

X012/701

NATIONAL
QUALIFICATIONS
2006

TUESDAY, 30 MAY
9.00 AM - 11.30 AM

CHEMISTRY
ADVANCED HIGHER

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

SECTION A – 40 marks

Instructions for completion of **SECTION A** are given on page two.

For this section of the examination you must use an **HB pencil**.

SECTION B – 60 marks

All questions should be attempted.

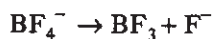
Answers must be written clearly and legibly in ink.



1. Sodium vapour street lamps emit yellow light because

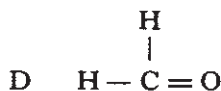
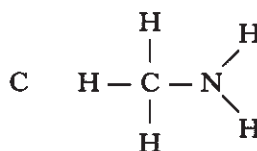
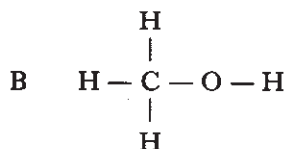
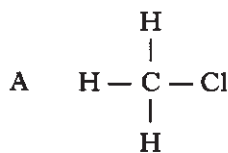
- A sodium vapour is burning and giving out a yellow glow
- B sodium vapour filters out all the light from the filament except yellow
- C energy corresponding to yellow light is given out as electrons in sodium move to higher energies
- D energy corresponding to yellow light is given out as electrons in sodium move to lower energies.

2. What is the change in the three-dimensional arrangement of the bonds round the B atom in the following reaction?



- A Square planar to trigonal planar
 - B Tetrahedral to trigonal planar
 - C Tetrahedral to pyramidal
 - D Square planar to pyramidal
3. Which of the following oxides is amphoteric?
- A Aluminium oxide
 - B Calcium oxide
 - C Copper(II) oxide
 - D Sulphur dioxide
4. The electrical conductivity of semiconductors
- A decreases with increasing temperature
 - B increases with increasing temperature
 - C decreases on exposure to light
 - D increases with the removal of dopant atoms.

5. Which of the following molecules has the greatest number of non-bonding electron pairs (lone pairs)?



6. A white solid gives a lilac flame colour. It reacts with water releasing hydrogen gas and forming a strongly alkaline solution.

The solid could be

- A calcium oxide
- B potassium oxide
- C calcium hydride
- D potassium hydride.

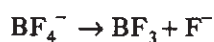
7. Hund's rule states that

- A it is impossible to define both the position and momentum of an electron simultaneously
- B electrons occupy orbitals in order of increasing energy
- C electrons occupy degenerate orbitals singly with parallel spins before spin pairing occurs
- D the energy of an electron in an atom is quantised.

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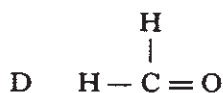
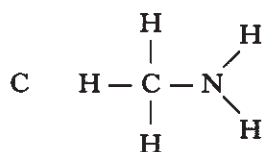
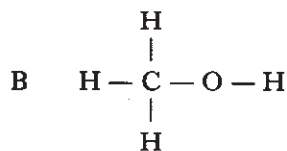
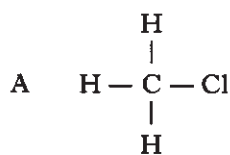
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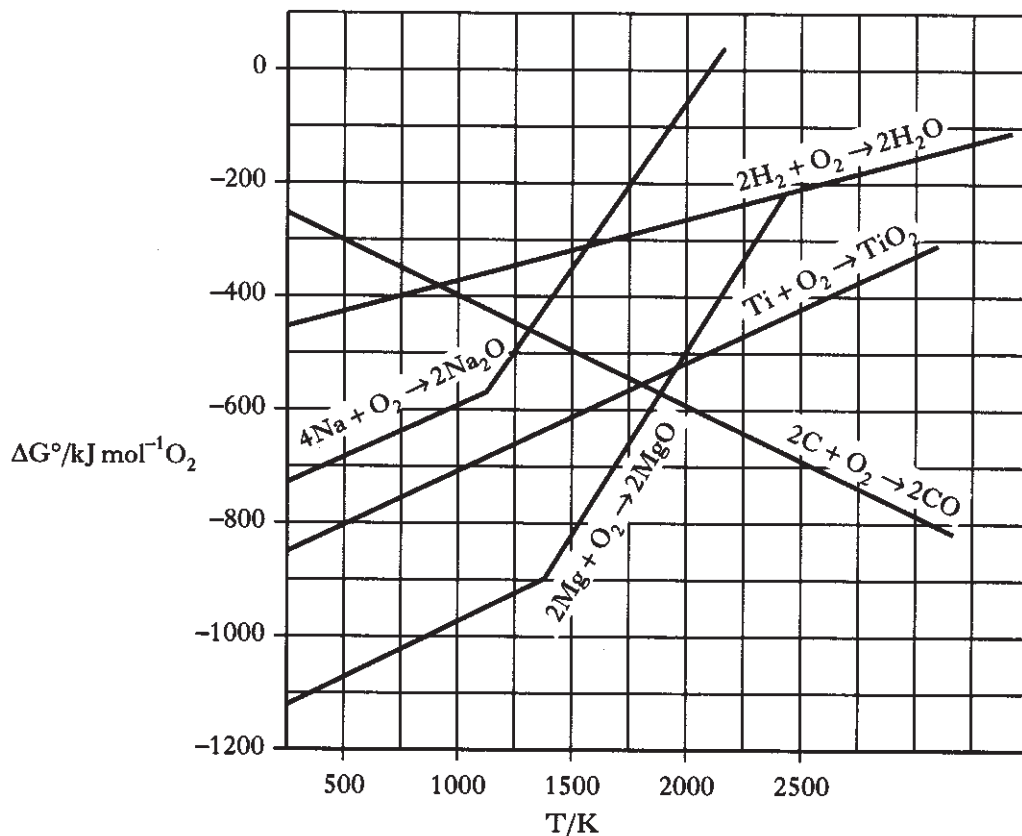
15. The use of an indicator is **not** appropriate in titrations involving
- A hydrochloric acid solution and methylamine solution
 - B nitric acid solution and potassium hydroxide solution
 - C methanoic acid solution and ammonia solution
 - D propanoic acid solution and sodium hydroxide solution.
16. In the presence of bright light, hydrogen and chlorine react explosively. One step in the reaction is shown below.
- $$\text{H}_2(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{H}(\text{g})$$
- Using information from the Data Booklet, the enthalpy change, in kJ mol^{-1} , for this step is calculated as
- A -189
 - B -4
 - C +4
 - D +189.
17. For which of the following reactions does the ΔH° value correspond to **both** the enthalpy of combustion of an element and the enthalpy of formation of a compound?
- A $\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$
 - B $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\ell)$
 - C $2\text{Na}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{O}(\text{s})$
 - D $\text{Mg}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO}(\text{s})$
18. In which of the following reactions would the energy change represent the lattice enthalpy of sodium chloride?
- A $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$
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19. A Born-Haber cycle can be used to calculate the lattice enthalpy of sodium chloride. Which of the following is **not** required in the calculation?
- A The bond enthalpy of chlorine
 - B The first ionisation energy of chlorine
 - C The first ionisation energy of sodium
 - D The enthalpy of formation of sodium chloride
20. Which of the following reactions results in a **decrease** in entropy?
- A $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
 - B $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
 - C $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - D $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
21. The equilibrium constant for a particular hydrolysis reaction has the value 3×10^4 at 25°C . From this we can conclude that, at 25°C , this hydrolysis reaction is
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 - B feasible
 - C exothermic
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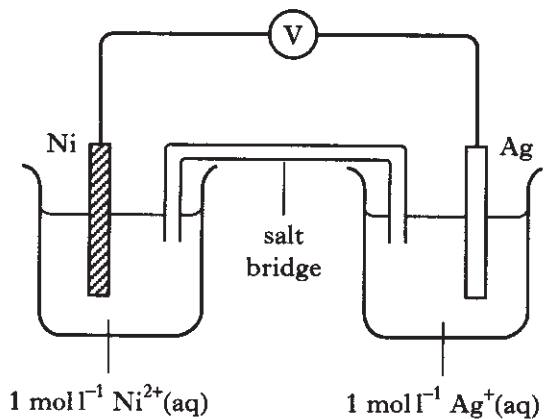
22.



The reduction of TiO_2 to Ti is thermodynamically feasible at 1500 K using

- A hydrogen
- B magnesium
- C carbon
- D sodium.

23.

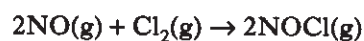


In the cell, which of the following is reduced?

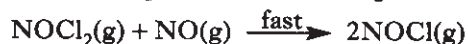
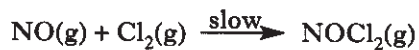
(Assume standard conditions.)

- A $\text{Ni}(\text{s})$
- B $\text{Ni}^{2+}(\text{aq})$
- C $\text{Ag}(\text{s})$
- D $\text{Ag}^+(\text{aq})$

24. For the reaction



the suggested mechanism is



The rate equation is

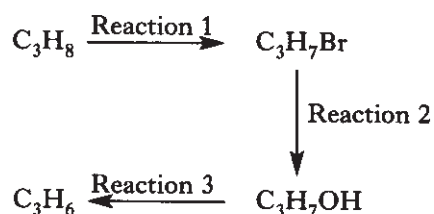
- A $\text{rate} = k[\text{NO}][\text{Cl}_2]$
- B $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$
- C $\text{rate} = k[\text{NOCl}_2][\text{NO}]$
- D $\text{rate} = k[\text{NO}_2]^2[\text{NOCl}_2][\text{Cl}_2]$.

25. In a series of experiments, P and Q reacted to form R. The times taken to produce a fixed concentration of R were recorded.

Experiment	Initial [P] /mol l ⁻¹	Initial [Q] /mol l ⁻¹	Time/s
1	0.05	0.05	46
2	0.05	0.10	23
3	0.10	0.05	46

The rate equation for this reaction is

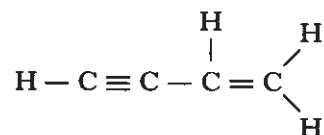
- A rate = k[P]
 B rate = k[Q]
 C rate = k[Q]²
 D rate = k[P][Q].
26. Which line in the table correctly describes the types of reaction in the following sequence?



	Reaction 1	Reaction 2	Reaction 3
A	addition	substitution	dehydration
B	addition	addition	condensation
C	substitution	substitution	dehydration
D	substitution	addition	condensation

27. When ethene reacts with bromine in the presence of potassium chloride, CH₂BrCH₂Cl and CH₂BrCH₂Br are both formed. The first of these two compounds is produced because chloride ions
- A compete with ethene to form an ionic intermediate
 B compete with bromide ions in attacking a cyclic ion intermediate
 C attack the CH₂BrCH₂Br which had originally formed, displacing the less reactive bromide ions
 D react with bromine to give chlorine which then attacks the ethene.

28. Which line in the table has the correct number and type of bonds in



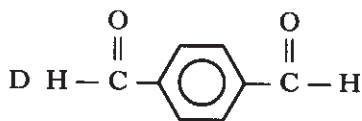
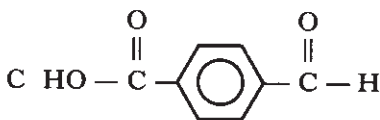
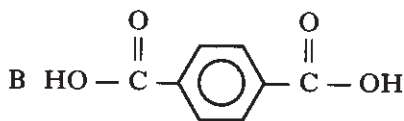
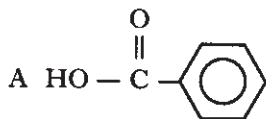
	Number of σ-bonds	Number of π-bonds
A	7	3
B	7	2
C	5	2
D	5	5

29. Which of the following best describes the bonding in alkanes?
- A sp² hybridisation of the carbon atoms giving sigma bonds only
 B sp² hybridisation of the carbon atoms giving sigma and pi bonds
 C sp³ hybridisation of the carbon atoms giving sigma bonds only
 D sp³ hybridisation of the carbon atoms giving sigma and pi bonds
30. Which of the following represents a termination step in a chain reaction?
- A Cl• + Cl• → Cl₂
 B Cl• + CH₄ → CH₃• + HCl
 C CH₃• + Cl₂ → CH₃Cl + Cl•
 D Cl₂ → Cl• + Cl•

31. Which one of the following statements about ethoxyethane is **not** correct?
- A It burns readily in air.
 B It is isomeric with butan-1-ol.
 C It has a higher boiling point than butan-1-ol.
 D It may be prepared from sodium ethoxide and bromoethane.

[Turn over


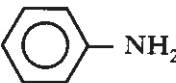
32. Which of the following, when reacted with ethane-1,2-diol, would form a polyester?



33. Which of the following can be oxidised by Tollens' reagent?

- A CH_3COCH_3
 B CH_3CHO
 C CH_3OH
 D $(\text{CH}_3)_2\text{CHOH}$

34. Which of the following is the strongest base?

- A $\text{CH}_3\text{CH}_2\text{OH}$
 B 
 C $\text{CH}_3\text{CH}_2\text{NH}_2$
 D 

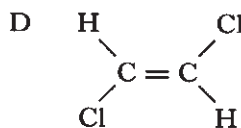
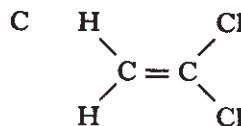
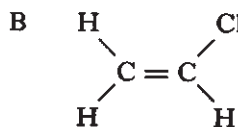
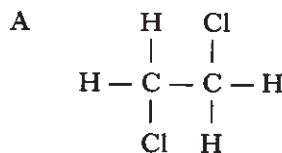
35. Naphthalene, C_{10}H_8 , has the following structure.



The number of moles of hydrogen gas required for the complete hydrogenation of 12.8 g naphthalene will be

- A 0.1
 B 0.4
 C 0.5
 D 0.8.

36. Which of the following compounds has a geometric isomer?



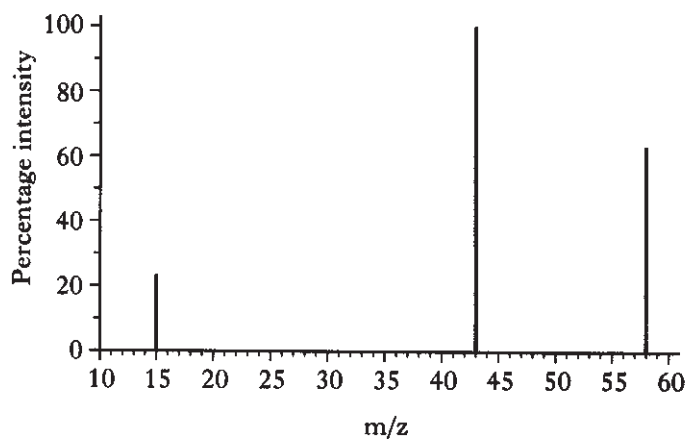
37. An analysis of an organic compound found in meteorite rocks shows the following percentage composition by mass.

$$\text{C} = 37.5\% \quad \text{H} = 12.5\% \quad \text{O} = 50\%$$

The empirical (simplest) formula for the compound is

- A CH_4O
 B C_3HO_4
 C $\text{C}_3\text{H}_{12}\text{O}_3$
 D CH_2O_2 .

38. A simplified mass spectrum of an organic compound is shown.



Which of the following compounds gave this spectrum?

- A Propane
- B Propan-1-ol
- C Propan-2-ol
- D Propanone

39. Which of the following analytical techniques depends on the vibrations within molecules?

- A Colorimetry
- B Atomic emission spectroscopy
- C Infra-red absorption spectroscopy
- D Mass spectroscopy

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

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

[END OF SECTION A]

Candidates are reminded that the answer sheet for Section A MUST be placed INSIDE the front cover of your answer book.

[Turn over

SECTION B

All answers must be written clearly and legibly in ink.

Marks

1. Molten iron, made in a blast furnace, often contains sulphur and phosphorus impurities which must be removed.

Bubbling carbon dioxide gas through molten iron removes the sulphur.

The carbon dioxide gas is produced by the decomposition of calcium carbonate.



(a)

Substance	Standard enthalpy of formation, $\Delta H^\circ/\text{kJ mol}^{-1}$	Standard entropy, $S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
CO ₂	-393.5	213.8
CaCO ₃	-1206.9	92.9
CaO	-635.1	38.1

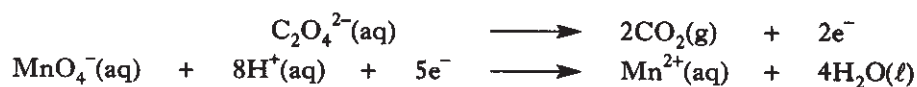
For the decomposition of calcium carbonate, use the data in the table to calculate:

- (i) the standard enthalpy change, ΔH° , in kJ mol^{-1} ; 1
- (ii) the standard entropy change, ΔS° , in $\text{J K}^{-1} \text{mol}^{-1}$; 1
- (iii) the theoretical temperature at which the reaction just becomes feasible. 2
- (b) The phosphorus impurity is removed by first converting it into the oxide, P₄O₁₀. This oxide then reacts with calcium oxide to produce a useful fertiliser.
- (i) Calculate the oxidation number of phosphorus in P₄O₁₀. 1
- (ii) Name the fertiliser formed. 1
- (6)**

2. 25.0 cm³ of an acidified solution of potassium oxalate, K₂C₂O₄, was heated to 80 °C and titrated with a standard solution of 0.020 mol l⁻¹ potassium permanganate, KMnO₄.

The end-point was reached when 22.5 cm³ of KMnO₄ solution had been added.

The ion-electron equations for the reactions involved are:



- (a) How would the end-point of the titration be determined? 1
- (b) Write the redox equation for the reaction. 1
- (c) Calculate the concentration of the potassium oxalate solution used in this titration. 3
- (5)**

3. The table shows two quantum numbers for the 10 electrons in a neon atom.

Electron	First Quantum Number (n)	Second Quantum Number (ℓ)
1	1	0
2	1	0
3	2	0
4	2	0
5	2	1
6	2	1
7	2	1
8	2	1
9	2	1
10	2	1

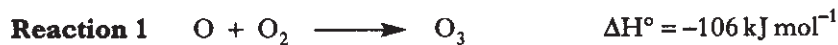
- (a) Write the electronic configuration for a neon atom in terms of s and p orbitals. 1
- (b) Electrons 5 to 10 can be described as degenerate.
What is meant by the term "degenerate"? 1
- (c) The second quantum number, ℓ , is related to the shape of the orbitals.
Draw the shape of an orbital when $\ell = 1$. 1
- (d) What are the first and second quantum numbers for the outer electron in a sodium atom? 1
- (4)**

[Turn over

4. In the stratosphere, oxygen molecules absorb ultraviolet radiation and break up to form oxygen atoms.



- (a) The bond enthalpy of $\text{O}=\text{O}$ is 497 kJ mol^{-1} . Calculate the wavelength, in nm, of the ultraviolet radiation required to break up 1 mole of oxygen molecules into oxygen atoms. 3
- (b) Some of the oxygen atoms react with oxygen molecules to produce ozone, O_3 .



Other oxygen atoms react to produce oxygen molecules.



Oxygen atoms can also react with ozone to produce oxygen molecules.



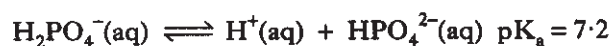
- (i) Use Hess's law to calculate the standard enthalpy change, in kJ mol^{-1} , for **Reaction 3**. 1
- (ii) A Lewis dot diagram for an oxygen molecule is



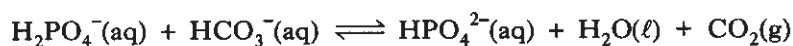
Draw a similar diagram for an ozone molecule. 1

(5)

5. Solutions of NaH_2PO_4 are acidic because the H_2PO_4^- ion partially dissociates.



- (a) Write the expression for the acid dissociation constant, K_a . 1
- (b) Calculate the pH of 0.1 mol l^{-1} NaH_2PO_4 solution. 2
- (c) NaH_2PO_4 is used with NaHCO_3 in baking powders, to produce carbon dioxide.



Explain how HCO_3^- acts as a base in this reaction. 1

(4)

6. Most cars are powered by the combustion of petrol which consists mainly of octane isomers. Currently research is being carried out on replacing petrol with hydrogen as a fuel.

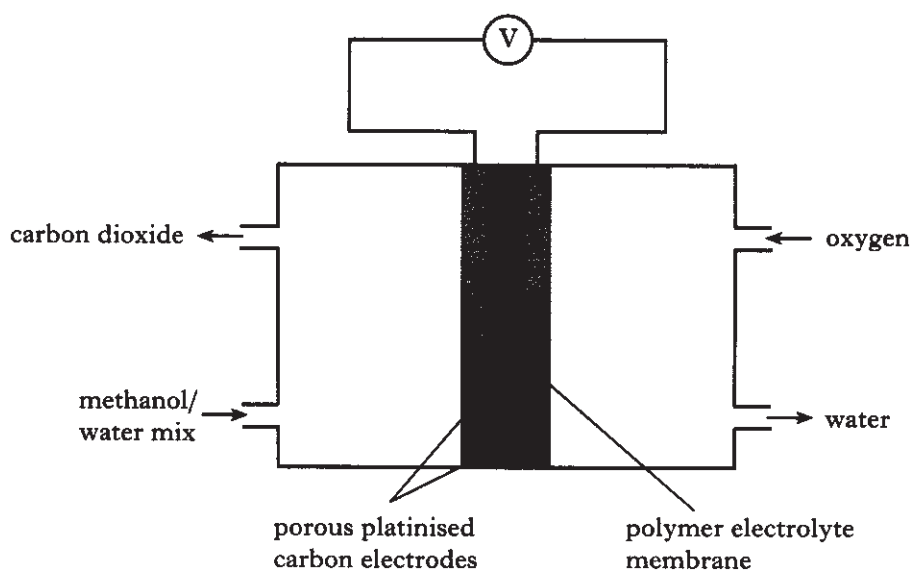
(a)

Fuel	Combustion Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$
Hydrogen	$\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$	-286
Petrol	$\text{C}_8\text{H}_{18} + 12\frac{1}{2}\text{O}_2 \longrightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$	-5100

Calculate the energy produced per gram of each fuel.

1

- (b) Research is also being carried out on replacing engines with fuel cells such as the direct methanol fuel cell shown.



The overall cell reaction is



The ion-electron equation for the oxidation of methanol is

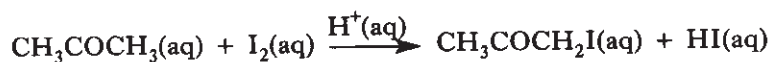


The standard reduction potential for oxygen is 1.23 V.

- Write the ion-electron equation for the reduction of oxygen. 1
 - The emf of the cell measured under standard conditions is 1.20 V.
Calculate the standard **reduction** potential for the ion-electron reaction involving the methanol. 1
 - Calculate the standard free energy change, ΔG° , in kJ per mole of methanol, for the cell reaction. 3
- (6)

[Turn over

7. In a PPA, the kinetics of the acid-catalysed propanone/iodine reaction were studied.

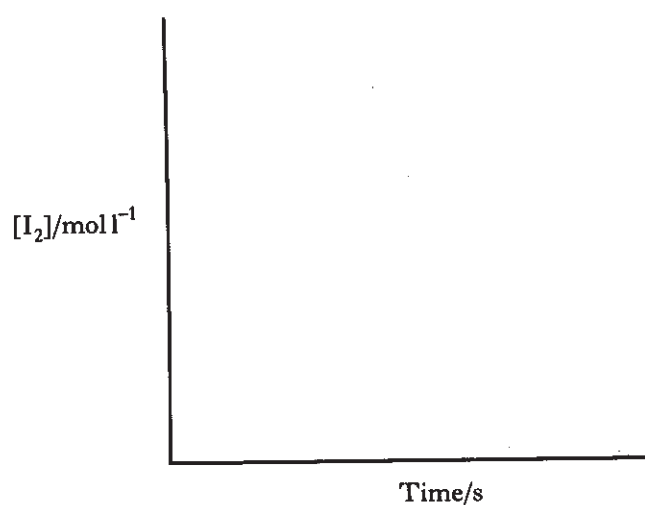


The reaction is first order with respect to propanone and first order with respect to the hydrogen ions which catalyse the reaction. The order with respect to iodine is unknown. The rate equation is

$$\text{Rate} = k[\text{I}_2]^x[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

The aim of the experiment was to determine x .

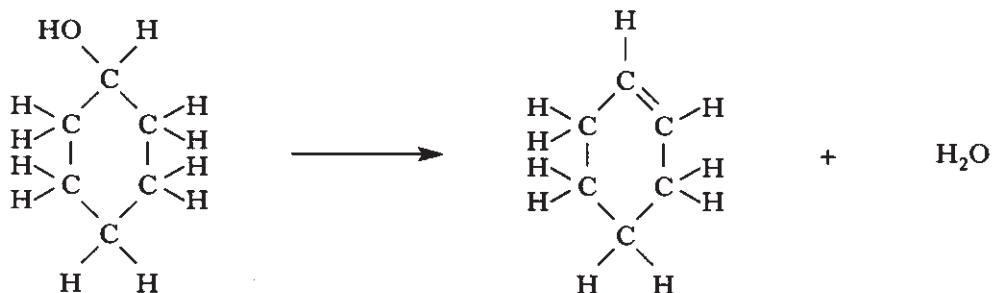
- (a) How did the initial concentrations of the propanone and acid compare with that of the iodine to allow the value of x to be determined? 1
- (b) The experiment proved that the order of the reaction with respect to iodine was zero. Copy the axes shown and sketch the graph which would be obtained.



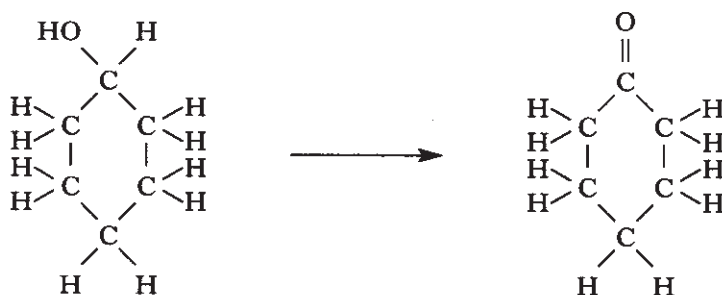
- (c) What is the overall order of the reaction? 1
- (d) What are the units for the rate constant, k ? 1

(4)

8. In a PPA, cyclohexene was prepared from cyclohexanol by dehydration.



- (a) Which reagent was used to convert cyclohexanol to cyclohexene? 1
- (b) Distillation was used to separate the cyclohexene product from the reaction mixture because cyclohexanol has a higher boiling point than cyclohexene.
Explain why cyclohexanol has the much higher boiling point. 1
- (c) To purify the cyclohexene distillate, a saturated sodium chloride solution was added to it in a separating funnel.
Why was sodium chloride solution used instead of water? 1
- (d) Cyclohexanol can also be oxidised to the cycloketone, cyclohexanone.



Ketones can be identified using 2,4-dinitrophenylhydrazine solution (Brady's reagent).
How would this be used to identify the ketone as cyclohexanone? 2

(5)

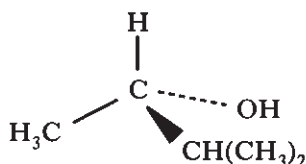
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9. Mixtures of the isomers of the alcohol, $C_5H_{11}OH$, are used as solvents for resins and oily materials.

The shortened structural formulae for four of these isomers are shown in the table.

Isomer	Shortened structural formula
A	$(CH_3)(C_2H_5)CHCH_2OH$
B	$(CH_3)_3CCH_2OH$
C	$(CH_3)_2(C_2H_5)COH$
D	$(C_2H_5)_2CHOH$

- (a) Which isomer is the tertiary alcohol? 1
- (b) Another isomer of $C_5H_{11}OH$ displays optical isomerism.
One of its optical isomers is shown below.



Draw a diagram representing the other optical isomer. 1

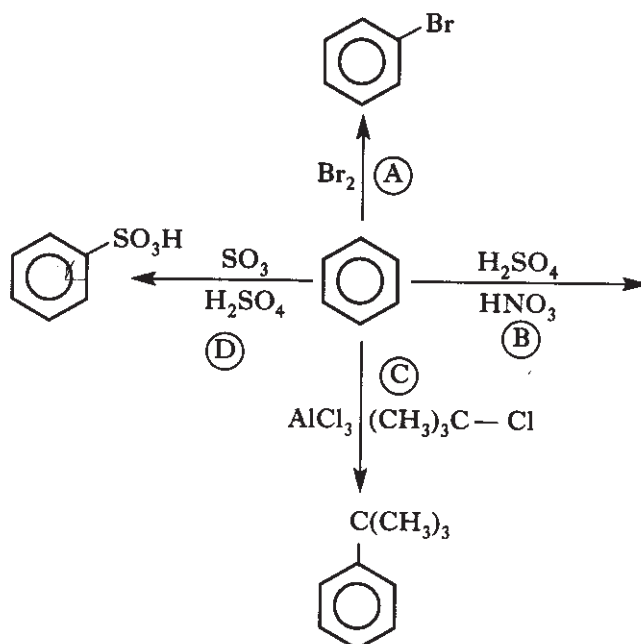
- (c) One of the four isomers, A to D, in the table above, is also optically active.
Draw a similar diagram to that shown in part (b) to represent one of its optical isomers. 1
(3)

10. Fusel alcohols are components of fusel oil which is obtained during the process of brewing beer. They contribute to the flavour of the beer and are also the major cause of hangovers. The most important fusel alcohols are

3-methylbutan-1-ol
2-methylbutan-1-ol
propan-1-ol.

- (a) Give a reason why propan-1-ol is the most soluble of these alcohols in water. 1
- (b) Other flavours found in beer are caused by esters.
Esters can be formed by reacting alcohols with carboxylic acids.
- (i) What can be used in place of carboxylic acids to form esters? 1
- (ii) What advantage is there in using this type of reagent? 1
(3)

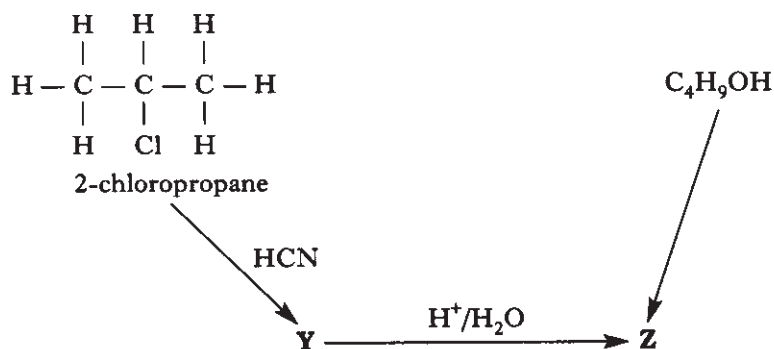
11. Benzene is one of the most important aromatic feedstocks in the chemical industry. Four electrophilic substitution reactions which benzene undergoes are shown.



- (a) (i) Which catalyst is required to carry out reaction (A)? 1
- (ii) What is the organic product in reaction (B)? 1
- (iii) The specific name for reaction (C) is alkylation.
 What is the specific name for reaction (D)? 1
- (b) Both benzene and graphite have delocalised electrons.
 Suggest why benzene does not conduct electricity. 1
- (4)**

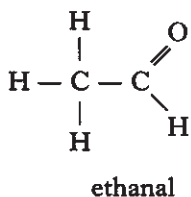
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12. The diagram illustrates two methods of preparing compound **Z**.

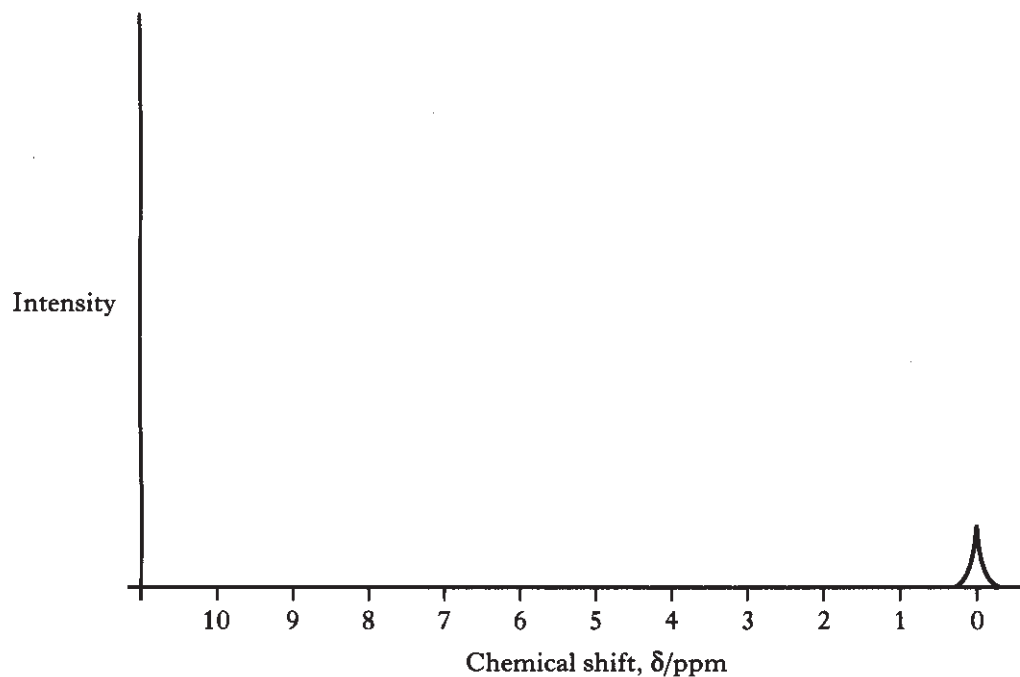


- (a) Draw a structural formula for compound **Y**. 1
- (b) Compound **Z** has the molecular formula $\text{C}_4\text{H}_8\text{O}_2$.
Name **and** draw a structural formula for compound **Z**. 2
- (c) (i) Name the alcohol, $\text{C}_4\text{H}_9\text{OH}$, used to prepare compound **Z**. 1
(ii) Which reagent could be used to convert $\text{C}_4\text{H}_9\text{OH}$ to compound **Z**? 1
- (d) The conversion of 2-chloropropane into compound **Y** proceeds by an $\text{S}_{\text{N}}2$ mechanism.
(i) Explain what is meant by the abbreviation $\text{S}_{\text{N}}2$. 2
(ii) Draw a structural formula for the transition state in this reaction. 1
- (8)**

13. A proton nmr spectrum was produced for ethanal.



(a) Copy and complete the following diagram to show the approximate positions and relative heights of the two peaks in the proton nmr spectrum of ethanal.



2

(b) Which reference substance is used in proton nmr spectroscopy and causes the peak at $\delta = 0$ ppm?

1
(3)

[END OF QUESTION PAPER]