion.

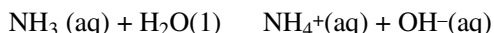
(2)

(ii) In what way is the H—N—H bond angle in ammonia different from that in the ammonium ion? Explain the difference in the values.

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(2)

(c) Ammonia is very soluble in water. The solution contains the following equilibrium:



Ammonia and ammonium compounds may be introduced into rivers from sewage treatment plants. The Environment Agency monitors levels which, depending on river conditions, are allowed to be between 5 and 10 mg of nitrogen (measured as nitrogen atoms) per dm³ of water.

(i) Calculate the number of moles of ammonia that, on dissolving in water, would give a nitrogen atom content of 10 mg dm⁻³.

(2)

(ii) Aqueous ammonia is much more toxic in a river than the aqueous ammonium ion. The proportion of the two species present depends on the pH of the water. State, with a reason, whether a high or a low pH favours a small concentration of aqueous ammonia.

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(2)

- (iii) River samples could be analysed for both NH_3 and NH_4^+ by converting NH_4^+ to ammonia and distilling the ammonia into a known excess of hydrochloric acid; the residual acid could then be estimated by titration.

What would you do to convert all the NH_4^+ ion into ammonia?

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(2)
(Total 15 marks)

2. Nuclear medicine makes wide use of a metastable form of an isotope of technetium, $^{99m}_{43}\text{Tc}$.

$^{99m}_{43}\text{Tc}$ is made by the decay of $^{99}_{42}\text{Mo}$.

$^{99m}_{43}\text{Tc}$ has a half-life of 6 hours, decaying by gamma emission to $^{99}_{43}\text{Tc}$.

$^{99m}_{43}\text{Tc}$ is injected into the blood stream and is used to monitor blood flow, for example through the heart or the kidney.

- (a) $^{99m}_{43}\text{Tc}$ is obtained from a generator which contains $^{99}_{42}\text{Mo}$. This can be made by neutron bombardment of $^{98}_{42}\text{Mo}$ in a nuclear reactor.

- (i) Write an equation representing the conversion of $^{98}_{42}\text{Mo} \rightarrow ^{99m}_{43}\text{Mo}$ by neutron bombardment.

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(1)

- (ii) $^{99}_{42}\text{Mo}$ decays to $^{99m}_{43}\text{Tc}$. Write an equation representing this decay.

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(1)

- (iii) $^{99m}_{43}\text{Tc}$ decays by emission of a gamma ray only. Suggest why this is the most advantageous type of decay in this application given that the activity is monitored externally.

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(1)

- (iv) Explain why hospitals that make use of $^{99m}_{43}\text{Tc}$ generate this nuclide on the premises immediately before use.

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(1)

- (b) $^{99m}_{43}\text{Tc}$ is injected as the compound NaTcO_4 .

Technetium and manganese are in the same group of the Periodic Table. E^\ominus for the reduction of TcO_4^- to Tc^{2+} is +0.85 V; that for MnO_4^- to Mn^{2+} is +1.52 V.

- (i) What is the oxidation state of technetium in NaTcO_4 ?

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(1)

- (ii) An acidified solution of NaTcO_4 might be expected to react with iodide ions to give iodine, the technetium being reduced to Tc^{2+} . Derive an equation to represent this reaction.

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(3)

- (iii) Which of the two oxoanions TcO_4^- and MnO_4^- is the stronger oxidising agent? Give a reason for your answer.

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(2)

- (iv) Technetium in the ion TcO_4^- has no unshared electrons. Suggest the shape of TcO_4^- ions, giving your reasons.

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(2)

- (c) Solutions of TcO_4^- and Tc^{2+} ions are both colourless. Describe in *outline* how the concentration of TcO_4^- ions in solution might be determined based on its reaction with iodide ions.

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(3)

(Total 15 marks)

3. This question deals with various aspects of the chemistry of Group 2 of the Periodic Table.

- (a) The cement, glassmaking and iron–smelting industries make use of the reaction



Limestone is heated above 1000 °C in a kiln through which air is blown. Find the enthalpy change for the reaction, using the following data:

	$\text{CaCO}_3(\text{s})$	$\text{CaO}(\text{s})$	$\text{CO}_2(\text{g})$
$\Delta H_f / \text{kJ mol}^{-1}$	–1207	–635	–394

(2)

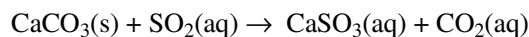
- (b) If the reaction is performed in a closed container, an equilibrium mixture is formed:



Write the expression for K_p for the equilibrium. State and explain the effect of an increase in temperature on the position of the equilibrium.

(4)

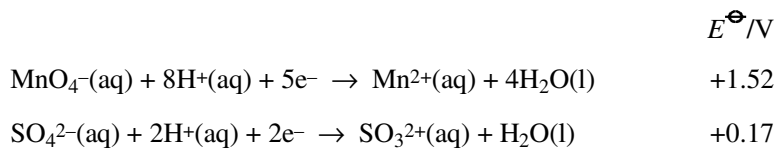
- (c) Sulphur dioxide emissions from the burning of fossil fuels are a concern because of the formation of acid rain. The flue gases from power stations have their sulphur dioxide content reduced by passing them through an aqueous suspension of finely crushed limestone. The reaction occurring is



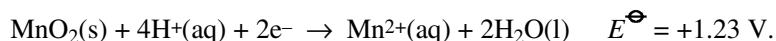
The calcium sulphite formed is then oxidised to sparingly soluble calcium sulphate, which is used in the building industry. On the basis of the reaction above, comment on the relative acid strengths of sulphurous acid, H_2SO_3 , and of carbonic acid, H_2CO_3 giving reasons for your answer.

(3)

- (d) The calcium sulphite produced could be oxidised in several ways. Use the following reduction potentials in answering this question.



- (i) Derive the equation for the oxidation of sulphite ions by manganate(VII) ions, and state why the reaction is feasible. (3)
- (ii) Calcium sulphite is in practice oxidised by oxygen in the air. Suggest why this reaction is used in a power station rather than oxidation with manganate(VII) ions. (2)
- (e) The concentration of sulphur dioxide in flue gases could be determined by titration of an acidified sample of calcium sulphite with potassium manganate(VII) solution.
- A suspension of calcium sulphite obtained from treatment of 100 dm³ of flue gases was acidified and titrated with 0.020 mol dm⁻³ potassium manganate(VII) solution; 41.5 cm³ was required. Calculate the percentage of SO₂ by volume in the flue gas. The molar volume of a gas at the temperature and pressure of the experiment is 24 dm³. (4)
- (f) One difference between the chemistries of calcium and manganese is that manganese can undergo disproportionation reactions whereas calcium cannot.
- (i) Explain in terms of the electronic structures of calcium and of manganese why disproportionation is a feature of the chemistry of many of the elements of the d-block but of none of those in the s-block. (4)
- (ii) Derive the half equation for the reduction of manganate(VII) ions in acidic solution to MnO₂. Given that E^{\ominus} for this reduction is +1.67 V, show that manganese(IV) oxide will not disproportionate to MnO₄⁻ and Mn²⁺ in acid solution.

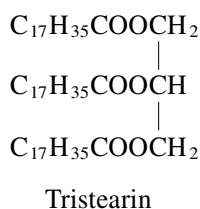


(3)
(Total 25 marks)

4. Sodium hydroxide is a very important substance. Potassium hydroxide is also important but it is produced in smaller quantities and is costlier. For some purposes, potassium hydroxide is necessary; it will take part in substitution, elimination, hydrolysis, acid-base and redox processes.

- (a) Suggest how potassium hydroxide is manufactured. A detailed account of the manufacturing plant is **not** required. (3)

- (b) (i) Potassium hydroxide can be used in substitution reactions with halogenoalkanes. 2-bromo-2-methylpropane is known to react with hydroxide ions via an S_N1 mechanism. Give the rate equation for the reaction, and justify it by giving the mechanism and explaining the relationship between the rate equation and the mechanism. What is the role of the hydroxide ions in this reaction? (6)
- (ii) The halogenoalkane could contain chlorine, bromine, or iodine. Explain what effect, if any, the nature of the halogen has on the rate of the reaction. (2)
- (c) Potassium hydroxide is used for elimination reactions of halogenoalkanes because it is more soluble in the solvent ethanol than sodium hydroxide is. 2-Bromobutane gives two organic products when reacted with potassium hydroxide in ethanol, one of these having two stereoisomers. Give structural formulae for all three product molecules and explain the existence of the stereoisomeric forms in terms of the orbitals involved. What is the role of the hydroxide ions in this reaction? (6)
- (d) Tristearin is an ester found in animal fats, especially beef tallow, which can be hydrolysed by potassium hydroxide solution. Write an equation to represent the reaction, and state the importance of the potassium-containing product. (4)



- (e) Potassium hydroxide solution reacts with chlorine at room temperature. Write the ionic equation for this reaction and explain the nature of the reaction. (4)
- (Total 25 marks)**

5. Organometallic compounds are very important in both industrial and laboratory chemistry. Lead and magnesium are amongst the most significant of the metals that are used.

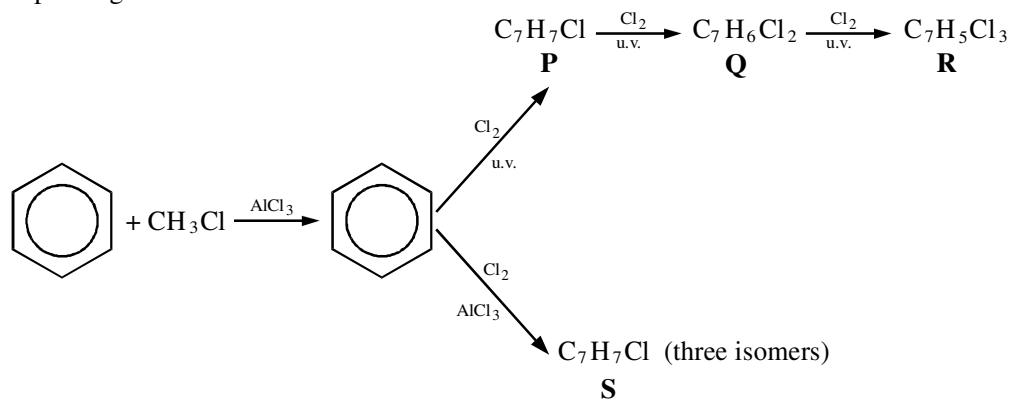
- (a) The most significant organolead compound is lead tetraethyl, $(\text{C}_2\text{H}_5)_4\text{Pb}$. It is a liquid, and is used to prevent pre-ignition in petrol engines.
- (i) Explain what pre-ignition is, how it arises, and why it is a problem. (3)
- (ii) State and explain the nature of the bonding in lead tetraethyl. (2)
- (iii) Lead tetraethyl is made by reaction between bromoethane and a lead/sodium alloy. Write an equation to represent this reaction, and suggest why such an alloy is used rather than lead metal alone. (3)

- (iv) Suggest why lead tetraethyl is a much more toxic material than, say, lead(II) chloride. (2)
- (v) Explain the nature of the substitute fuel which has enabled leaded fuel to be gradually phased out. (1)
- (b) Pyrophoric lead is a variety of very finely powdered lead.
- (i) Pyrophoric lead is spontaneously flammable in air. Suggest why this is, and write an equation to represent the reaction which occurs. (2)
- (ii) If ethanoyl chloride is reacted with pyrophoric lead in an inert solvent, a compound **X** is obtained together with another inorganic lead compound.
- X** contains, by mass, 55.8% carbon and 6.98% hydrogen, the remainder being oxygen. The relative molecular mass of the organic compound is 86. Deduce the molecular formula of **X** and draw its structural formula. (3)
- (c) The 1912 Nobel Prize for Chemistry was awarded in part to Victor Grignard for the development of the reagent which bears his name. The Grignard reagent can be used to prepare alcohols and carboxylic acids.
- (i) Use a Grignard reagent of your choice to illustrate, with equations, each of these synthetic pathways. (6)
- (ii) By considering the polarity of the bonds in the Grignard reagent, state with reasons the mechanistic nature of the reactions considered in (i). (3)
- (Total 25 marks)**
6. The reactions of chlorine are important in both inorganic and organic chemistry, the chemistries of the resulting compounds also being linked.
- (a) Chlorine reacts with aluminium in a similar fashion to its reaction with iron.
- (i) Sketch an apparatus which you could use to make aluminium chloride from aluminium and dry chlorine, indicating one safety precaution specific to this reaction. (3)
- (ii) Explain in terms of bonding and structure why aluminium chloride sublimes and has a relative molecular mass of 267. (3)
- (iii) Show by means of ionic equations why dissolving aluminium chloride in water produces an acidic solution. By further consideration of the equilibria present explain why the addition of aqueous sodium hydroxide solution results initially in a white precipitate, which dissolves upon further addition of sodium hydroxide. (6)

- (iv) Aluminium was first produced by the reaction of sodium with aluminium chloride. Write an equation representing the reaction and explain why, although it is apparently simpler than the electrolysis of purified bauxite it is not more economical.

(2)

- (b) Aluminium chloride is used as a catalyst in the reaction of benzene with chloromethane. The methylbenzene produced can then itself react with chlorine in one of two ways, depending on the conditions:



- (i) Suggest a mechanism for the reaction of chloromethane with benzene.

(4)

- (ii) Suggest a structural formula for any one of the three isomers of compound **S** produced by the reaction shown.

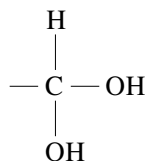
(1)

- (c) Compound **Q** has both chlorine atoms attached to the same carbon atom.

- (i) Draw the structure of **Q**.

(1)

- (ii) **Q** will react with sodium hydroxide solution under suitable conditions in a nucleophilic substitution reaction, both chlorine atoms being substituted. It might therefore be expected that the product will contain the structure.



In practice, this reacts further to give an aldehyde and water. Use the bond enthalpies given to suggest why this is so.

	C—O	C—H	C=O	H—O
Bond enthalpy/kJ mol ⁻¹	358	413	736	464

(4)

- (iii) Suggest the structure of the product when **R** is reacted with sodium hydroxide solution.

(1)

(Total 25 marks)