

A Level

Chemistry

Session: 1984 June
Type: Question paper
Code: 9250

CHEMISTRY

ADVANCED LEVEL

PAPER 1

(Two and a half hours)

9250/1

Answer five questions, including one question from each of the Sections A, B, C, D and any one other.

Candidates are advised not to attempt questions on Options for which they have not been prepared.

Candidates are not permitted to answer both the Biochemistry question and the Food Chemistry question, on this paper.

Begin each answer on a fresh sheet of paper.

Mathematical tables, squared paper and a Data Booklet are available.

In this paper, nitrous acid may be read as nitric(III) acid,

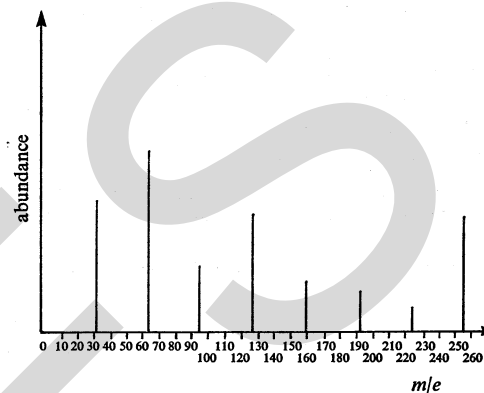
peroxodisulphate(VI) as persulphate,
sulphate as sulphate(VI).
sulphuric acid as sulphuric(VI) acid.

SECTION A

- 1 Write an essay on *intermolecular forces*. Your answer should include an account of how the different types of intermolecular forces arise, their relative strengths and how they influence the physical properties of various substances. [20 marks]

- 2 Interpret each of the following observations as fully as you can.

(a) The mass spectrum of sulphur vapour is as shown below.



- (b) The principal oxidation states of sulphur are II, IV and VI.
(c) When aqueous ammonia is added to aqueous magnesium sulphate a white precipitate is obtained. However, when the experiment is repeated in the presence of dissolved ammonium sulphate, no precipitate is obtained.
(d) A relatively small increase in temperature can cause a large increase in the rate of a chemical reaction; for example, it is sometimes said that a 10 °C rise in temperature approximately doubles the rate of a reaction. [4 × 5 marks]

- 3 Define *enthalpy change of formation* and *lattice energy*. [4 marks]

Discuss the factors that determine the magnitude of a lattice energy. [5 marks]

Draw Born-Haber cycles for the formation of (a) crystalline potassium chloride, (b) an aqueous solution of potassium chloride. Use these cycles to calculate (i) the enthalpy change of formation of potassium chloride, (ii) the enthalpy change of solution of potassium chloride.

Data

Enthalpy term	$\Delta H/\text{kJ mol}^{-1}$
Enthalpy change of atomisation of potassium	+ 90
Enthalpy change of atomisation of chlorine	+121
First ionisation energy of potassium	+418
Electron affinity of chlorine*	-364
Enthalpy change of hydration of potassium ion	-322
Enthalpy change of hydration of chloride ion	-364
Lattice energy of potassium chloride	-701

*i.e. the enthalpy change for the process $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$.

Comment briefly on your answer to (ii) in relation to the solubility of potassium chloride in water. [9 + 2 marks]

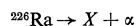
SECTION B

4 (a) Give a concise account of the chemistry of the elements in Group II of the Periodic Table (beryllium, magnesium, calcium, strontium and barium), referring in your answer to **all** of the following aspects:

- (i) the variation in first ionisation energy of the elements,
- (ii) the reducing power of the elements,
- (iii) the thermal decomposition of the carbonates,
- (iv) the variation in solubility of the sulphates. [3 + 3 + 5 + 5 marks]

(b) (i) The element radium, Ra, is also in Group II of the Periodic Table. Use the *Data Booklet* to predict the approximate magnitude of the standard electrode potential for this element. [2 marks]

(ii) The radioactive decay of the isotope radium-226 can be represented by the following equation.



State, giving reasons, the group of the Periodic Table to which element X belongs. [2 marks]

5 State and explain what happens in **each** of the following experiments. Write balanced equations for the reactions that occur where possible.

- (a) Aqueous sodium hydroxide is gradually added to aqueous aluminium sulphate until it is present in excess.
- (b) A few drops of silicon tetrachloride are added to water containing universal indicator solution.
- (c) Ammonium sulphate is warmed with aqueous sodium hydroxide and a strip of filter paper which has been immersed in aqueous copper(II) sulphate is held just above the mouth of the test tube.
- (d) Aqueous chlorine is shaken with aqueous potassium iodide to which a few drops of an organic solvent such as tetrachloromethane have been added. [4 × 5 marks]

SECTION C

6 What do you understand by the terms (a) *structural isomerism*, (b) *cis-trans isomerism*? [4 marks]

A gaseous hydrocarbon X contains 85.7% of carbon by mass. When 0.140 g of X was introduced into a gas syringe, its volume (after correction to s.t.p.) was found to be 56.0 cm³. When X was shaken with aqueous bromine the latter was decolourised.

Three structural isomers A, B and C of the hydrocarbon X were found to have the following properties.

- (i) A exists as a pair of *cis-trans* isomers.
- (ii) B underwent oxidation under certain conditions to produce methanal and a compound Y (empirical formula C₃H₆O) which gave an orange precipitate with 2,4-dinitrophenylhydrazine reagent and a red-brown precipitate on boiling with Fehling's solution.
- (iii) C can be obtained by the dehydration of 2-methylpropan-2-ol.

Deduce the **full** structural formula of **each** of the isomers A, B and C, explaining your reasoning and giving balanced equations where possible. [16 marks]

7 Each of five reagent bottles, from which the labels have been removed, is known to contain a different one of the following liquids:

- (a) HCO₂H, (b) CH₃CO₂H, (c) CH₃COCl, (d) CH₃CH₂CH₂Cl, (e) CH₃CH₂CH₂I.

Describe how you would identify **each** liquid by means of chemical tests that can be readily carried out in a school laboratory. You should name the reagents, and give the essential reaction conditions, the observations made and the conclusions drawn from the observations.

Note A chemical test is required for **each** liquid – it is not sufficient to identify the fifth liquid by elimination. [5 × 4 marks]

8 (a) How, and under what conditions, does nitrous acid react with (i) ethylamine, (ii) phenylamine? [6 marks]

Outline the industrial importance of the reaction of an aromatic amine with nitrous acid. [3 marks]

(b) What functional groups are present in the molecule of an amino acid? [2 marks]

Aminoethanoic acid is a high melting point solid which is soluble in water giving a neutral solution, but insoluble in ethoxyethane ('ether'). Draw a **full** structural formula for aminoethanoic acid which is consistent with these observations and explain how you arrive at your answer. [5 marks]

(c) Describe, with the aid of structural formulae, the process involved in the formation of the peptide linkages in a protein. [4 marks]

SECTION D

PHASE EQUILIBRIA – Standard Option A

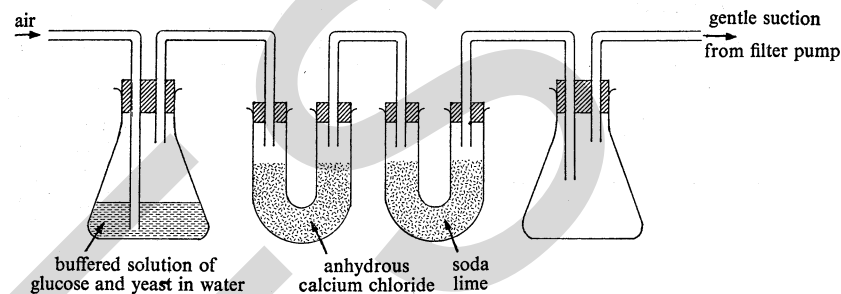
- 9 (a) What do you understand by the term *eutectic mixture*? [2 marks]
 Camphor (melting point 176 °C) and naphthalene (melting point 80 °C) form a eutectic mixture at 33 °C in which the mole fraction of camphor is 0.41. Use these data to construct the eutectic diagram for this system on the graph paper provided. [3 marks]
 Describe, with the aid of a sketch of the cooling curve, what happens when a melt containing 0.75 mole fraction of camphor is cooled. [5 marks]
 What is the physical nature of a camphor/naphthalene system in which the mole fraction of camphor is 0.50 at 50 °C? [2 marks]
- (b) (i) State *Raoult's law* as it applies to the vapour pressures of miscible liquids. [2 marks]
 (ii) Sketch the vapour pressure/composition diagram for a mixture of two liquids which shows a negative deviation from Raoult's law. [2 marks]
 (iii) Give **one** example of a liquid mixture which would show a negative deviation from Raoult's law and explain the basis of your choice. [4 marks]

FURTHER TRANSITION METAL CHEMISTRY – Standard Option B

- 10 (a) Discuss points of interest in the oxidation states shown by the first row d-block (transition) elements. [5 marks]
- (b) Explain **each** of the following observations as fully as you can.
- When aqueous potassium peroxodisulphate(VI), $K_2S_2O_8$, is added to an aqueous solution containing potassium iodide, sodium thiosulphate and starch a dark blue colour suddenly appears after a short delay. The appearance of this blue colour can be accelerated by the addition of a few drops of aqueous iron(III) chloride to the reactants.
 - When aqueous ammonia is gradually added to aqueous cobalt(II) chloride a blue precipitate is formed initially, but this dissolves in an excess of aqueous ammonia to give a pale brown solution. When the latter is allowed to stand in the air its colour gradually turns darker brown.
 - When copper(I) oxide is warmed with dilute sulphuric acid a pale blue solution containing a reddish-brown solid is obtained. [3 × 5 marks]

BIOCHEMISTRY – Special Option

- 11 The diagram below shows the apparatus which could be used to study the rate of metabolism of glucose by yeast under aerobic conditions.



- (a) Explain the use of the various pieces of apparatus and describe two ways in which you could measure the rate of metabolism. [12 marks]
- (b) How would you adapt the apparatus to study the metabolism of glucose under anaerobic conditions? [2 marks]
- (c) Write overall equations for the metabolism of glucose by yeast under (i) aerobic conditions, (ii) anaerobic conditions. [4 marks]
- (d) What control experiment is required in the investigation? [2 marks]

CHEMICAL ENGINEERING – Special Option

- 12 Discuss each of the following statements.
- Very large Liebig condensers are not employed as condensers in a manufacturing process. [4 marks]
 - Large scale filtration becomes slower as it proceeds. There are, however, two ways of overcoming this difficulty. [4 marks]
 - Turbulent flow is desirable in a heat exchanger as this reduces the time required for the fluid in the heat exchanger to cool. [4 marks]
 - A heat exchanger is often part of a pre-heat and cooling circuit in an exothermic manufacturing process. [4 marks]
 - Slurries are usually dried in a continuous process. [4 marks]

SOIL CHEMISTRY – Special Option

- 13 (a) Sketch labelled diagrams to illustrate the sheet structures of kaolinite (a 1:1 clay) and montmorillonite (a 2:1 clay). [6 marks]
 Which of these two structures is most responsible for the 'cracking' of soils in dry weather? Explain your answer. [4 marks]
- (b) (i) Explain how isomorphous substitution leads to the permanent cation exchange capacity of montmorillonite. [6 marks]
 (ii) Explain how a pH dependent cation exchange capacity occurs on sheet silicate structures. [4 marks]

FOOD CHEMISTRY – *Special Option*

- 14 (a) Many food materials are produced which are surplus to immediate requirements and deteriorate on storage and become inedible.
- (i) Briefly describe the ways in which food materials deteriorate. [10 marks]
- (ii) Outline the principles and disadvantages of an osmotic method and a thermal method of food preservation and state the food materials best preserved by each method. [6 marks]
- (b) Outline the chemical changes which can take place when (i) meat, (ii) cabbage is cooked. [4 marks]
- (c) Suggest why fresh market produce may be of lower nutritional value than some frozen foods. [4 marks]

POLYMERS – *Special Option*

- 15 (a) Explain the function of the initiator and the reasons for initially heating then cooling the reaction vessel in the manufacture of poly(phenylethene) (polystyrene) from phenylethene. Why is it usual to have more than one initiator? [10 marks]
- (b) One form of poly(phenylethene) is highly crystalline at room temperature whereas other forms are less crystalline. Explain these differences with the aid of suitable diagrams. [4 marks]
- (c) Explain, with equations, why co-polymers of phenylethene and buta-1,3-diene can be used both for making car tyres and for making containers for dairy products. [6 marks]

SPECTROSCOPY – *Special Option*

- 16 By using suitable examples, explain the following features of the various branches of spectroscopy.
- (a) The use of $M + 1$ and $M + 2$ peaks in mass spectroscopy. [5 marks]
- (b) The addition of D_2O to a sample in n.m.r. spectroscopy. [5 marks]
- (c) The use of the Beer–Lambert law in u.v./visible spectroscopy. [5 marks]
- (d) The absorption of energy causing colour in octahedral transition metal complexes. [5 marks]

You should use diagrams to illustrate your answers where appropriate.

CHEMISTRY

9250/2

ADVANCED LEVEL

PAPER 2

(One and a half hours)

Answer six questions, including at least four from Section A, in the spaces provided on the question paper. Candidates are advised not to attempt questions on Options for which they have not been prepared. Candidates are not permitted to answer both the Biochemistry question and the Food Chemistry question on this paper.

Each question carries ten marks.

Mathematical tables and a Data Booklet are available.

All working must be shown.

Wherever they are appropriate, units must be quoted in numerical answers.

In this question paper, relative molecular mass may be read as molecular weight,
 sulphuric acid as sulphuric(VI) acid,
 phosphoric(V) acid as phosphoric acid.

SECTION A

- 1 For each of the two reactions below you are asked to (i) write a balanced equation, (ii) state what you would expect to observe. It is not necessary to name the products nor to state the conditions required for successful reaction.
- (a) potassium chloride and concentrated sulphuric acid
- (i)
- (ii) [2 marks]
- (b) potassium iodide and concentrated sulphuric acid
- (i)
- (ii) [2 marks]
- (c) In the light of your answer to (b) suggest why phosphoric(V) acid is used to make gaseous hydrogen iodide from potassium iodide.
-
- [1 mark]
- (d) A hot glass rod is plunged separately into gas jars containing hydrogen chloride and hydrogen iodide.

- (i) For each gas state what you would observe and write an equation for any reaction that occurs.

.....

.....

.....

.....

[2 marks]

- (ii) Comment on the role of the hot glass rod.

.....

[1 mark]

- (iii) Comment on the enthalpy changes which control what happens in (d) (i).

.....

.....

.....

[2 marks]

- 2 Weighed samples of ethanedioic acid, $(\text{CO}_2\text{H})_2$, and ethanol are mixed together and sealed in a glass vessel which is maintained at constant temperature for several hours until equilibrium is reached.

- (a) Write a balanced equation for the reaction.

.....

[1 mark]

- (b) Outline how the ethanedioic acid remaining in the equilibrium mixture may be estimated, mentioning all the additional reagents you may require.

.....

.....

.....

.....

.....

[3 marks]

- (c) (i) Write an expression for the equilibrium constant of this reaction.

[1 mark]

- (ii) The initial mass of anhydrous ethanedioic acid used was 90 g and it was reacted with 92 g of ethanol. At equilibrium there were 36 g of ethanedioic acid remaining. Calculate the value of the equilibrium constant.

- (iii) Explain why the equilibrium constant does not have any units.

.....

.....

[4 marks]

[1 mark]

3 (a) Complete the table below.

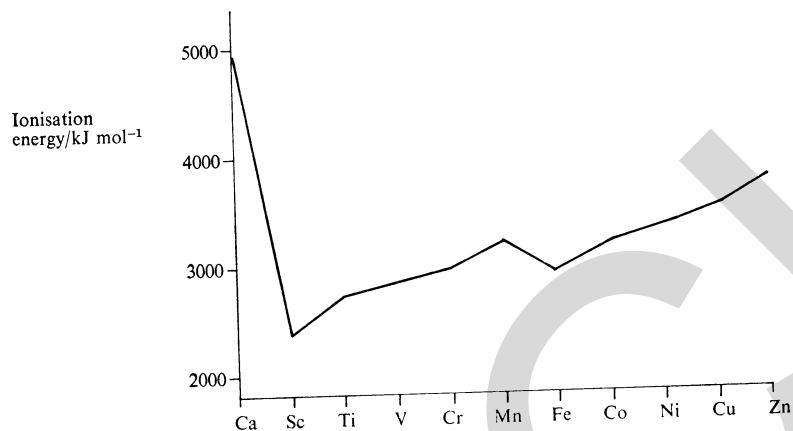
Ion	Ca ²⁺	Mn ²⁺	Fe ²⁺	Ni ²⁺	Cu ²⁺
Number of electrons in 3d shell in ion					
Colour of ion in aqueous solution					

[5 marks]

(b) (i) Define, in terms of an element *M*, what is meant by the third ionisation energy.

[1 mark]

The graph below shows the third ionisation energies for the elements Ca to Zn inclusive.



(ii) Why is the third ionisation energy of calcium so much higher than those of the other elements?

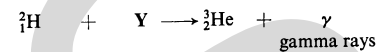
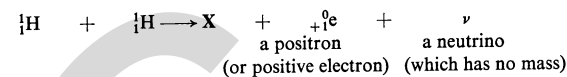
[1 mark]

(iii) Why is the third ionisation energy of scandium the lowest value of the sequence?

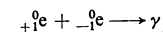
[1 mark]

(iv) Suggest a reason why the third ionisation energy of iron is lower than that of manganese.

[2 marks]

4 Under the conditions prevailing in the centre of a star like the sun, where the temperature is about 1.6×10^7 K, hydrogen ${}^1_1\text{H}$ undergoes nuclear changes according to the following sequence of reactions.

The positrons are annihilated by meeting electrons, with the consequent production of gamma rays.



(a) (i) Identify the nuclei X, Y and Z, giving their atomic symbols, atomic numbers and mass numbers.

X

Y

Z

[3 marks]

(ii) What new element has been formed from hydrogen?

[1 mark]

(b) The energy associated with radiation of frequency f is given by the equation $E = hf$, where h is the Planck constant.(i) Use the values on page 4 of the *Data Booklet* to calculate the energy in joules associated with one quantum of gamma radiation of wavelength 50 pm. (1 picometre (pm) = 10^{-12} m.)(ii) How much energy will be associated with the formation of L quanta of gamma radiation? L is the Avogadro constant and is also to be found on page 4 of the *Data Booklet*.

[3 marks]

(c) In addition to hydrogen, the following elements have been found in reasonable quantities in the sun:

He C O Ne Si S Ca Fe

(i) Suggest how these elements can be identified in the sun.

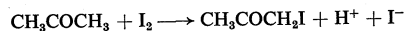
.....

.....

- (ii) Use the Periodic Table on page 3 of the *Data Booklet* to find what these elements have in common, and comment upon their possible origin.

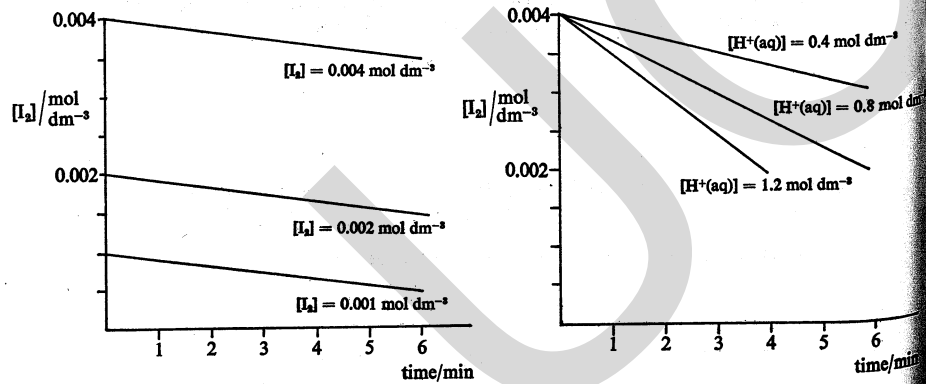
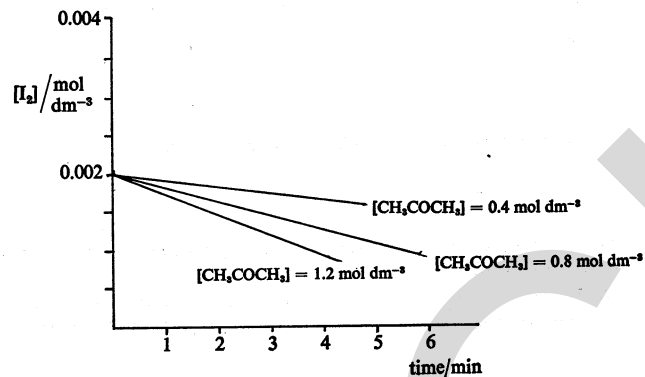
[3 marks]

- 5 Iodine and propanone react together in aqueous acidic solution according to the equation



The rate of the reaction can be measured by recording the reduction of the concentration of the iodine by the decrease in the intensity of its colour as measured in a colorimeter.

Three sets of separate experiments were performed in which the initial concentration of each of the reactants, iodine, propanone and acid was varied in turn, the other two being kept constant. The results are shown below in graphical form.



- (a) (i) How is the rate of reaction found from a graph of concentration of reagent against time?

[1 mark]

- (ii) Use the graphs to find how the rate of the reaction varies with the concentration of propanone, iodine and acid, expressing your answers in the form rate $\propto [\text{X}]^n$ where X is each reactant in turn.

propanone:

iodine:

acid:

[3 marks]

- (iii) Write a full rate expression for the reaction, using the rate constant, k .

[1 mark]

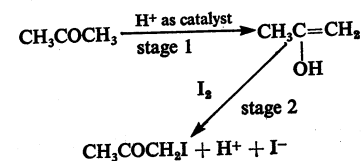
- (iv) What is the total order of the reaction?

[1 mark]

- (v) What are the units of the rate constant, k ?

[1 mark]

A mechanism for the reaction is suggested in the following scheme.



- (b) In the light of your answers in (a) what can you say about the relative rates of the two stages given in the mechanism above? Explain your reasoning.

[2 marks]

- (c) In what way (if at all) do the conditions of this reaction differ from those of the tri-iodomethane (CHI_3) reaction?

[1 mark]

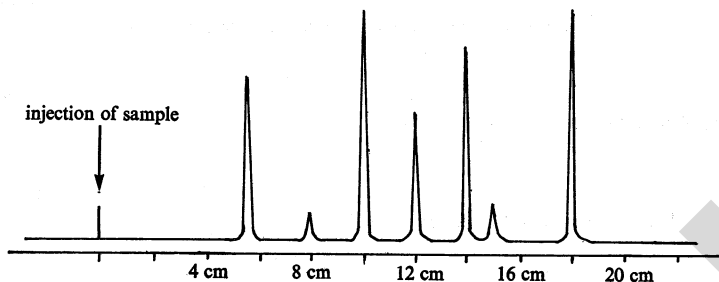
SECTION B

PHASE EQUILIBRIA – Standard Option A

- 6 (a) The retention times of some organic liquids on a certain gas-liquid chromatography column at 150 °C are given below.

Compound	Retention time/s	Compound	Retention time/s
methanol	6	propanone	11
ethanol	24	butanone	20
propan-1-ol	36	pentan-2-one	26
propan-2-ol	30	pentan-3-one	28
		cyclohexanone	33

A mixture of liquids was injected, under the same conditions, on to the same column and the following trace was obtained.



- (i) Given that the paper in the recorder moves at 0.5 cm s^{-1} , what compounds can you identify in the mixture? (Not all the peaks can be identified.)
-
-
- [3 marks]
- (ii) State two processes that are involved in the separation process in the chromatography column.
- (i)
- (ii)
- [2 marks]
- (iii) Suggest why the retention time for propan-2-ol is much longer than that for propanone even though their relative molecular masses are very similar.
-
-
- [1 mark]
- (b) (i) The different nitration products of phenol can be readily separated by thin-layer chromatography using trichloromethane as solvent. Draw and label a diagram of the apparatus you would use to put this separation into effect.

[2 marks]

- (ii) How could the presence of 4-nitrophenol be shown among the nitration products? 4-nitrophenol is yellow and soluble in ethanol. Either write your answer below or use your diagram in (b) (i) above.
-
-
-
- [2 marks]

FURTHER TRANSITION METAL CHEMISTRY – Standard Option B

- 7 (a) Titanium is obtained from its chief ore, rutile, TiO_2 . The first stage is to make titanium(IV) chloride by heating rutile with coke at about 1000 °C in an atmosphere of chlorine.
- (i) Write a balanced equation for this stage.
-
- [1 mark]
- (ii) Titanium(IV) chloride cannot be stored exposed to the air. Explain, with an equation, why this is so.
-
-
- [2 marks]
- (iii) Titanium(IV) chloride is reduced by using a more electropositive metal. Which metal is used?
-
- (iv) Write a balanced equation for the reduction.
-
- (v) What precautions need to be observed in this reduction?
-
-
- [3 marks]
- (b) Give one major use of an alloy of titanium and state what physical or chemical property is involved in your chosen use.
-
-
-
- [2 marks]

[2 marks]

- (c) It was once thought that iron would be superseded by titanium in several of its uses as a metal. There are several reasons why this is unlikely; mention two of them.

.....

 [2 marks]

BIOCHEMISTRY – Special Option

If this question is attempted, you are not permitted to answer the Food Chemistry question as well.

- 8 (a) Proteins, such as enzymes, require a precise three dimensional structure in order to function, so why does the translation of information from DNA to protein require only the order of amino acid sequence to be controlled?

.....

 [2 marks]

- (b) Explain what is meant by
 (i) a competitive (reversible) inhibitor of an enzyme

.....

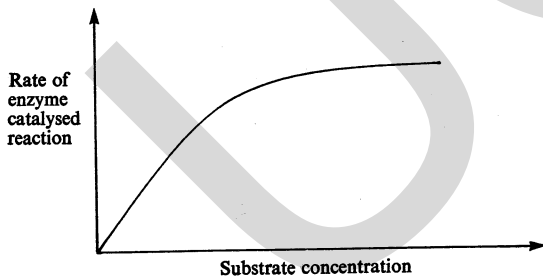
 [2 marks]

- (ii) a non-competitive (irreversible) inhibitor of an enzyme

.....

 [2 marks]

- (c) The graph below shows the variation in the rate of an enzyme-catalysed reaction with no inhibitor present.



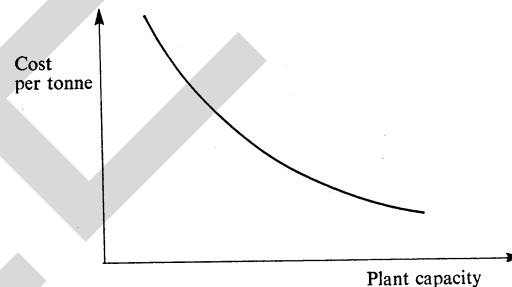
Sketch, on the axes above, the shapes of the curves that show the effect on the enzyme-catalysed reaction of (i) a competitive inhibitor, (ii) a non-competitive inhibitor. Explain their shapes below.

.....

 [4 marks]

CHEMICAL ENGINEERING – Special Option

- 9 (a) In the chemical industry it is generally true that for a continuous process the manufacturing cost per tonne of product falls as the plant capacity increases, as shown below.



Give two reasons why such plants with a very high capacity are unusual.

- (i) [1 mark]
 (ii) [1 mark]

(b)	Plant capacity	Capital cost ratio	Labour cost ratio per tonne	Fixed cost ratio per tonne
	750 tonnes/day	2	2	4
	1500 tonnes/day	3	1	3

For each of the above ratios suggest one reason why the cost for the 1500 tonnes/day plant is not double that for the 750 tonnes/day plant.

Capital cost ratio

Labour cost ratio

Fixed cost ratio

[6 marks]

- (c) Originally the manufacture of ethanoic and sulphuric acids was uneconomic. State how each process became viable.

[2 marks]

SOIL CHEMISTRY – Special Option

- 10 On an imaginary planet, plants require the same nutrients and growing conditions as on Earth except that the additional macronutrient element, emium (*Em*), is needed. Emium forms Em^{2+} and Em^{3+} ions although plants will only accept emium in its Em^{2+} form. The standard redox potential $Em^{3+}(aq)/Em^{2+}(aq)$ is + 0.86 V and Em^{2+} has an ionic size identical to Na^+ . Emium is unable to form covalent bonds.

- (a) Explain how you would expect the strength of adhesion of $Em^{2+}(aq)$ at cation exchange sites to compare with:

(i) $K^+(aq)$,

[2 marks]

(ii) $Mg^{2+}(aq)$.

[2 marks]

- (b) Explain whether you would expect Em^{3+} to be supplied to plants largely from organic or inorganic material.

[1 mark]

- (c) A plant suffering from an emium deficiency shows yellowing on its newer leaves which curl up if the deficiency is marked.

(i) What does this suggest about the mobility of the Em^{3+} ion in the plant?

[1 mark]

- (ii) How do the symptoms of the deficiency compare with a potassium ion deficiency?

[1 mark]

- (iii) Under what physical conditions would an emium deficiency be likely to occur? Explain your answer.

[3 marks]

FOOD CHEMISTRY – Special Option

If this question is attempted, you are not permitted to answer the Biochemistry question as well.

- 11 A white mixture **T** was extracted from the root system of a plant and was thought to be commercially valuable as a foodstuff. It was found to be partially soluble in cold water and the residue dissolved readily in hot dilute hydrochloric acid, giving a clear colourless solution.
- (a) From the information given, suggest one specific food component apparently absent in **T**. Explain your reasoning.

[2 marks]

- (b) The water insoluble portion of **T**, being readily soluble in dilute hydrochloric acid, was thought to have reacted with it.

(i) Name two food components which could do so.

[2 marks]

- (ii) Name the products of the reaction between dilute hydrochloric acid and the food components in (b) (i).

[2 marks]

(c) Name one other possible constituent of T and indicate how the concentration of this could be determined.

.....

[3 marks]

(d) T was found to have a long shelf life, needing little further processing after initial extraction. What does this tell you about the nature of T?

.....

[1 mark]

POLYMERS – Special Option

12 (a) Describe with the aid of an equation how you would prepare a small sample of nylon in the laboratory.

.....

[4 marks]

(b) In what way, other than scale of operation, is the manufacture of nylon (i) similar to, (ii) different from the laboratory process?

(i)

(ii)

[2 marks]

(c) Draw the repeat unit of a polyester such as Terylene.

[2 marks]

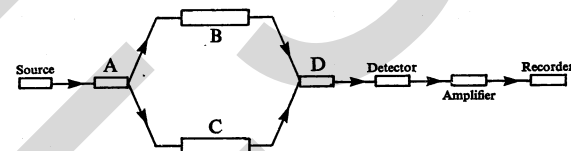
(d) Give two advantages of nylon and Terylene over cotton fibres.

.....

[2 marks]

SPECTROSCOPY – Special Option

13



The diagram above represents a double-beam infra-red spectrometer.

(a) Identify the parts labelled A, B, C and D above.

A

B

C

D

State the function of each of the parts A to D.

A

B

C

D

[4 marks]

(b) Describe three ways in which a sample of benzoic acid might be prepared for infrared analysis.

(i)

.....

.....

(ii)

.....

(iii)

.....

.....

[3 marks]

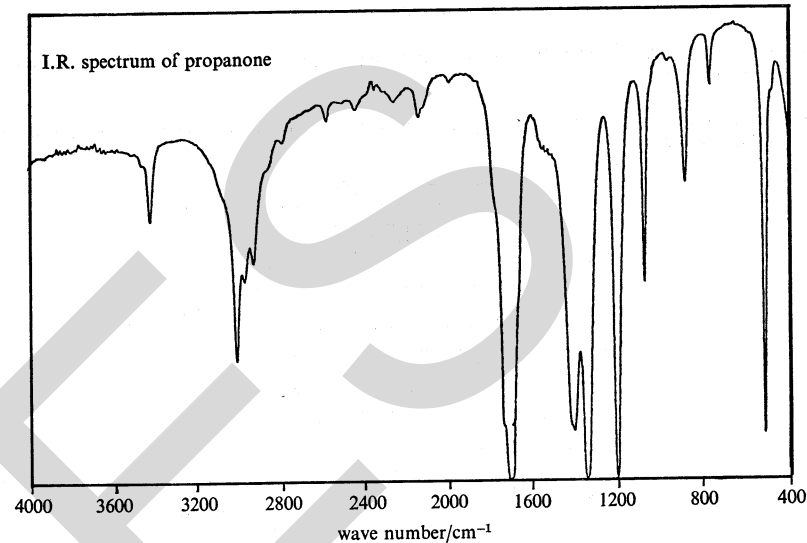
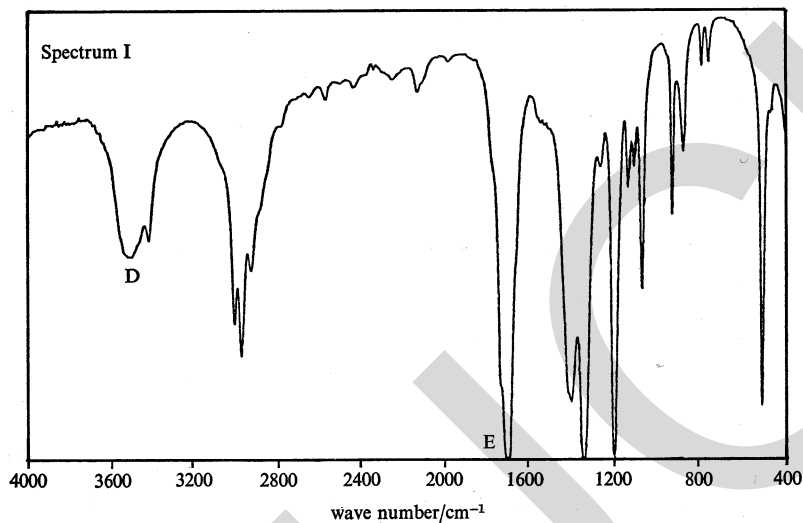
(d) A student had prepared an impure sample of propanone and obtained spectrum I from his product. By comparison with the spectrum of pure propanone, suggest what the impurity might be and the identities of the functional groups causing the absorptions labelled D and E.

Impurity

Peak D

Peak E

[3 marks]



CHEMISTRY

9250/3

ADVANCED LEVEL

PAPER 3

(One hour)

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO

Read these notes carefully

This test is composed of forty questions. For each question, five suggested answers are given. You are to select the most appropriate one and indicate it on the separate answer sheet.

For each type of question, instructions about how to choose the most appropriate answer are given.

Read the instructions on the separate sheet very carefully.

Ask any questions now before the test begins.

Attempt all the questions. Marks will not be deducted for wrong answers: your total score on this test will be the number of correct answers given.

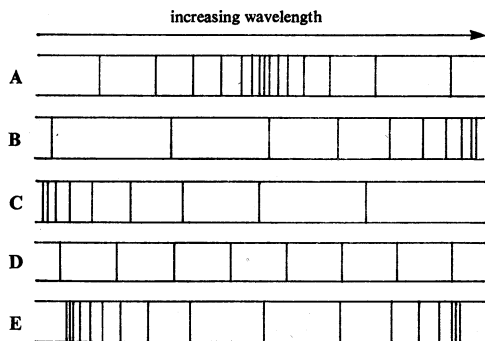
Mathematical tables are available. Data Booklets are not to be used.

*In this paper, dichromate(VI) may be read as dichromate,
 manganese(IV) oxide as manganese dioxide,
 manganate(VII) as permanganate,
 nitric acid as nitric(V) acid,
 sulphate as sulphate(VI),
 sulphuric acid as sulphuric(VI) acid,
 sulphur(VI) oxide as sulphur trioxide.*

Section A

Five possible answers, labelled A, B, C, D and E are given for each question. Choose the one which you consider to be correct.

- 1 Which diagram best represents the appearance of the line spectrum of atomic hydrogen in the visible region?



- 2 10 dm³ of polluted air is passed through lime water so that all the carbon dioxide present is precipitated as calcium carbonate. The mass of calcium carbonate formed is 0.05 g. What is the percentage, by volume, of carbon dioxide in the air sample? [C, 12; O, 16; Ca, 40; 1 mol of gas under experimental conditions has a volume of 24 dm³.]

- A 0.03
B 0.05
C 0.12
D 0.3
E 0.6

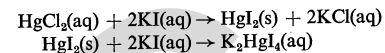
- 3 For complete oxidation, 1 mol of an organic compound requires 3 mol of oxygen gas. Which one of the following could the compound be?

- A ethanal
B ethane
C ethanoic acid
D ethanol
E methanol

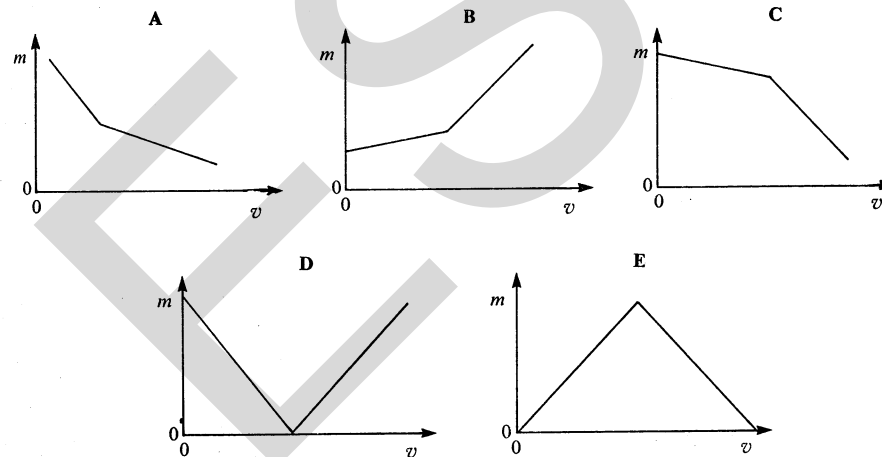
- 4 Which one of the following equations relates to the first ionisation energy of bromine?

- A $\frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{Br}^-(\text{g}) - \text{e}^-$
B $\frac{1}{2}\text{Br}_2(\text{g}) \rightarrow \text{Br}^-(\text{g}) - \text{e}^-$
C $\text{Br}(\text{g}) \rightarrow \text{Br}^-(\text{g}) - \text{e}^-$
D $\text{Br}(\text{g}) \rightarrow \text{Br}^+(\text{g}) + \text{e}^-$
E $\frac{1}{2}\text{Br}_2(\text{g}) \rightarrow \text{Br}^+(\text{g}) + \text{e}^-$

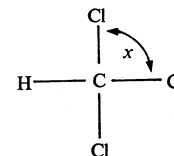
- 5 When an excess of aqueous potassium iodide is added to aqueous mercury(II) chloride, the following reactions occur:



Which one of the following diagrams shows how the mass m of the precipitate varies with the volume v of aqueous potassium iodide added?



- 6 What is the value of the bond angle marked x in the molecule of trichloromethane?

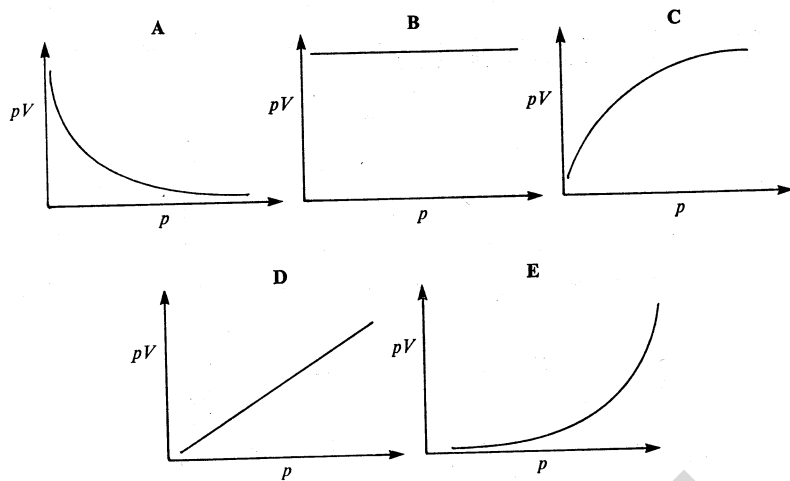


- A less than 90°
B exactly 90°
C approximately 107°
D exactly 109.5°
E more than 109.5°

- 7 What is the co-ordination number of a sodium ion in the sodium chloride lattice?

- A 1 B 2 C 4 D 6 E 8

- 8 Consider a fixed mass of an ideal gas at constant temperature and occupying a vessel of volume V at a pressure p . Which graph below, A, B, C, D or E, best shows the relationship between the product pV and p ?



- 9 When a current of 8 A is passed through molten aluminium oxide using inert electrodes for 100 minutes, what will be the approximate volume of gas liberated measured at s.t.p.? [1 mol of gas at s.t.p. occupies 22.4 dm³; Faraday constant = 9.6×10^4 C mol⁻¹.]

- A 2.8 dm³
 B 5.6 dm³
 C 8.4 dm³
 D 11.2 dm³
 E 22.4 dm³

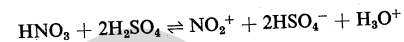
- 10 Which one of the following systems will have an increased proportion of products at equilibrium, in separate experiments, *both* when the pressure is reduced at constant temperature *and* when the temperature is increased at constant pressure?

- A $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ $\Delta H = -92$ kJ mol⁻¹
 B $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ $\Delta H = +57$ kJ mol⁻¹
 C $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ $\Delta H = -197$ kJ mol⁻¹
 D $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $\Delta H = +53$ kJ mol⁻¹
 E $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ $\Delta H = -950$ kJ mol⁻¹

- 11 If the solubility products of the following ionic compounds all had the same *numerical* value, which one would have the lowest solubility in moles of solute per dm³?

- A PQ
 B RS_2
 C T_2U
 D VW_3
 E X_2Y_2

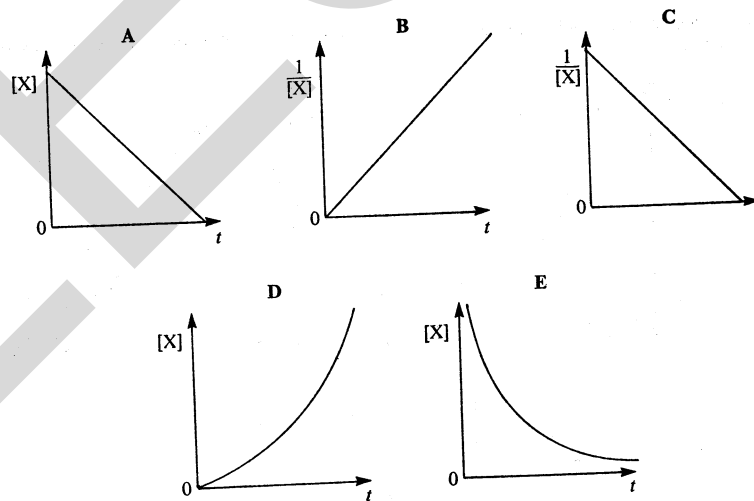
- 12 The following reaction occurs in a mixture of concentrated nitric acid and concentrated sulphuric acid:



Which one of the following statements about this reaction is correct?

- A The nitric acid acts as an oxidising agent.
 B The sulphuric acid acts as a base.
 C The sulphuric acid acts as a dehydrating agent.
 D Addition of H_2O will reduce the NO_2^+ concentration.
 E HNO_3 and NO_2^+ are a conjugate acid-base pair.

- 13 In the following graphs, $[X]$ is the concentration of a particular reactant X at various times t for five different reactions A, B, C, D and E. Which one of these reactions is first order with respect to this reactant (all other reactants may be assumed to be present in a large excess)?



- 14 Which one of the following groups contains a basic, an acidic and an amphoteric oxide?

- | | | | |
|---|---------------------------|-------------------------|---------------------------|
| A | Na_2O | MgO | Al_2O_3 |
| B | P_4O_{10} | SO_3 | Cl_2O |
| C | Al_2O_3 | SiO_2 | P_4O_{10} |
| D | Na_2O | MgO | SO_3 |
| E | MgO | Al_2O_3 | Cl_2O |

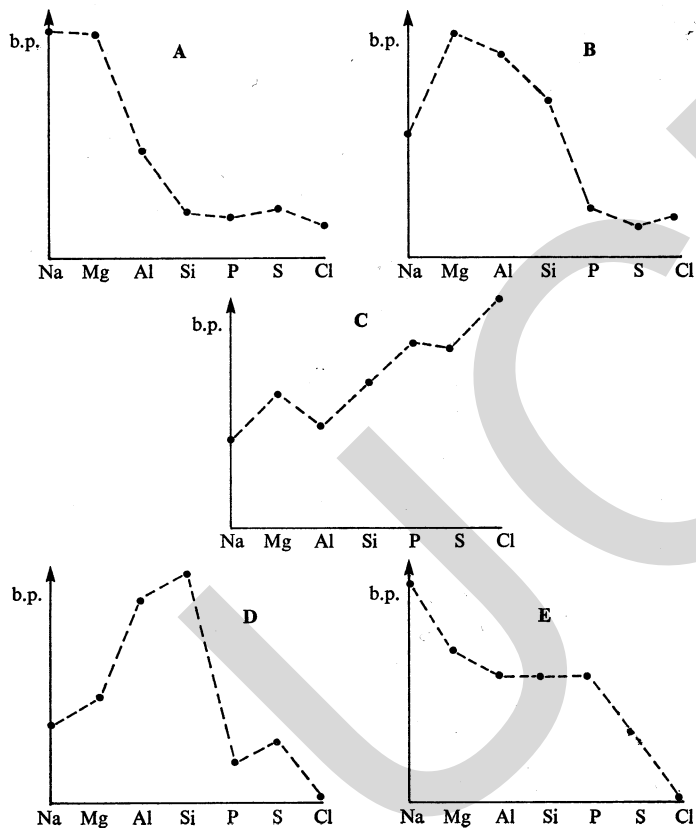
15 Consider the data in the table below.

substance	standard enthalpy change (heat) of combustion/kJ mol ⁻¹
hydrogen (g)	-300
carbon (s)	-400
benzene (l)	-3350

What is the standard enthalpy change of formation of liquid benzene calculated to be?

- A -4050 kJ mol⁻¹
 B -850 kJ mol⁻¹
 C -50 kJ mol⁻¹
 D +50 kJ mol⁻¹
 E +1250 kJ mol⁻¹

16 Which graph below best represents the variation in the boiling points of the elements sodium to chlorine?



17 The fact that BaSO₄ is precipitated immediately solutions of barium chloride and sodium sulphate are mixed indicates that

- A Ba(OH)₂ is a very weak base.
 B BaSO₄ forms a predominantly covalent molecule.
 C BaSO₄ is strongly hydrated.
 D BaSO₄ has a very high solubility product.
 E free Ba²⁺(aq) and SO₄²⁻(aq) most probably exist in the initial solutions.

18 A piece of aluminium foil is treated with aqueous mercury(II) chloride in order to expose a clean metal surface. The foil is washed and then left to stand in water. Bubbles of gas are evolved.

What do the final products include?

- A aluminium oxide and chlorine
 B aluminium chloride and hydrogen
 C aluminium hydroxide and hydrogen
 D aluminium hydroxide and oxygen
 E aluminium hydride and oxygen

19 Which one of the following properties of the elements of Group IV of the Periodic Table shows a decrease with increasing relative atomic mass?

- A first ionisation energy
 B the basic character of the oxides
 C the ionic character of the compounds
 D the stability of the +2 oxidation state
 E the ease of hydrolysis of the tetrahalides

20 What changes in oxidation number take place when copper reacts with concentrated nitric acid to give a blue solution and a brown, acidic gas?

	change in oxidation number copper	nitrogen
A	1	1
B	1	2
C	2	1
D	2	2
E	2	3

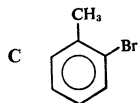
21 Which one of the following statements is most likely to be true for astatine, the element below iodine in Group VII of the Periodic Table?

- A Potassium astatide and hot dilute sulphuric acid react to form white fumes of hydrogen astatide.
 B Astatine and aqueous potassium chloride react to form aqueous potassium astatide and chlorine.
 C Sodium astatide and hot concentrated sulphuric acid react to form astatine.
 D Silver astatide and dilute aqueous ammonia react to form a solution of a soluble complex.
 E Astatine is a coloured liquid at s.t.p.

- 22 The dark blue colour of the solution formed when an excess of ammonia is added to a solution of copper(II) sulphate is due to the presence of the ion
- A $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$
 B $[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$
 C $[\text{Cu}(\text{NH}_3)_5(\text{H}_2\text{O})]^{1+}$
 D $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
 E $[\text{Cu}(\text{OH})_4(\text{H}_2\text{O})_2]^{2-}$

- 23 Which one of the following structures will have *cis-trans* isomers?

- A $\text{CH}_3\text{BrC}=\text{CCl}_2$
 B $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$

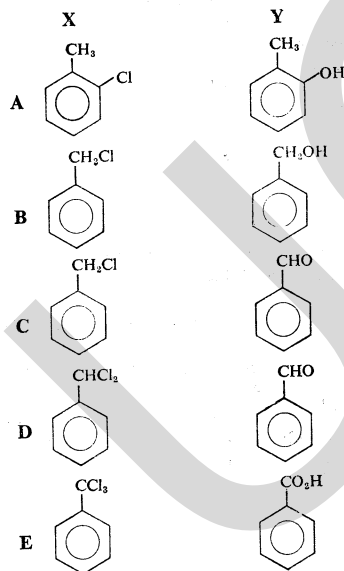


- D $\text{CH}_2=\text{C}(\text{CH}_3)_2$
 E $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{H}$

- 24 The reaction of bromine with ethene is an example of

- A free-radical addition.
 B electrophilic substitution.
 C electrophilic addition.
 D nucleophilic substitution.
 E nucleophilic addition.

- 25 Chlorine is passed into boiling methylbenzene in the absence of a halogen carrier. The product X of this reaction gives on hydrolysis a compound Y, which gives a precipitate with 2,4-dinitrophenylhydrazine. What are X and Y likely to be?



- 26 Which one of the following substances may be used to oxidise ethene to ethane-1,2-diol in high yield?

- A copper(II) oxide
 B hydrogen peroxide, catalysed by manganese(IV) oxide
 C cold aqueous alkaline potassium manganate(VII)
 D Fehling's solution (alkaline copper(II) sulphate solution)
 E potassium dichromate(VI) and concentrated sulphuric acid

- 27 Which one of the following is the correct order for the ease of hydrolysis (under identical conditions) for chlorobenzene, chloroethane and ethanoyl chloride?

	<i>most readily hydrolysed</i> →	← <i>least readily hydrolysed</i>
A	chlorobenzene	chloroethane
B	chloroethane	chlorobenzene
C	chloroethane	ethanoyl chloride
D	ethanoyl chloride	chlorobenzene
E	ethanoyl chloride	chloroethane

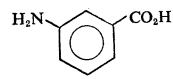
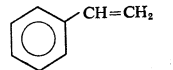
- 28 Which one of the following statements is true for $\text{HOCH}_2\text{CO}_2\text{H}$ and for $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$?

- A Both are insoluble in water.
 B Both react with aqueous sodium hydroxide.
 C Both react with 2,4-dinitrophenylhydrazine.
 D Both form zwitterions.
 E Both are obtained by the hydrolysis of proteins.

- 29 Which one of the following compounds will react with its own oxidation product (an oxidation which involves no loss of carbon) to give a sweet-smelling liquid?

- A propanal
 B propanoic acid
 C propan-1-ol
 D propan-2-ol
 E propanone

- 30 Which one of the following compounds could be used by itself to form a condensation polymer?

- A $\text{HO}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H}$
 B $\text{HOCH}_2\text{CH}_2\text{OH}$
 C 
 D $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$
 E 

Section B

For each of the questions in this section one or more of the three numbered statements 1 to 3 may be correct. Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements which you consider to be correct). The responses A to E should be selected on the basis of

A	B	C	D	E
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct	3 only is correct

No other combination of statements is used as a correct response.

31 Which of the following observations can be made when aqueous sodium hydroxide and aqueous ammonia are each gradually added to separate portions of aqueous zinc sulphate until they are present in excess?

- 1 A white precipitate is formed initially in both experiments.
- 2 A colourless solution is obtained with an excess of aqueous sodium hydroxide.
- 3 A colourless solution is obtained with an excess of aqueous ammonia.

32 The bonding in an ionic compound will show more covalent character if

- 1 the radius of the cation is large rather than small.
- 2 the radius of the anion is large rather than small.
- 3 the charge on the cation is large rather than small.

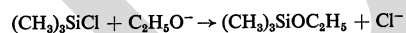
33 Which of the following statements about the properties of graphite are correct?

- 1 Graphite can be used as a lubricant.
- 2 Graphite is a good conductor of electricity in the direction parallel to the planes containing hexagonal rings of carbon but a poor conductor perpendicular to these planes.
- 3 Carbon-to-carbon distances between the planes of hexagonal rings are greater than carbon-to-carbon distances within those planes.

34 The solubility of calcium hydroxide in water is lowered by the addition of

- 1 sodium hydroxide.
- 2 calcium chloride.
- 3 barium sulphate.

35 For the reaction



which of the following statements are likely to be true?

- 1 It involves nucleophilic attack by $\text{C}_2\text{H}_5\text{O}^-$.
- 2 Cl^- is displaced by $\text{C}_2\text{H}_5\text{O}^-$.
- 3 The oxygen-carbon bond is not broken.

A	B	C	D	E
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct	3 only is correct

No other combination of statements is used as a correct response.

36 When a mixture of two gases is sparked, an explosion occurs. Which of the following mixtures would show this behaviour?

- 1 H_2 and O_2
- 2 H_2 and Cl_2
- 3 H_2 and N_2

37 The equilibrium yield of sulphur(VI) oxide by the oxidation of sulphur dioxide in the Contact process is increased by

- 1 lowering the total pressure.
- 2 raising the temperature.
- 3 increasing the partial pressure of air.

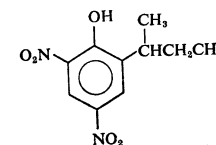
38 A compound of general formula $\text{C}_n\text{H}_{2n}\text{O}_2$ could

- 1 contain two carbonyl groups.
- 2 be an acid.
- 3 be an ester.

39 Which of the following statements about phosphorus compounds are correct?

- 1 The gaseous hydride, PH_3 , is weakly basic.
- 2 The chloride, PCl_3 , is readily hydrolysed by water.
- 3 An acidic oxide has the empirical formula P_2O_5 .

40 Binapacryl is used as a fungicide.



From an examination of its structure shown above, it can be deduced that

- 1 its aqueous solution will be acidic.
- 2 it cannot exist in optically active forms.
- 3 it will react with ethanol in the presence of concentrated sulphuric acid to give an ester.

CHEMISTRY

9250/4

(ADVANCED LEVEL)

PRACTICAL TEST

(ALTERNATIVE A)

(Three and a quarter hours)

Answer all questions.

Record your answers on this question paper in the places indicated.

For your calculations you may wish to use the following relative atomic masses:

Fe, 55.8; Zn, 65.4

Mathematical tables are available. Data Booklets are **not** to be used.

You will not be allowed to start work with the apparatus for the first fifteen minutes.

In this paper, relative atomic mass may be read as atomic weight,

relative molecular mass as molecular weight,

sulphuric acid as sulphuric(VI) acid.

- 1 Copper(II) ions in aqueous solution react with a substance X to form a complex ion. You are required to determine how many moles of copper(II) ions react with one mole of X to form this complex.

FA 1 is an aqueous solution of copper(II) ions.

SUMMER 1984

FA 2 is 0.100 mol dm⁻³ aqueous sodium thiosulphate.Using a burette, place between 22.0 and 24.0 cm³ of FA 1 into a 250 cm³ volumetric flask and make up to the mark with distilled water. Shake this solution and label it FA 3.

Dilution of FA 1

Final burette reading/cm ³	
Initial burette reading/cm ³	
Volume of FA 1/cm ³	

[2 marks]

Pipette 25.0 cm³ of FA 3 into a conical flask, add about 10 cm³ of aqueous potassium iodide and titrate the iodine produced against FA 2. Add starch indicator near the end-point, that is when the brown colour has almost disappeared. The end point is reached when the dark blue colour (formed with the starch indicator) just disappears. Repeat the titration as many times as you think necessary to obtain accurate results.

Results

Burette readings

	Rough	Accurate	
Titration number		1	
Final reading/cm ³			
Initial reading/cm ³			
Volume of FA 2 /cm ³			

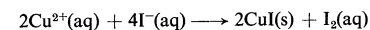
[10 marks]

Summary

..... cm³ of FA 3 required cm³ of FA 2. Indicate clearly how you obtained this value of the volume of FA 2 from your results.

[2 marks]

- (a) Copper(II) ions react with iodide ions according to the following equation.



Thiosulphate ions react with iodine according to the following equation.



Calculate the number of moles of copper(II) ions in 25.0 cm³ of FA 3.

[2 marks]

Pipette 25.0 cm³ of FA 3 into a conical flask and then, using a second pipette, add 25.0 cm³ of FA 4. FA 4 contains 0.090 mol dm⁻³ of substance X.

Add about 10 cm³ of aqueous potassium iodide to the flask which now contains the complex ion together with unreacted copper(II) ions. Titrate the iodine produced as before, using starch as indicator.

Note. This titre should be considerably less than in the previous titration. Repeat the titration as many times as you think necessary to obtain accurate results.

Results

Burette readings

	Rough	Accurate	
Titration number		1	
Final reading/cm ³			
Initial reading/cm ³			
Volume of FA 2 /cm ³			

[10 marks]

Summary

..... cm³ of FA 3, after treatment with X, required cm³ of FA 2.
Indicate clearly how you obtained this value for the volume of FA 2 from your results.

[2 marks]

- (b) Calculate the number of moles of copper(II) ions which remained in the flask after addition of X to 25.0 cm³ of FA 3.

[2 marks]

- (c) Calculate the number of moles of X contained in 25.0 cm³ of FA 4.

[1 mark]

- (d) Calculate the number of moles of copper(II) ions which react with one mole of X.

[2 marks]

- 2 You are required to obtain values for the enthalpy changes associated with several chemical reactions. Assume throughout this question that the aqueous copper(II) ions in FA 1 have a concentration of 1.0 mol dm⁻³.

Place 30 cm³ of FA 1 into the plastic cup provided. Note the temperature of this solution and, using a measuring cylinder, add 30 cm³ of 2.0 mol dm⁻³ aqueous sodium hydroxide. Stir the mixture with the thermometer and note the highest temperature reached.

Results

Final temperature/ °C	
Initial temperature/ °C	
Temperature rise/ °C	

[4 marks]

- (a) How many moles of copper(II) ions were placed in the plastic cup?

[1 mark]

- (b) How many moles of sodium hydroxide were added to the cup?

[1 mark]

- (c) Write an equation for the reaction which took place.

[1 mark]

- (d) If 4.5 J are required to raise the temperature of 1 cm³ of solution by 1 °C, calculate the enthalpy change for the reaction given in (c).

[3 marks]

Rinse out the plastic cup, place 25 cm³ of FA 1 into it and add 25 cm³ of water using a measuring cylinder. Note the temperature of this mixture and then pour in all the iron filings from the container labelled FA 5. Stir with the thermometer and note the highest temperature reached.

Results

Final temperature/ °C	
Initial temperature/ °C	
Temperature rise/ °C	

[4 marks]

(e) How many moles of copper(II) ions were placed in the plastic cup?

[1 mark]

(f) Assuming that you were supplied with 6 g of FA 5, calculate the number of moles of iron added to the cup.

[1 mark]

(g) Write an equation for the reaction which took place.

[1 mark]

(h) If 4.5 J are required to raise the temperature of 1 cm³ of solution by 1 °C, calculate the enthalpy change for the reaction given in (g).

[3 marks]

Rinse out the plastic cup once more and place 50 cm³ of FA 1 into it. Weigh the tube of zinc powder provided, FA 6, note the temperature of the liquid in the cup and then add the zinc to the solution of copper(II) ions. Stir with the thermometer and note the highest temperature reached. Reweigh the tube which contained FA 6 to determine the mass of zinc used.

Results

Final temperature/ °C	
Initial temperature/ °C	
Temperature rise/ °C	

Mass of tube and zinc provided/ g	
Mass of tube after using zinc/ g	
Mass of zinc used in experiment/ g	

[6 marks]

(i) How many moles of copper(II) ions were placed in the plastic cup?

[1 mark]

(j) How many moles of zinc were added to the cup?

[1 mark]

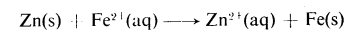
(k) Write an equation for the reaction which took place.

[1 mark]

(l) If 4.5 J are required to raise the temperature of 1 cm³ of solution by 1 °C, calculate the enthalpy change for the reaction given in (k).

[3 marks]

(m) Use the values of enthalpy changes calculated above to evaluate the enthalpy change occurring in the following reaction:



[2 marks]

- 3 Carry out the following experiments with the solids **FA 7** and **FA 8**. In all tests, the reagent should be added gradually until no further change is observed. Record your observations and the deductions you make from them in the spaces provided. Deduce what you can about the anions in **FA 7** and the cations in **FA 8**. Observations should include details of colour changes, precipitates, and tests on gases evolved, and you should indicate clearly at which stage in a test a change occurs.

<i>Test</i>	<i>Observation [4 marks]</i>	<i>Deduction [3 marks]</i>
Tests on FA 7 (a) Dissolve a small amount of FA 7 in dilute hydrochloric acid and add aqueous barium chloride.		
(b) Carefully , add concentrated sulphuric acid to a small quantity of FA 7 .		

<i>Test</i>	<i>Observation [3 marks]</i>	<i>Deduction [3 marks]</i>
(c) Dissolve FA 7 in aqueous sodium hydroxide. Warm the mixture and retain it for test (d).		
(d) Cool the mixture from (c) and add a little aluminium powder (or Devarda's alloy). Warm carefully.		
(e) Dissolve FA 7 in dilute sulphuric acid and add aqueous chlorine (or aqueous sodium chlorate(I)). Add the organic solvent provided and shake the mixture.		

Test	Observation [2 marks]	Deduction [2 marks]
(f) Dissolve FA 7 in dilute nitric acid and add aqueous lead(II) nitrate. Heat the mixture and then cool under a tap.		

Anions present are

By considering the appearance of FA 7 together with results of the above tests, suggest a possible cation which could be present

[2 marks]

Test	Observation [4 marks]	Deduction [3 marks]
Tests on FA 8 (g) Describe the appearance of FA 8.		
(h) Warm FA 8 with dilute nitric acid. Cool, filter off any undissolved solid and use the filtrate for tests (i) to (iv).		
(i) Add aqueous sodium hydroxide.		
(ii) Add aqueous ammonia. Filter and acidify the filtrate with dilute sulphuric acid.		

<i>Test</i>	<i>Observation [3 marks]</i>	<i>Deduction [3 marks]</i>
(iii) Add dilute sulphuric acid. Filter and add aqueous sodium hydroxide to the filtrate.		
(iv) Add aqueous potassium iodide. Warm and then cool under a tap.		

The cations in FA 8 are.....

[1 mark]