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JC 2 PRELIMINARY EXAMINATION in preparation for General Certificate of Education Advanced Level

Higher 2

CHEMIST	RY		9647/01
CLASS		INDEX NUMBER	
CANDIDATE NAME			

Paper 1 Multiple Choice

Additional Materials: Data Booklet Multiple Choice Answer Sheet

# READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in. Write in soft pencil. Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

## Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

30 August 2016

1 hour

#### Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Carbon disulfide, CS<sub>2</sub>, is a volatile liquid used in the production of cellophane which is used for food packaging.

On combustion, CS<sub>2</sub> is oxidised as follows:

 $CS_2(g) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$ 

A 20 cm<sup>3</sup> sample of carbon disulfide vapour is ignited with 100 cm<sup>3</sup> of oxygen. The final volume of gas after burning is treated with an excess of aqueous alkali.

Which percentage of this final volume dissolves in alkali? (All volumes are measured at room temperature and pressure.)

- **A** 20%
- **B** 40%
- **C** 60%
- **D** 80%
- 2 Consider the following half-equations

$$\begin{array}{cccc} C_2O_4^{2-} & \longrightarrow & 2CO_2 + 2e^- \\ Fe^{2+} & \longrightarrow & Fe^{3+} + e^- \\ MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O \end{array}$$

What volume of 0.01 mol dm<sup>-3</sup> potassium manganate(VII) is needed to completely oxidise  $25.0 \text{ cm}^3$  of an acidified solution of 0.01 mol dm<sup>-3</sup> FeC<sub>2</sub>O<sub>4</sub>?

- **A** 5 cm<sup>3</sup>
- **B** 7.5 cm<sup>3</sup>
- **C** 10 cm<sup>3</sup>
- **D** 15 cm<sup>3</sup>

3 Which electronic configuration represents an element that forms a simple ion with a charge of -3?

- A 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>1</sup>
- **B** 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>3</sup>
- **C** 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>1</sup>4s<sup>2</sup>
- D 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>3</sup>4s<sup>2</sup>

- A carbon dioxide contains double covalent bonds while silicon dioxide contains single covalent bonds.
- **B** instantaneous dipole induced dipole attractions are weaker than permanent dipole permanent dipole attractions.
- **C** carbon-oxygen bonds are less polar than silicon-oxygen bonds.
- **D** van der Waals' forces are much weaker than covalent bonds.
- 5 Under which conditions will the behaviour of a gas be **most** ideal?

	pressure	temperature
Α	high	high
в	high	low
С	low	high
D	low	low

6 The enthalpy changes involving some oxides of nitrogen are given below:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$	$\Delta H$ = +180 kJ mol <sup>-1</sup>
$2NO_2(g) + \frac{1}{2}O_2(g) \rightarrow N_2O_5(g)$	$\Delta H = -55 \text{ kJ mol}^{-1}$
$N_2(g) + \frac{5}{2}O_2(g) \rightarrow N_2O_5(g)$	$\Delta H$ = +11 kJ mol <sup>-1</sup>

What is the enthalpy change, in kJ mol<sup>-1</sup>, of the following reaction?

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

A -114 B +114 C -136 D +136

7 A typical protein forms hundreds of hydrogen bonds and thousands of van der Waals' forces in folding from primary to tertiary structures.

Which of the following thermodynamic state functions of the protein best represents the folding process?

	∆ <b>G / kJ mol⁻¹</b>	∆ <i>H I</i> kJ mol <sup>-1</sup>	∆S/JK <sup>-1</sup> mol <sup>-1</sup>
Α	_	_	_
в	+	_	+
С	_	+	_
D	+	+	_

**8** When 1 mole of carbon dioxide gas solidifies as dry ice, 25.2 kJ of heat energy is evolved. The sublimation temperature of carbon dioxide is –78.5 °C.

What is the entropy change when 132 g of carbon dioxide gas solidifies at this temperature?

- A +130 J K<sup>-1</sup>
- **B** –130 J K<sup>-1</sup>
- **C** +389 J K<sup>-1</sup>
- **D** –389 J K<sup>-1</sup>
- **9** A student set up the hydrogen electrode shown in the diagram below.



What would have to be changed to make this a standard hydrogen electrode?

- **A** the acid solution used
- **B** the temperature of the gas and of the acid solution
- **C** the pressure of the gas
- **D** the metal comprising the electrode

**10** Use of the Data Booklet is relevant to this question.

Using inert electrodes, a current was passed through two beakers containing aqueous silver sulfate and aqueous copper(II) nitrate, connected in series under standard conditions.



What is the ratio of the mass of silver to copper deposited after the current was passed for *t* minutes?

- **A** 0.59 **B** 0.85
- **C** 1.70 **D** 3.40
- 11 A nitrogen-hydrogen mixture, initially in the mole ratio of 1:3, reached equilibrium with ammonia when 50% of the nitrogen had reacted. The total equilibrium pressure was p.

$$N_2(g) + 3H_2(g) \implies 2NH_3(g)$$

What was the partial pressure of ammonia in the equilibrium mixture?

Α	p	В	p	С	p	D	2р
	3		4		6		7

**12** Solid calcium hypochlorite pellets, Ca(C*l*O)<sub>2</sub>(s), are added to swimming pools to form HC*l*O(aq), which kills disease-causing bacteria and algae.

 $Ca(ClO)_2(s) \square Ca^{2+}(aq) + 2ClO^{-}(aq)$ 

 $ClO^{-}(aq) + H_2O(l)$   $HClO(aq) + OH^{-}(aq)$ 

What is the effect on the solubility of calcium hypochlorite and bacterial growth when pH decreases?

	solubility of calcium hypochlorite	effect on bacterial growth
Α	decreases	more favourable
В	decreases	less favourable
С	increases	more favourable
D	increases	less favourable

**13** The dissociation constant,  $K_{w}$ , for the ionisation of water,  $H_2O \square H^+ + OH^-$ , at different temperatures is given below.

temperature / °C	Kw
0	1.15 x 10 <sup>-15</sup>
25	1.00 x 10 <sup>-14</sup>
50	5.50 x 10 <sup>-14</sup>

What can be deduced from this information?

- **A** Only at 25 °C are  $[H^+]$  and  $[OH^-]$  equal.
- **B** The equilibrium lies furthest to the right at 0°C.
- **C** The forward reaction is exothermic.
- **D** The pH of water decreases as temperature increases.
- 14 A sparingly soluble salt, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> dissociates in aqueous solution as follows:

Given that the solubility product,  $K_{sp}$  of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is **Q**, what is the value of [Mg<sup>2+</sup>] in a saturated solution?

**A** 
$$(\frac{9Q}{4})^{\frac{1}{5}}$$
 **B**  $(\frac{Q}{27})^{\frac{1}{3}}$  **C**  $(\frac{Q}{108})^{\frac{1}{5}}$  **D**  $(\frac{9Q}{64})^{\frac{1}{3}}$ 

**15.** The reaction of hydrogen peroxide with iodide ions in an acidic solution is first order with respect to hydrogen peroxide as well as iodide ions, and zero order with respect to hydrogen ions.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(I) + I_2(aq)$$

Two experiments were carried out. Which pair of diagrams represents the variation of  $[H_2O_2]$  and  $[H^+]$  with time?



**16** Aluminium is an element in the third period, Na to Ar, of the Periodic Table.

What is true for aluminium?

- A Aluminium has the highest melting point of the elements in this period.
- **B** Aluminium is the only element in this period whose chloride reacts with water to form an acidic solution.
- **C** Aluminium is the only element in this period which can exist, at room temperature and pressure, as solid and conduct electricity.
- **D** Aluminium is the only element in this period whose oxide reacts with both acids and bases.
- 17 Which of the following statements regarding Group II elements or their compounds is correct?
  - A Magnesium chloride has a higher melting point than barium chloride.
  - **B** Magnesium is a stronger reducing agent than strontium.
  - **C** Calcium hydroxide is more thermally stable than barium hydroxide.
  - **D** Strontium reacts more readily with oxygen than radium.
- **18** Which of the following statements about astatine, the element below iodine in Group VII of the periodic table, is **incorrect**?
  - A Silver astatide is insoluble in aqueous ammonia.
  - **B** Hydrogen astatide is less stable to heat than hydrogen iodide.
  - **C** Sodium astatide and hot concentrated sulfuric acid react to form astatine.
  - **D** Astatine and aqueous potassium chloride react to form aqueous potassium astatide and chlorine.

What are the formulae of the copper species in the blue and yellow solution?

	blue	yellow
Α	CuCl <sub>2</sub>	[CuCl <sub>4</sub> ] <sup>2-</sup>
в	CuCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	[CuCl <sub>6</sub> ] <sup>4-</sup>
С	Cu(OH) <sub>2</sub>	$CuCl_2(H_2O)_4$
D	[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	[CuCl <sub>4</sub> ] <sup>2-</sup>

20 Four carbon-carbon bonds are labelled in the diagram.



Which bonds are made up of an sp<sup>2</sup>–sp<sup>2</sup> overlap?

- A w and y only
- B w, x and y only
- C w, x, y and z
- **D** x and y only
- 21 When heated with chlorine, the hydrocarbon 3,3-dimethylpentane undergoes free radical substitution. In the propagation step, the free radical X<sup>•</sup> is formed by the loss of one hydrogen atom.

How many different forms of X • are theoretically possible?

**A** 2 **B** 3 **C** 4 **D** 5

**22** Bromoethene,  $CH_2$ =CHBr, is unreactive to nucleophiles whereas 3-bromopropene,  $CH_2$ =CHCH<sub>2</sub>Br is very reactive by comparison.

What explains the lack of reactivity of CH<sub>2</sub>=CHBr?

- A Substituted alkenes undergo only electrophilic addition.
- **B** The C=C double bond and the Br atom are both electron withdrawing which stabilises  $CH_2$ =CHBr.
- **C** The electrons on the Br atom delocalise into the  $\pi$  bond.
- **D** The presence of the  $\pi$  bond prevents free rotation of the C-Br bond this decreasing the reactivity.
- **23** Phosgene,  $COCl_2$ , is a colourless gas that gained infamy as a chemical weapon during World War I. It is formed when trichloromethane,  $CHCl_3$ , is left exposed to the atmosphere.

Below is a reaction scheme that involves trichloromethane and phosgene:

 $\mathsf{CHC}l_3 \longrightarrow \mathsf{COC}l_2 \longrightarrow \mathsf{COC}l(\mathsf{OH}) \longrightarrow \mathsf{CO}_2 + \mathsf{HC}l$ 

Which of the following type of reaction is **not** being observed in the reaction scheme?

- A oxidation
- **B** elimination
- **C** electrophilic addition
- **D** nucleophilic substitution
- **24** A chlorine-containing organic compound, **X**, undergoes an elimination reaction when treated with hot ethanolic potassium hydroxide solution.

What is **X**?

- **A**  $CH_2Cl_2$
- $\textbf{B} \qquad C_2 C \mathit{l}_6$
- C (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>Cl
- **D**  $(CH_3)_3CCH_2Cl$

**25** Dopamine is an important organic chemical that helps control the brain's reward and pleasure centres. It also helps regulate movement and emotional responses.



Which of the following statements about dopamine is incorrect?

- **A** It is able to rotate plane-polarized light.
- **B** It is soluble in water due to zwitterion formation.
- **C** It migrates to the negative electrode of an electrolytic cell at pH 14.
- **D** The acidity of dopamine will increase when aqueous bromine is added.
- 26 Two bottles containing the following reagents had their labels removed.



Which one of the following reagents can be used to distinguish between them?

- A sodium metal
- **B** sodium hydroxide
- **C** hot acidified potassium manganate(VII)
- D hot acidified potassium dichromate

**27** Marijuana (cannabis) is the most widely used illegal drug in many developed countries. Medical studies have shown that the active ingredient in marijuana, tetrahydrocannabinol, might provide medical benefits to some patients.



In the following reactions, the remains unaltered.

Which reaction will tetrahydrocannabinol undergo?

- A It reacts with aqueous bromine to incorporate up to 2 atoms of bromine in each molecule.
- **B** It reacts with hot acidified potassium dichromate(VI) to form a green solution.
- **C** It reacts with dilute nitric acid to form a substitution product.
- **D** It reacts with ethanoic acid to form a sweet-smelling product.
- **28** A student carried out an experiment to study the ease of hydrolysis of a series of chlorinated compounds, and recorded the observations based on the addition of acidified silver nitrate solution.

	time taken for precipitate to appear			
	shortest			longest
Α	$C_6H_5Cl$	CH <sub>2</sub> ClCONH <sub>2</sub>	CH <sub>3</sub> COC <i>l</i>	COCl <sub>2</sub>
В	$CH_2ClCONH_2$	$C_6H_5Cl$	$COCl_2$	$CH_3COCl$
С	CH₃COC <i>l</i>	$COCl_2$	$C_6H_5Cl$	$CH_2ClCONH_2$
D	$COCl_2$	CH <sub>3</sub> COC <i>l</i>	$CH_2ClCONH_2$	$C_6H_5Cl$

Which of the following gives the expected results?

**29** In the following two-step synthesis, **Y** a solid which is insoluble in water, is one of the components in the final reaction mixture.

13



- **30** Benzylamine has the formula  $C_6H_5CH_2NH_2$  and is a common precursor in organic synthesis. Which of the following statements about benzylamine is correct?
  - A It decolourises aqueous Br<sub>2</sub>.
  - **B** It can be produced by reduction of  $C_6H_5CH_2CN$ .
  - **C** It reacts with  $CH_3COOH$  to form  $C_6H_5CH_2NHCOCH_3$ .
  - **D** It reacts with excess  $CH_3CH_2Cl$  to form the compound,  $C_{13}H_{22}NCl$ .

## Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	В	C	D
1, 2 and 3	1 and 2	2 and 3	1 only
are	only are	only are	is
correct	correct	correct	correct

No other combination of statements is used as a correct response.

**31** Gaseous particle **Y** has a proton (atomic) number *n* and a charge of +1.

Gaseous particle **Z** has a proton (atomic) number of n+1 and is isoelectronic with **Y**.

Which statement correctly describes Y and Z?

- 1 Y has a larger radius than Z.
- 2 Y requires more energy than Z when a further electron is removed from each particle.
- **3** Y releases more energy than Z when an electron is added to each particles.
- 32 Which of the following molecules will form a hydrogen bond with another of its own molecules?
  - 1 CH<sub>3</sub>NH<sub>2</sub>
  - 2 CH<sub>3</sub>CHO
  - 3 CH<sub>3</sub>CH<sub>2</sub>F

**33** The graph below shows the results of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied but that of amylase was kept constant.



Which conclusions can be deduced from these results?

- 1 When [maltose] is low, the rate is first order with respect to [maltose].
- 2 When [maltose] is high, the rate is independent of [maltose].
- **3** When [maltose] is high, the rate is independent of [amylase].
- **34** With reference to the *Data Booklet* and the data below, deduce which of the following statements are correct.

Half-equation	E <sup>θ</sup> IV
$VO_2^+(aq) + 2H^+(aq) + e^- \Box VO^{2+}(aq) + H_2O(I)$	+1.00
$VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \Box V^{3+}(aq) + H_2O(I)$	+0.34
$V^{3+}(aq) + e^{-} = V^{2+}(aq) + H_2O(I)$	-0.26

- 1 An excess of zinc is capable of reducing  $VO_2^+(aq)$  to  $V^{2+}(aq)$  in acidic conditions.
- **2** Fe<sup>3+</sup>(aq) is capable of oxidising  $V^{2+}(aq)$  to  $VO_2^+$  (aq) in acidic conditions.
- 3  $Zn^{2+}(aq)$  ions will oxidise  $V^{2+}(aq)$  ions to  $V^{3+}(aq)$  ions.

indicator	working pH range	colour change	
	working prinange	Acid	Alkali
chlorophenol red	4.8 - 6.4	Yellow	Red

**35** The working range and colour change of chlorophenol red is given below.

Two drops of this indicator are added to each of the three aqueous solutions listed below.

Which solution has its colour correctly stated?

	solution	colour
1	aluminium oxide added to water	Red
2	0.1 mol dm <sup>-3</sup> of CH <sub>3</sub> COOH ( $K_a$ = 1.8 x 10 <sup>-5</sup> mol dm <sup>-3</sup> )	Yellow
3	solution of sodium ethanoate and ethanoic acid in 1:2 proportion [p $K_a$ of ethanoic acid = 4.7]	Orange

**36** Use of the Data Booklet is relevant to this question.

Which statements about the trends in properties of the hydrogen halides are correct?

- 1 Volatility decreases in the order: HF > HCl > HBr > HI.
- 2 Thermal stability increases in the order: HI < HBr < HCl < HF.
- **3** Ease of oxidation increases in the order: HF < HCl < HBr < HI.
- **37** Nickel is purified by a method called the Mond process. The equation of the first step of the purification is shown below.

 $Ni(s) + 4CO(g) \longrightarrow Ni(CO)_4(I)$ 

Which of the following statements are correct?

- 1 CO is a monodentate ligand.
- 2 Ni in Ni(CO)<sub>4</sub> has a co-ordination number of 4.
- **3** The oxidation number of Ni in Ni(CO)<sub>4</sub> is zero.

**38** Compound **X** is a synthetic precursor of *meloscine*, an alkaloid isolated from the New Caledonian plant *Melodinus Scandens Forst*.



Which of the following statements about its reactions are correct?

- 1 1 mol of **X** reacts with 2 mol of HBr(g) when heated.
- **2** 1 mol of **X** reacts with 4 mol of  $Br_2(aq)$  at room temperature.
- 3 1 mol of X reacts with 2 mol of  $CH_3COCl$  at room temperature.

**39** Which of the following reactions give products that does not rotate the plane of polarised light?

- 1 1–bromobutane refluxed with aqueous KOH
- 2 butanone reacted with HCN, trace amount of NaOH
- **3** but–1–ene reacted with bromine dissolved in organic solvent
- 40 Which of the following could result in the loss of the tertiary structure of a protein?
  - 1 addition of weak acid
  - 2 addition of alcohol
  - **3** addition of AgNO<sub>3</sub> solution

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JC 2 PRELIMINARY EXAMINATION 2 in preparation for General Certificate of Education Advanced Level

Higher 2

CHEMIST	RY		9647/01
CLASS		INDEX NUMBER	
CANDIDATE NAME			

Paper 1 Multiple Choice

Additional Materials: Data Booklet Multiple Choice Answer Sheet

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Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

## Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

30 August 2016

1 hour

### Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Carbon disulfide, CS<sub>2</sub>, is a volatile liquid used in the production of cellophane which is used for food packaging.

On combustion, CS<sub>2</sub> is oxidised as follows.

 $CS_2(g) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$ 

A 20 cm<sup>3</sup> sample of carbon disulfide vapour is ignited with 100 cm<sup>3</sup> of oxygen. The final volume of gas after burning is treated with an excess of aqueous alkali.

Which percentage of this final volume dissolves in alkali? (All volumes are measured at room temperature of pressure.)

- **A** 20%
- **B** 40%
- **C** 60%
- **D** 80%

**Answer: C** 

1 mole of CS<sub>2</sub> reacts with 60cm<sup>3</sup> of O<sub>2</sub>, remaining volume of O<sub>2</sub> = 40 cm<sup>3</sup> produces 1 mole of CO<sub>2</sub> 20 cm<sup>3</sup> of CS2 produces 20 cm<sup>3</sup> of CO<sub>2</sub> and 40 cm<sup>3</sup> of SO<sub>2</sub> Total volume of gases at the end of reaction = 40 + 20 + 40 = 100 cm<sup>3</sup> Both CO<sub>2</sub> and SO<sub>2</sub> are acidic gases which will react with NaOH Hence % of final volume dissolved in alkali 60/100 x 100% = 60%

2 Consider the following half-equations

 $\begin{array}{ccc} C_2O_4{}^{2-} & \longrightarrow & 2CO_2 + 2e^- \\ Fe^{2+} & \longrightarrow & Fe^{3+} + e^- \\ MnO_4{}^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O \end{array}$ 

What volume of 0.01 mol dm<sup>-3</sup> potassium manganate(VII) is needed to completely oxidise  $25.0 \text{ cm}^3$  of an acidified solution of 0.01 mol dm<sup>-3</sup> FeC<sub>2</sub>O<sub>4</sub>?

A  $5 \text{ cm}^3$ 

- **B** 7.5 cm<sup>3</sup>
- **C** 10 cm<sup>3</sup>

**D** 15 cm<sup>3</sup>

Answer: D

Combining eqns:



**3**   $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O x3$ Overall equation:  $3MnO_4^- + 5FeC_2O_4 \longrightarrow 10CO_2 + 5Fe^{3+} + 3Mn^{2+} + 12H_2O$ 

Amount of FeC<sub>2</sub>O<sub>4</sub>= 25/100 x 0.01 = 0.00025 mol Mole ratio of FeC<sub>2</sub>O<sub>4</sub>  $\cdot$  MnO<sub>4</sub><sup>-</sup> = 5 : 3 Amount of MnO<sub>4</sub><sup>-</sup> = 3/5 x 0.00025 = 0.00015 mol Volume of MnO<sub>4</sub><sup>-</sup> = 0.00015 / 0.01 = 0.015 dm<sup>3</sup> = 15 cm<sup>3</sup>

- 3 Which electronic configuration represents an element that forms a simple ion with a charge of -3?
  - **A**  $1s^22s^22p^63s^23p^1$

## **B** 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>3</sup>

- **C** 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>1</sup>4s<sup>2</sup>
- D 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>3</sup>4s<sup>2</sup>

## Answer: B

- A : Group III element : + 3 ion
- B: Group V : -3 ion

C and D are transition elements – forms positively charged ions

- 4 Carbon dioxide is a gas at room temperature while silicon dioxide is a solid because
  - A carbon dioxide contains double covalent bonds while silicon dioxide contains single covalent bonds.
  - **B** instantaneous dipole induced dipole attractions are weaker than permanent dipole permanent dipole attractions.
  - **C** carbon-oxygen bonds are less polar than silicon-oxygen bonds.
  - **D** van der Waals' forces are much weaker than covalent bonds.

### Answer D

Carbon dioxide is a simple molecules with weak can der waal's forces of attraction between molecules while silicon dioxide is a giant covalent structure with strong covalent bonds. Thus, less amt of energy is required to overcome the weaker VDW forces of attraction between  $CO_2$  molecules, resulting in lower boiling point.

5 Under which conditions will the behaviour of a gas be **most** ideal?

	pressure	temperature
Α	high	high
в	high	low
C	Low	high
D	Low	low

Answer: C

Gas behave most ideally at high temperatures and low pressures.

At high temperatures, particles have sufficient energy to overcome the intermolecular forces of attraction.

At low pressures, particles are very far apart. The volume of the particles is negligible to the volume of container which they moves in; intermolecular forces of attraction is negligible.

6 The enthalpy changes involving some oxides of nitrogen are given below:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$	$\Delta H = +180 \text{ kJ mol}^{-1}$
$2NO_2(g) + \frac{1}{2}O_2(g) \rightarrow N_2O_5(g)$	$\Delta H = -55 \text{ kJ mol}^{-1}$
$N_2(g) + \frac{5}{2}O_2(g) \rightarrow N_2O_5(g)$	$\Delta H = +11 \text{ kJ mol}^{-1}$

What is the enthalpy change, in kJ mol<sup>-1</sup>, of the following reaction?

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

**A** –114 **B** +114 **C** –136 **D** +136

**Answer: A** 

Reverse Equation 1: $2NO(g) \rightarrow N_2(g) + O_2(g)$	$\Delta H = -180 \text{ kJ mol}^{-1}$
Reverse Equation 2: $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$	$\Delta H$ = +55 kJ mol <sup>-1</sup>
Equation 3 remains: $N_2(g) + \frac{5}{2}O_2(g) \rightarrow N_2O_5(g)$	$\Delta H = +11 \text{ kJ mol}^{-1}$
Sum up these 3 equations: $2NO(g) + O_2(g) \rightarrow 2NO(g)$	$_{2}(g) \Delta H = -180+55+11$ = -114 kJ mol <sup>-1</sup>

Which of the following thermodynamic state functions of the protein best represents the folding process?

	$\Delta G$ / kJ mol <sup>-1</sup>	∆ <i>H I</i> kJ mol <sup>−1</sup>	$\Delta$ S/JK <sup>-1</sup> mol <sup>-1</sup>
A	_	_	_
В	+	_	+
С	_	+	_
D	+	+	_

#### **Answer: A**

When hydrogen bonds and van der Waals' forces are formed, heat will be released. Thus  $\Delta H$  is negative.

When the protein is folded from primary to tertiary structures, the system becomes less disordered. Thus  $\Delta S$  is negative.

The process of protein folding is spontaneous. Thus,  $\Delta G$  is negative.

**8** When 1 mole of carbon dioxide gas solidifies as dry ice, 25.2 kJ of heat energy is evolved. The sublimation temperature of carbon dioxide is –78.5 °C.

What is the entropy change when 132 g of carbon dioxide gas solidifies at this temperature?

- **C** +389 J K<sup>-1</sup>
- D –389 J K<sup>-1</sup>

Answer: D

This is a phase change reaction.  $\Delta G = 0$ 

$$\Delta G = \Delta H - T\Delta S$$
  

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$
  

$$\Delta S = \frac{-25200 - 0}{-78.5 + 273}$$
  

$$\Delta S = \frac{-25200}{194.5}$$
  

$$\Delta S = -129.56 \text{ J K}^{-1}$$
  

$$\Delta S \text{ when 132 g of carbon dioxide gas solidifies = -129.56 \text{ x} \frac{132}{44} = -389 \text{ J}$$

K<sup>-1</sup>

**9** A student set up the hydrogen electrode shown in the diagram below.



What would have to be changed to make this a standard hydrogen electrode?

- A the acid solution used
- **B** the temperature of the gas and of the acid solution
- **C** the pressure of the gas
- **D** the metal comprising the electrode

## Answer:A

In 1.0 mol dm<sup>-3</sup> sulfuric acid,  $[H^+] = 2.0$  mol dm<sup>-3</sup>. To make the electrode a standard hydrogen electrode, either change the acid to a 1.0 mol dm<sup>-3</sup> monoprotic acid (option **A**), or halve the concentration of sulfuric acid used.

**10** Use of the Data Booklet is relevant to this question.

Using inert electrodes, a current was passed through two beakers containing aqueous silver sulfate and aqueous copper(II) nitrate, connected in series under standard conditions.



What is the ratio of the mass of silver to copper deposited after the current was passed for *t* minutes?

Α	0.59		В	0.85
С	1.70		D	<mark>3.40</mark>
Answer: D	)			

It = n<sub>e</sub>F  

$$n_e \text{ transferred} = \frac{\text{It}}{\text{F}}$$
  
 $Cu^{2+} + 2e^- \rightarrow Cu$   
 $n_{Cu} = \frac{\text{It}}{2\text{F}}$   
 $Ag^+ + e^- \rightarrow Ag$   
 $n_{Ag} = \frac{\text{It}}{\text{F}}$   
 $\frac{\text{mass of Ag formed}}{\text{mass of Cu formed}} = \frac{Ar \text{ x no. of moles of Ag formed}}{Ar \text{ x no. of moles of Cu formed}} = \frac{108 \text{ x } \frac{\text{It}}{\text{F}}}{63.5 \text{ x } \frac{\text{It}}{2\text{F}}} = 3.40$ 

11 A nitrogen-hydrogen mixture, initially in the mole ratio of 1:3, reached equilibrium with ammonia when 50% of the nitrogen had reacted. The total equilibrium pressure was p.

$$N_2(g) + 3H_2(g) \implies 2NH_3(g)$$

What was the partial pressure of ammonia in the equilibrium mixture?

A С D В  $\frac{p}{6}$ р <u>2p</u> р 3 4 Ans A  $N_2(g) + 3H_2(g) \implies$  $2NH_3(g)$ Initial amt 3x Х Change x/2 3x/2 Х Eqm amt x/2 3x-3x/2Х Total final pressure = sum of eqm partial pressure = x/2 + (3x-3x/2) + x = p $3x = p \rightarrow x = p/3$ 

**12** Solid calcium hypochlorite pellets, Ca(C*l*O)<sub>2</sub>(s), are added to swimming pools to form HC*l*O(aq), which kills disease-causing bacteria and algae.

 $Ca(ClO)_2(s) \Box Ca^{2+}(aq) + 2ClO^{-}(aq)$ 

 $ClO^{-}(aq) + H_2O(l) \square HClO(aq) + OH^{-}(aq)$ 

What is the effect on the solubility of calcium hypochlorite and bacterial growth when pH decreases?

	Solubility of calcium hypochlorite	Effect on bacterial growth
Α	decreases	more favourable
В	decreases	less favourable
С	increases	more favourable
D	increases	less favourable

### Answer: D

When pH decreases, [H<sup>+</sup>] increases and [OH<sup>-</sup>] decreases, equilibrium position of second equation shift to the right and [HC*l*O] increases. Bacterial growth will be **less favourable**.

When [C/O<sup>-</sup>] decreases, equilibrium position of first equation shift to the right and **solubility of calcium hypochlorite increases**.

**13** The dissociation constant,  $K_{w}$ , for the ionisation of water,  $H_2O \square H^+ + OH^-$ , at different temperatures is given below.

temperature / °C	$\kappa_w$
0	1.15 x 10 <sup>-15</sup>
25	1.00 x 10 <sup>-14</sup>
50	5.50 x 10 <sup>-14</sup>

What can be deduced from this information?

- A Only at 25 °C are  $[H^+]$  and  $[OH^-]$  equal.
- **B** The equilibrium lies furthest to the right at 0°C.
- **C** The forward reaction is exothermic.
- **D** The pH of water decreases as temperature increases.

#### Answer: D

Option A is wrong as [H<sup>+</sup>] and [OH<sup>-</sup>] are equal at all temperature for pure water.

Option B is wrong as the equilibrium lies furthest to the right at  $50^{\circ}$ C (as shown by K<sub>w</sub> value).

Option C is wrong as the forward reaction is endothermic. When temperature increases,  $K_w$  increases. This shows that equilibrium lies to the right.

Option D is correct as the forward reaction is endothermic. When temperature increases,  $K_w$  increases. This shows that equilibrium lies to the right. [H<sup>+</sup>] increases and this leads to decrease in pH.

**14** A sparingly soluble salt, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> dissociates in aqueous solution as follows:

Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> □ 3 Mg<sup>2+</sup> + 2 PO<sub>4</sub><sup>3-</sup>

Given that the solubility product,  $K_{sp}$  of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is **Q**, what is the value of [Mg<sup>2+</sup>] in a saturated solution?

**A** 
$$(\frac{9Q}{4})^{\frac{1}{5}}$$
 **B**  $(\frac{Q}{27})^{\frac{1}{3}}$  **C**  $(\frac{Q}{108})^{\frac{1}{5}}$  **D**  $(\frac{9Q}{64})^{\frac{1}{3}}$ 

**Answer: A** 

 $Mg_{3}(PO_{4})_{2} \square 3 Mg^{2+} + 2 PO_{4}^{3-}$  Change -x + 3x + 2xEquilibrium 3x 2x  $K_{sp} = [Mg^{2+}]^{3} [PO_{4}^{3-}]^{2}$   $Q = (3x)^{3} (2x)^{2}$   $Q = (27x^{3}) (4x)$   $x = (\frac{Q}{108})^{\frac{1}{5}}$   $[Mg^{2+}] = 3 \times (\frac{Q}{108})^{\frac{1}{5}}$   $= (\frac{243Q}{108})^{\frac{1}{5}}$   $= (\frac{9Q}{4})^{\frac{1}{5}}$ 

**15.** The reaction of hydrogen peroxide with iodide ions in an acidic solution is first order with respect to hydrogen peroxide as well as iodide ions, and zero order with respect to hydrogen ions.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(I) + I_2(aq)$$

Two experiments were carried out. Which pair of diagrams represents the variation of  $[H_2O_2]$  and  $[H^+]$  with time?



## Ans B

Given in question: Rate =  $k[H_2O_2][I^-]$ ,

For expt 1: [I<sup>-</sup>] is first order

The graph of [H<sub>2</sub>O<sub>2</sub>] against time is a downward sloping curve with decreasing gradient.

Rate =  $k'[H_2O_2]$  where  $k' = k[I^-]$ 

For expt 2:

[H+] is zero order. The graph of [H<sup>+</sup>] against time is a decreasing straight line with a constant gradient. Rate = k' where  $k' = k[I^-][H_2O_2]$ 

**16** Aluminium is an element in the third period, Na to Ar, of the Periodic Table.

What is true for aluminium?

- A Aluminium has the highest melting point of the elements in this period.
- **B** Aluminium is the only element in this period whose chloride reacts with water to form an acidic solution
- **C** Aluminium is the only element in this period which can exist, at room temperature and pressure, as solid and conduct electricity.
- **D** Aluminium is the only element in this period whose oxide reacts with both acids and bases.

Answer: D

Period 3 trends

Aluminium is the only amphoteric oxide in third period.

- 17 Which of the following statements regarding Group II elements or their compounds is <u>correct</u>?
  - A Magnesium chloride has a higher melting point than barium chloride.
  - **B** Magnesium is a stronger reducing agent than strontium.
  - **C** Calcium hydroxide is more thermally stable than barium hydroxide.
  - **D** Strontium reacts more readily with oxygen than radium.

Answer:

 $MgCl_2$  has a larger magnitude of lattice energy than  $BaCl_2$  since ionic radius of  $Mg^{2+}$  is smaller than that of  $Ba^{2+}$  ion.

Mg is a weaker reducing agent or undergoes oxidation less readily than Sr since  $E^{\circ}(Mg^{2+}/Mg)$  is less negative than  $E^{\circ}(Sr^{2+}/Sr)$ .

Ca(OH)<sub>2</sub> is less thermally stable than Ba(OH)<sub>2</sub> as Ca<sup>2+</sup> has a higher charge density than Ba<sup>2+</sup> (due to the smaller ionic radius of Ca<sup>2+</sup>. Ca<sup>2+</sup> polarises the electron cloud of OH- ions and weakens the O-H bond in the hydroxide ions to a greater extent, thus less energy is required for the decomposition of Ca(OH)<sub>2</sub>.

The reactivity of Group II metals increases down the group due to increasing reducing power of the metals down the Group. Since Sr is above Ra in Group II, Sr is expected to react less readily with oxygen than Ra.

- **18** Which of the following statements about astatine, the element below iodine in Group VII of the periodic table, is **incorrect**?
  - A Silver astatide is insoluble in aqueous ammonia.
  - **B** Hydrogen astatide is less stable to heat than hydrogen iodide.
  - **C** Sodium astatide and hot concentrated sulfuric acid react to form astatine.
  - D Astatine and aqueous potassium chloride react to form aqueous potassium astatide and chlorine.

## Answer:

AgI is insoluble in both dilute and concentrated NH<sub>3</sub> and since Ksp of AgX decreases down the group, AgAt is expected to be less soluble in both dilute and concentrated NH<sub>3</sub> than AgI. H-At bond is weaker than H-I bond since At atom is bigger and more diffuse leading to less effective orbital overlap in H-At bond.

Since reducing power of the halides increases down the group and NaI reacts with conc  $H_2SO_4$  to give  $I_2$ , NaAt is similarly expected to react with conc  $H_2SO_4$  to give  $I_2$ .

 $At_2$  cannot undergo displacement reaction with KCl since  $At_2$  is a weaker oxidising agent (or less likely to undergo reduction) than  $Cl_2$  as oxidising power of halogen decreases down the group.

**19** When copper(II) chloride is dissolved in water it gives a blue solution. When this solution is treated with an excess of concentrated hydrochloric acid it turns yellow.

	blue	yellow
Α	CuCl <sub>2</sub>	[CuCl <sub>4</sub> ] <sup>2-</sup>
в	$CuCl_2(H_2O)_4$	[CuCl <sub>6</sub> ] <sup>4-</sup>
C Cu(OH) <sub>2</sub>		CuC <i>l</i> <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>
D	[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	[CuCl <sub>4</sub> ] <sup>2-</sup>

What are the formulae of the copper species in the blue and yellow solution?

## Answer: D

When copper(II) chloride dissolves in water, it dissociates into  $Cu^{2+}$  and  $Cl^{-}$  ions. The  $Cu^{2+}$  ions exist in the hydrated form,  $[Cu(H_2O)_6]^{2+}$ , which is blue in colour.

When excess conc HCl is added, ligand exchange occurs, where the Cl<sup>-</sup> ligand displace the  $H_2O$  ligands to form  $[CuCl_4]^{2-}$ , according to the following equation.

 $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$ 

20 Four carbon-carbon bonds are labelled in the diagram.



13

Which bonds are made up of an sp<sup>2</sup>-sp<sup>2</sup> overlap?

- **A** w and y only
- **B** w, x and y only
- C w, x, y and z
- **D** x and y only

## Answer: B

All the carbons are sp2, except the bond for z where the carbon in C=C is sp hybridized.

21 When heated with chlorine, the hydrocarbon 3,3-dimethylpentane undergoes free radical substitution. In the propagation step, the free radical X<sup>•</sup> is formed by the loss of one hydrogen atom.

$$CH_{3} CH_{2} - CH_{2}CH_{2}CH_{3} + Cl \bullet \longrightarrow X \bullet + HCl$$

$$CH_{3}CH_{2} - CH_{2}CH_{3} + Cl \bullet \longrightarrow X \bullet + HCl$$

How many different forms of **X**<sup>•</sup> are theoretically possible?





**22** Bromoethene,  $CH_2$ =CHBr, is unreactive to nucleophiles whereas 3-bromopropene,  $CH_2$ =CHCH<sub>2</sub>Br is very reactive by comparison.

What explains the lack of reactivity of CH<sub>2</sub>=CHBr?

- A Substituted alkenes undergo only electrophilic addition.
- **B** The C=C double bond and the Br atom are both electron withdrawing which stabilises CH<sub>2</sub>=CHBr.
- **C** The electrons on the Br atom delocalise into the  $\pi$  bond.
- **D** The presence of the  $\pi$  bond prevents free rotation of the C-Br bond this decreasing the reactivity.

Answer: C

For halogen-containing organic compounds, reactivity to nucleophiles (such as OH-) depends on the bond strength of C-X bonds. The unreactivity of bromoethene with nucleophile possibly suggest stronger C-Br bonds, as a result of the p orbital of Br overlapping with  $\pi$  bonds, hence having partial double-bond character.

Phosgene, COC<sup>1</sup>/<sub>2</sub>, is a colourless gas that gained infamy as a chemical weapon during World War I. It is formed when trichloromethane, CHC<sup>1</sup>/<sub>3</sub>, is left exposed to the atmosphere.Below is a reaction scheme that involves trichloromethane and phosgene:

 $CHCl_3 \longrightarrow COCl_2 \longrightarrow COCl(OH) \longrightarrow CO_2 + HCl$ 

Which of the following type of reaction is **not** being observed in the reaction scheme?

- A Oxidation
- **B** Elimination
- C Electrophilic addition
- **D** Nucleophilic substitution

Ans: C

$CHCl_3$		$COCl_2$	$\rightarrow$	COC <i>l</i> (OH)		$CO_2 + HCl$
	Oxidation	nucleo	ophilic sub	stitution	elimination	n in the second s

**24** A chlorine-containing organic compound, **X**, undergoes an elimination reaction when treated with hot ethanolic potassium hydroxide solution.

What is X?

- A  $CH_2CI_2$
- **B** C<sub>2</sub>C*I*<sub>6</sub>
- $C \qquad (CH_3)_2 CHCH_2 CI$
- **D**  $(CH_3)_3CCH_2C/$

Answer: C

To undergo elimination, there must be a hydrogen atom on the carbon atom adjacent to the carbon atom bearing the halogen atom. Only option C fulfils this criterion.

**25** Dopamine is an important organic chemical that helps control the brain's reward and pleasure centres. It also helps regulate movement and emotional responses.





Which of the following statements about dopamine is incorrect?

- A It is able to rotate plane-polarized light.
- **B** It is soluble in water due to zwitterion formation.
- **C** It migrates to the negative electrode of an electrolytic cell at pH 14.
- **D** The acidity of dopamine will increase when aqueous bromine is added.

Ans: C

Option A: Dopamine indeed contains a chiral carbon and exhibits optical activity

Option B: Dopamine is able to exist as a zwitterion RCH(NH3<sup>+</sup>)(COO<sup>-</sup>) which is able to form ion-dipole interactions with water.

Option C: At pH 14, the COOH group is deprotonated. The predominant form is the anionic form, which should migrate to the positive electrode instead of the negative electrode.

Option D: When aqueous bromine is added, electrophilic substitution occurs with the introduction of Br into the benzene ring. Br is electron withdrawing and is able to disperse the negative charge on the oxygen atoms in the anion, thus increasing the acidity of the compound.

26 Two bottles containing the following reagents had their labels removed.



Which one of the following reagents can be used to distinguish between them?

- A sodium metal C
  - C hot acidified potassium manganate(VII)D hot acidified potassium dichromate

- B sodium hydroxide
- Ans: D

Option A: Both compounds react with Na. Effervescence will be seen for both compounds. Gas evolved will extinguish lighted splint with a 'pop' sound.



and effervescence will be seen for both. Gas evolved will form white ppt with Ca(OH)<sub>2</sub>.

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Option D:  $C_{I}$   $C_{I}$  reacts with hot acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> via oxidation of primary alcohol (orange solution turns green).  $C_{I}$   $C_{H_3}$  does not undergo side chain oxidation as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is a weaker oxidizing agent than KMnO<sub>4</sub>.

17

27 Marijuana (cannabis) is the most widely used illegal drug in many developed countries. Medical studies have shown that the active ingredient in marijuana, tetrahydrocannabinol, might provide medical benefits to some patients.

OH

tetrahydrocannabinol

In the following reactions, the

<sup>o</sup> remains unaltered.

Which reaction will tetrahydrocannabinol undergo?

- A It reacts with aqueous bromine to incorporate up to 2 atoms of bromine in each molecule.
- **B** It reacts with hot acidified potassium dichromate(VI) to form a green solution.
- **C** It reacts with dilute nitric acid to form a substitution product.
- **D** It reacts with ethanoic acid to form a sweet-smelling product.

#### Ans: C

Option **A** is incorrect because both alkene group and phenol group will react with aqueous  $Br_2$  to incorporate **3 Br atoms**, forming the following products:



Option **B** is incorrect.  $K_2Cr_2O_7$  is not strong enough to oxidise side-chain of benzene and alkene. Phenol is not oxidised as well.

Option **C** is correct. Dilute nitric acid reacts with phenol functional group via electrophilic substitution to form the following product:

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[Turn over

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18

Option **D** is incorrect. Phenol functional group does not react readily with ethanoic acid (even in the presence of conc.  $H_2SO_4$  as catalyst). Hence, no ester will be formed. (To form the ester, the phenol should be treated with aq. NaOH to generate a stronger phenoxide ion before added into ethanoyl chloride)

**28** A student carried out an experiment to study the ease of hydrolysis of a series of chlorinated compounds, and recorded the observations based on the addition of acidified silver nitrate solution.

	time taken for precipitate to appear							
	shortest			longest				
Α	C <sub>6</sub> H₅C/	$CH_2C/CONH_2$	CH₃COC/	COC/2				
В	CH <sub>2</sub> C/CONH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Cl	COCl <sub>2</sub>	CH₃COC/				
С	CH <sub>3</sub> COC/	COCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Cl	CH <sub>2</sub> C/CONH <sub>2</sub>				
D	COCI2	CH <sub>3</sub> COC/	CH <sub>2</sub> C/CONH <sub>2</sub>	C <sub>6</sub> H₅C <i>l</i>				

Which of the following gives the expected results?

### Ans: D

 $COCl_2$  and  $CH_3COCl$  more reactive as the highly electronegative O and Cl atoms that are bonded to acyl carbon make it more electron deficient (or more  $\delta$ + charged), thus attract nucleophiles more readily.  $COCl_2$  hydrolyses more rapidly than  $CH_3COCl$  as the former has its acyl carbon more electron deficient due to its additional Cl atom.

In addition, the acyl carbon atoms are  $sp^2$  hybridised, so they have trigonal planar arrangement with respect to C, resulting in less steric hindrance for the approach of nucleophiles compared to the  $sp^3$  C atom (that is bonded to Cl in CH<sub>2</sub>ClCONH<sub>2</sub>).

 $CH_2C/CONH_2$  is the next most reactive as the C atom bonded to only one highly electronegative Cl atom is less electron deficient (or less  $\delta$ + charged) compared to  $COCl_2$  and  $CH_3COCl$ .

 $C_6H_5Cl$  is a halogenoarene (or aryl halide) where its Cl atom is bonded directly to benzene ring. The p orbital of Cl overlaps with the  $\pi$  electron cloud of benzene ring resulting its lone pair being delocalized into benzene and double bond character in its C-Cl bond. Since its C-Cl is most difficult to break, nucleophilic substitution (or hydrolysis) cannot occur. **29** In the following two-step synthesis, **Y** a solid which is insoluble in water, is one of the components in the final reaction mixture.

19



The reaction of X with NH<sub>3</sub> produces a mixture of products. Use Chipman is one of the products which contains an amine group and an acyl chloride group. The amine group is nucleophilic and undergo intramolecular reaction with the electron-deficient C of the acyl chloride to form a cylic product.

Since reaction with  $PCI_5$  converts -COOH to -COCI and  $-CH_2OH$  to  $-CH_2CI$  (as shown in **X**), the product should not contain -COO- or  $-CH_2OH$  group. Hence, by elimination of options, B, C and D are incorrect.
**30** Benzylamine has the formula  $C_6H_5CH_2NH_2$  and is a common precursor in organic synthesis.

Which of the following statements about benzylamine is correct?

- A It decolourises aqueous Br<sub>2</sub>.
- **B** It can be produced by reduction of  $C_6H_5CH_2CN$ .
- **C** It reacts with  $CH_3COOH$  to form  $C_6H_5CH_2NHCOCH_3$ .
- **D** It reacts with excess  $CH_3CH_2C/to$  form the compound,  $C_{13}H_{22}NC/.$
- (A)  $-CH_2NH_2$  group is not strongly activating, hence benzylamine,  $C_6H_5CH_2NH_2$ , cannot undergo easy electrophilic substitution with aqueous  $Br_2$ . This is not to be confused with phenylamine,  $C_6H_5NH_2$ .
- (B) When  $C_6H_5CH_2CN$  undergoes reduction,  $C_6H_5CH_2CH_2NH_2$  is produced, not  $C_6H_5CH_2NH_2$ .
- (C)  $C_6H_5CH_2NH_2$  undergoes acid base reaction, not condensation reaction, with  $CH_3COOH$  to give  $C_6H_5CH_2NH_3^+CH_3COO^-$ . An amide is formed from condensation between a primary or secondary amine and *acyl halide*.
- (D) A quaternary ammonium salt (shown below) is formed from successive nucleophilic substitutions (polyalkylation).



# Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

Α	В	С	D
1, 2 and 3	1 and 2	2 and 3	1 only
are	only are	only are	is
correct	correct	correct	correct

No other combination of statements is used as a correct response.

**31** Gaseous particle **Y** has a proton(atomic) number *n* and a charge of +1.

Gaseous particle **Z** has a proton(atomic) number of n+1 and is isoelectronic with **Y**.

Which statement correctly describes **Y** and **Z**?

# **1 Y** has a larger radius than **Z**.

- 2 Y requires more energy than Z when a further electron is removed from each particle.
- **3 Y** releases more energy than **Z** when an electron is added to each particles.

# Ans: D

Statement 1 (correct) Y (less protons) and isoelectronic with Z has a lower nuclear charge and has a larger radius. Statement 2: (wrong) Z has a higher nuclear charge and hold electrons more strongly(stronger attraction) and hence requires more energy.

- **32** Which of the following molecules will form a hydrogen bond with another of its own molecules?
  - 1 CH<sub>3</sub>NH<sub>2</sub>
  - **2** CH<sub>3</sub>CHO
  - 3 CH<sub>3</sub>CH<sub>2</sub>F

Answer: D Option 1: There is H-bonding between  $CH_3NH_2$ . Option 2: No H-bonding as O is not directly bonded to H atom. Option 3: No H-bonding as F is not directly bonded to H atom.

**33** The graph below shows the results of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied but that of amylase was kept constant.



Which conclusions can be deduced from these results?

- **1** When [maltose] is low, the rate is first order with respect to [maltose].
- 2 When [maltose] is high, the rate is independent of [maltose].
- 3 When [maltose] is high, the rate is independent of [amylase].

Answer: B Answer: B

Option 1:

At **low substrate concentration**[maltose], not all of the active sites are occupied.

- rate  $\infty$  [maltose]  $\Rightarrow$  reaction is **first order** with respect to the maltose.

Option 2:

At **high** [maltose], all the active sites are occupied, i.e. the active sites of the enzyme [amylase] become **saturated** with maltose.

- Any increase in [maltose] will not have any effect on the reaction rate.
- The reaction is **zero order** with respect to the maltose.

Option 3: If substrate is not the limiting factor, increasing enzyme amylase concentration **will increase** the rate of reaction, as there will be more active sites of enzyme.

**34** With reference to the *Data Booklet* and the data below, deduce which of the following statements are correct.

Half-equation	E <sup>e</sup> /N
$VO_2^+(aq) + 2H^+(aq) + e^- \Box VO^{2+}(aq) + H_2O(l)$	+1.00
$VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \cup V^{3+}(aq) + H_2O(I)$	+0.34
$V^{3+}(aq) + e^{-} = V^{2+}(aq) + H_2O(I)$	-0.26

- **1** An excess of zinc is capable of reducing  $VO_2^+(aq)$  to  $V^{2+}(aq)$  in acidic conditions.
- **2** Fe<sup>3+</sup>(aq) is capable of oxidising  $V^{2+}(aq)$  to  $VO_2^+$  (aq) in acidic conditions.
- **3**  $Zn^{2+}(aq)$  ions will oxidise  $V^{2+}(aq)$  ions to  $V^{3+}(aq)$  ions.

Answer: D

Answer: D

Half-equation	E <sup>θ</sup> /V
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76

#### Option 1:

Excess Zn is the reducing agent which can reduce  $VO_2^+(aq)$  to  $VO^{2+}(aq)$ Ecell = +1.00 - (-0.76) =1.76V > 0 Excess Zn can further reduce  $VO^{2+}(aq)$  to  $V^{3+}(aq)$  : Ecell = +0.34 - (-0.76) = 1.10V > 0 Excess Zn can further reduce  $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$  : Ecell: -0.26 - (-0.76) = 0.50V > 0 Quick thinking for MCQ: Since Ecell = Ered - Eoxi > 0 for reaction to proceed (Zn is oxidised), Ered - (-0.76) > 0 Ered - 0.76 for reaction to proceed

Option 2: wrong Quick thinking for MCQ: Since Ecell = Ered – Eoxi > 0 for reaction to proceed (Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup>), +0.77 - Eoxi > 0Eoxi < + 0.77 for reaction to proceed

Fe<sup>3+</sup> can oxidise V<sup>2+</sup> to VO<sup>2+</sup> but not VO<sub>2</sub><sup>+</sup>

$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(I)$	+1.00
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77

 $E\overline{cell} = +0.77 - 1.00 = -0.23v < 0$ 

Another factor:  $Fe^{3+}$  is not in excess, successive oxidation of vandadium compounds may not occur.

# **35** The working range and colour change of Chlorophenol red is given below.

Indicator	Marking pH range	Colour change		
Indicator		Acid	Alkali	
Chlorophenol red	4.8 - 6.4	Yellow	Red	

Two drops of this indicator are added to each of the three aqueous solutions listed below.

Which solution has its colour correctly stated?

IJC P1 MS

	Solution	Colour
<mark>1</mark>	Aluminium oxide added to water	Red
<mark>2</mark>	0.1 mol dm <sup>-3</sup> of CH <sub>3</sub> COOH (K <sub>a</sub> = 1.8 x 10 <sup>-5</sup> mol dm <sup>-3</sup> )	Yellow
3	Solution of sodium ethanoate and ethanoic acid in 1:2 proportion [p $K_a$ of ethanoic acid = 4.7]	Orange

24

#### Answer: B

Option 1 is correct.

Aluminium oxide does not dissolve in water and it gives a pH 7 solution. According to the working pH range of this indicator, the color is red.

Option 2 is correct.

 $[H^+] = \sqrt{K_a[acid]}$ =  $\sqrt{1.8X10^{-5}[0.1]}$ =  $1.342 \times 10^{-3} \text{ mol dm}^{-3}$ 

 $\therefore$  pH = - log<sub>10</sub> (1.342 × 10<sup>-3</sup>) = <u>2.87</u>

According to the working pH range of this indicator, the color shown for a solution of pH 2.87 is yellow.

Option 3 is incorrect.  $pH = pK_a + log \frac{[salt]}{[acid]} = 4.7 + log 0.5 = 4.7 - 0.3 = 4.4$ According to the working pH range of this indicator, the color shown for a solution of pH 4.4 is yellow and not orange.

**36** Use of the Data Booklet is relevant to this question.

Which statements about the trends in properties of the hydrogen halides are correct? 1 Volatility decreases in the order: HF > HC/ > HBr > HI.

- 2 Thermal stability increases in the order: HI < HBr < HC/ < HF.
- 3 Ease of oxidation increases in the order: HF < HC/ < HBr < HI.

Ans: C

**Option 1:** Volatility is inversely proportional to the boiling point. The higher the boiling point, the less volatile the substance. HF has stronger intermolecular hydrogen bonding that requires more energy to break while the strength of instantaneous dipole-induced dipole interaction increases from HCI to HBr to HI due to increasing polarizability of electron cloud of the molecules. Thus the correct trend of volatility is HF < HI < HBr < HCI.

**Option 2:** Thermal stability of hydrogen halides depend on the bond strength of H-X. The stronger the H-X bond, the more thermally stable the hydrogen halides. Down the group, the valence orbital is more diffused, as there is less effective orbital overlap between the valence orbitals of hydrogen and halogen OR down the group, as the atomic size of halogen increases,

the H-X bond length increases. As such, the H-X bond strength is weaker, and less thermally stable. Therefore, the trend of increasing thermal stability (HI < HBr < HCI < HF) is correct.

**Option 3:** The ease of oxidation or reducing power of the halides increases down the group due to the less positive  $E^{e}(X_{2}/X)$  down the group. Hence, the trend is correct.

**37** Nickel is purified by a method called the Mond process. The equation of the first step of the purification is shown below.

$$Ni(s) + 4CO(g) \longrightarrow Ni(CO)_4(I)$$

Which of the following statements are correct?

- 1 CO is a monodentate ligand.
- 2 Ni in Ni(CO)<sub>4</sub> has a co-ordination number of 4.

### 3 The oxidation number of Ni in Ni(CO)<sub>4</sub> is zero.

#### Ans: A

CO is a monodentate ligand as it forms one dative bond (using the lone pair of electron on the carbon atom) per formula unit.

Ni in Ni(CO)<sub>4</sub> has 4 dative or coordinate bonds formed with 4 CO ligands, thus its coordination number is 4.

Since the charges of the complex compound,  $Ni(CO)_4$  and CO ligands are zero, the charge of Ni is zero too.

**38** Compound **X** is a synthetic precursor of *meloscine*, an alkaloid isolated from the New Caledonian plant *Melodinus Scandens Forst*.



#### compound X

Which of the following statements about its reactions are correct?

- 1 1 mol of **X** reacts with 2 mol of HBr(g) when heated.
- **2** 1 mol of **X** reacts with 4 mol of  $Br_2(aq)$  at room temperature.
- **3** 1 mol of **X** reacts with 2 mol of  $CH_3COCl$  at room temperature.

#### Ans: C

Option 1: Incorrect. 1 mol of X reacts with 3 mol of HBr.

Each C=C will undergo electrophilic addition with HBr. 1° alcohol will undergo nucleophilic substitution with HBr, heat.

#### **Option 2: Correct**

Each C=C will undergo electrophilic addition with  $Br_2(aq)$ . Phenylamine will undergo electrophilic substitution with 2 mol of  $Br_2$  to form the di-substituted product.

### Option 3: Correct

1° alcohol will undergo condensation reaction with  $CH_3COCl$  to form an ester. Phenylamine will undergo condensation reaction with 1 mol of  $CH_3COCl$  to form amide.

- **39** Which of the following reactions give products that **does not** rotate the plane of polarised light?
  - 1 bromobutane refluxed with aqueous KOH
  - 2 Butanone reacted with HCN, trace amount of NaOH
  - **3** But–1–ene reacted with bromine dissolved in organic solvent

#### Ans: A

Option 1: 1-bromobutane is a 1° halogenoalkane hence it will react with aq KOH via  $S_N2$  mechanism. Since the product does not contain a chiral carbon, it is unable to rotate plane of polarised light.

Option 2: Butanone reacts with HCN via nucleophilic addition. As the nucleophiles can attack the carbonyl carbon (trigonal planar in shape) either from the top or the bottom of the plane with equal chance, it results in a racemic mixture Hence, even though the products are chiral, they are unable to rotate plane of polarised light.

Option 3: But-1-ene reacts with bromine via electrophilic addition. As the electrophile can attack the C atom of the carbocation intermediate is trigonal planar in shape, either from the top or the bottom of the plane with equal chance, it results in a racemic mixture Hence, even though the products are chiral, they are unable to rotate plane of polarised light.

- 40 Which of the following could result in the loss of the tertiary structure of a protein?
  - **1** Addition of weak acid
  - 2 Addition of alcohol
  - **3** Addition of AgNO<sub>3</sub> solution

#### Ans: A

Note: The tertiary structure of proteins refers to the 3D arrangement of the protein due to the folding of a polypeptide chain. Folding is due to R group (side chain) interactions.

Option 1: Addition of weak acid pH can change the ionic charges on amino acid residues (i.e. groups containing acidic COOH or basic  $NH_2$  groups) and hence disrupt the ionic interactions.

 $\Rightarrow$  In acidic conditions), protonation occurs, i.e.  $-COO^-$  is converted to -COOH.

Option 2: Alcohol can disrupt the original hydrogen bonds between polar R groups thereby disrupting their normal folding.

Option 3: Metal ions (Ag<sup>+</sup>) are positively charged cations. They compete with positively charged groups (e.g.  $-NH_3^+$ ) for attraction to negatively charged groups (e.g.  $-COO^-$ ), hence disrupting the original ionic interactions.

1	С	6	А	11	А	16	D	21	В	26	D	31	D	36	С
2	D	7	А	12	D	17	А	22	С	27	С	32	D	37	А
3	В	8	D	13	D	18	D	23	С	28	D	33	В	38	С
4	D	9	А	14	А	19	D	24	С	29	А	34	D	39	А
5	С	10	D	15	В	20	В	25	С	30	D	35	В	40	А

A = 10

B = 6

C = 9

D = 15



JC 2 PRELIMINARY EXAMINATION in preparation for General Certificate of Education Advanced Level

Higher 2

CANDIDATE NAME		
CLASS	INDEX NUMBER	

# CHEMISTRY

Paper 2 Structured Questions

Candidates answer on the Question Paper

Additional Materials: Data Booklet

# READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group. Write in dark blue or black pen. You may use pencil for any diagrams, graphs or rough working. Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **<u>all</u>** questions in the space provided. A Data Booklet is provided.

You are advised to show all working in calculations. You are reminded of the need for good English and clear presentation in your answers. You are reminded of the need for good handwriting. Your final answers should be in 3 significant figures.

You may use a calculator.

The number of marks is given in brackets [] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

For Examiner's Use Section A 1 12 2 17 3 10 4 18 5 15 Significant figures Handwriting Total 72

This document consists of **17** printed pages and **1** blank page.

9647/02

18 August 2016 2 hours

# Answer <u>ALL</u> questions on the spaces provided.

# 1 Planning

Using the information below, you are to write a plan for determining number of molecules of water of crystalisation, *n*, in barium chloride crystals,  $BaCl_2.nH_2O$  where n = 1,2 or 3. The basis of this investigation is a technique known as *precipitation titration* with the use of silver nitrate solution, AgNO<sub>3</sub>(aq).

AgCl, Ag<sub>2</sub>CrO<sub>4</sub> and BaCrO<sub>4</sub> are sparing soluble salts and relevant information about these salts are given in the table below.

compound	colour	numerical value of $K_{sp}$ at 25 ° C
AgC <i>l</i>	white	2.0 × 10 <sup>-10</sup>
Ag <sub>2</sub> CrO <sub>4</sub>	red	2.0 × 10 <sup>-12</sup>
BaCrO <sub>4</sub>	yellow	1.0 × 10 <sup>-10</sup>

Some barium chloride crystals, BaC $l_2.nH_2O$ , is dissolved to make up 250.0 cm<sup>3</sup> of standard solution. Approximately 10 cm<sup>3</sup> of 0.2 mol dm<sup>-3</sup> of reagent **X** solution is added to a portion of this standard solution to precipitate the barium ions *before* a few drops of K<sub>2</sub>CrO<sub>4</sub> indicator solution is added. A titration is then carried out on this portion of solution against silver nitrate solution, AgNO<sub>3</sub>(aq). Ag<sub>2</sub>CrO<sub>4</sub> would just precipitate only when almost all of the  $Cl^-$  ions have been precipitated as AgC*l*. The titration is repeated until a more reliable average value, **V** cm<sup>3</sup>, can be determined.

(a) (i) Identify reagent X.

[1]
 (ii) A student suggested that BaCrO<sub>4</sub> is more soluble than Ag<sub>2</sub>CrO<sub>4</sub> as BaCrO<sub>4</sub> has larger numerical value of K<sub>sp</sub> than Ag<sub>2</sub>CrO<sub>4</sub>.
 Suggest whether this student's claim is valid.
 [1]
 (iii) Suggest why reagent X is added *before* a few drops of K<sub>2</sub>CrO<sub>4</sub> indicator solution is added.
 [1]
 (iii) Suggest why reagent X is added *before* a few drops of K<sub>2</sub>CrO<sub>4</sub> indicator solution reaction is added.

- (b) You may assume that you are provided with
  - 0.10 mol dm<sup>-3</sup> silver nitrate
  - 0.2 mol dm<sup>-3</sup> of reagent **X** solution
  - 10 g of barium chloride crystals, BaCl<sub>2</sub>.nH<sub>2</sub>O
  - Potassium chromate solution, K<sub>2</sub>CrO<sub>4</sub>(aq)
  - The equipment and materials normally found in a school or college laboratory.

Your plan should include the following

- brief, but specific details of the apparatus you would use, bearing in mind the levels of precision they offer
- details, including quantities, for preparation of 250.0 cm<sup>3</sup> of BaCl<sub>2</sub> solution from barium chloride crystals, BaCl<sub>2</sub>.nH<sub>2</sub>O
- essential details of the titration procedure
- an outline of how the results obtained, including V cm<sup>3</sup>, would be used to determine n, in barium chloride crystals (BaCl<sub>2</sub>.nH<sub>2</sub>O)


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	[8]
(c)	Explain why this titration cannot be conducted under acidic or alkaline medium.
	[1]
	[Total: 12]

For Examiner's Use

2 This question is about the oxides of nitrogen and its reactions. Oxides of nitrogen constitute air pollutants originating from emission of car exhaust that cause acid rain and photochemical smog.

The two gases of NO and  $N_2O_4$  slowly react to form the blue compound,  $N_2O_3$  according to the following equation.

 $2NO(g) + N_2O_4(g) \implies 2N_2O_3(g)$ 

(a) (i) Draw the dot and cross diagrams of the two molecules, NO and  $N_2O_3$ . The  $N_2O_3$  molecule contains a N-N bond.

[2]

(ii) From your answer in (a)(i), suggest why the forward reaction is likely to occur.

..... .....[1]

(b) In an experiment, a mixture containing NO and  $N_2O_4$  was introduced into a 1.48 dm<sup>3</sup> evacuated vessel was allowed to reach equilibrium at 280 K. The equilibrium pressure is 98.9 kPa.

Calculate the total number of moles of gases at equilibrium, assuming the gases behave ideally.

(c) Two colourless gases NO and  $N_2O_4$  slowly react to form the blue compound,  $N_2O_3$  according to the following equation.

 $2NO(g) + N_2O_4(g) \implies 2N_2O_3(g)$ 

Equimolar mixtures of NO and  $N_2O_4$  are mixed at varying pressure P but at two different temperatures of 300 K and 330 K, and the variation in colour intensity was monitored over a period of time.

The graphs below show the variation of the colour intensity with pressure at temperatures of 300 K and 330 K.



(d) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g).$$

In an experiment, the amount of  $Cl_2(g)$  was kept in *large excess* while the initial partial pressure of NO(g) was varied at constant temperature of 500K. The table below shows the experimental results obtained.

time / s	P <sub>NO</sub> / atm	(Rate / P <sub>NO</sub> ) / s <sup>-1</sup>	(Rate / (P <sub>NO</sub> ) <sup>2</sup> ) / (atm <sup>-1</sup> s <sup>-1</sup> )
0	0.917	1.033 × 10 <sup>-4</sup>	1.126 × 10 <sup>-4</sup>
1000	0.827	9.312 × 10⁻⁵	1.126 × 10 <sup>-4</sup>
2000	0.753	8.486 × 10 <sup>-5</sup>	1.127 × 10 <sup>-4</sup>
3000	0.691	7.788 × 10⁻⁵	1.127 × 10 <sup>-4</sup>
4000	0.638	7.190 × 10⁻⁵	1.127 × 10 <sup>-4</sup>

(i) Suggest why the amount of  $Cl_2(g)$  was kept in *large excess*.

.....[1]

(ii) Using the data from the table above, deduce the order of reaction with respect to NO(g).

.....[1]

(iii) In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with  $Cl_2(g)$  at a constant temperature of 500 K. The partial pressure of  $Cl_2(g)$  was recorded at time intervals of 30 s. The data obtained are tabulated below.

time / s	partial pressure of Cl <sub>2</sub> (g) / atm	time / s	partial pressure of Cl <sub>2</sub> (g) / atm
0	0.78	300	0.49
30	0.76	330	0.46
60	0.72	360	0.44
90	0.70	390	0.42
120	0.66	420	0.39
150	0.63	450	0.38
180	0.59	480	0.36
210	0.57	510	0.34
240	0.54	540	0.33
270	0.52	570	0.32

Write the rate Hence, calcu	e equation for this reaction. late the rate constant, including its units	
		[3]
Ono nossiblo	mechanism of the reaction is given below	[3]
		<b>.</b> .
Step I	$NO(g) + C_2(g) \implies NOC_2(g)$	fast
Step II	$NOC I_2(g) + NO(g) \longrightarrow 2NOC I(g)$	slow
Explain whetl	ner it is consistent with the observed kinetic	s data in <b>(d)(iv)</b> .
		[2]
		[Total: 17]

**3** Organic compounds can undergo combustion. Chemical companies produce containers filled with butane for use by campers.

The enthalpy change of combustion of butane is  $-3000 \text{ kJ mol}^{-1}$ .

(a) (i) Define the term standard enthalpy of combustion of butane.


(ii) Calculate the mass of water at 25 °C that could be brought to the boiling point by the combustion of 1.2 dm<sup>3</sup> of butane gas. Assume 75 % of the heat from the butane is absorbed by the water.

- [2]
- (b) Explain in terms of structure and bonding, why butanone has a higher boiling point than pentane.

(c) Organic compounds are also widely used for pharmaceutical purposes such as ephedrine which is an anti-asthmatic and stimulant. Ephedrine can be converted into ethylephedrine via a  $S_N2$  reaction.



Ephedrine

Ethylephedrine

- (i) Suggest the reagent that can be used to perform this conversion.
- .....[1]
- (ii) Explain why an  $S_N 2$  mechanism is favoured for this reaction.

 	 [1]

(d) Complete hydrolysis of proteins produces individual units of amino acids, but partial hydrolysis can break the protein down into dipeptide or tripeptide fragments.

Partial hydrolysis of a tetrapeptide (containing four amino acid residues) produces the following three dipeptides, as well as the individual amino acids.

NH<sub>2</sub>CH<sub>2</sub>CONHCH(CH<sub>3</sub>)CO<sub>2</sub>H NH<sub>2</sub>CH<sub>2</sub>CONHCH<sub>2</sub>CO<sub>2</sub>H NH<sub>2</sub>CH(CH<sub>3</sub>)CONHCH(CH<sub>3</sub>)CO<sub>2</sub>H

(i) Define the *primary structure* of a protein.

.....

.....[1]

(ii) Deduce the order in which the amino acids are bonded together in the tetrapeptide.

.....[1]

(iii) Suggest suitable reagents and conditions to hydrolyse the tetrapeptide into its individual amino acids.

.....

.....[1]

[Total: 10]

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4 (a) A 0.031 mol dm<sup>-3</sup> solution of a base, MOH, has a pH of 12.5. (M is a metal.)

25 cm<sup>3</sup> of the solution of MOH was titrated with 0.025 mol dm<sup>-3</sup> propanoic acid,  $CH_3CH_2COOH$ , at 25 °C. The pH of the solution was followed using a pH meter and the following titration curve was obtained.



(iii) Explain, with the aid of an equation, why the pH when V cm<sup>3</sup> of propanoic acid was added, is greater than 7.



(b) The colour of blackberries is due to a compound known as cyanidin. Cyanidin is a weak organic acid which may be represented by CyH. In aqueous solution, CyH dissociates slightly:

 $\begin{array}{rcl} \text{CyH (aq)} & \stackrel{\longrightarrow}{\longrightarrow} & \text{Cy}^{-}(\text{aq}) & + & \text{H}^{+}(\text{aq}) \\ \text{red} & & \text{purple} \end{array}$ 

The colours of CyH and Cy<sup>-</sup> are indicated in the above equation. Acid dissociation constant,  $K_a$ , of CyH is 5.0 x 10<sup>-5</sup> mol dm<sup>-3</sup> at 25 °C.

A glass of blackberry juice has a pH of 3.00 at 25 °C. Calculate the ratio of the red to purple form in the juice, and hence predict its colour.

[3]

(c) When chlorine is bubbled through cold sodium hydroxide solution and acidified silver nitrate solution, only half of the chlorine that has dissolved is precipitated as silver chloride. When the sodium hydroxide is hot, up to five–sixth of the chlorine can be precipitated. Explain the observations, giving balanced equations where appropriate.

(d) The table below gives data about some physical properties of the elements calcium, nickel and copper.

	calcium	nickel	copper
atomic radius / nm	0.197	0.124	0.128
electronic configuration	[Ar]4s <sup>2</sup>	[Ar]3d <sup>8</sup> 4s <sup>2</sup>	[Ar]3d <sup>10</sup> 4s <sup>1</sup>

(i) What do you understand by the term *transition element*?

.....[1]

(ii) Although the nickel and copper atoms have more electrons than the calcium atom, the atomic radii of nickel and copper are smaller than that of calcium.

Suggest an explanation for this.

 	[3]

(e) The following are some reactions involving copper(II) nitrate.



- 5 Benzene reacts with propanoyl chloride and 1-phenylpropan-1-one is formed in the reaction.
  - (a) State the reagents and conditions needed to convert 1-phenylpropan-1-one into compound **Q**. Show the structure of the intermediate in the box provided.



(b) Describe the mechanism in Step 1 in part (a). In your answer, you should show all charges and lone pairs and show the movement of electrons by curly arrows.

(C) The 2,4-D weed killer,  $C_8H_6Cl_2O_2$  is widely used on cereal crops, pastures and orchards. Compound R is an isomer of the weed killer under development to improve its properties. It is an aromatic compound which contains **three** functional groups.

The following tests are carried out in the order given. In each case, state all deductions about the compound **R** you can make at **that** stage. When identifying the functional groups, your answers should be unambiguous.

(i) When Compound **R** is treated with Na,  $C_8H_5Cl_2O_2Na$  is formed.

deduction(s)	
	[1]
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(ii)	When Fehling's solution is added to Compound ${\bf R},$ red brick precipitate is obtained.	
	deduction(s)	
	[1]	
(iii)	When 1 mole of Compound ${f R}$ is boiled with ethanolic silver nitrate, 287 g of white precipitate is formed.	
	deduction(s)	
(iv)	When Compound <b>R</b> is treated with concentrated nitric acid, $C_8H_3Cl_2N_3O_8$ is	
	formed.	
	<ol> <li>What type of reaction takes place?</li> </ol>	
	<ol> <li>Name the functional group present in Compound R that is confirmed by this reaction.</li> </ol>	
	[2]	
(v)	You now have enough information to determine the structural formula of R.	
	1. Draw the fully displayed structure of <b>R</b> .	
	<b>2.</b> Explain clearly why you have placed each of the aromatic substituent groups in their particular positions.	
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INNOVA JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION in preparation for General Certificate of Education Advanced Level **Higher 2** 

# CHEMISTRY

Paper 3 Free Response

26 August 2016 2 hours

9647/03

Candidates answer on separate paper.

Additional Materials: Writing Papers Data Booklet Cover Page

# READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in. Write in dark blue or black pen on both sides of the paper. You may use a soft pencil for any diagrams, graphs or rough working. Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions. Begin each question on a fresh sheet of paper.

You are advised to show all working in calculations. You are reminded of the need for good English and clear presentation in your answers. You are reminded of the need for good handwriting. Your final answers should be in 3 significant figures.

At the end of the examination, fasten all your work securely together. The number of marks is given in the brackets [] at the end of each question or part question.

This document consists of **12** printed pages.



Innova Junior College

### Answer any **four** questions.

1 Data concerning the elements of group II of the Periodic Table, at 298K, are given in the table. Further data may be found in the *Data Booklet*. M refers to elements of group II.

	1 <sup>st</sup> and 2 <sup>nd</sup> IE of M	$\Delta H_{atom of} M$	$\Delta H_{hydration}$ of M <sup>2+</sup>	<i>Е</i> <sup>ө</sup> / V
	/ kJ mol <sup>-1</sup>	/ kJ mol <sup>-1</sup>	/ kJ mol <sup>-1</sup>	
Ca	1740	178	-1650	-2.87
Sr	1608	164	-1480	-2.89

(a) The electrode reduction potential *E*<sup>e</sup> of Group II elements gives an indication of the ease with which the following reaction occurs:

 $M(s) \longrightarrow M^{2+}(aq) + 2e$  Reaction 1

The *enthalpy change of reaction 1* can be related to the following factors:

- *first and second ionisation energy* of the element
- enthalpy change of atomisation and
- enthalpy change of hydration of its gaseous ion.
- (i) Construct an energy cycle relating the factors above, and use the values given above to calculate the enthalpy change of *Reaction 1* for calcium. [3]
- (ii) By quoting appropriate data from *Data Booklet*, explain the difference in enthalpy change of hydration of calcium and strontium ions. [2]
- (b) Calcium oxide is the key ingredient for the process of making cement.

When calcium is burned in oxygen, calcium oxide is produced. When 1.50 g calcium is burned in air, a mixture of ionic solids calcium oxide and red brown solid is formed.

The red brown solid has the following composition by mass: Ca, 81.1%; N,18.9%.

Adding water to the red brown solid produces calcium hydroxide and 19.2 cm<sup>3</sup> of ammonia gas at room temperature and pressure.

- (i) Calculate the formula of the red brown solid. [1]
- (ii) Write an equation for the reaction between red brown solid with water. [1]
- (iii) Write equations for the reactions of calcium with air and use them to calculate the mass of CaO formed when 1.5 g of calcium is burnt in air. [3]
- (c) Calcium oxide is normally made by heating calcium carbonate to a temperature above 825°C. A gas which turns lime water chalky is produced in the process.
  - (i) Write an equation for the decomposition of CaCO<sub>3</sub>. [1]
  - (ii) Explain why barium carbonate decomposes at a higher temperature than calcium carbonate. [2]

(d) Methylcyclohexene reacts with hydrogen bromide to form alkyl bromides.

$$+ HBr - C_7H_{13}Br$$

methylcyclohexene

- (i) The above reaction could produce two isomers with molecular formula C<sub>7</sub>H<sub>13</sub>Br. However, when the reaction is carried out, mainly one product is formed. Give the structural formula of the major product, explaining your answer. [2]
- (ii) Describe the mechanism of the reaction between hydrogen bromide and methylcyclohexene, C<sub>6</sub>H<sub>9</sub>CH<sub>3</sub>, showing curly arrows, charges, dipoles and any relevant lone pairs. [3]
- (iii) Unsymmetrical dihalides reacts with alkene in a similar way as hydrogen halides. Predict the structure of the product when IBr reacts with methylcyclohexene, and explain your answer by considering the polarity within the molecule IBr. [2]

[Total: 20]

- 2 Alcohols and carboxylic acids have many scientific, medical and industrial uses worldwide.
  - (a) Methanol is made from the following gaseous reaction.

$$CO(g) + 2H_2(g) \Rightarrow CH_3OH(g)$$

A 1:2 mixture of CO and  $H_2$  was pumped into a sealed reactor at 6 atm and then heated to 227 °C and maintained at this temperature for some time. When equilibrium was reached, the partial pressure of CH<sub>3</sub>OH was found to be 1.6 atm.

- (i) Write an expression for  $K_p$  for the reaction. Hence, determine the value of  $K_p$  stating its units. [3]
- (ii) Suggest the effect on the position of equilibrium and value of *K*<sub>p</sub> when methanol is removed from the reaction vessel. Explain your answer. [2]
- (b) Grignard reagent, RMgX, is an important reagent in organic synthesis. Grignard reagents are prepared by the addition of activated magnesium on an alkyl halide or aryl halide in non-polar solvents such as ether in anhydrous conditions.

$$R \xrightarrow{\circ} CH_2 \xrightarrow{\circ} X + Mg \xrightarrow{\sim} R \xrightarrow{\circ} CH_2 \xrightarrow{\circ} MgX \qquad X = Cl \text{ or } Br$$

An example of a Grignard reagent reacting with a ketone to form an alcohol via a two stage process is given below:



R' and R" could be alkyl / aryl group / H atoms

- (i) Suggest the type of reaction occurred between the Grignard reagent and the carbonyl compound in Stage 1 and 2. [2]
- (ii) Suggest the structural formula of the final organic product formed when



is reacted with propanone,  $CH_3COCH_3$ , in a similar twostep process. [1]

(iii) Deduce the structures of a suitable Grignard reagent, RMgBr, and a suitable carbonyl compound, R'R"CO, to synthesize the following alcohol, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH(OH)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>.

(iv) The Grignard reagent CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>MgBr can be readily converted into a carboxylic acid by using carbon dioxide.

Suggest the structural formula of the organic product formed. [1]

- (v) The product formed by using Grignard reagent in (b) (iii) does not rotate the plane polarised light. Explain your reasoning. [2]
- (c) Describe and explain the relative acidities of phenol, benzoic acid and phenylmethanol. [3]
- (d) Lactic acid, glycolic acid and salicylic acid are three organic acids commonly used in chemical peel.



Suggest a simple chemical test that can be used to distinguish each of the following pairs. State what you would observe for each chemical test.

- **1.** lactic acid from glycolic acid, and
- **2.** glycolic acid from salicylic acid.

[4]

[Total: 20]

- 3 Aluminium, is the third most abundant element (after oxygen and silicon) found in the Earth's crust. Aluminium reacts readily with carbon to form aluminium carbide,  $Al_4C_3$ .
  - (a) Aluminium carbide can react with protic reagents such as hydrochloric acid to produce methane gas and aluminium(III) chloride.
    - (i) Write a balanced equation for the reaction between aluminium carbide and hydrochloric acid. [1]
    - (ii) Using the equation in (a)(i), calculate the maximum volume of methane gas that can be produced when 12.0 g of aluminium carbide reacts with 250 cm<sup>3</sup> of 2.0 mol dm<sup>-3</sup> hydrochloric acid at standard temperature and pressure.

[3]

(b) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.



The reaction occurs in several steps.

• The first step is the reaction between Cl<sub>2</sub> and AlCl<sub>3</sub>.

 $Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$ 

• The benzene ring is then attacked by the  $Cl^+$  cation in the second step.

 $AlCl_3$  reacts in a similar way with halogenoalkanes and acyl chlorides, producing a carbocation that can then attack a benzene ring.

Using the reactions described above as parts of a synthesis route, a student suggested the following route to form phenyl 4-phenylbutanoate, from benzene.



- (i) Explain why step 1 has to be carried out in an anhydrous condition. [1]
- (ii) Draw the carbocation formed in step 1.

[1]

(iii) A student suggested that A could have the following structure:



By quoting appropriate data in the *Data Booklet*, explain why the structure suggested by the student is less likely to be formed. [2]

- (iv) Give appropriate reagents and conditions necessary for steps 2 and 3. [2]
- (v) Suggest the reagents and conditions for each of the two steps in route **B**. [2]
- (vi) Predict the structure of the product of each of the following reactions. Both compounds E and F react with 2,4-dinitrophenylhydrazine. [2]



- (vii) Describe and explain the relative ease of hydrolysis of the two compounds C and D. [2]
- (c) By considering the structure and bonding, explain why
  - (i) the boiling point of aluminium fluoride is higher than that of aluminium chloride.

(ii) salicylic acid, OH is less soluble in water than benzoic acid, .

[Total: 20]

4 The *Strecker synthesis* is a term used for a series of chemical reactions that synthesize an amino acid from an aldehyde or ketone. This reaction requires acid and HCN is supplied from cyanide salts.

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One example of the Strecker synthesis is a multikilogram scale synthesis of amino acids.

- (a) Name the type of reaction occurring in *Stage 2* and state the reagent and conditions used in this reaction. [2]
- (b) In Stage 1, ammonia formed from the reaction between KCN and NH<sub>4</sub>Cl reacts with the aldehyde.
   Suggest an equation for the formation of ammonia from the reaction between KCN and NH<sub>4</sub>Cl and describe the role of KCN in stage 1. [2]
- (c) Explain why isobutyramide is less basic than 3-aminobutan-2-one.



(d) Predict the outcomes of the following reactions starting from isobutyramide, drawing the structures of the intermediate J and the products K and L.



(e) Compound P,  $C_9H_{12}O_2$ , shows optical activity and does not react with aqueous potassium carbonate. However, it is soluble in aqueous potassium hydroxide. When P reacts with hot acidified potassium dichromate(VI), the solution turns from orange to green. P also decolourises aqueous bromine to form a white precipitate, Q,  $C_9H_{10}O_2Br_2$ .

Upon heating with concentrated sulfuric acid, **P** gives only compound **R**,  $C_9H_{10}O$ , which displays geometric isomerism. **R** gives compound **S** and ethanoic acid on reacting with hot acidified potassium manganate(VII) solution.

Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved. [7]

(f) The structure of squaric acid is shown below.



- (i) State the functional groups in squaric acid.
- (ii) Squaric acid is a stable molecule although it has high angle strain associated with a four-membered ring. It is a strong diprotic acid with a pK<sub>a</sub> values 1.5 and 3.4 respectively. Explain the high acidity of squaric acid.

[Total: 20]

- **5** Iron is, by mass, the most common element on Earth, forming much of Earth's outer and inner core. Iron and its compounds have been used as catalysts in many reactions. For example, aqueous iron(II) chloride can be used to catalyse the reaction between I<sup>-</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, to form I<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> ions.
  - (a) (i) Write an equation to represent the *third* ionisation energy of Fe. [1]
    - (ii) Write the electronic configuration for  $Fe^{2+}$ . Hence, suggest why the third ionisation energy of <sub>26</sub>Fe is lower than that of <sub>25</sub>Mn. [2]
    - (iii) State the type of catalysis for the reaction between I<sup>-</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> that is catalysed by aqueous iron(II) chloride.
       [1]
    - (iv) The reaction between I<sup>-</sup> and  $S_2O_8^{2-}$  can also be catalysed by aqueous cobalt(II) chloride. Using relevant  $E^{\Theta}$  values from the *Data Booklet*, explain why cobalt(II) chloride can be a catalyst for this reaction. [2]
  - (b) A green solution of aqueous iron(II) chloride is reacted with acidified potassium manganate(VII). The resultant solution D is treated with aqueous sodium carbonate to form a reddish brown precipitate E, together with a colourless gas which forms white precipitate in aqueous calcium hydroxide. When aqueous NH<sub>4</sub>SCN is added to D, a blood red solution is formed.

(i) Explain why aqueous iron(II) chloride is coloure	d. [2]
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- (ii) Identify precipitate E. [1]
- (iii) Suggest the type of reaction that has occurred for the formation of the blood red solution. [1]

(c) Iron is also used in making iron-air battery which is a low-cost and environmental friendly rechargeable energy source. An iron-air battery comprises of iron electrode, porous carbon-containing air electrode. The electrolyte used is aqueous potassium hydroxide.

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At the iron electrode, iron is oxidised to magnetite, Fe<sub>3</sub>O<sub>4</sub>, during discharging, according to the following reaction:

 $3Fe + 8OH^- \longrightarrow Fe_3O_4 + 4H_2O + 8e$ 

At the air electrode, oxygen is reduced to form hydroxide ions.

- (i) Write the half-equation for the reaction that occurred at the air electrode during discharging. [1]
- (ii) During discharging, the cell acts as a power source and the overall reaction occurred is as follows:

 $3Fe + 2O_2 \longrightarrow Fe_3O_4$ 

Suggest, with explanation, for the sign of the  $\Delta G^{\Theta}$  for this reaction. [1]

(iii) The battery is capable of producing an e.m.f. of 1.28V. By using suitable data from the *Data Booklet*, suggest a value for the E<sup>e</sup> of the Fe<sub>3</sub>O<sub>4</sub>|Fe electrode reaction.
 [1]

During charging, at the iron electrode, magnetite and water undergo the following reaction:

 $Fe_3O_4 + 4H_2O + 8e \longrightarrow 3Fe + 8OH^-$ 

At the same electrode, a competing side-reaction occurs where water reacts to form hydrogen gas according to the following reaction:

 $2H_2O + 2e \longrightarrow H_2 + 2OH^-$
- (iv) Calculate the amount of electrons that was required to produce  $H_2$  gas. [1]
  - (v) A current of 9.5 A is supplied to the battery during the 1-hour charging.

Use this information and your answer in **(c)(iv)** to calculate the amount of iron produced during the charging. [2]

(d) The separator used in the iron-air battery is an organic polymeric membrane, made from compound X.

Compound **X** has a molecular formula  $C_3H_3N$ . On heating with dilute sulfuric acid, **X** forms compound **Y**,  $C_3H_4O_2$ . Both **X** and **Y** decolourise aqueous bromine, however, only **Y** reacts with sodium carbonate to form gas which forms white precipitate in  $Ca(OH)_2(aq)$ .

Suggest structures for compounds **X** and **Y**, giving reasons for your answers. [4]

[Total: 20]