X012/13/02

NATIONAL QUALIFICATIONS 2012

MONDAY, 14 MAY
1.00 PM – 3.30 PM

CHEMISTRY
ADVANCED HIGHER

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet.

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.

SECTION A

Read carefully

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

2 For this section of the examination you must use an **HB pencil** and, where necessary, an eraser.

3 Check that the answer sheet you have been given has **your name**, **date of birth**, **SCN** (Scottish Candidate Number) and **Centre Name** printed on it.

Do not change any of these details.

4 If any of this information is wrong, tell the Invigilator immediately.

5 If this information is correct, **print** your name and seat number in the boxes provided.

6 The answer to each question is **either** A, B, C or D. Decide what your answer is, then, using your pencil, put a horizontal line in the space provided (see sample question below).

7 There is **only one correct** answer to each question.

8 Any rough working should be done on the question paper or the rough working sheet, **not** on your answer sheet.

9 At the end of the exam, put the **answer sheet for Section A inside the front cover of your answer book**.

Sample Question

To show that the ink in a ball-pen consists of a mixture of dyes, the method of separation would be

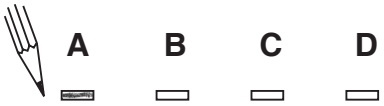
A chromatography

B fractional distillation

C fractional crystallisation

D filtration.

The correct answer is **A**—chromatography. The answer **A** has been clearly marked in **pencil** with a horizontal line (see below).



Changing an answer

If you decide to change your answer, carefully erase your first answer and using your pencil, fill in the answer you want. The answer below has been changed to **D**.

1. Which of the following is **not** a form of electromagnetic radiation?

A α radiation

B γ radiation

C UV radiation

D X-rays

2. An ion, $\mathbf{X^{3+}}$, contains 55 electrons.

In which block of the Periodic Table would element **X** be found?

A s

B p

C d

D f

3. Which of the following statements is **true** about a $Co^{2+}(g)$ ion?

A It has 5 unpaired electrons.

B It has 8 electrons in s orbitals.

C It has 13 electrons in the third shell.

D Its electrons with the highest energy are in 3d orbitals.

4. In absorption spectroscopy, as the concentration of an ionic solution decreases, the radiation transmitted

A increases in intensity

B decreases in intensity

C increases in wavelength

D decreases in wavelength.

5. Neon gas discharge lamps produce a red glow because electrons in neon atoms are

A absorbing radiation from the blue end of the visible spectrum

B emitting radiation from the red end of the visible spectrum

C emitting radiation from the blue end of the visible spectrum

D absorbing radiation from the red end of the visible spectrum.

6. Which of the following molecules has three atoms in a straight line?

A H_2O

B SF_6

C CH_4

D C_2H_3Br

7. Which of the following ligands is bidentate?

A CN^-

B NH_3

C H_2O

D $H_2NCH_2CH_2NH_2$

8. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Adding PCl_3 to the above system will

A increase the value of the equilibrium constant

B decrease the value of the equilibrium constant

C increase the concentration of PCl_5 and decrease the concentration of Cl_2

D decrease the concentration of PCl_5 and increase the concentration of Cl_2.

9. $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$

The solubility product (K_s) for silver chloride is given by the expression

$$K_s = [Ag^+(aq)]\,[Cl^-(aq)]$$

The formula mass of AgCl is 143·4.

$K_s = 1{\cdot}80 \times 10^{-10}$ at 25 °C.

The solubility of silver chloride, in mol l^{-1}, at 25 °C is

A $1{\cdot}80 \times 10^{-10}$

B $3{\cdot}60 \times 10^{-10}$

C $1{\cdot}34 \times 10^{-5}$

D $2{\cdot}68 \times 10^{-5}$.

[Turn over

10. At a particular temperature, 8·0 mole of NO_2 was placed in a 1 litre container and the NO_2 dissociated by the following reaction:

$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

At equilibrium the concentration of NO(g) is $2{\cdot}0\ mol\,l^{-1}$.

The equilibrium constant will have a value of

A 0·11

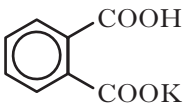
B 0·22

C 0·33

D 9·00.

11. A buffer solution can **not** be made from

A CH_3CH_2COOH and CH_3CH_2COONa

B 

C HNO_3 and $NaNO_3$

D NH_3 and NH_4Cl.

12. $5{\cdot}0\ cm^3$ of a solution of hydrochloric acid was diluted to exactly $250\ cm^3$ with water. The pH of this diluted solution was 2·00.

The concentration of the original undiluted solution, in $mol\,l^{-1}$, was

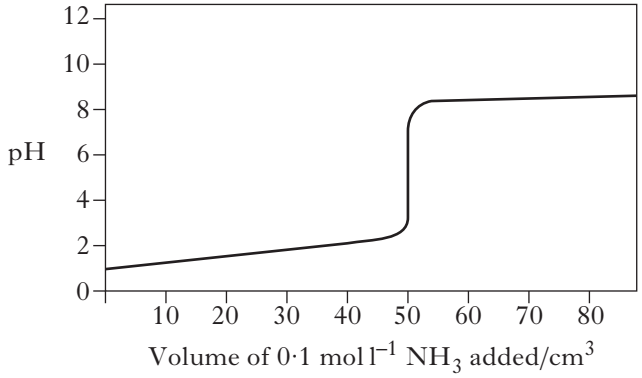
A $2{\cdot}0 \times 10^{-2}$

B $4{\cdot}0 \times 10^{-2}$

C $4{\cdot}0 \times 10^{-1}$

D $5{\cdot}0 \times 10^{-1}$.

13. The graph below shows the pH changes when $0{\cdot}1\ mol\,l^{-1}$ ammonia solution is added to $50\ cm^3$ of $0{\cdot}1\ mol\,l^{-1}$ hydrochloric acid solution.



Which line in the table shows an indicator which is **not** suitable for use in determining the equivalence point for the above reaction?

	Indicator	pH range of indicator
A	methyl orange	3·1 – 4·4
B	bromophenol red	5·2 – 6·8
C	bromothymol blue	6·0 – 7·6
D	phenolphthalein	8·3 – 10·0

14. $C(s) + O_2(g) \rightarrow CO_2(g)\ \ \Delta H° = -396\,kJ\ mol^{-1}$

$Pb(s) + \frac{1}{2}O_2(g) \rightarrow PbO(s)\ \ \Delta H° = -210\,kJ\ mol^{-1}$

$PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)\ \ \Delta H° = -74\,kJ\ mol^{-1}$

What is the value of $\Delta H°$, in $kJ\ mol^{-1}$, for the following reaction?

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

A –260

B –112

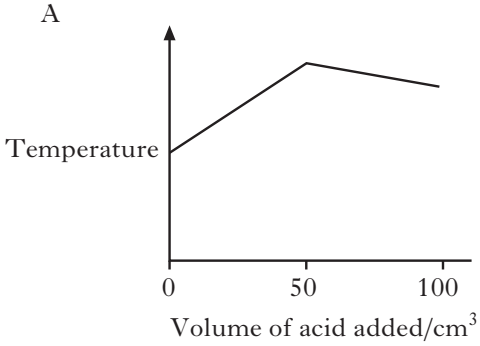
C +112

D +260

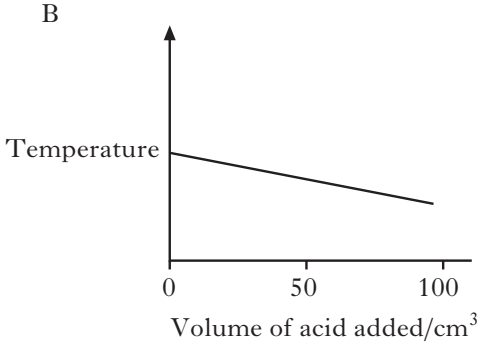
15. $50\,cm^3$ of $1\ mol\,l^{-1}$ sodium hydroxide is placed in a beaker.

Which of the following graphs shows how the temperature of the solution in the beaker would change as $100\,cm^3$ of $1\ mol\,l^{-1}$ hydrochloric acid is gradually added?

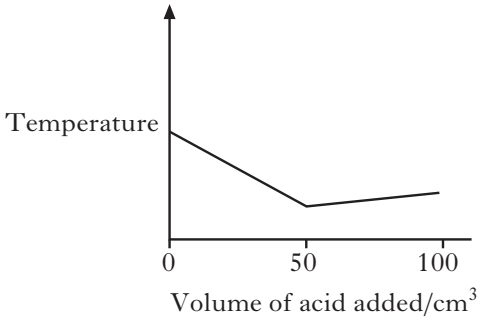
A



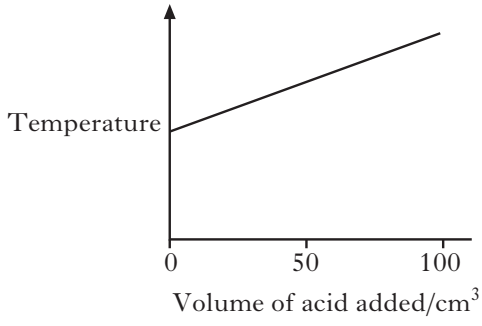
B



C



D



16. Which of the following enthalpy changes can **not** be measured directly by experiment?

A Enthalpy of formation of methane

B Enthalpy of combustion of hydrogen

C Enthalpy of formation of carbon dioxide

D Enthalpy of combustion of carbon monoxide

17.

Bond	Bond enthalpy/kJ mol^{-1}
H—H	432
Cl—Cl	243
H—Cl	428

Using the above data, the standard enthalpy of formation of HCl(g), in kJ mol^{-1}, is

A –90·5

B –123·5

C –181

D –247.

18. Which of the following equations represents a step that is **not** involved in the Born Haber cycle for the formation of rubidium iodide?

A $I_2(s) \rightarrow I_2(g)$

B $I_2(g) \rightarrow 2I(g)$

C $I(g) \rightarrow I^+(g) + e^-$

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

19. $Cr^+(g) \rightarrow Cr^{3+}(g) + 2e^-$

The energy required for this change per mole of chromium(III) ions is

A 2259 kJ

B 3000 kJ

C 4600 kJ

D 5259 kJ.

[Turn over

20. For any liquid, $\Delta S_{vapourisation} = \dfrac{\Delta H_{vapourisation}}{T_b}$

where T_b = boiling point of that liquid.

For many liquids,

$\Delta S_{vapourisation} = 88\ J\ K^{-1}\ mol^{-1}$.

Assuming that this value is true for water and that its $\Delta H_{vapourisation} = 40{\cdot}6\ kJ\ mol^{-1}$, then the boiling point of water is calculated as

A 0·46 K

B 2·17 K

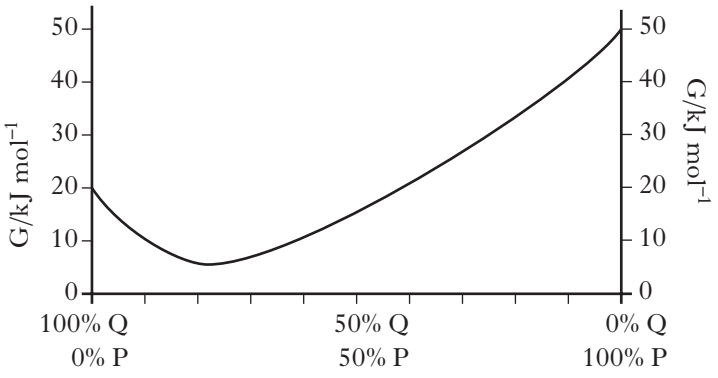
C 373 K

D 461 K.

21. Which line in the table is correct for the enthalpy change and entropy change when steam condenses?

	ΔH	**ΔS**
A	+ve	+ve
B	+ve	–ve
C	–ve	–ve
D	–ve	+ve

22.



Assuming that liquids P and Q are in their standard states when 100 % of either is present, what is the value of $\Delta G°$, in $kJ\ mol^{-1}$, for the reaction represented by the stoichiometric equation,

$$Q(\ell) \rightarrow P(\ell)?$$

A –15

B –30

C +30

D +45

23. 2-Bromobutane reacts with potassium hydroxide in ethanol to produce two unsaturated products.

The type of reaction involved is

A addition

B elimination

C oxidation

D substitution.

24. The reaction between chlorine and ethane to give chloroethane is an example of a chain reaction.

Which of the following is a propagation step in this reaction?

A $Cl_2 \rightarrow Cl\bullet + Cl\bullet$

B $C_2H_5\bullet + Cl\bullet \rightarrow C_2H_5Cl$

C $C_2H_5\bullet + C_2H_5\bullet \rightarrow C_4H_{10}$

D $C_2H_5\bullet + Cl_2 \rightarrow C_2H_5Cl + Cl\bullet$

25. Which of the following molecules is likely to produce the most stable carbocation intermediate in a substitution reaction?

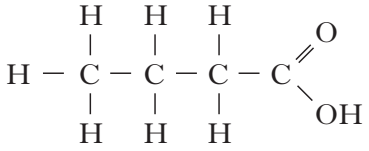
A CH_3CH_2I

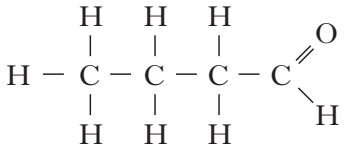
B $(CH_3)_3CCl$

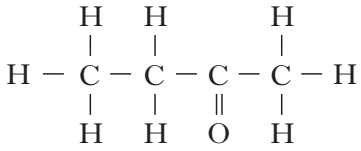
C CH_3CH_2Cl

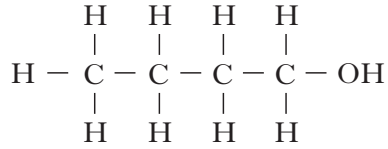
D $CH_3CHICH_2CH_3$

26. Which of the following compounds will have the highest boiling point?

A 

B 

C 

D 

27. Which of the following is an **essential** property of a solvent to be used for recrystallisation purposes?

A Insoluble in water

B A low boiling point

C Ability to dissolve more solute when hot than when cold

D Ability to dissolve more solute when cold than when hot

28. Which of the following is correct for the reaction of propene with hydrogen bromide?

A 1-Bromopropane is the only product.

B 1-Bromopropane is the major product.

C 2-Bromopropane is the only product.

D 2-Bromopropane is the major product.

29. Hybrid orbitals can be formed by the mixing of s and p orbitals.

Which of the following hybrid orbitals are most likely to be involved in the bonding in ethyne?

A sp

B sp^2

C sp^3

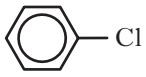
D s^2p

30. Carbon dioxide has the following structure.

O = C = O

Which line in the table shows the correct numbers of σ and π bonds in a molecule of carbon dioxide?

	Number of σ bonds	**Number of π bonds**
A	0	2
B	2	2
C	4	0
D	0	4

31. **P** 

Q CH_2=CHCl

R CH_2=$CHCH_2$Cl

Which of the above molecules is/are planar?

A **P** only

B **P** and **Q** only

C **Q** and **R** only

D **P**, **Q** and **R**

[Turn over

32. Which of the following can be distinguished by making 2,4-dinitrophenylhydrazone derivatives?

A Ethanal and propanal

B Propan-1-ol and propan-2-ol

C Ethanoic acid and benzoic acid

D Methoxyethane and ethoxyethane

33. Which of the following could be the molecular formula for a ketone?

A C_3H_8O

B C_3H_6O

C C_2H_4O

D CH_2O

34. Which of the following compounds would dissolve in water to give an alkaline solution?

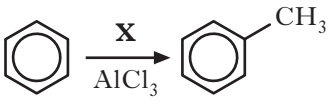
A CH_3CH_2CN

B CH_3CH_2CHO

C $CH_3CH_2CH_2OH$

D $CH_3CH_2CH_2NH_2$

35.



Which of the following compounds could be **X**?

A CH_4

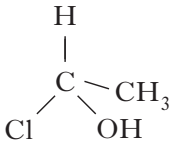
B CH_3Cl

C CH_2Cl_2

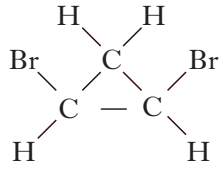
D CH_3OH

36. Which of the following has a geometric isomer?

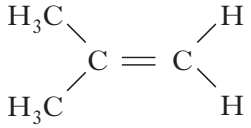
A



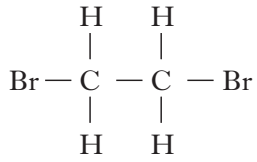
B



C



D



37. Combustion analysis of hydrocarbon **X** showed that it contained 82·7% carbon and 17·3% hydrogen.

The molecular formula for **X** could be

A CH_3

B C_2H_6

C C_2H_5

D C_4H_{10}.

38. The number of waves per centimetre is known as the

A wavenumber

B wavelength

C frequency

D intensity.

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

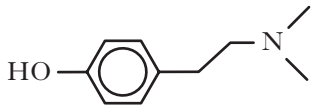
A Colorimetry

B Mass spectroscopy

C Proton nmr spectroscopy

D Infra-red absorption spectroscopy

40.



The active structural fragment of several pain-killing molecules is shown.

What term best describes this structural fragment?

A Agonist

B Receptor

C Antagonist

D Pharmacophore

[*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 for SECTION B on *Page ten*

SECTION B

Marks

60 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

1. Semiconductors are used in a wide variety of applications.

(*a*) In Blu-ray DVD players, light of wavelength 405 nm is produced from a gallium(III) nitride laser.

(i) Calculate the energy, in kJ mol^{-1}, corresponding to this wavelength. **2**

(ii) Write the electronic configuration of gallium(III) in terms of s, p and d orbitals. **1**

(*b*) The electrical conductivity of the semiconductor gallium arsenide increases on exposure to light.

What name is given to this phenomenon? **1**

(*c*) Doped silicon is also used as a semiconductor.

What is the main current carrier in silicon doped with boron? **1**

(5)

2. The nitrate ion, NO_3^-, can be converted into either nitrous acid, HNO_2 or nitrogen monoxide, NO.

The oxidation state of nitrogen in NO is +2.

(*a*) Calculate the oxidation state of nitrogen in

(i) NO_3^-

(ii) HNO_2. **1**

(*b*) Write a balanced ion-electron equation for the reduction of nitrous acid into the compound $H_2N_2O_2$. **1**

(*c*) Nitrogen is also present in the cyanide ion, CN^-.

Name the complex ion $[Cu(CN)_2]^-$. **1**

(3)

Marks

3. Two common crystal lattice structures adopted by ionic compounds can be described as simple cubic and face-centred cubic.

(*a*) What determines the type of structure adopted by a particular ionic compound? **1**

(*b*) Sodium chloride has a face-centred cubic structure which has 6:6 coordination.

Explain what 6:6 coordination means. **1**

(*c*) Caesium chloride has a simple cubic structure which has 8:8 coordination.

Which potassium halide is most likely to have 8:8 coordination? **1**

(*d*) Many ionic compounds are soluble in water.

(i) Which two factors determine whether the enthalpy of solution is exothermic or endothermic? **1**

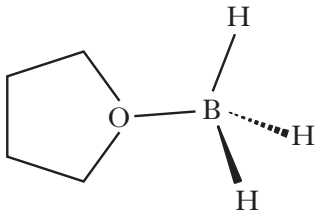
(ii) The enthalpy of solution of sodium chloride is 0 kJ mol^{-1}.

Suggest what makes the dissolving of sodium chloride in water a feasible process. **1**

(5)

4. BH_3 in the gas phase is very reactive. It readily combines with the compound tetrahydrofuran, C_4H_8O, to make a more stable compound.

$$BH_3 + C_4H_8O \rightarrow C_4H_8OBH_3$$



(*a*) What is the shape of a BH_3 molecule? **1**

(*b*) In the more stable compound a dative covalent bond exists between the boron and oxygen.

How does this dative covalent bond form? **1**

(*c*) To which class of organic compound does tetrahydrofuran belong? **1**

(3)

[Turn over

Marks

5. As part of an investigation a student was analysing the metallic content of a key known to be composed of a copper/nickel alloy.

The key was dissolved in nitric acid and the resulting solution diluted to 1000 cm^3 in a standard flask using tap water. Three 25·0 cm^3 samples of the nitrate solution were pipetted into separate conical flasks and approximately 10 g of solid potassium iodide were added. Iodine was produced as shown in the equation.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

The liberated iodine was titrated against standardised 0·102 mol l^{-1} sodium thiosulphate solution. Starch indicator was added near the end point of the titration.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

The results, for the volume of thiosulphate used, are given in the table.

	Titration 1	Titration 2	Titration 3
Final volume/cm^3	16·30	31·50	46·80
Initial volume/cm^3	0·30	16·30	31·50
Volume added/cm^3	16·00	15·20	15·30

(*a*) From the results calculate the mass of copper in the key. **3**

(*b*) Suggest how the accuracy of the analysis could be improved. **1**

(*c*) The student then tried to analyse the original nitrate solution for nickel using EDTA as in a PPA experiment. The value obtained for the nickel content was much greater than the true value.

Give the main reason why the value obtained was higher than the true value. **1**

(5)

Marks

6. A student was trying to determine the partition coefficient of propanedioic acid between the two solvents, hexane and water.

$$\text{propanedioic acid}_{(\text{water})} \rightleftharpoons \text{propanedioic acid}_{(\text{hexane})}$$

The following series of steps were carried out.

Step A. 25 cm^3 water and 25 cm^3 hexane were pipetted into apparatus X.

Step B. A measured mass of propanedioic acid was added to the solvents in apparatus X.

Step C. The mixture was shaken for approximately 2 minutes and allowed to settle.

These steps were repeated with different masses of propanedioic acid.

(*a*) Name apparatus X. **1**

(*b*) A series of titrations were carried out which enabled the student to work out the equilibrium concentrations of propanedioic acid in the two solvents. The values obtained are given in the table below.

Mass of propanedioic acid used/g	Concentration of propanedioic acid in water/mol l^{-1}	Concentration of propanedioic acid in hexane/mol l^{-1}
0·31	0·24	0·031
0·44	0·30	0·038
0·61	0·37	0·048

Use these results to calculate a value for the partition coefficient. **1**

(*c*) The student repeated the experiment several weeks later using the same chemicals. The values obtained are given in the table below.

Mass of propanedioic acid used/g	Concentration of propanedioic acid in water/mol l^{-1}	Concentration of propanedioic acid in hexane/mol l^{-1}
0·93	0·57	0·083

Give the reason why this experiment produces a different value for the partition coefficient compared to the value calculated earlier. **1**

(*d*) Why would no partition take place if ethanol had been used instead of hexane? **1**

(4)

[Turn over

Marks

7. Balsamic vinegar is a dark brown liquid containing ethanoic acid. The pH of a sample of balsamic vinegar was 2·5.

(*a*) Calculate the concentration of ethanoic acid in the sample of balsamic vinegar. **2**

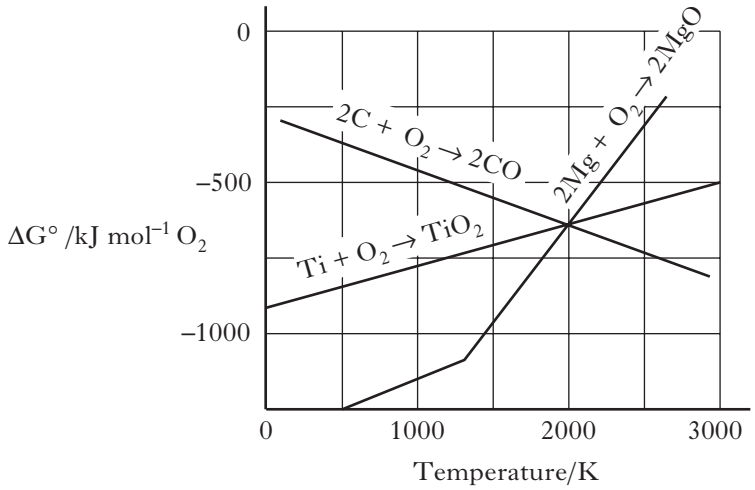
(*b*) A student chose to use a pH meter rather than use an indicator for the titration of balsamic vinegar with sodium hydroxide.

Apart from being more accurate, suggest why the student chose to use a pH meter rather than an indicator for this particular titration. **1**

(*c*) Write the formula for the conjugate base of ethanoic acid. **1**

(4)

8. Part of an Ellingham diagram is shown below.



(*a*) Using the Ellingham diagram give the temperature **range** over which magnesium will reduce titanium dioxide to titanium. **1**

(*b*) Suggest why the line labelled $2C + O_2 \rightarrow 2CO$ slopes downward. **1**

(*c*) Suggest why the gradient of the line labelled $2Mg + O_2 \rightarrow 2MgO$ changes at approximately 1360 K. **1**

(3)

9. Silver oxide cells are used in hearing aids. Zinc is the negative electrode and silver(I) oxide is the positive electrode. The overall cell reaction is represented by the equation

$$Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$$

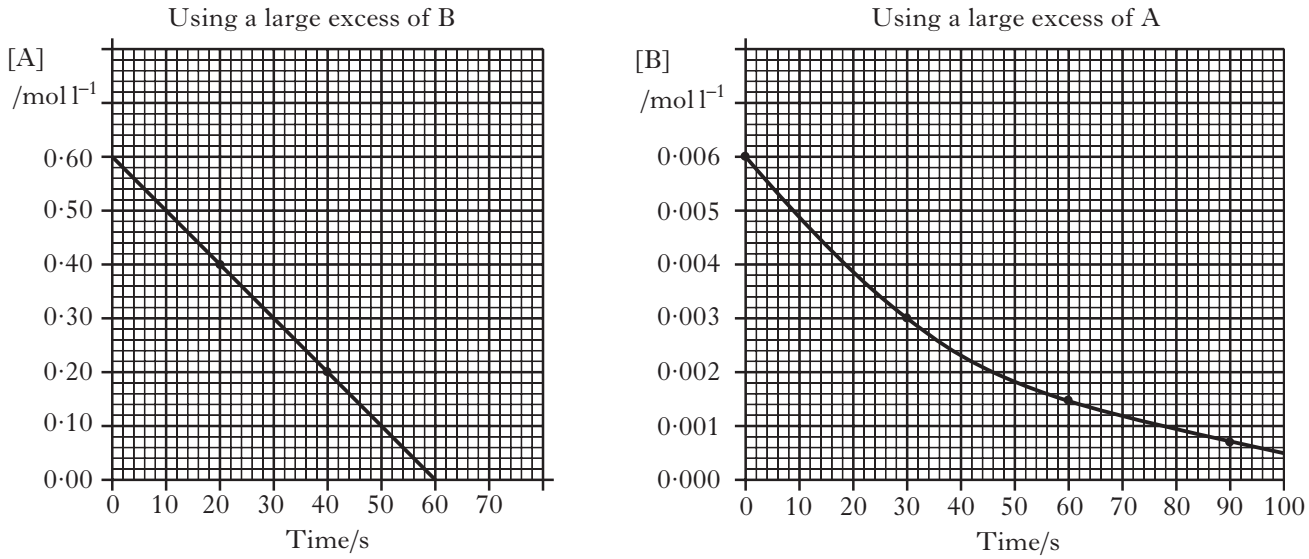
The free energy change for the cell is –279·8 kJ per mole of zinc.

Calculate the voltage produced by the cell. **(3)**

Marks

10. The graphs show how the concentrations of reactants A and B change with time for the reaction

$$A + B \rightarrow C$$



(*a*) What is the order of reaction with respect to A? **1**

(*b*) What is the order of reaction with respect to B? **1**

(*c*) What are the units of the rate constant in this reaction? **1**

(3)

11. Both lithium aluminium hydride, $LiAlH_4$, and phosphorus pentachloride, PCl_5, react vigorously with water producing different gases.

(*a*) Name the gas produced when water reacts with

(i) lithium aluminium hydride **1**

(ii) phosphorus pentachloride. **1**

(*b*) Phosphorus pentachloride will also react with any compound containing a hydroxyl group. A chlorine atom replaces the hydroxyl group. For example,

$$C_6H_5COOH \xrightarrow{PCl_5} C_6H_5COCl \quad \text{or} \quad CH_3COOH \xrightarrow{PCl_5} CH_3COCl$$

(i) What type of organic compound is produced in these reactions? **1**

(ii) Draw a structural formula for the ester formed when C_6H_5COCl reacts with propan-2-ol. **1**

(iii) What is the advantage of using C_6H_5COCl instead of benzoic acid in this esterification reaction? **1**

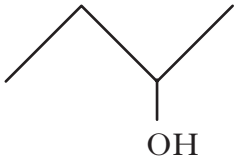
(5)

Marks

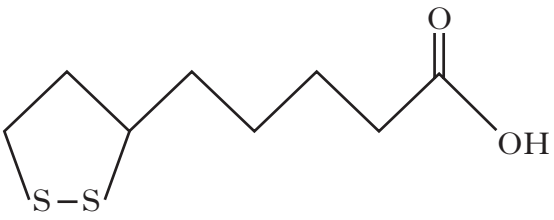
12. Skeletal structural formulae are used to show structures of molecules more simply than full structural formulae.

For example, pent-1-ene can be represented as

and butan-2-ol as



Lipoic acid has recently been used as a food supplement. The skeletal structural formula of lipoic acid is shown below.



(*a*) Write the molecular formula of lipoic acid. **1**

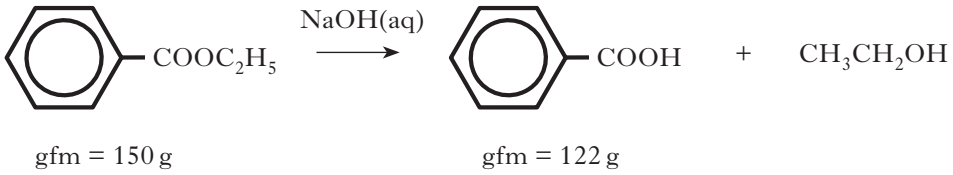
(*b*) (i) Lipoic acid is optically active. Copy the skeletal structural formula of lipoic acid and circle the carbon atom responsible for the optical activity of lipoic acid. **1**

(ii) Why does this carbon atom make lipoic acid optically active? **1**

(3)

Marks

13. In a PPA, benzoic acid is prepared from ethyl benzoate by refluxing with sodium hydroxide solution.



gfm = 150 g gfm = 122 g

(*a*) Why is the mixture refluxed rather than heated in an open beaker? **1**

(*b*) Name the type of reaction that is involved between ethyl benzoate and sodium hydroxide solution. **1**

(*c*) What does the procedure suggest should be added to the flask along with ethyl benzoate and sodium hydroxide solution? **1**

(*d*) What change in appearance of the contents of the flask indicates that the reaction is complete? **1**

(*e*) A yield of 73·2% of benzoic acid was obtained from 5·64 g of ethyl benzoate.

Calculate the mass of benzoic acid produced. **2**

(6)

14. (*a*) Benzene reacts with a "nitrating mixture" to produce nitrobenzene.

(i) Name the type of chemical reaction that takes place in the nitration of benzene. **1**

(ii) Nitrobenzene is reduced by reaction with a mixture of tin and concentrated hydrochloric acid to form an organic base.

Identify this organic base. **1**

(*b*) Benzene also reacts with sulphur trioxide dissolved in concentrated sulphuric acid to produce benzenesulphonic acid, $C_6H_5SO_3H$.

(i) Draw a structural formula for benzenesulphonic acid. **1**

(ii) Draw a Lewis electron dot diagram for sulphur trioxide. **1**

(4)

[Turn over for Question 15 on *Page eighteen*

Marks

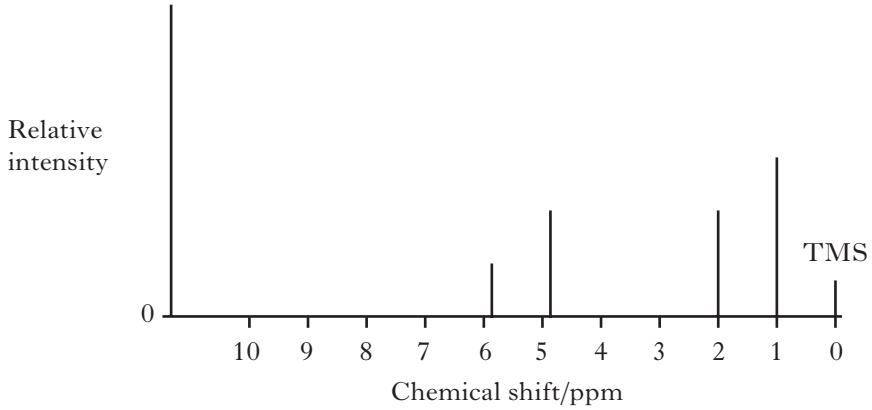
15. Chloroalkane **A** has molecular formula C_4H_9Cl. When **A** is heated with NaOH(aq), it undergoes an S_N2 reaction to form alcohol **B**.

Alcohol **B** can be oxidised by acidified potassium dichromate solution and it can also be dehydrated to produce a mixture of two alkenes which are structural isomers.

(*a*) Draw a structural formula for compound **A**. **1**

(*b*) Draw the structure of the transition state involved in this S_N2 reaction. **1**

(*c*) The simplified proton nmr spectrum of one of the alkenes is shown.



Sketch the proton nmr spectrum of the other alkene. **2**

(4)

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