X012/13/02

NATIONAL FRIDAY, 31 MAY QUALIFICATIONS 1.00 PM - 3.30 PM 2013 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 equation can be used to represent the second ionisation energy of the diatomic element, X?
 - $\begin{array}{lll} A & X_2(g) & \to X_2^{2^+}(g) + 2e^- \\ B & {}^{l_2}X_2(g) & \to X^{2^+}(g) + 2e^- \\ C & X^+(g) & \to X^{2^+}(g) + e^- \\ D & X(g) & \to X^{2^+}(g) + 2e^- \end{array}$
- **2.** Which of the following lists electromagnetic radiation bands in order of increasing frequency?
 - A Ultraviolet, visible, infra-red, radio
 - B Radio, infra-red, visible, ultraviolet
 - C Radio, microwave, ultraviolet, visible
 - D Visible, ultraviolet, X-ray, microwave
- **3.** Using information from the Data Booklet which one of the following metal salts will emit radiation of the highest frequency when placed in a Bunsen flame?
 - A Copper(II) sulphate
 - B Potassium chloride
 - C Barium chloride
 - D Lithium sulphate
- **4.** Which of the following indicators transmits only the lower frequencies of the visible spectrum at low pH?

Indicator	Colour in acid	Colour in alkali
А	Violet	Red
В	Green	Blue
С	Yellow	Violet
D	Red	Yellow

- 5. When electrons occupy degenerate orbitals, they do so in such a way as to maximise the number of parallel spins. This statement is known as
 - A the Pauli exclusion principle
 - B Heisenberg's uncertainty principle
 - C the aufbau principle
 - D Hund's rule.

- **6.** Which of the following represents the configuration of the highest energy electrons in an atom of a Group III element in the ground state?
 - $A = 3s^2 3p^1$
 - B $3s^23p^3$
 - C $4s^23d^1$
 - $D = 4s^24p^3$
- **7.** Which of the following analytical techniques would be most suitable to determine quantitatively the concentration of sodium ions in a urine sample?
 - A Mass spectrometry
 - B Infra-red spectroscopy
 - C Atomic emission spectroscopy
 - D Proton nuclear magnetic resonance spectroscopy
- **8.** Which of the following represents a valid Lewis electron dot diagram for ozone, O₃?



- **9.** Which of the following substances contains a dative covalent bond?
 - A NH₃
 - B NCl₃
 - C NH₄Cl
 - D CH₃NH₂
- **10.** Which of the following molecules has the greatest number of non-bonding electron pairs (lone pairs)?
 - $\begin{array}{ccc} A & H \\ & H C = O \\ B & H \end{array}$

$$\begin{array}{c} H = C - C \\ H = C - C \\ H \end{array}$$

$$\begin{array}{ccc} C & H & H \\ I & I & \checkmark \\ H - C - N \\ I & H \\ H & H \end{array}$$

$$\begin{array}{ccc}
 D & H \\
 I & I \\
 H - C - O - H \\
 I \\
 H
\end{array}$$

11. The following diagram represents a square-planar structure.

Where _____ and _____ represent bonding electron pairs

and ^(c) represents a non-bonding electron pair (lone pair).

Which of the following species could have the structure shown above?

- A SF₄
- B NH₄⁺
- C XeF₄
- D AlH₄-



The graph shows how the electrical conductivity varies with temperature in

- A a metal
- B an ionic solid
- C a semiconductor
- D a superconductor.
- **13.** Which of the following compounds contains hydride ions?
 - A NH₃
 - B HCl
 - $C H_2S$
 - D CaH₂
- **14.** In which of the following reactions does the oxidation state of copper neither increase nor decrease?
 - $\mathbf{A} \quad \mathbf{Zn} + \mathbf{CuSO}_4 \rightarrow \mathbf{ZnSO}_4 + \mathbf{Cu}$
 - B $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$
 - $\mathbf{C} \qquad \mathrm{FeCl}_2 + \mathrm{CuCl}_2 \rightarrow \mathrm{FeCl}_3 + \mathrm{CuCl}$
 - D Cu + $4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$
- **15.** 100 cm^3 of $0.500 \text{ mol } l^{-1} \text{ AgNO}_3(aq)$ is reacted with excess $\text{CaCl}_2(aq)$.

What mass of precipitate forms?

- $\mathrm{A} \qquad 7{\cdot}17\,\mathrm{g}$
- B 8.95 g
- C 12.6 g
- D 14·3 g

16. When a salt, formula $Ni(H_2O)_6.K_2(SO_4)_2$, is dissolved in water, the solution contains the ions $Ni(H_2O)_6^{2+}$, K^+ and SO_4^{2-} .

The total number of moles of ions in one litre of $0.01 \text{ mol } l^{-1}$ solution is

- A 0.01
- B 0.03
- C 0.05
- D 0.10.
- 17. What volume of $0.2 \text{ mol } l^{-1}$ potassium sulphate is required to make, by dilution with water, one litre of a solution with a **potassium** ion concentration of $0.1 \text{ mol } l^{-1}$?
 - $A = 100 \text{ cm}^3$
 - $B = 250 \text{ cm}^3$
 - $C = 400 \, \text{cm}^3$
 - $D = 500 \text{ cm}^3$
- **18.** Phosphoric acid is a weak acid and undergoes partial dissociation according to the equation

 $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$

The position of equilibrium would be shifted to the right by the addition of

- A a catalyst
- B sulphuric acid
- C sodium hydroxide
- D sodium dihydrogenphosphate.
- **19.** Caffeine can be extracted from coffee dissolved in water using the solvent dichloromethane (CH_2Cl_2) .

 $caffeine(aq) \rightleftharpoons caffeine(CH_2Cl_2)$

Which of the following, when increased, will change the value of the partition coefficient for this equilibrium?

- A Temperature
- B Mass of coffee
- C Volume of water
- D Volume of dichloromethane

20. Substance **X** is distributed between equal volumes of two immiscible liquids as shown in the diagram. The number of dots represents the relative distribution of **X** in the two liquids at equilibrium.





The partition coefficient for this system is

- A 0.46
- B 0.50
- C 2.00
- D 2·17.
- **21.** Which of the following decreases when an aqueous solution of ethanoic acid is diluted?
 - A pH
 - B $[H^+]$
 - С рКа
 - D The degree of dissociation
- **22.** Iodide ions are oxidised by acidified nitrite ions according to the equation

 $2\mathrm{NO_2^-} + 2\mathrm{I^-} + 4\mathrm{H^+} \rightarrow 2\mathrm{NO} + \mathrm{I_2} + 2\mathrm{H_2O}$

Addition of sodium ethanoate to the reaction mixture slows down the formation of iodine.

The most likely explanation for this effect is that ethanoate ions

- A remove iodine
- B reduce the concentration of iodide ions
- C react with nitrite ions
- D react with hydrogen ions.

- **23.** Which of the following indicators should be used in the titration of potassium hydroxide solution with ethanoic acid solution?
 - A Phenolphthalein, pH range 8.0 9.8
 - B Bromothymol blue, pH range 6.0 7.6
 - C Methyl red, pH range $4 \cdot 2 6 \cdot 2$
 - D Methyl orange, pH range 3.1 4.4
- **24.** The following diagram illustrates the catalysed and uncatalysed reaction pathways for a reversible reaction.



The activation energy for the reverse uncatalysed reaction is given by

- A s-r
- B p + s
- C = q p
- D p + r.

25. The element X can exist in two forms, as X=X, or as X₈ with the following cubic structure.



The X—X bond dissociation enthalpy is 163 kJ mol^{-1} .

The X=X bond dissociation enthalpy is 944 kJ mol^{-1} .

Which of the following is the value of ΔH , in kJ mol⁻¹, for the reaction

$$X_8(g) \rightarrow 4X_2(g)$$
?

A –2472

- В -1820
- C +1820
- D +2472

26. Which of the following sets of information would enable the bond enthalpy of a C=C double bond to be calculated?

	Enthalpy of formation of	Enthalpy of combustion of	Enthalpy of sublimation of	(Mean) bond enthalpy of
А	ethene	ethene		С—Н, Н—Н
В	benzene	benzene		С—Н, Н—Н
С	ethene		carbon	С—Н, Н—Н
D	benzene		carbon	С—Н, Н—Н

- **27.** In which of the following changes will there be an increase in entropy?
 - A $CO_2(g) \rightarrow CO_2(s)$
 - B Combustion of ethanol
 - C Hydrogenation of ethene
 - D Phenylethene \rightarrow poly(phenylethene)
- **28.** One mole of which of the following chlorides would have the greatest entropy at **750** °C?
 - A Sodium chloride
 - B Calcium chloride
 - C Potassium chloride
 - D Magnesium chloride
- **29.** The conversion of butanoic acid into butan-1-ol is an example of
 - A elimination
 - B substitution
 - C oxidation
 - D reduction.

30.



Which line in the table is correct for the types of reaction taking place at (1), (2) and (3)?

	Reaction ①	Reaction 2	Reaction ③
Α	substitution	elimination	substitution
В	substitution	reduction	substitution
C	addition	reduction	condensation
D	addition	elimination	substitution

31. Bromine reacts with propene to produce 1,2-dibromopropane.

A possible intermediate in the reaction is

32. Which of the following represents an initiation step in a chain reaction?

Η

A $Cl_2 \rightarrow 2Cl \bullet$

Η

Η

- $B \qquad CH_3 \bullet + CH_3 \bullet \to C_2H_6$
- $\mathbf{C} \qquad \mathbf{C}\mathbf{H}_4 + \mathbf{C}\mathbf{l} \bullet \to \mathbf{C}\mathbf{H}_3\mathbf{C}\mathbf{l} + \mathbf{H} \bullet$
- $\mathbf{D} \quad \mathbf{CH}_3 \bullet + \mathbf{Cl}_2 \to \mathbf{CH}_3 \mathbf{Cl} + \mathbf{Cl} \bullet$
- **33.** Which of the following compounds would be expected to have the highest boiling point?
 - A Pentanal
 - B Pentan-2-ol
 - C Pentan-2-one
 - D Ethoxypropane

34. Which line in the table shows a general formula which does **not** match the homologous series?

	General formula	Homologous series
А	$C_nH_{2n}O$	alkanals
В	$C_nH_{2n}O_2$	alkanoic acids
С	$C_nH_{2n+2}O$	alkanols
D	$C_nH_{2n}O$	ethers

- **35.** The Williamson synthesis for the preparation of unsymmetrical ethers (ROR') starting with an alcohol and a halogenoalkane is summarised in the general equations:
 - Step 1: ROH + Na \rightarrow RO⁻Na⁺ + $\frac{1}{2}$ H₂

Step 2: $RO^-Na^+ + R'X \rightarrow ROR' + Na^+X^-$

Using propan-2-ol and 2-chlorobutane, the unsymmetrical ether formed would be

- A CH₃CH₂CH₂OCH(CH₃)CH₂CH₃
- $B \qquad CH_3CH_2CH_2OCH_2CH_2CH_2CH_3$
- $C \qquad CH_3CH(CH_3)OCH_2CH_2CH_2CH_3$
- D CH₃CH(CH₃)OCH(CH₃)CH₂CH₃
- **36.** Which of the following is the strongest base?
 - A CH₃CH₂OH



C CH₃CH₂NH₂

D
$$()$$
 NH₂

37. Phenylamine reacts with hydrochloric acid.



The products are



38.



Which species initially attacks the benzene molecule in the above reaction?



The above reaction is an example of

- A addition
- B oxidation
- C elimination
- D substitution.
- **40.** Most medicines work by binding to receptors. Receptors are usually
 - A nucleophiles
 - B electrophiles
 - C free radicals
 - D protein molecules.

[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

60 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

1.	(<i>a</i>)	Name a dopant which could be added to germanium to make a p-type semiconductor.	1
	(<i>b</i>)	What is the charge carrier in a p-type semiconductor?	1
			(2)

2. Burning magnesium continues to burn when placed in a gas jar of carbon dioxide according to the equation

burning spoon
$$gas jar$$
 $gas jar$ $gag carbon dioxide$ $S^{\circ}/JK^{-1} mol^{-1}$ $Mg(s)$ $33 \cdot 0$ $CO_2(g)$ 214 $MgO(s)$ $27 \cdot 0$ $C(s)$ $5 \cdot 70$

 $2\mathrm{Mg}(s) + \mathrm{CO}_2(g) \rightarrow 2\mathrm{MgO}(s) + \mathrm{C}(s)$

- (a) Using the values from the table above, calculate ΔS° for the reaction.
- (b) Using the information below and your answer to (a), calculate ΔG° for the burning of magnesium in carbon dioxide.

$$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s) \qquad \Delta H^\circ = -493 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ = -394 \text{ kJ mol}^{-1} \qquad 3$$
(4)

1

3. The Born-Haber cycle diagram shows the theoretical process involved in the formation of rubidium chloride from the elements rubidium and chlorine.



- (a) Write the equation which represents the standard enthalpy of formation of rubidium chloride. 1 Use the Data Booklet to find the value for enthalpy change $\Delta H_{(4)}$. *(b)* 1 *(c)* What name is given to the enthalpy change represented by ΔH_{3} ? 1 Calculate the value for enthalpy change $\Delta H_{(5)}$. (d)1 (4)
- 4. In a PPA the manganese content of a steel paper clip is determined by converting the manganese into purple permanganate ions, the concentration of which is measured using colorimetry. At the start of the activity, a calibration graph has to be drawn.

(<i>a</i>)	What data must be collected to allow the calibration graph to be drawn?	1
(<i>b</i>)	Which colour of filter or wavelength of light should be used in this procedure?	1
(<i>c</i>)	A weighed sample of the paper clip is dissolved in 2 mol l ⁻¹ nitric acid in a beaker covered with a watch glass which is placed in a fume cupboard because a toxic gas is produced.	
	Name this toxic gas.	1
(<i>d</i>)	Colorimetry is not used to determine potassium content because potassium ions are not coloured. The concentration of potassium ions in a compound can be determined using atomic absorption spectroscopy at a wavelength of 405 nm.	
	Calculate the energy, in kI mol ^{-1} , of this radiation.	2

Calculate the energy, in kJ mol⁻¹, of this radiation.

Marks



The absorption spectrum of a solution of sodium tetrachlorocobaltate(II) is shown above.

(<i>a</i>)	Predict the most likely colour of the solution.	1
<i>(b)</i>	Write the electronic configuration for a cobalt(II) ion in terms of s, p and d orbitals.	1
(<i>c</i>)	Write the formula for the tetrachlorocobaltate(II) ion.	1
		(3)

6. Propanoic acid is a weak acid. Sodium propanoate is a salt which can be formed from it. Both propanoic acid and sodium propanoate can be used as mould inhibitors.

(<i>a</i>)	Calculate the pH of $0.10 \text{ mol } l^{-1}$ propanoic acid solution.	2
(<i>b</i>)	0.20 moles of sodium propanoate are added to 100 cm^3 of the $0.10 \text{ mol } l^{-1}$ solution of propanoic acid.	
	Calculate the pH of the buffer solution formed.	2

(4)

Marks

7.	(<i>a</i>)	Calculate the emf of a $Cr(s) Cr^{3+}(aq) Fe^{2+}(aq) Fe(s)$ cell operating under standard conditions.	Marks 1
	(<i>b</i>)	Calculate the free energy change, ΔG° , in kJ per mole of chromium, for this cell reaction.	3
	(c)	Use the Ellingham diagram below to explain whether zinc or aluminium should be chosen to extract chromium from chromium oxide.	1
ΔG°/k]	∫ mol	$ \begin{array}{c} 0 \\ -100 \\ -200 \\ -300 \\ -400 \\ -400 \\ -500 \\ -600 \\ -600 \\ -600 \\ -700 \\ -800 \\ -900 \\ -1000 \\ -1100 \\ \end{array} $	
		0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200 Temperature/°C	

(5)

8. A kinetics study was carried out on the reaction between a halogenoalkane, C₄H₉Br, and aqueous sodium hydroxide.

$$C_4H_9Br$$
 + NaOH \rightarrow C_4H_9OH + NaBr

The following results were obtained.

$[C_4H_9Br]/mol l^{-1}$	[NaOH]/mol l ⁻¹	Initial Rate/mol l ⁻¹ s ⁻¹
8.0×10^{-4}	0.10	0.12
1.6×10^{-3}	0.10	0.30
1.6×10^{-3}	0.20	0.30
$3 \cdot 2 \times 10^{-3}$	0.40	0.60

- (a) What is the order of reaction with respect to
- (i) the halogenoalkane
 (ii) the sodium hydroxide?
 1
 (b) Write the rate equation for the reaction.
 (c) Calculate a value for the rate constant, k, including the appropriate units.
 (d) There are four structural isomers of C₄H₉Br.
 (i) From the above results, which isomer is most likely to have been used?
 (ii) Explain your answer to (d)(i).

9. Nickel(II) ions react quantitatively with dimethylglyoxime $(C_4H_8O_2N_2)$ forming a complex which precipitates out as a red solid. The equation for the reaction and the structure of the complex are shown below.

$$Ni^{2+} + 2C_4H_8O_2N_2 \rightarrow Ni(C_4H_7O_2N_2)_2 + 2H^+$$



Relative formula mass = 288.7

- (a) What is the coordination number of nickel in the complex?
- (b) When 0.968 g of an impure sample of nickel(II) sulphate, NiSO₄.7H₂O, was dissolved in water and reacted with dimethylglyoxime, 0.942 g of the red precipitate was formed.

Calculate the percentage, by mass, of nickel in the impure sample of nickel(II) sulphate.

2 (3)

1

Marks

10. A student devised the following reaction sequence.



(<i>b</i>)	What experimental condition would be required in step (2)?	1
(c)	Draw a structural formula for product \mathbf{X} .	1
(<i>d</i>)	What type of reaction is taking place in step ④?	1
(<i>e</i>)	Draw a structural formula for product Y .	1

(5)

1

11. Methylamphetamine (also known as "speed") and caffeine are stimulants.

A "designer drug" with a structure related to methylamphetamine is ecstasy. Ecstasy tablets are sometimes contaminated with a substance called 4-MTA.



12. In a PPA, cyclohexene is prepared from cyclohexanol using a dehydrating agent.

<i>(a)</i>	Which dehydrating agent is used in the PPA?	1
(b)	(i) When the reactants have been heated gently for about 15 to 20 minutes, the mixture is allowed to cool. Separation of the product is carried out by adding saturated sodium chloride solution to the reaction mixture and vigorously shaking them together for about a minute and allowing them to settle and form two layers.	
	Why is saturated sodium chloride solution used rather than water?	1
	(ii) Which piece of apparatus is used in this part of the procedure ?	1
(<i>c</i>)	The identity of the product can be verified by using infra-red spectroscopy.	
	Predict one difference that would be observed between the infra-red spectra of cyclohexene and cyclohexanol.	1
		(4)

Marks

13. The diagram below shows a reaction sequence starting from compound A which is pentan-2-ol ($C_5H_{12}O$).



Compound **B** can exist as two geometric isomers.

Compound **C** is pent-1-ene.

Compound \mathbf{D} is the oxidation product of compound \mathbf{A} .

(a)	Name and draw the structural formulae for the two geometric isomers of compound B .	2
(<i>b</i>)	Name compound D .	1
(<i>c</i>)	Compound E is a cyanohydrin.	
	(i) Name the type of reaction occurring when D is converted into E .	1
	(ii) Draw a structural formula for compound E .	1
(<i>d</i>)	Name or draw a structural formula for compound F .	1
		(6)

3

- 14. 5.00 g of an organic compound **A** was burned completely producing 11.89 g of CO₂ and 6.08 g of H₂O as the only products.
 - (*a*) Using the information above, calculate the empirical formula for compound **A**.
 - (b) The infra-red spectrum of compound **A** is shown below.



Which bond is responsible for the peak at 1140 cm⁻¹?

- (c) The mass spectrum of compound **A** shows the molecular ion to have a mass/charge ratio of 74. Deduce the molecular formula of compound **A**.
- (*d*) The proton nmr spectrum of compound **A** is shown below.



Using all the above information, deduce the structural formula for compound A.

1 (6)

1

1

[END OF QUESTION PAPER]

Page nineteen

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