[0500/482] 1993

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER

Thursday, 13th May—1.30 p.m. to 3.10 p.m.

Dalziel High School

Chemistry Department

1993 CSYS

UCP 0500/482 6/5326

1. Which of the following contains approximately 6×10^{23} molecules?

A 16 g oxygen

B 40 g neon

C 58·5 g sodium chloride

D 160 g bromine

2. Which of the following molecules is non-planar?

A H_2O

B C_2H_4

C C_2H_2

D NH_3

3. A mixture of 1 volume of methane and 3 volumes of oxygen is sparked in a closed tube. The equation for the reaction occurring is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

What is the molar composition of the gas mixture at 110 °C after the reaction?

	Methane	Oxygen	Carbon dioxide	Steam
A	0	1	1	0
B	0	1	1	2
C	0	2	2	1
D	0	0	1	2

4. The atomic emission spectrum of hydrogen

A provides information about the bond vibrations in the hydrogen molecule

B consists of several series of lines, each series converging to a limit at the low frequency end

C provides information about the radiation emitted by excited electrons when they gain energy

D consists of several series of lines, each series converging to a limit at the high frequency end.

5. Which of the following represents the first ionisation energy for bromine?

A $\frac{1}{2}Br_2(\ell) \rightarrow Br^+(g) + e^-$

B $Br(g) \rightarrow Br^+(g) + e^-$

C $\frac{1}{2}Br_2(g) \rightarrow Br^+(g) + e^-$

D $Br(g) + e^- \rightarrow Br^-(g)$

6. The energy associated with electromagnetic radiation is directly proportional to the

A velocity of the radiation

B wavelength of the radiation

C reciprocal of the velocity of the radiation

D reciprocal of the wavelength of the radiation.

7. In which of the following does Y represent the mean bond dissociation enthalpy for (O—H) in water?

A $H_2O(g) \rightarrow O(g) + H_2(g)$ $\Delta H = 2 \times Y$

B $H_2O(g) \rightarrow O(g) + 2H(g)$ $\Delta H = Y$

C $H_2O(g) \rightarrow O(g) + H_2(g)$ $\Delta H = Y$

D $H_2O(g) \rightarrow O(g) + 2H(g)$ $\Delta H = 2 \times Y$

8. What is the concentration of hydrogen ions, in $mol\,l^{-1}$, of a solution of pH = 14?

A 0

B 10^{-14}

C 14

D 10^{14}

9. In which of the following does the bonding have most ionic character?

A Ammonia

B Sodium hydride

C Silicon hydride

D Hydrogen fluoride

[Turn over

10. The units for K_c for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \text{ are}$$

A $\quad mol\ l^{-1}$

B $\quad mol\ l^{-2}$

C $\quad$ non-existent

D $\quad mol^{-2}\ l^2$

11. In which of the following will an increase in pressure lead to an increase in concentration of the product(s)?

A $\quad H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

B $\quad 2N_2O_5(g) \rightleftharpoons 2N_2O_4(g) + O_2(g)$

C $\quad 2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

D $\quad N_2O_4(g) \rightleftharpoons 2NO_2(g)$

12. $25\ cm^3$ of sodium hydroxide solution require $30\ cm^3$ sulphuric acid ($1\ mol\ l^{-1}$) for complete neutralisation. The number of moles of sodium hydroxide neutralised are

A $\quad$ 0·03

B $\quad$ 0·06

C $\quad$ 1·20

D $\quad$ 2·40.

13. Which of the following indicators would you use in the titration of aqueous potassium hydroxide solution with aqueous ethanoic acid solution?

A $\quad$ Phenolphthalein, pH range 8·3–10·0

B $\quad$ Bromothymol blue, pH range 6·0–7·6

C $\quad$ Methyl red, pH range 4·2–6·3

D $\quad$ Methyl orange, pH range 3·1–4·4

14. A solution is made by mixing $100\ cm^3$ CH_3COOH ($0{\cdot}1\ mol\ l^{-1}$) and $100\ cm^3$ CH_3COONa ($0{\cdot}1\ mol\ l^{-1}$).

What will be the effect of diluting this mixture with $50\ cm^3$ water?

A $\quad$ The concentration and pH will decrease significantly.

B $\quad$ The concentration will decrease and the pH will increase significantly.

C $\quad$ The concentration will decrease but the pH will remain fairly constant.

D $\quad$ The concentration and pH will remain fairly constant.

15. Which of the following statements about the benzene molecule is **not** true?

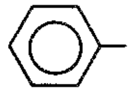
A $\quad$ It is planar.

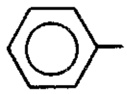
B $\quad$ It is susceptible to attack by electrophilic reagents.

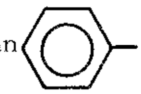
C $\quad$ The C—C bonds are equal in length.

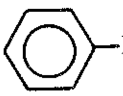
D $\quad$ It is readily attacked by bromine.

16. Which of the following is correct?

A $\quad CH_3OH$ is a stronger acid than —OH

B $\quad$ $-NH_2$ is a stronger base than CH_3NH_2

C $\quad CH_3COOH$ is a stronger acid than —OH

D $\quad C_2H_5OH$ is a stronger base than $-NH_2$

17. Which of the following will give rise to a secondary alcohol on hydrolysis?

A $\quad CH_3CH(CH_3)-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

B $\quad CH_3CH(CH_3)CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

C $\quad CH_3C(CH_3)_2-O-\overset{\displaystyle O}{\overset{\|}{C}}H$

D $\quad CH_3-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH(CH_3)CH_3$

18. A substance has a molecular formula C_7H_8O. It is slightly soluble in water, but very soluble in sodium hydroxide solution. It gives no vigorous reaction with sodium carbonate solution. Which of the following functional groups is most likely to be present in this compound?

A $\quad$ Carboxylic

B $\quad$ Phenolic

C $\quad$ Ketonic

D $\quad$ Aldehydic

19. An alcohol did not react with acidified dichromate solution, but gave an alkene when dehydrated with hot concentrated sulphuric acid. This alkene reacted with bromine water to form 1,2-dibromo-2-methylpropane.

Which of the following could have been the alcohol concerned?

A $CH_3-\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}H}-CH_2OH$

B $CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3$

C $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$

D $CH_3-\underset{\underset{\displaystyle C_2H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$

20. Which of the following compounds would liberate one mole of hydrogen gas if one mole of it reacts with two moles of sodium?

A C_2H_5OH

B CH_2OHCH_2OH

C CH_3COOH

D CH_3CHO

21. Which of the following can behave as an electrophile?

A $C_2H_5NH_2$

B HS^-

C NH_3

D NO_2^+

22. For the reaction $A + B \rightarrow C$, the following data were obtained.

Experiment	Initial concentration of A/mol l^{-1}	Initial concentration of B/mol l^{-1}	Initial rate of formation of C/mol l^{-1} s^{-1}
1	0·050	0·050	0·015
2	0·050	0·100	0·060
3	0·100	0·100	0·060

The rate law for this reaction is

A rate = $k[A]^2$

B rate = $k[A][B]$

C rate = $k[B]^2$

D rate = $k[A][B]^2$

23. The reaction $A + 2B \rightarrow C$ has a rate law of the form

$$\text{Rate} = k[A][B]$$

If the reaction proceeds by a two step process, then the rate determining step might be

A $A + B \rightarrow$ intermediate

B $B + B \rightarrow$ intermediate

C $A + B \rightarrow C$

D $B + AB \rightarrow C$

24. The rate law for the reaction

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$

can be expressed as either

Rate of production of $N_2 = k'[H_2][NO]^2$ or

Rate of production of $H_2O = k''[H_2][NO]^2$

Which of the following is true?

A $k' = k''$

B $k' = 2k''$

C $k'' = 2k'$

D The order of the reaction is 4.

[Turn over

25. The equilibrium constant for a reaction at 298 K is $> 10^6$.

Which of the following statements about the reaction is true?

A The activation energy for the forward reaction must be very small.

B ΔH° for the forward reaction must be negative.

C ΔG° for the forward reaction must be negative.

D ΔG° for the forward reaction must be positive.

26. Which of the following is **not** a redox reaction?

A $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

B $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2$

C $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

D $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

27. Which of the following statements best explains the fact that SiH_4 has a higher boiling point than CH_4?

(You may wish to consult the Data Booklet.)

A Si—H bonds are stronger than C—H bonds.

B There is stronger hydrogen bonding between SiH_4 molecules than between CH_4 molecules.

C SiH_4 has a higher molecular weight than CH_4.

D Methane exists as a gas at room temperature.

28. Which of the following statements regarding a chemical system in equilibrium is **never** true?

A The forward reaction and the reverse reaction have both stopped.

B The concentrations of the reactants are greater than the concentrations of the products.

C The rate of the forward reaction is equal to the rate of the reverse reaction.

D The concentrations of the reactants are less than the concentrations of the products.

29. Assuming the symbol [Ar] indicates complete filling of electron shells up to and including argon, the electron configuration of Mn^{2+} is

A [Ar] $3d^5$

B [Ar] $3d^5\ 4s^2$

C [Ar] $3d^3\ 4s^2$

D [Ar] $3d^4\ 4s^1$

30. Which of the following ions contains d-electrons?

A Ca^{2+}

B V^{3+}

C Sc^{3+}

D Ti^{4+}

The processes in questions **31, 32** and **33** may be placed in **one** of the following categories. A category may be used once, more than once, or not at all.

A ΔH positive, ΔS positive

B ΔH positive, ΔS negative

C ΔH negative, ΔS positive

D ΔH negative, ΔS negative

31. The condensation of water vapour.

32. The melting of ice.

33. The burning of liquid petrol.

34. In the electrochemical cell

$$Cr(s)/Cr^{3+}(aq)//Ag^+(aq)/Ag(s)$$

operating under standard conditions, which of the following is **not** true? (Refer to page 13 of the Data Booklet.)

A Oxidation takes place at the chromium electrode.

B The silver electrode decreases in mass.

C The potential difference is 1·54 V.

D Electrons flow from chromium to silver in the external circuit.

35. $Fe(III)[Fe(III)(CN)_6] \rightleftharpoons KFe(II)[Fe(III)(CN)_6] \rightleftharpoons K_2Fe(II)[Fe(II)(CN)_6]$

Berlin Green — Prussian Blue — Everitt's Salt

To form Prussian Blue, it would be necessary to

A oxidise Berlin Green and oxidise Everitt's Salt

B oxidise Berlin Green and reduce Everitt's Salt

C reduce Berlin Green and reduce Everitt's Salt

D reduce Berlin Green and oxidise Everitt's Salt.

36. Which of the following will increase the equilibrium constant for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

given that ΔH, left to right, is positive?

A Use of a catalyst

B Increase of pressure

C Increase of temperature

D Decrease of temperature

37. Which of the following statements is **not** likely to be true of a transition element M?

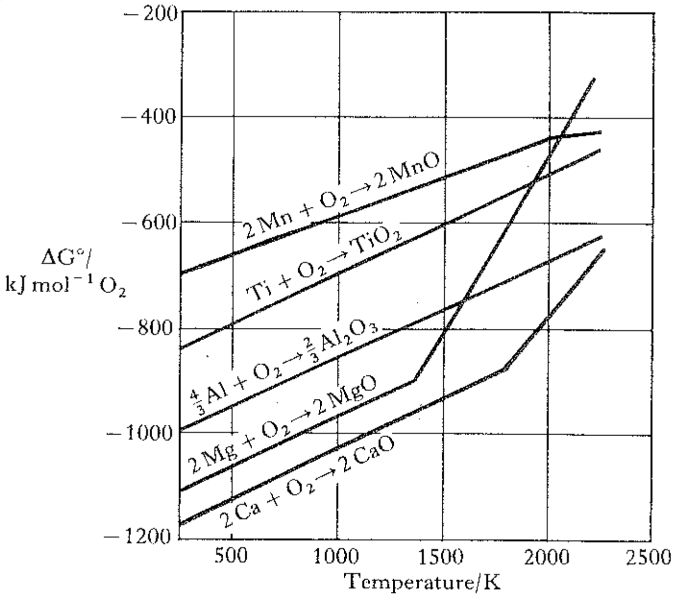
A It has a fixed valency.

B It forms a stable ion M^{2+}.

C It forms coloured compounds.

D Its atoms contain partly filled d-orbitals.

38.



The reduction of Al_2O_3 to Al is thermodynamically feasible at 2000 K using

A calcium

B magnesium

C manganese

D titanium.

[Turn over

39. The boxes in the grid below show the names of certain chemical compounds.

A	B	C
Aluminium chloride	Sodium ethanoate	Ammonium chloride
D	E	F
Sodium chloride	Copper(II) sulphate	Potassium nitrate

(*a*) Identify the compound(s) whose aqueous solution(s) has (have) a pH of less than 7.

(*b*) If an aqueous sodium carbonate solution is added to an aqueous solution of each of the above compounds, identify which will give a precipitate.

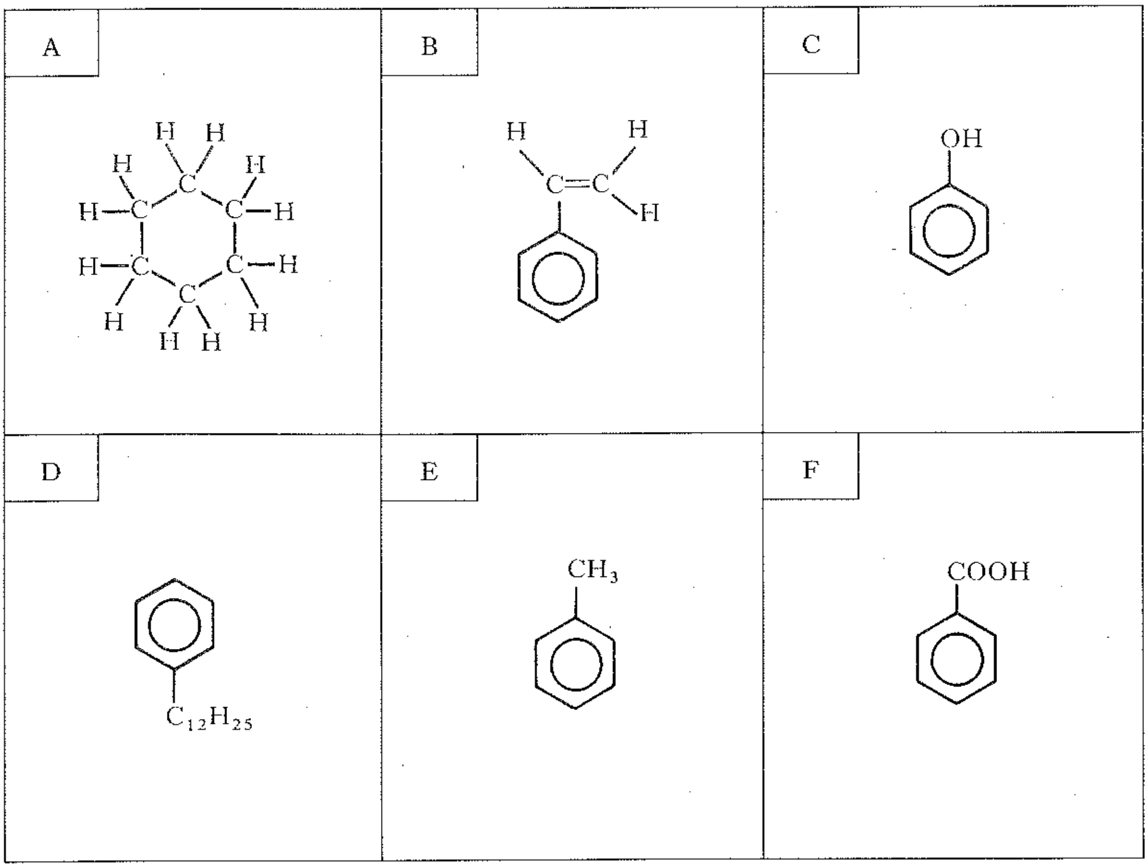
40. The boxes in the grid below show the equations for certain chemical reactions.

A	B	C
$Cl(g) + e^- \rightarrow Cl^-(g)$	$Na(g) \rightarrow Na^+(g) + e^-$	$Na(s) \rightarrow Na(g)$
D	E	F
$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow Na^+Cl^-(s)$	$Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s)$	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$

Identify the endothermic reaction(s).

[Turn over

41. The boxes in the grid below show the formulae of organic compounds used in industry.



Identify, in each case, a compound used to manufacture (by the shortest route)

(*a*) explosives

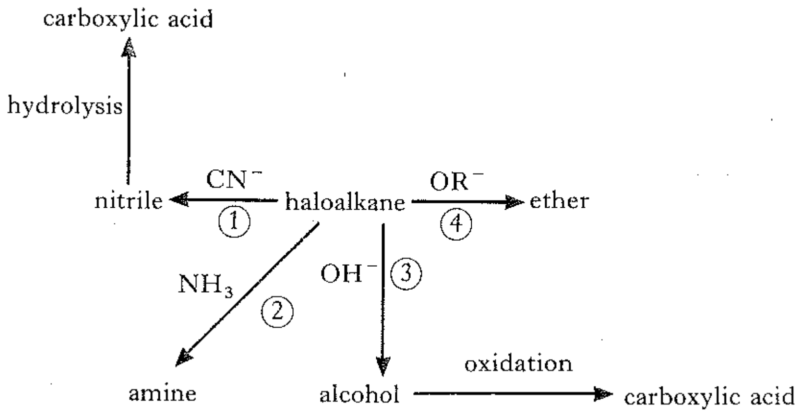
(*b*) a thermosetting plastic

(*c*) an ionic soapless detergent

(*d*) an addition polymer.

Marks

1. Haloalkanes are extremely versatile organic compounds, and are widely used in syntheses and preparations as indicated in the following flow diagram.



R = alkyl group

(*a*) Name the type of reaction involved in reactions 1 to 4. **1**

(*b*) Why can haloalkanes take part in the type of reaction in (*a*)? **1**

(*c*) How is the reagent OR^- obtained from an alcohol? **1**

(*d*) 1-bromopropane was used as the starting material for the preparation of carboxylic acids. Name the carboxylic acid formed

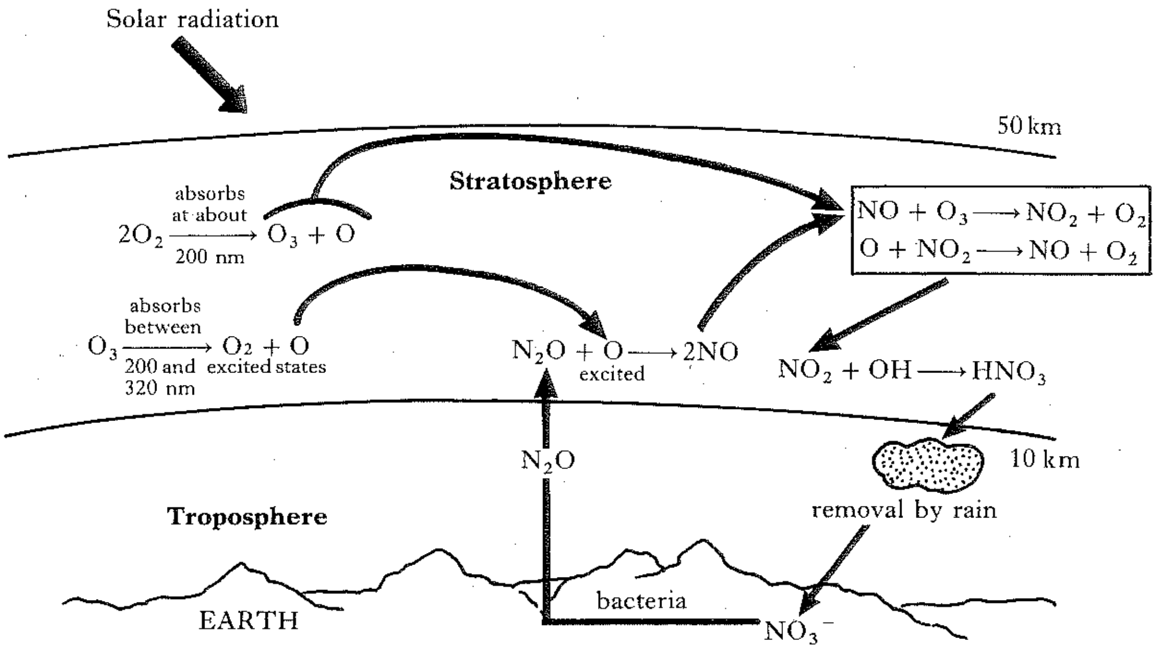
(i) via route 1,

(ii) via route 3. **2**

(5)

2. Use the data on page 14 of the Data Booklet to calculate the pH of a solution of propanoic acid of concentration $10^{-1}\,mol\,l^{-1}$. **(3)**

3.



Marks

Examine the diagram above, which shows the main natural processes affecting ozone in the stratosphere, and answer the questions below.

(*a*) How does the ozone in the stratosphere act as an essential filter for solar radiation? **1**

(*b*) The production of nitric oxide (nitrogen monoxide), NO, from nitrous oxide (dinitrogen monoxide), N_2O, in the lower stratosphere requires reaction with an oxygen atom in an excited state.

What is meant by an "excited state"? **1**

(*c*) Why is the nitric oxide regarded as a catalyst in the destruction of the ozone layer? **2**

(*d*) Why would the presence of large numbers of aircraft flying in the stratosphere be a threat to the ozone layer? **1**

(5)

[Turn over

Marks

4. Solid magnesium chloride exists in two forms—

anhydrous($MgCl_2$) and hydrated($MgCl_2 . 6H_2O$).

(*a*) Calculate the enthalpy change for the process

$$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

given the following data:

$$Mg^{2+}(g) \rightarrow Mg^{2+}(aq) \quad \Delta H = -1920\,kJ\,mol^{-1}$$

$$Cl^-(g) \rightarrow Cl^-(aq) \quad \Delta H = -364\,kJ\,mol^{-1}$$

Lattice enthalpy (anhydrous magnesium chloride) = $2493\,kJ\,mol^{-1}$ 3

(*b*) Calculate the enthalpy change for converting anhydrous magnesium chloride to hydrated magnesium chloride, given the following enthalpies of formation:

ΔH_f° (hydrated magnesium chloride) $= -2500\,kJ\,mol^{-1}$

ΔH_f° (anhydrous magnesium chloride) $= -642\,kJ\,mol^{-1}$

ΔH_f° (water) $= -286\,kJ\,mol^{-1}$ 3

(6)

5. Chlorine and fluorine react to produce a compound of formula ClF_3. This molecule contains three chlorine-fluorine single bonds. Each fluorine atom contributes **one** electron to the bonding.

(*a*) How many electron pairs (both bonded and non-bonded) surround the central chlorine atom in the molecule? 1

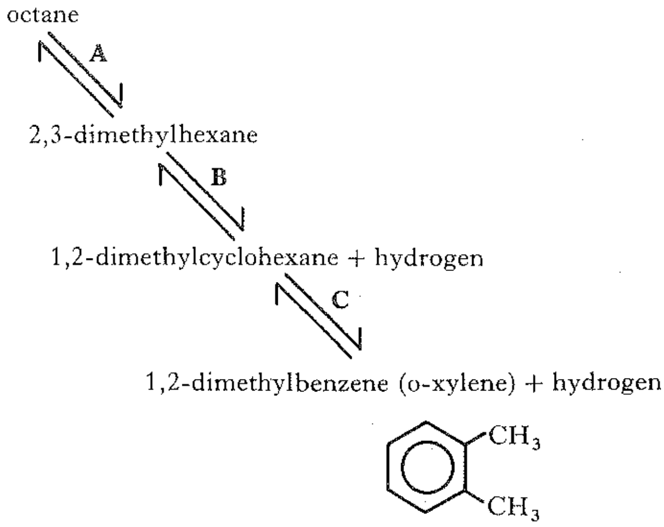
(*b*) What would be the three-dimensional arrangement of electron pairs (both bonded and non-bonded) around the chlorine atom? 1

(*c*) The fluorine atoms may occupy different positions in this shape giving rise to three possible shapes for the molecule. Draw **two** of these, showing the angles between the bonds. 2

(4)

Marks

6. In a catalytic reformer, straight chain alkanes are converted to branched chains, cycloalkanes and aromatic hydrocarbons. Consider the sequence shown below.



(*a*) Use the data in the table below to calculate ΔS° for the conversion of octane to o-xylene and hydrogen at 298 K.

Compound	$S^{\circ}/JK^{-1}\,mol^{-1}$
octane	463
o-xylene	352
hydrogen	131

3

(*b*) Calculate the minimum temperature at which the conversion in (*a*) becomes thermodynamically feasible, given that $\Delta H^{\circ} = 227\,kJ\,mol^{-1}$. **3**

(*c*) Explain why the conversion in (*a*) can be achieved at or above the temperature calculated in part (*b*), despite the fact that the equilibrium constant for reaction **A** is very much less than 1 at this temperature. **1**

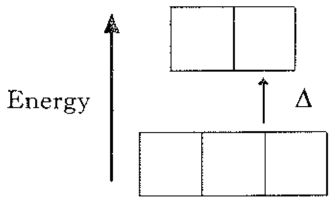
(7)

[Turn over

Marks

7. The d-orbitals in an isolated ion or atom of a transition metal are degenerate. As soon as an ion is surrounded by ligands, these orbitals are no longer degenerate but are split into two groups having different energies. In a complex ion with octahedral arrangement of ligands, $[MX_6]^n$, the relative energies of the d-orbitals are as shown below.

(M = transition metal, X = ligand, n = charge on the complex ion)



The energy difference, Δ, between the two groups of d-orbitals depends on the ligand X. The splitting ability of some ligands has been observed to be as follows.

$$H_2O < NH_3 < CN^-$$

The colour of many transition metal complex ions can be explained by electronic transitions between the two sets of d-orbitals.

(*a*) Explain why $[Fe(H_2O)_6]^{2+}$ is green. 2

(*b*) Predict the colour of $[Fe(CN)_6]^{4-}$, giving reasons for your answer. 3

Substances which are weakly attracted by a magnetic field are called paramagnetic substances. Paramagnetism is caused by the presence of unpaired electrons, as there is a small magnetic field created by a single spinning electron.

(*c*) Fe(II), which is present in both $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$, has six d-electrons. Of these two complex ions, only $[Fe(H_2O)_6]^{2+}$ is paramagnetic.

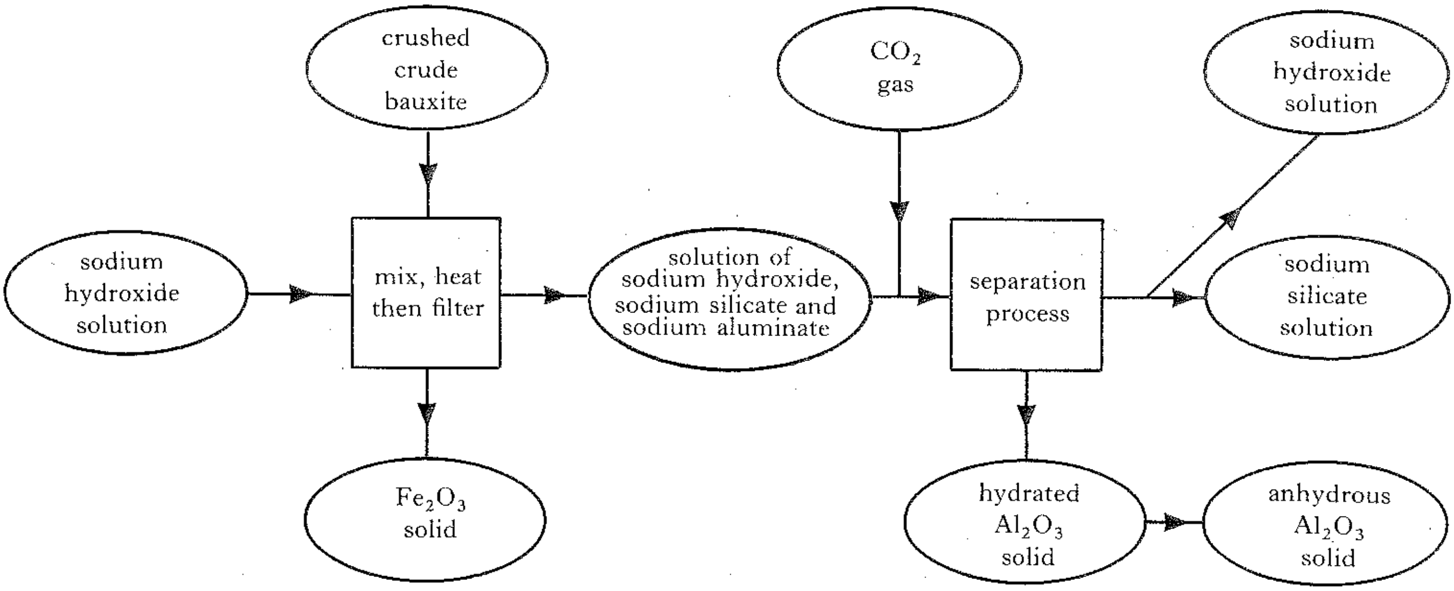
Using d-orbital diagrams, similar to the one above, show the d-electron arrangements of Fe(II) in each of these two complex ions and suggest why one complex ion is paramagnetic while the other is not. 4

(9)

8. 1·8 g of iron(II) ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 . 6H_2O$, was dissolved in 35 cm^3 of distilled water. The solution was then diluted to 50 cm^3 using dilute sulphuric acid. The final solution was titrated against potassium permanganate solution and 40 cm^3 of the permanganate solution was required to reach the end point at which all the iron(II) had been converted to iron(III).

Calculate the concentration of the potassium permanganate solution. **(4)**

9. Aluminium oxide is obtained from bauxite as shown in the flow diagram below.



Marks

(*a*) On what property of oxides does the initial separation of aluminium oxide and iron(III) oxide depend? **1**

(*b*) What role does carbon dioxide play in the overall process? **2**

(*c*) Identify the by-products of the process. **2**

(*d*) Suggest one addition to the above flow diagram which would make the process more economical. **1**

(6)

10. A company decided to produce relatively cheap platinum jewellery.

Their plan was to make plastic brooches or ear-rings which were then to be sprayed, first with silver(I) nitrate solution and then with a reducing agent. Electrolysis in a solution of a platinum(II) salt would then build up a coating of platinum on each item. The finished items were to look like solid platinum, but would be mainly plastic.

It was planned that electrolysis for 15 hours would deposit a total of 0·25 kg of platinum.

(*a*) Why was it necessary to spray the plastic items with silver(I) nitrate solution and then a reducing agent? **2**

(*b*) Suggest a suitable reducing agent. **1**

(*c*) Calculate the average current to be used in the electrolysis. **3**

(6)

11. The following is an extract from *Opportunities in Chemistry* – often referred to as the Pimentel Report, published in America by the National Academy Press in 1985.

"Since the 1960s, we've known that high levels of cholesterol correlate with heart ailments, the major cause of death in the United States. What we need is a Pac-Man to chomp up the cholesterol in the blood and reduce "hardening" of the arteries that carry blood from the heart (atherosclerosis). Now a lowly fungus – not unlike the famous mould, penicillium – may have shown us one.

A normally functioning human cell uses a dual system for meeting its cholesterol needs. First, the cell has its own factory to manufacture cholesterol. In addition, the cell's exterior has a number of lipoprotein receptors that can grab onto cholesterol-containing lipoproteins as they pass by in the bloodstream and pull them inside. The cell fixes the number of these Pac-Man-like receptors so that just the right amount of imported cholesterol is added to the factory-made product. If the inner cell cholesterol level falls too low, more receptors are added to extract more from the blood stream.

There's an idea! If the cell's cholesterol factory could be slowed down, would the cell produce more receptors to make up the difference from the blood stream supply? A chance to test this scenario came when a biochemist discovered that certain fungi produced something that inhibited cholesterol synthesis. Chemists joined in the plot, purified the effective compound, determined its structure, and named it COMPACTIN. Knowing its structure, chemists were able to synthesize close relatives of compactin that are even more potent. Chemical tests with these new chemicals indicate that the scheme works as planned."

Marks

Read the passage above, and answer the questions below.

(*a*) What determines the number of lipoprotein receptors on the exterior of human cells? **2**

(*b*) What is an inhibitor? **1**

(*c*) Explain how the inhibitor inside the cells reduces the level of cholesterol in the blood. **2**

(5)

12. Examine the reaction mechanism below:

$$A + B \xrightarrow{\text{fast}} C \qquad \underline{\text{step 1}}$$

$$2B + C \xrightarrow{\text{slow}} D + E \qquad \underline{\text{step 2}}$$

$$\text{Overall: } A + 3B \longrightarrow D + E$$

How would the rate of reaction depend on the concentrations of

(*a*) A and **1**

(*b*) B? **1**

(2)

Marks

13. Two aliphatic compounds A and B, which contain carbon, hydrogen and oxygen only, are isomers. They can both be oxidised as follows.

$$A \xrightarrow{\text{oxidation}} C$$

$$B \xrightarrow{\text{oxidation}} D$$

The table below shows the wavenumbers of the main absorptions in the infra red spectra caused by the functional groups in compounds A to D, between 1500 and 4000 cm^{-1} (absorptions caused by C—H bonds in alkyl components have been omitted):

Compound	Wavenumber(s)/cm^{-1}		
A	3300		
B	3350		
C		2750	1730
D			1700

In answering the following questions, you are advised to consult the data on page 15 of the Data Booklet.

(*a*) Examine the table above and identify the functional groups present in:

(i) A and B, **1**

(ii) C, **1**

(iii) D. **1**

(*b*) Describe a chemical test you could use to provide support for your answers to (ii) and (iii) of part (*a*). **3**

(*c*) Compound C will undergo further oxidation to produce compound E. Estimate the wavenumbers of the main infra red absorptions caused by the functional groups in compound E (only those between 1500 and 4000 cm^{-1}). **2**

(8)

[*END OF QUESTION PAPER*]