

X012/701

NATIONAL THURSDAY, 24 MAY
QUALIFICATIONS 9.00 AM – 11.30 AM
2001

CHEMISTRY
ADVANCED HIGHER

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet (1999 edition).

SECTION A—Part 1 Questions 1–30 and Part 2 Questions 31–33

Check that the answer sheet provided is for Chemistry Advanced Higher (Section A).

Fill in the details required on the answer sheet.

Rough working, if required, should be done only on this question paper, or on the rough working sheet provided—**not** on the answer sheet.

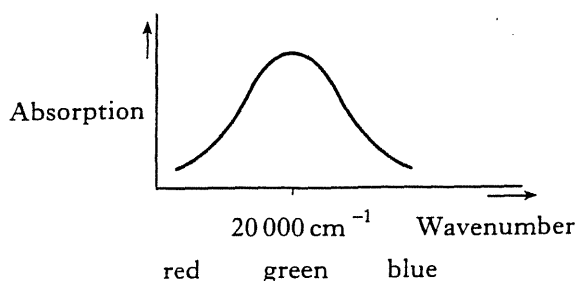
Instructions for completion of **Part 1** and **Part 2** are given on pages two and seven respectively.

SECTION B

All questions should be attempted.

1. If the wavelength of visible light from a tunable laser is increased
- the wavenumber increases
 - the velocity increases
 - the frequency increases
 - the colour changes towards red.

Questions 2 and 3 refer to the absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ below.



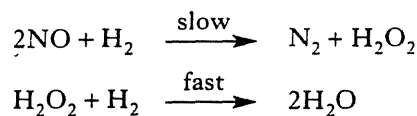
2. The colour which would be observed is
- blue
 - green
 - purple
 - yellow.
3. The colour is caused by
- electrons absorbing energy to jump from one d orbital to another d orbital
 - excited electrons dropping to the ground state
 - electrons absorbing energy to jump from the first to the second shell
 - electrons absorbing energy to jump from the second to the third shell.
4. Which of the following compounds shows most covalent character?
- CH_4
 - PH_3
 - NH_3
 - NaH

5. Manganese is in oxidation state +5 in
- MnO_4^-
 - MnO_4^{2-}
 - MnO_4^{3-}
 - $[\text{Mn}(\text{CN})_6]^{3-}$.

6. The formula $\text{C}_4\text{H}_{10}\text{O}$ could represent an alcohol ($\text{C}_4\text{H}_9\text{OH}$) or an ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$).

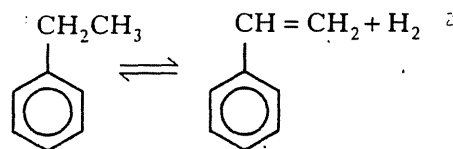
Which of the following statements would **not** be true about **both** compounds?

- They can be made by nucleophilic substitution from a halogenoalkane.
 - They have hydrogen bonds between their molecules.
 - They are used as solvents.
 - They are flammable.
7. The reaction between nitrogen monoxide (NO) and hydrogen occurs by the following mechanistic steps:



The order of this reaction will be

- 1
 - 2
 - 3
 - 4.
8. The following endothermic reaction is carried out in the gaseous state.



The conditions which most favour the forward reaction are

- high temperature and low pressure
- high temperature and high pressure
- low temperature and low pressure
- low temperature and high pressure.

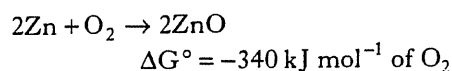
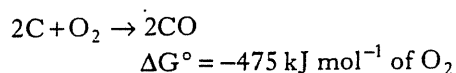
[Turn over

9. Salts having the empirical formula $\text{CrCl}_3(\text{H}_2\text{O})_6$ have been isolated in three isomeric forms. Analysis of one isomer showed one third of the total chlorine content was precipitated as silver(I) chloride by the addition of excess silver(I) nitrate solution.

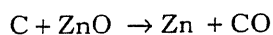
The formula of the isomer is

- A $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{Cl}^-)_3$
 B $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}(\text{Cl}^-)_2 \cdot \text{H}_2\text{O}$
 C $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+(\text{Cl}^-)_2 \cdot 2\text{H}_2\text{O}$
 D $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$

10. At 1400 K



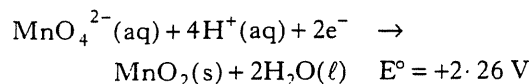
For the reaction



the standard free energy change at 1400 K is

- A $+67.5 \text{ kJ mol}^{-1}$
 B $-67.5 \text{ kJ mol}^{-1}$
 C $+135 \text{ kJ mol}^{-1}$
 D -135 kJ mol^{-1}
11. Which of the following correctly describes an atom of nickel in its ground state?
- A It has one empty d-orbital.
 B It contains 12 electrons in p-orbitals.
 C All orbitals in the 3rd shell are full.
 D It contains no unpaired electrons.

12. Given the standard reduction potential



what is the cell potential for the reaction of $\text{MnO}_4^{2-}(\text{aq})$ with $\text{SO}_3^{2-}(\text{aq})$ under standard conditions?

- A $+2.09 \text{ V}$
 B $+2.43 \text{ V}$
 C -2.09 V
 D -2.43 V

13. Some indicators and their pH ranges are shown below. Which is the most suitable indicator to use in a titration of 0.1 mol l^{-1} hydrochloric acid solution with 0.1 mol l^{-1} ammonia solution?

- A Methyl orange (4.2–6.3)
 B Bromothymol blue (6.0–7.6)
 C Phenol red (6.8–8.4)
 D Phenolphthalein (8.3–10.0)

14. $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 $\Delta H^\circ = 178 \text{ kJ mol}^{-1} \quad \Delta S^\circ = 161 \text{ JK}^{-1} \text{ mol}^{-1}$

This reaction is thermodynamically feasible

- A at any temperature
 B at all temperatures below 904 K
 C at all temperatures above 904 K
 D only at temperatures above 1106 K.

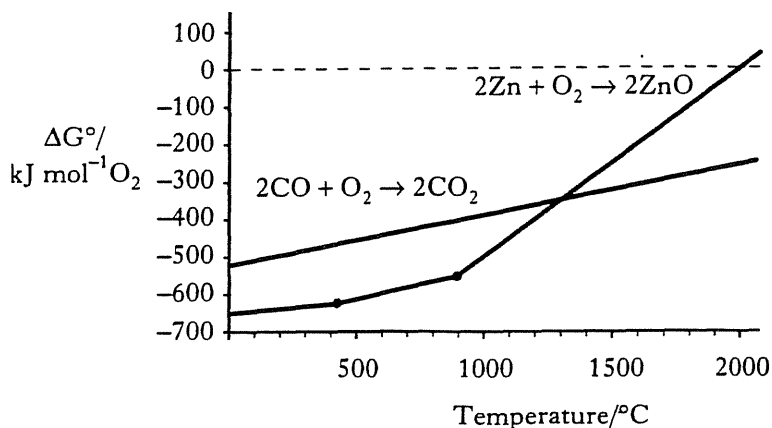
15. The conversion of benzene to monochlorobenzene using $\text{Cl}_2/\text{FeCl}_3$ involves

- A nucleophilic addition
 B nucleophilic substitution
 C electrophilic addition
 D electrophilic substitution.

16. The bond dissociation energy of HF is 569 kJ mol^{-1} . In which of the following is 569 kJ released?

- A $\text{HF}(\text{g}) \rightarrow \frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g})$
 B $\text{HF}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{F}(\text{g})$
 C $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{HF}(\text{g})$
 D $\text{H}(\text{g}) + \text{F}(\text{g}) \rightarrow \text{HF}(\text{g})$

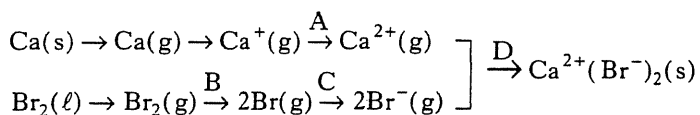
17.



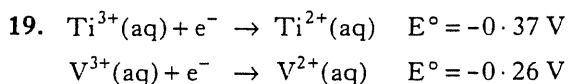
Carbon monoxide will reduce zinc oxide

- A at all temperatures below 1300 °C
 B only at a temperature of 1300 °C
 C at all temperatures above 1300 °C
 D only at temperatures above 2000 °C.

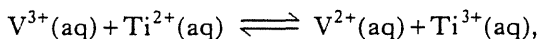
18. The diagram below shows the various energy steps involved in the formation of calcium bromide.



Which energy step labelled A, B, C or D is the most exothermic?



It can be concluded that, for the reaction

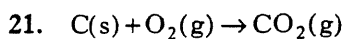


the standard free energy change and the equilibrium constant for the **forward** reaction will be

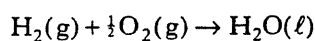
	ΔG°	K
A	negative	greater than 1
B	positive	greater than 1
C	negative	less than 1
D	positive	less than 1

20. The standard enthalpy of formation of solid calcium nitrate at 298 K is -937 kJ mol^{-1} . Which equation below correctly represents this formation process?

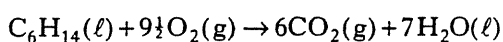
- A $\text{Ca}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{NO}_3)_2(\text{s})$
 B $\text{Ca}(\text{s}) + \text{N}_2(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{Ca}^{2+}(\text{NO}_3)_2(\text{s})$
 C $\text{Ca}(\text{g}) + \text{N}_2(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{Ca}^{2+}(\text{NO}_3)_2(\text{s})$
 D $\text{Ca}(\text{s}) + 2\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{Ca}^{2+}(\text{NO}_3)_2(\text{s})$



$$\Delta H^\circ = -394 \text{ kJ mol}^{-1}$$

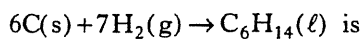


$$\Delta H^\circ = -286 \text{ kJ mol}^{-1}$$



$$\Delta H^\circ = -4160 \text{ kJ mol}^{-1}$$

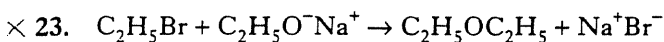
Using the above data, the standard enthalpy change for



- A $-3480 \text{ kJ mol}^{-1}$
 B $+3480 \text{ kJ mol}^{-1}$
 C -206 kJ mol^{-1}
 D $+206 \text{ kJ mol}^{-1}$.

× 22. Infra-red radiation can be used in the analysis and identification of organic compounds. Compared to visible radiation (light) infra-red radiation has a

- A shorter wavelength and higher frequency
 B longer wavelength and lower velocity
 C longer wavelength and lower frequency
 D shorter wavelength and higher velocity.



This is an example of

- A nucleophilic substitution.
 B electrophilic substitution
 C a condensation reaction
 D an addition reaction.

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24. Which of the following is most acidic?

- A Methanoic acid
- B Methanol
- C Phenol
- D Propanoic acid

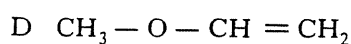
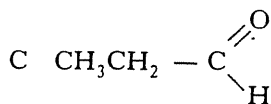
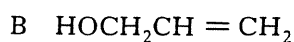
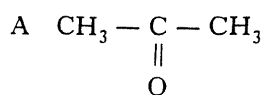
25. In the homologous series of amines, increase in chain length from CH_3NH_2 to $\text{C}_4\text{H}_9\text{NH}_2$ is accompanied by

	Volatility	Solubility in water
A	increased	increased
B	decreased	decreased
C	increased	decreased
D	decreased	increased

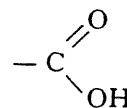
26. Which of the following can be used directly to distinguish between an aldehyde and a ketone?

- A 2, 4-Dinitrophenylhydrazine
- B Lithium aluminium hydride
- C Hydrogen cyanide
- D Ammoniacal silver(I) nitrate (Tollens' reagent)

27. Which of the following compounds is most likely to show an infra-red absorption at 2725 cm^{-1} ?

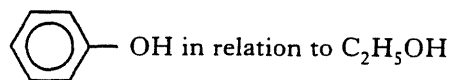


28. Select the statement which is true about the carboxyl group

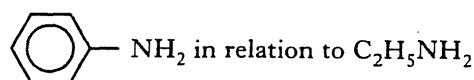


- A The $\text{C} = \text{O}$ and $-\text{OH}$ groups each retain their own properties, unaffected by the other.
- B The properties of the $\text{C} = \text{O}$ are changed but the $-\text{OH}$ is unaffected.
- C The properties of the $-\text{OH}$ are changed but the $\text{C} = \text{O}$ is unaffected.
- D The properties of the $\text{C} = \text{O}$ and the $-\text{OH}$ are each affected by the other.

29. Consider



and



The benzene ring makes

- A OH less acidic and NH_2 less basic
- B OH more acidic and NH_2 more basic
- C OH less acidic and NH_2 more basic
- D OH more acidic and NH_2 less basic.

30. Salbutamol is used to treat asthma. It behaves like the body's natural active compound by binding to receptors on the muscles of the airways. This relaxes the muscles and gives relief from breathing difficulties. Salbutamol is

- A an agonist
- B an antagonist
- C a pharmacophore
- D a receptor.

SECTION A

PART 2

In questions 31 to 33 of this part of the paper, an answer is given by circling in INK the appropriate letter (or letters) in the answer grids provided on Part 2 of the answer sheet.

In some questions, two letters are required for full marks.

If more than the correct number of answers is given, marks will be deducted.

In some cases the number of correct responses is NOT identified in the question.

This part of the paper is worth 10 marks.

SAMPLE QUESTION

A	CH ₄	B	H ₂	C	CO ₂
D	CO	E	C ₂ H ₆	F	N ₂

(a) Identify the diatomic **compound(s)**.

A	B	C
<input checked="" type="radio"/> D	E	F

The one correct answer to part (a) is D. This should be circled.

(b) Identify the **two** substances which burn to produce **both** carbon dioxide **and** water.

<input checked="" type="radio"/> A	B	C
D	<input checked="" type="radio"/> E	F

As indicated in this question, there are **two** correct answers to part (b). These are A and E.

Both answers are circled.

(c) Identify the substance(s) which can **not** be used as a fuel.

A	B	<input checked="" type="radio"/> C
D	E	<input checked="" type="radio"/> F

There are **two** correct answers to part (c). These are C and F.

Both answers are circled.

If, after you have recorded your answer, you decide that you have made an error and wish to make a change, you should cancel the original answer and circle the answer you now consider to be correct. Thus, in part (a), if you want to change an answer **D** to an answer **A**, your answer sheet would look like this:

<input checked="" type="radio"/> A	B	C
<input checked="" type="radio"/> D	E	F

If you want to change back to an answer which has already been scored out, you should enter a tick (✓) in the box of the answer of your choice, thus:

<input checked="" type="radio"/> A	B	C
✓ <input checked="" type="radio"/> D	E	F

31. The boxes in the grid below contain certain symbols used in chemistry.

A	ΔG°	B	K	C	ΔS°
D	k	E	ΔH°	F	ΔG

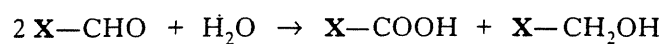
- Identify the **two** symbols which always have positive values when a solid melts.
- Identify the symbol which has a value greater or equal to one when a reaction is feasible.
- Identify the symbol which has a zero value when a chemical reaction is in a state of equilibrium.
- Identify the symbol whose usage is **not** relevant to thermodynamics.

32. The boxes in the grid below contain formulae of some compounds.

A	CO_2	B	PCl_5	C	AlCl_3
D	CuO	E	PCl_3	F	LiAlH_4

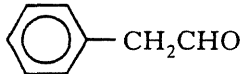
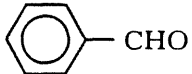
- Identify the **two** compounds which do **not** react with water to form an acidic solution.
- Identify the compound which has molecules that are trigonal bipyramidal in shape.
- Identify the compound which has linear molecules.
- Identify the compound(s) which can be used to reduce ethanal to ethanol.

- × 33. Some aldehydes can undergo the Cannizzaro reaction which can be represented by the following equation.



An aldehyde will react in this way provided that 'X' does **not** contain a $-\text{CH}_2-$ group attached to the functional group.

The boxes in the grid below contain names or formulae of certain aldehydes.

A		B		C	
			butanal		
D		E		F	
	methanal		$\text{C}_2\text{H}_5\text{CHO}$		3-methylbutanal

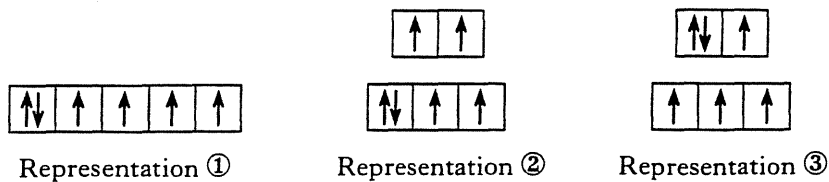
Identify the aldehyde(s) capable of undergoing the Cannizzaro reaction.

[Turn over

SECTION B

Marks

1. Under certain conditions the 3d electrons in the Fe^{2+} ion can be represented as

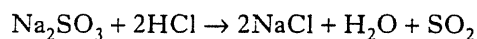


- (a) Give the full electronic configuration for the Fe^{2+} ion in terms of s, p and d electrons. 1
- (b) The orbitals shown in representation ① are degenerate.
What is meant by the term “degenerate”? 1
- (c) (i) Under which conditions could representation ① exist? 1
- (ii) Under which conditions could representation ② exist? 1
- (iii) What could cause the electronic configuration of the Fe^{2+} ion to change from representation ② to representation ③? 1
- (5)**

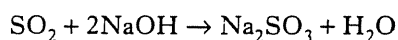
2. Meat fillings in pies can be preserved by addition of sodium sulphite.

The concentration of the sodium sulphite can be determined using the method outlined in steps 1, 2 and 3.

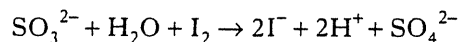
Step 1 Addition of hydrochloric acid to displace sulphur dioxide.



Step 2 Absorption of the sulphur dioxide in a solution of sodium hydroxide to form sodium sulphite solution.



Step 3 Titration of the sulphite ions against a standard solution of iodine.



A 10.0 g sample of meat filling, treated as above, released enough sulphur dioxide to react with 15.2 cm³ of 0.0020 mol l⁻¹ iodine solution.

- (a) Suggest a reason why steps 1 and 2 are carried out rather than adding the meat filling to water and titrating directly with iodine solution. 1
- (b) Which indicator would be used in the titration? 1
- (c) (i) Calculate the number of moles of iodine used in the titration. 1
- (ii) Calculate the % by mass of sodium sulphite in the sample of meat filling. 2
- (5)**

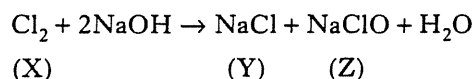
3. The halogens are all oxidising agents.

Fluorine is extracted from molten potassium fluoride by electrolysis.

Chlorine, bromine and iodine can be extracted from their potassium salts using a mixture of sulphuric acid and potassium permanganate.

- (a) (i) Write the ion-electron equation for the production of fluorine from molten potassium fluoride. 1
- (ii) Why can fluorine not be produced from potassium fluoride using acidified potassium permanganate? 1
- (b) In alkalis, halogens undergo **disproportionation**, a reaction in which the halogen molecule is simultaneously oxidised and reduced.

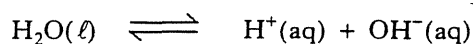
For example



Calculate the oxidation number of chlorine in each substance X, Y and Z and justify the use of the term disproportionation for this reaction. 2

(4)

4. The equilibrium in water can be represented by the equation



The ionic product for water (K_w) is $1.00 \times 10^{-14} \text{ mol}^2 \text{ l}^{-2}$ at 297 K.

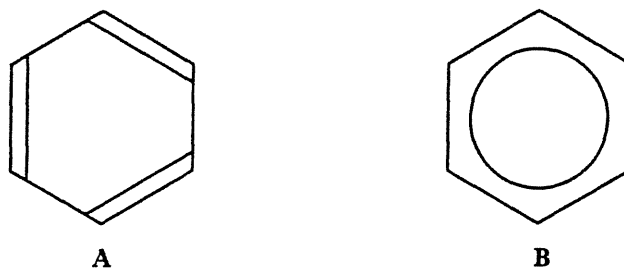
As shown in the table below, K_w is temperature dependent.

Temperature/K	$K_w/\text{mol}^2 \text{ l}^{-2}$
273	1.14×10^{-15}
283	2.93×10^{-15}
298	1.01×10^{-14}
323	5.48×10^{-14}
373	5.13×10^{-13}

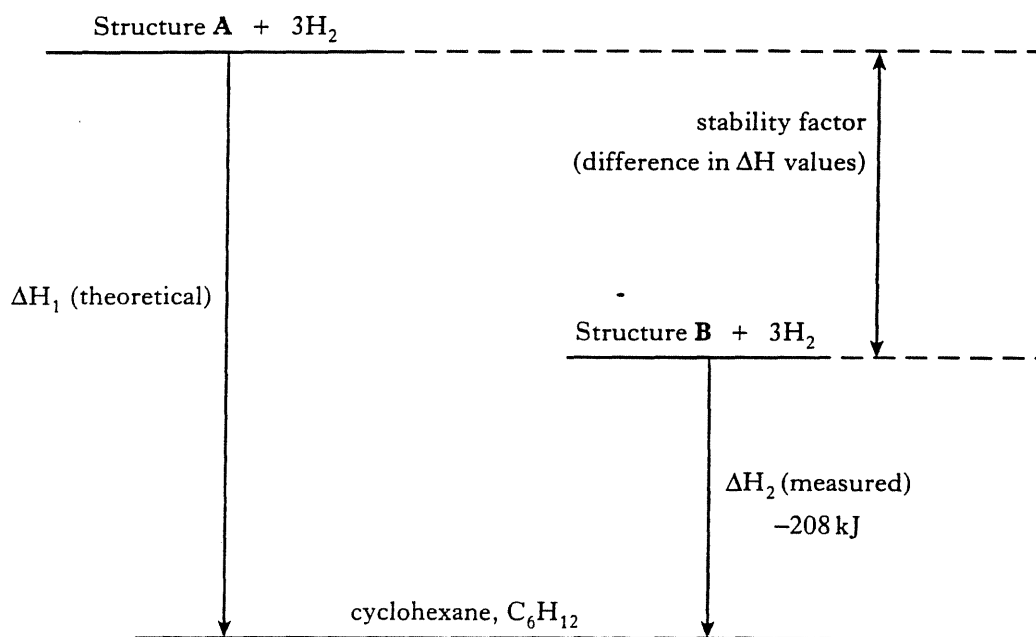
- (a) Write the expression for K_w . 1
- (b) Give a reason for the variation of K_w with temperature. 1
- (c) Calculate the pH of water at 323 K. 2
- (4)

[Turn over

5. The molecule benzene, formula C_6H_6 , has been described as involving alternating single and double carbon to carbon bonds as in diagram A. Diagram B is generally regarded as giving a more valid view of the structure.

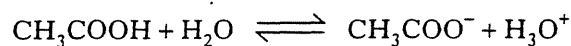


One piece of evidence which contradicts structure A is the hydrogenation data shown in the thermochemical cycle below.

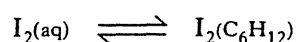


- (a) Give **one** other piece of evidence which contradicts structure A. 1
- (b) Using bond enthalpy data from page 9 of the Data Booklet, calculate ΔH_1 and hence the stability factor in the cycle above. 3
- (c) What feature of the bonding accounts for the relative stability of structure B? 1
- (5)**

6. When ethanoic acid is added to water the following equilibrium is established.



- (a) Identify the conjugate base of CH_3COOH . 1
- (b) 100 cm^3 of buffer solution was prepared by dissolving 3.74 g of sodium ethanoate (CH_3COONa) in 0.20 mol l^{-1} ethanoic acid solution. 1
- (i) Calculate the concentration of sodium ethanoate, in mol l^{-1} , in this buffer solution. 1
- (ii) Using data on page 12 of the Data Booklet, calculate the pH of this buffer solution. 2
- (iii) Explain why the addition of a small volume of sodium hydroxide solution will have little effect on the pH of this buffer solution. 2
- (6)**
7. 100 cm^3 of a 0.10 mol l^{-1} solution of iodine in aqueous potassium iodide was added to 50 cm^3 of cyclohexane and thoroughly shaken. The following equilibrium was established:

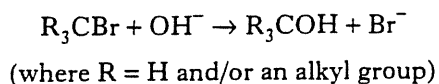


The partition coefficient, K , is equal to 0.40 .

- (a) Write the expression for the partition coefficient for this system. 1
- (b) (i) If x moles of iodine are present in the aqueous layer at equilibrium, calculate, in terms of x , the number of moles of iodine that must be present in the cyclohexane layer. 1
- (ii) Calculate the equilibrium concentration of iodine, in mol l^{-1} , in the aqueous layer. 2
- (c) If 25 cm^3 of cyclohexane had been used instead of 50 cm^3 what effect would this change have on:
- (i) the value of the partition coefficient;
- (ii) the equilibrium concentration of iodine in the cyclohexane layer? 2
- (6)**

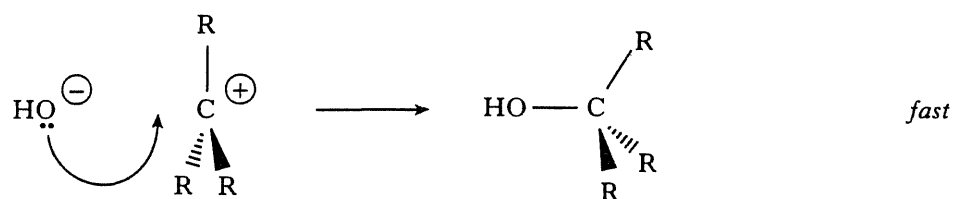
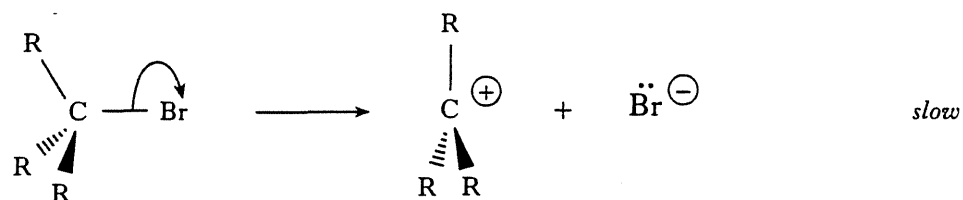
[Turn over

- × 8. Bromoalkanes undergo nucleophilic substitution when heated with aqueous sodium hydroxide solution.

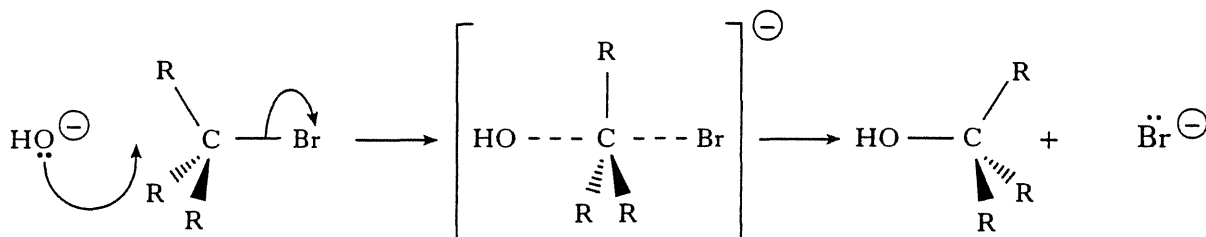


Two possible mechanisms for the reaction are outlined below.

Mechanism 1 (two-step process):



Mechanism 2 (single-step process):



- (a) Explain what is meant by the term, *nucleophilic substitution*. 2
- (b) A bromoalkane reacts as in **mechanism 1**.
Write the rate equation that would be obtained in a kinetic study of the reaction. 1
- (c) Another bromoalkane reacted as in **mechanism 2** and the following kinetic data were obtained:

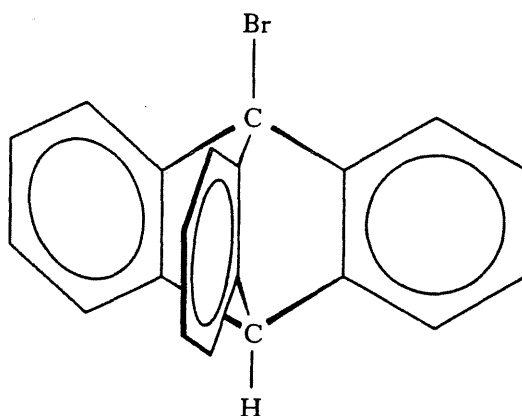
Experiment	Concentration of $\text{R}_3\text{CBr}/\text{mol l}^{-1}$	Concentration of $\text{NaOH}(\text{aq})/\text{mol l}^{-1}$	Relative rate
1	0.05	0.10	1
2	0.05	0.20	x
3	0.10	y	10

Determine values for x and y .

2

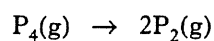
8. (continued)

- (d) Suggest why the compound shown below is unlikely to undergo reaction with sodium hydroxide by **mechanism 2**.

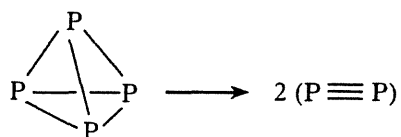


1
(6)

9. When phosphorus is heated the following transition occurs at 800 °C.



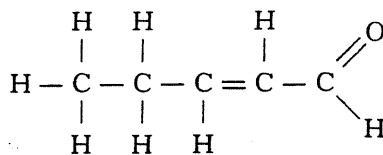
Using structural formulae, the transition may be represented as:



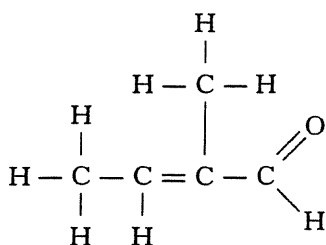
- (a) How many non-bonding electron pairs (lone pairs) are present in a P_4 molecule? 1
- (b) What is the bond angle in a P_4 molecule? 1
- (c) How many pi (π) bonds are present in a P_2 molecule? 1
- (d) Explain why there is an increase in entropy in the above transition. 1
- (4)

[Turn over

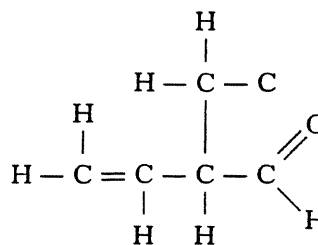
- × 10. An unsaturated aldehyde has the molecular formula C_5H_8O . The formulae of three of its structural isomers are drawn below.



A

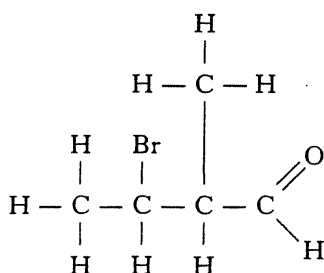


B

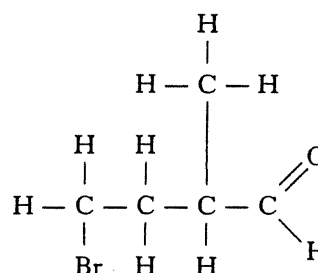


C

- (a) Which one of the above compounds does **not** exhibit **geometric isomerism**? 1
- (b) One of the above compounds exhibits **optical isomerism**.
Copy its structural formula and circle the chiral (asymmetric) carbon atom. 1
- (c) On treating compound C with hydrogen bromide two products, D and E, are formed.



D

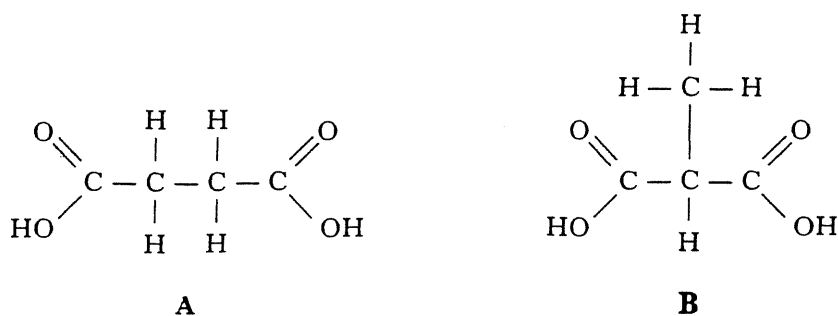


E

- (i) Outline the mechanism for the formation of D. 2
- (ii) According to Markovnikov's rule which of the two products is formed in greater yield? 1

(5)

11. The structures of the two dicarboxylic acids with molecular formula $C_4H_6O_4$ are drawn below.

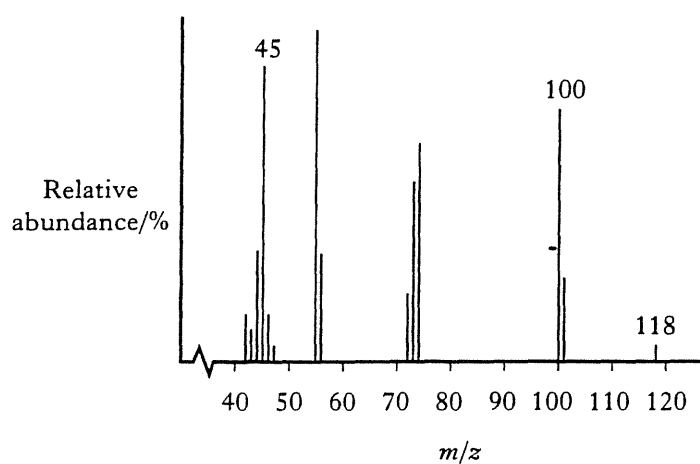


- (a) **A** is called butanedioic acid.

Name **B**.

1

- (b) The simplified mass spectrum of **A** is illustrated below.



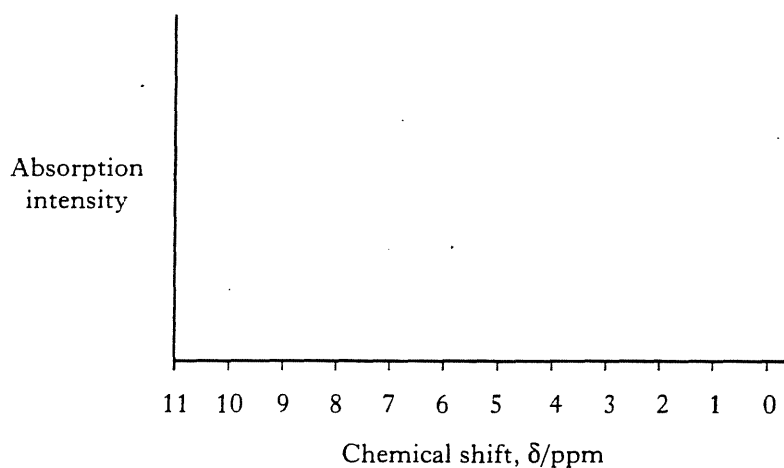
- (i) Write the formula for the ion which gives the peak at $m/z = 45$.

1

- (ii) What has been **lost** from molecule **A** to give the ion at $m/z = 100$?

1

- (c) Copy the following diagram and complete it to show the nmr spectrum of **A**.
(Use information on page 15 of the Data Booklet.)



2

(5)

[Turn over for Question 12 on Page eighteen

12. An alkali metal halide can adopt one or other of two different structures. They are:

- the “sodium chloride” type structure and
- the “caesium chloride” type structure.

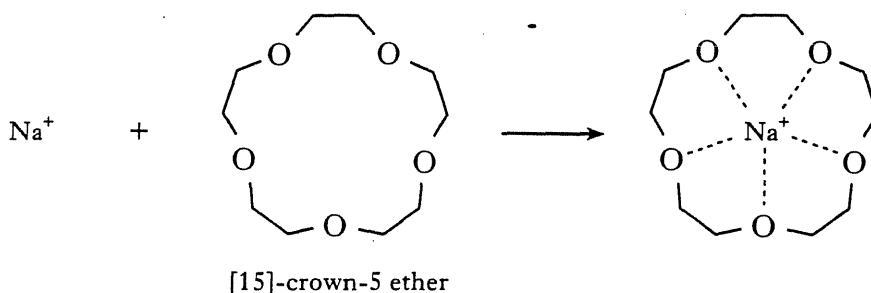
- (a) State the number of caesium ions which pack round each chloride ion in caesium chloride. 1
- (b) One way of predicting which structure an alkali metal halide will adopt is to calculate its radius ratio and compare it with those of sodium chloride and caesium chloride.

$$\text{The radius ratio of NaCl} = \frac{\text{radius of Na}^+}{\text{radius of Cl}^-} = \frac{95 \text{ pm}}{181 \text{ pm}} = 0.52$$

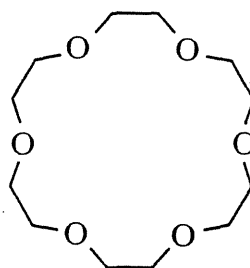
- (i) Calculate the radius ratio of CsCl. 1
- (ii) Predict which type of structure potassium fluoride is likely to adopt. 1
- (c) Alkali metal halides are generally insoluble in organic solvents but some dissolve in organic liquids called crown ethers.

A crown ether is a ring compound and it will bind certain metal ions depending on the size of its cavity.

Sodium chloride, for example, will dissolve in [15]-crown-5 ether because the diameter of the Na^+ ion (190 pm) matches closely the cavity diameter of the crown ether (170–220 pm).



Potassium chloride does **not** dissolve in [15]-crown-5 ether but does dissolve in:



- (i) Explain why potassium chloride will not dissolve in [15]-crown-5 ether. 1
- (ii) Suggest a name for the crown ether in which potassium chloride dissolves. 1

[END OF QUESTION PAPER]

(5)