1. This question is about shapes of molecules

Draw the three-dimensional shapes of the following molecules and mark any non-bonding lone pairs and bond angles;

a) NH_3

b) H_2O

c) BF_3

d) NO_2

e) ClO_2^-

(5)

2. This question is about lattice enthalpies

Standard enthalpy of formation CaO	-635 kJ mol^{-1}
Standard enthalpy of formation FeO	-278 kJ mol^{-1}
Standard enthalpy of atomisation Ca	+178 kJ mol^{-1}
Standard enthalpy of atomisation Fe	+416 kJ mol^{-1}
Standard molar 1st ionisation enthalpy Ca	+590 kJ mol^{-1}
Standard molar 2nd ionisation enthalpy Ca	+1145 kJ mol^{-1}
Standard molar 1st ionisation enthalpy Fe	+759 kJ mol^{-1}
Standard molar 2nd ionisation enthalpy Fe	+1561 kJ mol^{-1}
Standard enthalpy of atomisation (O) of O atoms	+249 kJ mol^{-1}
Combined standard molar 1st and 2nd electron affinity (O) of O atoms	+657 kJ mol^{-1}

(i) Using the data, calculate the lattice enthalpies/kJ mol^{-1} for iron(II) oxide and calcium oxide. (2)

(ii) Which metal oxide has the stronger lattice? (1)

(iii) Calculate the enthalpy change for the following reaction

$FeO_{(s)} + Ca_{(s)} \rightarrow CaO_{(s)} + Fe_{(s)}$ (1)

(iv) Explain whether it would be viable to use this reaction on an industrial scale? (1)

Iron(II) oxide can be readily oxidised to iron(III) oxide by warming in oxygen.
Calcium(III) oxide has never been formed.

(v) Explain why the two metal oxides, iron(II) oxide and calcium (II) oxide, differ. (1)

3. This question is about superconductors

Yttrium oxide, barium carbonate and copper oxide react in a solid state reaction at high temperature (900 °C) to form the superconductor **A** which contains 13.4%Y, 41.2%Ba and 28.6%Cu.

i) Assuming that the only element unaccounted for in **A** is oxygen, determine the empirical formula of **A**. (2)

ii) Given that the oxidation state of yttrium is +3 and barium is +2, calculate the average oxidation state of copper. (1)

iii) Reduction of A on a thermogravimetric analyser at 200 °C in hydrogen reduces all the copper 3+ in the material to copper 2+ and produces compound **B**. All the other elements remain in the same oxidation state. Given that the starting mass was 84.2 mg, what would be the mass of the remaining compound **B** after reduction? (Hint: consider the change in oxygen content for the two different compounds.) (2)

You will need to refer to your Periodic table for this question. (A_r yttrium = 88.9)

4. This question is about Iodine Number

This old method for determining the degree of unsaturation in a fat or oil is still used by most students following a food science course. You are asked to process the following experimental results.

Iodine monochloride is used to determine the degree of unsaturation in oils. The iodine monochloride adds rapidly to the carbon-carbon double bonds present. In an experiment, 0.127g of an unsaturated oil was treated with 25.00 cm^3 of 0.100 mol dm^{-3} iodine monochloride solution. The mixture was kept in the dark until the reaction was complete. The unreacted iodine monochloride was then treated with an excess of aqueous potassium iodide, forming iodine. The liberated iodine was found to react with 40.00 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate.

(i) Suggest why it is necessary to keep the mixture of oil and iodine monochloride in the dark. (1)

(ii) Write an equation for the reaction between iodine monochloride and potassium iodide. (1)

(iii) Calculate the number of moles of sodium thiosulfate which were used in the titration. (1)

(iv) Calculate the number of moles of iodine liberated, given that iodine reacts with sodium thiosulfate according to the equation:

$$I_2(aq) + 2Na_2S_2O_3(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$$

Hence calculate the number of moles of unreacted iodine monochloride. (1)

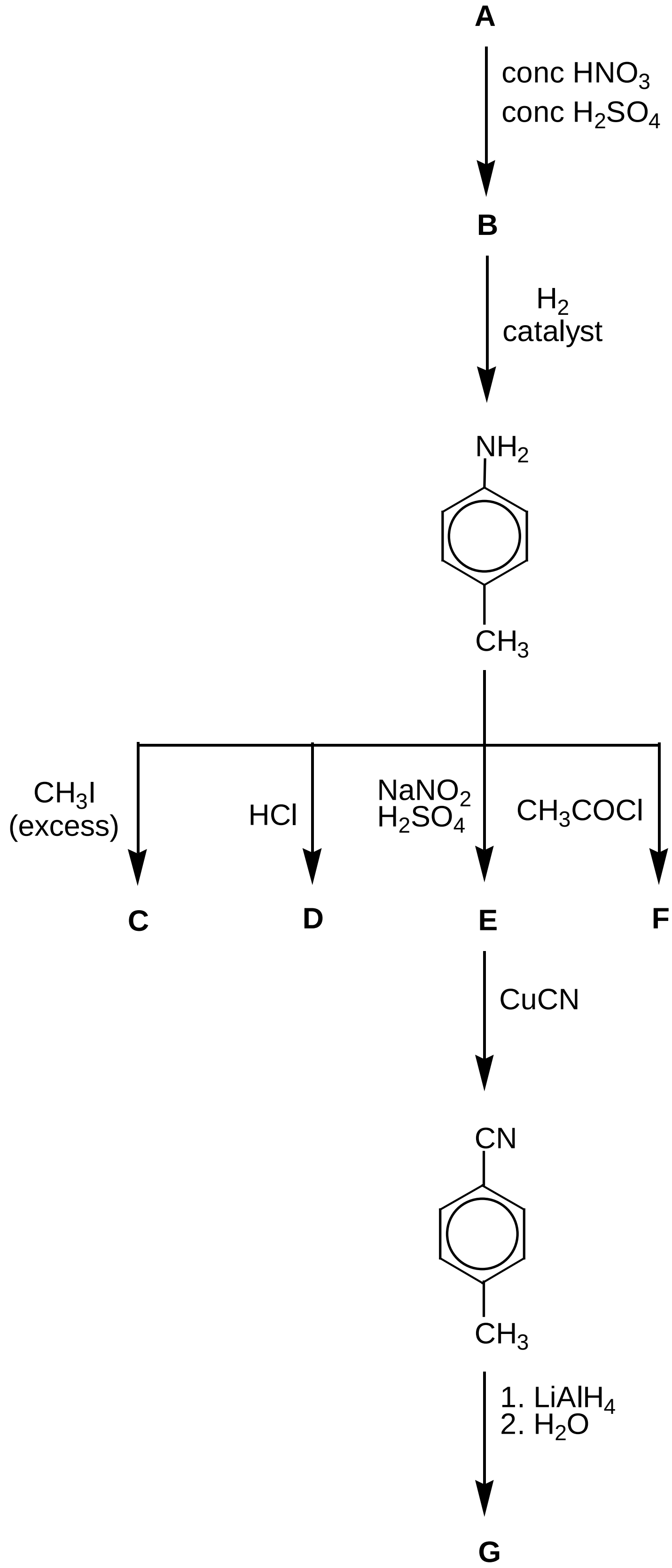
(v) Calculate the number of moles of iodine monochloride that reacted with the unsaturated oil. (1)

Direct addition of iodine to an unsaturated oil is slower than the addition of iodine monochloride. However, unsaturation is quoted as the **iodine number**. The iodine number is the number of grammes of iodine that in theory can be added to 100 g of oil.

(vi) Calculate the **iodine number** of this oil, given that one mole of iodine monochloride is equivalent to one mole of iodine molecules. (1)

5. This question is about organic compounds

Draw the structures for compounds **A-G** in the following synthesis:



(6)

6. This question is about metal nitrates

On heating, Group I metal nitrates such as sodium nitrate(V) decompose giving the metal nitrate(III) and oxygen, while Group 2 metal nitrates, eg magnesium nitrate(V), decompose giving the oxide, nitrogen dioxide and oxygen.

a) Write balanced equations for these two reactions. (2)

15.35g of a mixture of sodium nitrate(V) and magnesium nitrate(V) was heated in a fume cupboard until no more gases were evolved. The water soluble part of the residue was used to prepare 1.00 dm^3 of solution. 10.00 cm^3 of this solution was reacted with 20.00 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) solution, acidified with dilute sulfuric acid. The nitrate(III) half equation is:-

$$NO_2^-{}_{(aq)} + H_2O_{(l)} \rightarrow NO_3^-{}_{(aq)} + 2H^+_{(aq)} + 2e^-$$

b) Write an overall equation for the reaction between nitrate(III) ions and permanganate(VII) ions. (1)

The excess potassium manganate(VII) required 10.00 cm^3 of 0.0500 mol dm^{-3} ethanedioic acid solution for complete reaction. The ethanedioate half equation is:-

$$(COO)_2^{2-}{}_{(aq)} \rightarrow 2\,CO_{2(g)} + 2e^-$$

c) Write an overall equation for the reaction between ethanedioate ions and manganate(VII) ions. (1)

d) Calculate the mass of each nitrate in the mixture. (2)

e) What was the mole ratio of oxygen to nitrogen dioxide in the gases given off on heating? (1)

7. This question is about the identification of unknown organic compounds

Tollens' reagent is used to test for aldehydes – when an aldehyde is warmed with Tollens' reagent, metallic silver is formed.
Chemical explanation: aldehydes are oxidised by Ag^+ in alkaline solution. The Ag^+ is reduced to metallic silver, which can be seen on the inside of a test tube.
Ketones give no reaction to this test.

Compound **A** (C_5H_9OCl) is an aliphatic organic compound which gives a positive test with 2,4-dinitrophenylhydrazine (DNP), but does **not** give a silver mirror with Tollens' reagent (ammoniacal silver nitrate). It does **not** decolourise bromine water. It does **not** have any stereoisomers.

A is reacted with sodium borohydride to produce **B** ($C_5H_{11}OCl$).

B is then reacted with conc sulfuric acid to produce **C, D** and **E** (C_5H_9Cl). **C** does not have any stereoisomers, but **D** and **E** are **geometric stereoisomers** of one another.

B is then warmed with potassium cyanide in ethanol to produce **F** ($C_6H_{11}ON$).

F is then warmed with dilute sulfuric acid to produce **G** ($C_6H_{12}O_3$). **G**, on further heating with concentrated sulfuric acid produced a sweet smelling liquid **H** ($C_6H_{10}O_2$).

Give displayed structural formulae for compounds A-H.

(8)

8. This is a question about rates of chemical reactions

Bromate(V) ions react with bromide ions in the presence of acid to produce bromine.

(a) Write an ionic equation for this reaction. (1)

A number of experiments were set up with different volumes of bromate(V), bromide and acid, and the initial rate was measured in each case.

Some typical results are shown below using a strong monoprotic acid HX.

Experiment	Volume of 1.00 mol dm^{-3} bromate(V) / cm^3	Volume of 1.00 mol dm^{-3} bromide / cm^3	Volume of 1.00 mol dm^{-3} HX / cm^3	Volume of H_2O / cm^3	Initial rate / mol dm^{-3} s^{-1}
1	5.0	25.0	30.0	40.0	1.68×10^{-5}
2	5.0	25.0	60.0	10.0	6.70×10^{-5}
3	10.0	25.0	30.0	35.0	3.37×10^{-5}
4	15.0	50.0	30.0	5.0	1.00×10^{-4}

(b) Calculate the partial orders with respect to

(i) bromate(V) ions,

(ii) bromide ions,

(iii) hydrogen ions. (2)

(c) Calculate the value of the reaction rate constant, k, for this reaction, including its units.

(2)

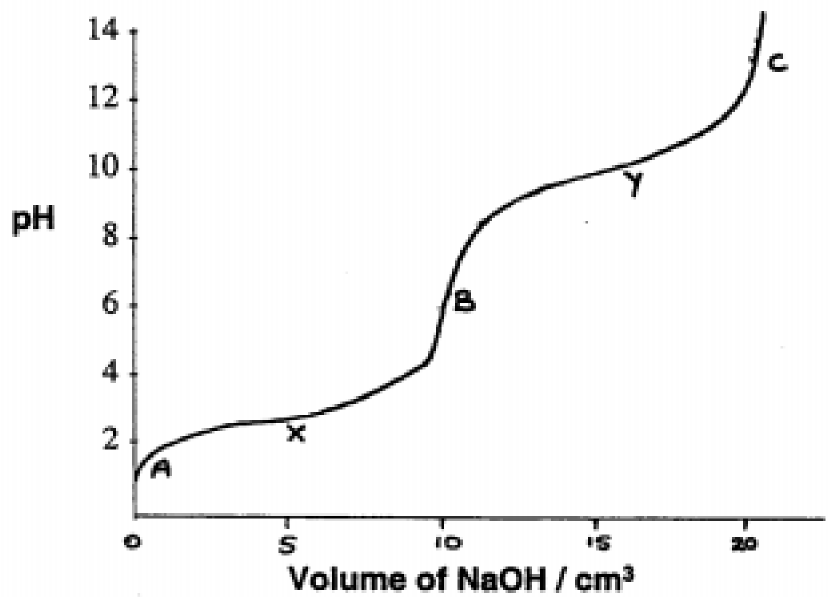
(d) Calculate the new initial rate if 0.100 mol dm^{-3} ethanoic acid (which has pK_a 4.76) had been used instead of the 1.00 mol dm^{-3} HX in experiment 1. (3)

9. This question is about the acid-base properties of glycine

Amino acids show both acidic and basic properties. In acidic solution, glycine, NH_2CH_2COOH, is completely protonated and exists as the conjugate acid.

$$H_3N^+CH_2CO_2^- \quad + \quad H^+ \rightleftharpoons H_3N^+CH_2CO_2H$$

The ion, $H_3N^+CH_2CO_2H$, has pK_a values of 2.35 and 9.78. The titration curve for glycine hydrochloride is shown below. The salt behaves as a dibasic acid:



a) Identify the major species present during the titration at each of the points A, B and C on the titration curve. (2)

b) Indicate which pK_a refers to which acidic hydrogen in the ion:

$$H_3N^+CH_2CO_2H \qquad (1)$$

c) Explain how you know that the pH at point X on the titration curve is 2.35. (1)

d) (i) Give the balanced equations for the dissociations corresponding to the pK_a values of 2.35 (pK_a1) and 9.78 (pK_a2). (1)

(ii) State the equilibrium expressions for K_a1 and K_a2. (1)

e) Calculate the ratio $[H_3N^+CH_2CO_2^-] / [H_3N^+CH_2CO_2H]$ at pH 4. (2)