1 During strenuous exercise, pyruvic acid, $CH_3COCOOH$, is converted to lactic acid, $CH_3CH(OH)COOH$, which builds up in our muscles due to limited oxygen availability.

(a) Such anaerobic respiration is catalysed by the enzyme lactate dehydrogenase, with concomitant conversion of NADH to NAD^+. NADH plays a key role in the production of energy through redox reactions. NADH and NAD^+ are cofactors, substances that act with and are essential to the activity of an enzyme.

(i) Write a balanced equation for anaerobic respiration. Using the data given in the table below, calculate the value of E^θ_{cell} for this reaction.

Electrode reaction	E^θ /V
$2e^- + H^+ + NAD^+ \rightleftharpoons NADH$	–0.32
$2e^- + 2H^+ + CH_3COCOOH \rightleftharpoons CH_3CH(OH)COOH$	+0.89

C

(ii) It is not possible to use E^θ values reliably to decide whether a chemical reaction will occur. Suggest a reason for this.

(iii) The activity of lactate dehydrogenase hinges on the active site Fe^{2+} contained in a heme group which can be oxidized to Fe^{3+}. Suggest a mechanism for the catalysis of anaerobic respiration by lactate dehydrogenase. Support your answers with relevant E^θ values given above and from the *Data Booklet*.
You may represent the reduced and oxidised forms of the enzyme as LDH–Fe^{2+} and LDH–Fe^{3+}.

(iv) After exercising, we do not stop panting immediately because we need to breathe in additional oxygen so that lactic acid can be reconverted back to pyruvic acid. Both breathing and heart rates increase until the excess lactic acid level normalizes.
Write a balanced equation for the conversion of lactic acid back to pyruvic acid. Calculate the value of E^θ_{cell} for this reaction, with the help of the *Data Booklet*.

[8]

(b) (i) Using bond energy data obtained from the *Data Booklet*, calculate the enthalpy change of reaction, ΔH, for the conversion of pyruvic acid into lactic acid.

$$CH_3COCOOH(l) + H_2(g) \rightarrow CH_3CH(OH)COOH(l)$$

(ii) Given that the actual enthalpy change of this reaction is -110 kJ mol^{-1}, suggest a reason for the discrepancy between your calculated ΔH value in **(b)(i)** and the actual ΔH value.

(iii) Acid-base neutralisation takes place when pyruvic acid reacts with barium hydroxide.

Rank barium hydroxide, pyruvic acid, and its salt in increasing melting point. Explain your answer.

[6]

(c) Muscles work by contracting and relaxing. Both processes are triggered by an electrical impulse. Calcium causes muscles to contract while magnesium relaxes them. **Y** is another element in Group II.

Element	Mg	Ca	**Y**
$E^{\ominus}$ /V	–2.37	–2.87	–2.95
Decomposition temperature of carbonates /K	470	1170	1770

(i) Predict the relative melting points of magnesium and calcium.

(ii) With the help of the *Data Booklet*, calculate the enthalpy change, ΔH when Mg and Ca ionise to Mg^{2+} and Ca^{2+} respectively.

(iii) How does the trend in ΔH calculated in **(c)(ii)** relate to the $E^{\ominus}$ values?
Hence, predict the relative reducing powers of magnesium and calcium.

(iv) Account for the difference between the decomposition temperature of $CaCO_3$ and **Y**CO_3.

[6]

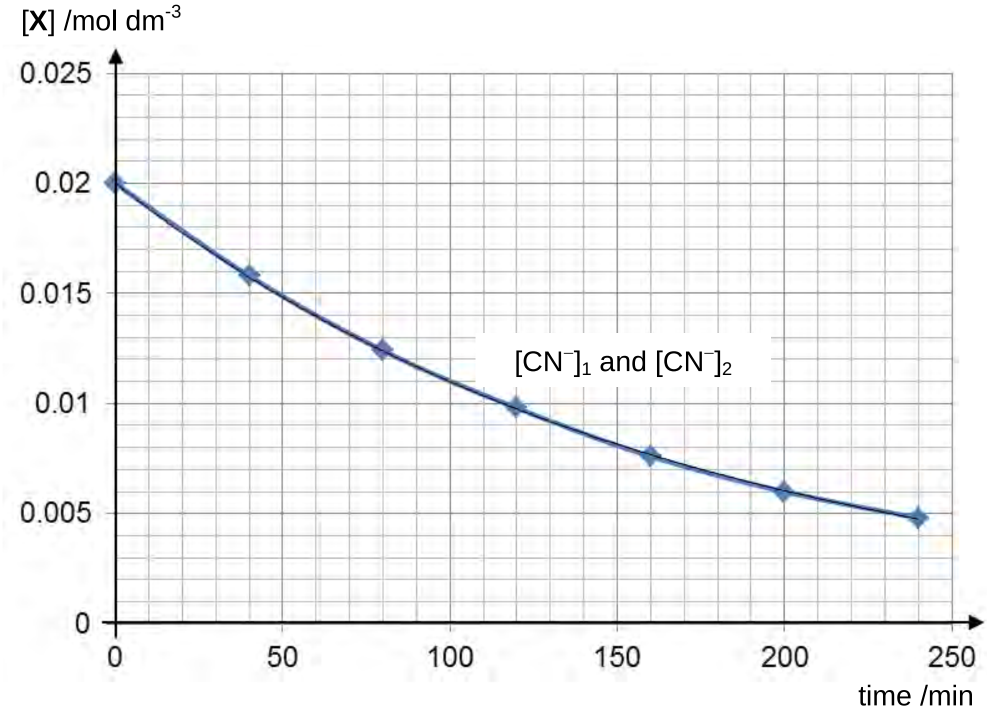
[Total: 20]

2 **(a)** Compound **X**, $CH_3CH{=}CHCHClCH_3$, reacts with alcoholic KCN according to the following equation:

$$CH_3CH{=}CHCHClCH_3 + CN^- \rightarrow CH_3CH{=}CHCH(CN)CH_3 + Cl^-$$

To investigate the above reaction, two separate experiments were performed using different initial concentrations of CN^-. In each experiment, the concentration of **X** in the reaction mixture was determined at different times as the reaction progresses. The same graph was obtained in both experiments, as shown below:

The following results were obtained:



(i) Explain why the reaction requires an alcoholic instead of an aqueous medium to take place.

(ii) Referring to the graphs above, deduce the order of reaction with respect to each of the reactants, CN^- and **X**.

(iii) State, with a reason, whether the reaction proceeds by the S_N1 or S_N2 mechanism.

(iv) Hence, sketch a well labelled reaction pathway diagram for the reaction, given that the reaction is exothermic.

(v) Suggest why the reaction of **X** is more likely than that of $CH_3CH_2CH_2CHClCH_3$ to exhibit the mechanism stated in **(ii)**.

[9]

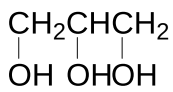
(b) The enzymatic hydrolysis of glycerides in oils is recently attempted industrially as an energy-saving method due to mild reaction conditions required. An enzyme such as lipase, is commonly used to speed up the rate of the hydrolysis of glycerides for the production of three fatty acids and glycerol, as shown by the structures below:

RCOOH

R'COOH

R''COOH

fatty acids

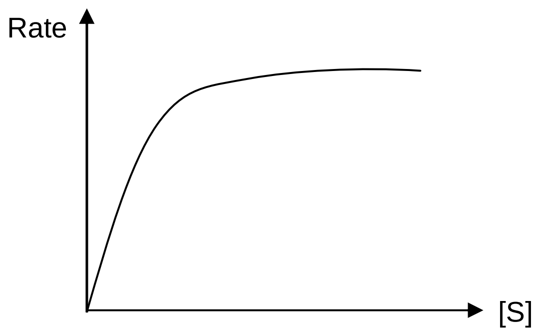


glycerol

(i) Draw the structural formula of glyceride and identify the functional group in the glyceride.

(ii) State the number of sigma and pi bonds surrounding the carbon atom in the functional group stated in **(i)**. Hence, identify the type of hybridisation of the carbon atom in the functional group.

(iii) The following graph shows how the rate of enzymatic hydrolysis of glyceride varies with increasing substrate concentration, [S] with a fixed amount of lipase used under fixed temperature. Suggest an explanation for the shape of the curve.



(iv) Besides using catalyst, the rate of reaction can also be increased by increasing the temperature. The rate of hydrolysis of glyceride is doubled when temperature increased by 10°C. If the rate of reaction at T °C is *r*, determine the new temperature if the rate is increased to 16*r*. Explain your answer.

[6]

(c) In an experiment involving the decomposition of ammonia, nickel is used as a catalyst to speed up the rate of decomposition of ammonia at 500°C in a reactor of volume 10 dm^3.

(i) State the type of catalysis which nickel exhibits and explain how its presence speeds up the rate of decomposition of ammonia.

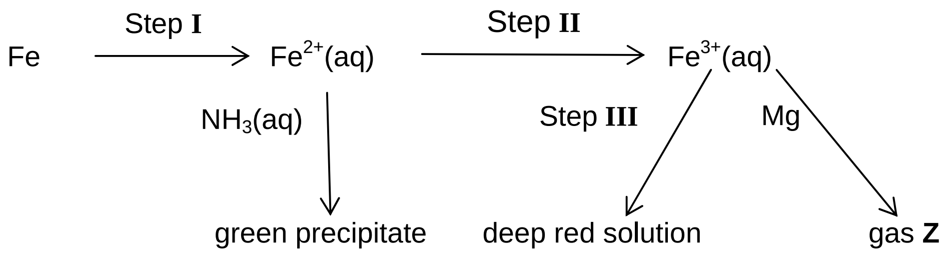
(ii) It was found that at equilibrium of decomposition for the experiment, 90% of the 6.80 g ammonia has decomposed. Calculate the total pressure of the gas mixture after reaction.

[5]

[Total: 20]

3 This question concerns the transition elements iron and chromium, together with their compounds.

(a) Iron is the fourth most common element in the Earth's crust. It is the most common element (by mass) forming much of Earth's outer and inner core.
Some reactions of iron are given below:



(i) State the reagents that could be used for Steps I to III.

(ii) Identify the gas **Z** and write an equation for its formation.

(iii) Describe what you would expect to observe when solid calcium carbonate is added to an aqueous solution of Fe^{3+}.

[6]

(b) The following data are given:

	Iron	Aluminium
Atomic radius / nm	0.116	0.143
Ionic radius / nm	0.076 (Fe^{2+}) 0.064 (Fe^{3+})	0.050

Explain why the atomic radius of iron is smaller than that of aluminium but the ionic radii of iron(II) and iron(III) are larger than that of Al^{3+}.

[2]

(c) Chromium is the hardest of all known metal elements in the Periodic Table. It is also odourless and tasteless. The name of the element is derived from the Greek word "chrōma" meaning colour, because many of its compounds are intensely coloured. The metal also reacts with oxygen to form a series of oxides.

One of these oxides, CrO_2, is often used to coat cassette tapes, due to its high conductivity and ferromagnetic properties, which provide a good high audio-frequency response.

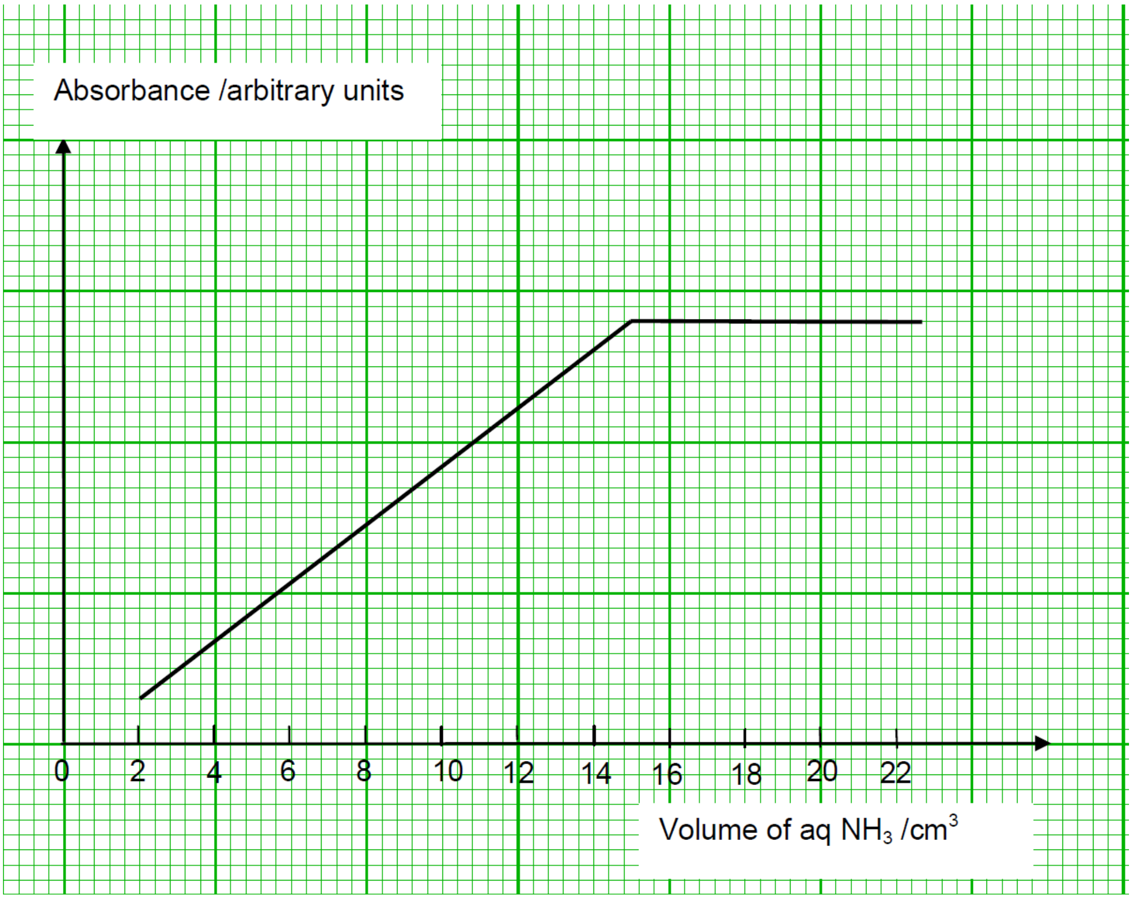
When the oxide from a length of tape was dissolved in dilute sulfuric acid, it disproportionates to give Cr^{3+} and $Cr_2O_7^{2-}$. The resulting solution needed 20.0 cm^3 of 0.015 mol dm^{-3} Fe^{2+} solution to reduce the $Cr_2O_7^{2-}$ completely to Cr^{3+}.

(i) Suggest equations for the disproportionation of CrO_2 in acid solution and for the reaction of $Cr_2O_7^{2-}$ with Fe^{2+} in acid solution.

(ii) Use the data to calculate the mass of CrO_2 in the length of cassette tape.

[4]

(d) The formula of a complex ion can sometimes be found by using a colorimeter. An aqueous solution of chromium(III) sulfate is green but if aqueous ammonia is added, the solution turns violet.
To eleven containers each containing 20.0 cm^3 of 0.050 mol dm^{-3} of chromium(III) sulfate, different volumes of 0.40 mol dm^{-3} aqueous ammonia was added. The first container had 2 cm^3 of the aqueous ammonia added, the second 4 cm^3 and so on. Distilled water was added to make up the total volume to 50 cm^3. A sample from each container was then placed in a colorimeter and the reading was recorded. The results are shown in the figure below:



(i) Explain the shape of the graph obtained.

(ii) Determine the formula of the complex.

(iii) Account for the difference in colours between the chromium-ammonia complex and the aqueous chromium(III) ion.

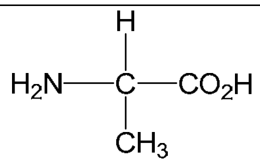
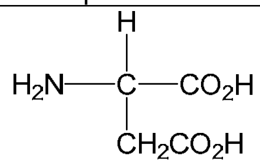
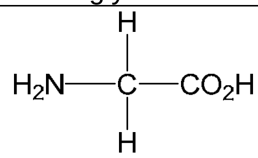
[8]
[Total: 20]

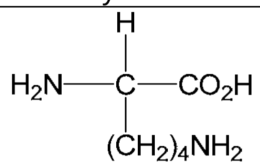
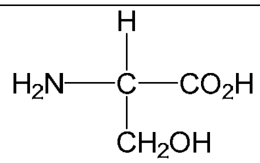
4 **(a)** Ovalbumin is the predominant protein in egg white. Structurally, it consists of 33 % α–helices, 5 % β–pleated sheets and 62 % random coil folded into a globular shape.

Draw a diagram to show how two strands in ovalbumin can be involved in maintaining a β–pleated sheet structure. Label any bonds established between the strands.

[2]

(b) Some of the amino acids found in ovalbumin are as follows:

alanine	aspartic acid	glycine
		

lysine	serine
	

The various methods of egg preparation are based on the principle of protein denaturation, which is accompanied by a change in the taste and appearance of the egg.

In your answers to this part of the question, reference should be made to the amino acids in the above table where appropriate.

(i) When an egg is boiled, the egg white changes from a transparent and colourless liquid into a white and opaque solid mass. Describe the structural changes that have taken place in the denaturation of ovalbumin which led to the change in appearance.

(ii) The Chinese delicacy known as "century egg" is prepared by coating the eggs with an alkaline clay paste. Through the process, the egg white becomes a dark brown, translucent jelly.
Suggest how the alkaline clay paste might interact with ovalbumin to bring about denaturation.

[5]

(c) At low temperatures, 1, 3, 5–trimethylbenzene reacts with HF and BF_3 to form a yellow solid **A**. **A** has the formula $C_9H_{13}BF_4$ and conducts an electric current in the molten state. When heated, **A** evolves BF_3 and regenerates 1, 3, 5–trimethylbenzene.

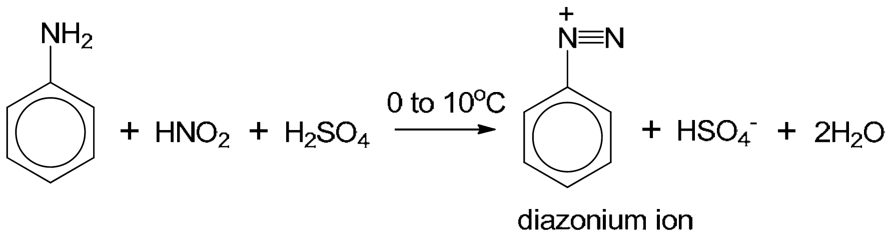
The formation of **A** provides strong confirmation for the mechanism of aromatic electrophilic substitution.

(i) HF and BF_3 react to generate the electrophile. By using the Lewis theory of acids and bases, construct an equation for the reaction between HF and BF_3.

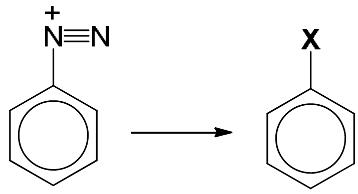
(ii) Outline the mechanism for this reaction, showing clearly how 1, 3, 5–trimethylbenzene and BF_3 are regenerated when **A** is heated. Hence, suggest a structure for **A**.

[4]

(d) A fairly stable diazonium salt can be prepared by treating a primary aromatic amine with nitrous acid in a cool solution:



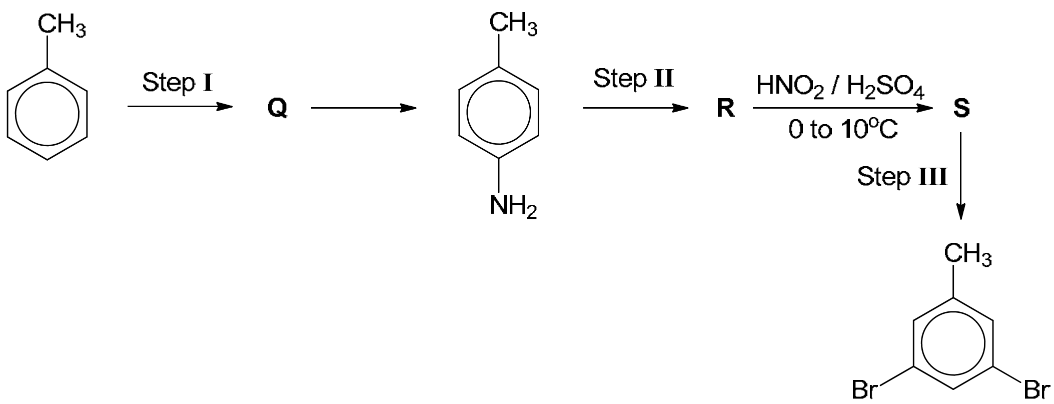
In a process named the Sandmeyer reaction, the –$\overset{+}{N}\equiv N$ group can be replaced by a new group –**X** when the appropriate reagents are used:



Some possible identities of **X** together with the corresponding reagents are shown below:

Identity of **X**	reagents and conditions
-Br	HBr and CuBr, room temperature
-H	H_3PO_2, room temperature
-OH	$Cu(NO_3)_2$ and Cu_2O, room temperature

This highly versatile reaction is widely used in the synthesis of aromatic compounds. An example is shown below, with methylbenzene as the starting compound:

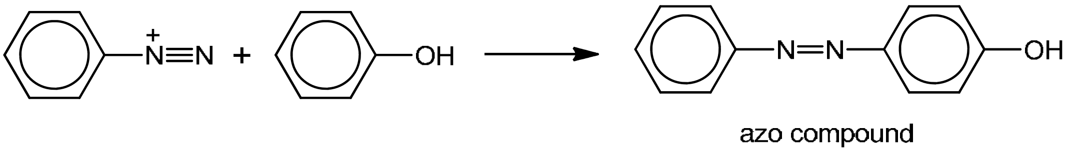


(i) Deduce the structures of **Q**, **R** and **S**.

(ii) Hence, state the reagents and conditions for effecting steps **I**, **II** and **III**.

[6]

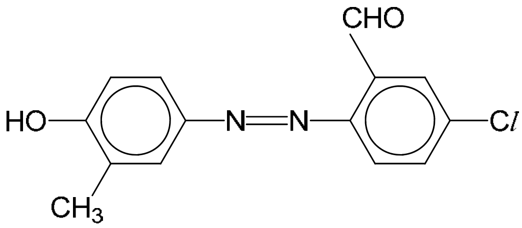
(e) Under the proper conditions, diazonium salts undergo a coupling reaction with phenol to obtain a brightly coloured azo compound:



The process is a typical electrophilic substitution reaction in which the positively charged diazonium ion acts as the electrophile that attacks the strongly activated benzene ring in phenol.

(i) As shown above, substitution typically takes place at the para rather than at the ortho position relative to –OH, i.e. position 4 rather than 2. Give a reason why this occurs.

(ii) The structure of an azo compound, **H**, is given below:



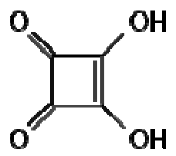
H

Deduce the structure of the amine and phenol that can be used as starting materials to synthesize **H**.

[3]

[Total: 20]

5 **(a)** Quadratic acid, used medically in the treatment of wart, is an unusual organic compound with molecular formula, $C_4H_2O_4$ and has the following structure:



(i) Suggest what you would see when quadratic acid reacts with:

1. 2,4-dinitrophenylhydrazine agent

2. ethanoyl chloride

Write a balanced equation for each reaction that occurs.

(ii) Quadratic acid is unusually acidic for an alcohol with a pK_a value of 1.5. Explain why this is so.

[4]

(iii) An aqueous solution of quadratic acid is titrated against aqueous sodium hydroxide.

An acid-base indicator (HIn) has a K_a value of 3.00 x 10^{-5} mol dm^{-3}.

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

The acidic form of the indicator (HIn) is red and the basic form (In^-) is blue. Given that the indicator appears red when it contains at least 75% of HIn, and appears blue when it contains at least 75% of In^-.

What is the pH range for colour change of this indicator? Based on your answer, briefly explain if this indicator is suitable for the quadratic acid titration.

[2]

(b) A large shipment of quadratic acid is contaminated with boracic acid, BH_3O_3, which is widely used as an insecticide.

The standard enthalpy change of combustion of quadratic acid is –1.26 x 10^3 kJ mol^{-1}. However, boracic acid does not burn as it is in the fully oxidised state.

When a 4.91 g sample of contaminated quadratic acid is burned in a bomb calorimeter, the temperature increases by 3.5 ^oC.

(i) Define standard enthalpy change of combustion of quadratic acid.

(ii) Given that the heat capacity of the calorimeter is 13.6 kJ K^{-1}, calculate the percentage by mass of boracic acid in the sample of contaminated quadratic acid.

(iii) Draw the displayed formula of boracic acid to illustrate its shape with respect to the boron and oxygen atoms. Indicate the bond angles clearly on the diagram.

[5]

(c) Hydrogen cyanide has been used in America to execute convicted murderers. A carbonyl–based antidote has been developed.

(i) Name and outline the mechanism of the reaction between propanone and hydrogen cyanide.

(ii) The carbonyl–based antidote **X** has molecular formula $C_4H_6O_2$.

X reacts with hydrogen cyanide to form **Y**, $C_6H_8O_2N_2$. **Y** reacts with excess hot acidified potassium dichromate(VI) solution to produce **Z**, $C_6H_8O_6$. 2.16 g of **Z** (M_r = 176) was dissolved in 250 cm^3 of water. 25.0 cm^3 of the solution required 24.50 cm^3 of 0.100 mol dm^{-3} of sodium hydroxide for complete neutralisation.

Calculate the amount of sodium hydroxide that will be neutralised by one mole of **Z**. Hence suggest possible structural formulae of **X**, **Y** and **Z**.

[6]

(d) Lead azide, $Pb(N_3)_2$, is used as a shock-sensitive detonator in car airbags. The impact of a collision causes lead azide to be converted into an enormous amount of gas that fills the airbag.

(i) In the determination of solubility product, K_{sp} of lead azide, 25.0 cm^3 of a saturated solution of lead azide was passed through a cation exchange column and the column washed down through with water. The washings required 10.50 cm^3 of 6.00 x 10^{-3} mol dm^{-3} of NaOH(aq) for complete neutralisation. The lead(II) ions in the saturated solution replaced all the H^+ ions from the cation exchange column such that

$$Pb^{2+}(aq) + 2H^+(column) \rightarrow Pb^{2+}(column) + 2H^+(aq)$$

Calculate the solubility product of lead azide, stating its units.

(ii) Draw the Lewis structure of the azide ion.

[3]

[Total: 20]