

# **Cambridge International AS & A Level**

CANDIDATE NAME		
CENTRE NUMBER		CANDIDATE NUMBER
CHEMISTRY		9701/43
Paper 4 A Leve	I Structured Questions	October/November 2020

2 hours

You must answer on the question paper.

You will need: Data booklet

#### INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

#### INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].

2

Answer **all** the questions in the spaces provided.

1 Nitrogen monoxide, NO, reacts with oxygen to form nitrogen dioxide, NO<sub>2</sub>.

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

The rate equation for the forward reaction is shown.

rate = 
$$k[NO]^2[O_2]$$

(a) Complete the following table.

the order of reaction with respect to [NO]	
the order of reaction with respect to $[O_2]$	
the overall order of reaction	

[1]

[2]

(b) Two separate experiments are carried out at 30 °C to determine the rate of the forward reaction.

experiment	[NO]/moldm <sup>-3</sup>	$[O_2]/moldm^{-3}$	rate/moldm <sup>-3</sup> s <sup>-1</sup>	
1	0.00300	0.00200	1.51 × 10 <sup>-4</sup>	
2		0.00500	$6.05  imes 10^{-5}$	

(i) Use the data for experiment 1 to calculate the value of the rate constant, *k*. State the units of *k*.

*k* = ..... units = .....

(ii) Calculate the value of [NO] in experiment 2.

[NO] = ..... mol dm<sup>-3</sup> [1]

(c) Define the term *rate-determining step*.

......[1]

(d) Peroxodisulfate ions,  $S_2O_8^{2-}$ , react with iodide ions, I<sup>-</sup>.

$$S_2O_8^{2-}$$
 +  $2I^- \rightarrow 2SO_4^{2-}$  +  $I_2$ 

The rate equation for the reaction in the absence of any catalyst is shown.

rate = 
$$k[S_2O_8^{2-}][I^-]$$

(i) Suggest equations for a two-step mechanism for this reaction, stating which of the two steps is the rate-determining step.

(ii) A large excess of peroxodisulfate ions is mixed with iodide ions. Immediately after mixing,  $[I^-] = 0.00780 \text{ mol dm}^{-3}$ . Under the conditions used, the half-life of  $[I^-]$  is 48 seconds.

Calculate the iodide ion concentration 192 seconds after the peroxodisulfate and iodide ions are mixed.

iodide ion concentration = ..... mol dm<sup>-3</sup> [1]

[Total: 8]

**2** (a) The lattice energies of three ionic compounds are given.

compound	lattice energy/kJmol-1
LiF(s)	-1022
CaO(s)	-3513
SrO(s)	-3310

(i) Define the term *lattice energy*.

..... (ii) Explain why the lattice energy of CaO is more exothermic than the lattice energy of LiF. ......[1] (iii) Use the data in the table to estimate approximate values for the lattice energies of magnesium oxide and barium oxide.  $\Delta H_{\text{latt}}$ MgO(s) = ..... kJ mol<sup>-1</sup>  $\Delta H_{\text{latt}} \text{BaO}(s) = \dots \text{kJmol}^{-1}$ [1] (b) (i) Write an equation for the reaction between BaO and  $H_2O$ . Include state symbols. State and explain how the solubilities of the hydroxides of the Group 2 elements vary (ii) down the group. ......[4] (c) Use the following data and relevant data from the *Data Booklet* to calculate a value for the lattice energy of magnesium fluoride,  $MgF_2(s)$ .

You might find it helpful to construct an energy cycle. Show your working.

electron affinity of F(g)	$= -348  \text{kJ}  \text{mol}^{-1}$
enthalpy change of atomisation of Mg(s)	= +147 kJ mol <sup>-1</sup>
enthalpy change of formation of $MgF_2(s)$	$= -1102  kJ  mol^{-1}$

 $\Delta H_{\text{latt}} MgF_2(s) = \dots [3]$ 

(d) (i)		Define the term <i>electron affinity</i> .
(i	i)	The electron affinity of carbon, $C(g)$ , is $-120 \text{ kJ mol}^{-1}$ .
		Suggest an explanation for the difference between the electron affinity of fluorine and the electron affinity of carbon.
		[Total: 15]

**3** (a) Identify the substances liberated at the anode and at the cathode during the electrolysis of aqueous sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>(aq).

anode ..... cathode .....[1]

(b) When molten sodium chloride is electrolysed, chlorine is liberated at the anode and sodium is liberated at the cathode.

A sample of molten sodium chloride is electrolysed for 1.50 hours using a current of 4.50A.

Calculate the volume of chlorine and the mass of sodium that are liberated under room conditions.

volume of chlorine = ..... dm<sup>3</sup> mass of sodium = ..... g [4] (c) The equation representing the standard electrode potential,  $E^{\circ}$ , for the reduction of  $MnO_4^{-}(aq)$  to  $Mn^{2+}(aq)$  in acid solution is given.

 $MnO_4^{-}(aq) + 8H^+(aq) + 5e^- \Longrightarrow Mn^{2+}(aq) + 4H_2O(I) \qquad E^{\circ} = +1.52V$ 

(i) Draw a diagram of the apparatus that would be used to measure the  $E^{\circ}$  value of this half-cell. Your diagram should be fully labelled to identify all apparatus, substances and conditions.

[4]

(ii) Use the Data Booklet to identify a substance that could be used to oxidise Mn<sup>2+</sup> ions to MnO₄<sup>-</sup> ions under standard conditions.

Write an equation for the reaction.

.....[2]

[Total: 11]

4	(a)	(i)	Give the mathematical expression for each of the terms pH and $K_{\rm w}$
-	(4)	(י)	one the mathematical expression for each of the terms pri and A

(ii) Calculate the pH of  $0.027 \text{ mol dm}^{-3} \text{ NaOH}(aq)$ .

pH = ..... [1]

[2]

(b) The  $K_a$  value of chloric(I) acid, HClO, is  $3.72 \times 10^{-8}$  mol dm<sup>-3</sup>.

Calculate the pH of  $0.010 \text{ mol dm}^{-3} \text{ HC}lO(\text{aq})$ .

pH = ..... [1]

(c) Water and octan-1-ol form two layers when mixed.

Ethanamide is more soluble in water than it is in octan-1-ol. When 1.00g of ethanamide is added to  $50.0 \text{ cm}^3$  of water and this is then shaken with  $50.0 \text{ cm}^3$  of octan-1-ol, it is found that the water layer contains 0.935g of ethanamide at equilibrium.

(i) Calculate the partition coefficient,  $K_{pc}$ , for ethanamide in water and octan-1-ol.

*K*<sub>pc</sub> = ..... [1]

(ii) The 50.0 cm<sup>3</sup> of water containing 0.935g of ethanamide is then shaken with 100.0 cm<sup>3</sup> of pure octan-1-ol under the same conditions.

Calculate the mass of ethanamide that is dissolved in the 100.0 cm<sup>3</sup> of octan-1-ol at equilibrium.

mass of ethanamide = ..... g [2]

[Total: 7]

- **5** A solution is made by dissolving  $CuSO_4 \cdot 5H_2O$  in an excess of aqueous ammonia. This solution contains the copper complex  $[Cu(NH_3)_4]^{2+}$ .
  - (a) (i) Write an expression for the  $K_{\text{stab}}$  of  $[Cu(NH_3)_4]^{2+}$ .

$$K_{\rm stab}$$
 =

- (ii) State the colour of the solution of  $[Cu(NH_3)_4]^{2+}$ .

The solution of  $[Cu(NH_3)_4]^{2+}$  is heated gently in a fume cupboard so that  $NH_3$  is released. Some  $NH_3$  remains in solution and some forms  $NH_3$  gas. The colour of the solution changes; a precipitate of  $Cu(OH)_2$  forms and is collected.

A sample of  $Cu(OH)_2$  is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, **Y**.

A sample of  $Cu(OH)_2$  is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, **Z**.

 $[Cu(NH_3)_4]^{2+}$ , **Y** and **Z** are different colours.

(b) Suggest an equation for the reaction of  $[Cu(NH_3)_4]^{2+}$  to form  $Cu(OH)_2$  as the aqueous solution of  $[Cu(NH_3)_4]^{2+}$  is heated.

......[1]

(c) Suggest an equation for the reaction of  $Cu(OH)_2$  with concentrated hydrochloric acid, forming **Y**.

(d) Complete the table with the colour and geometry of complex Y and the colour, geometry and formula of complex Z.

	Y	Z
colour of complex		
geometry of complex		
formula of complex		

[2]

[1]

(e) Explain why complexes Y and Z are coloured and why their colours are different.

 (a) When 1.0 mol dm<sup>-3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq) is added to a solution containing Ag<sup>+</sup>(aq) ions, a linear complex, **P**, is formed.  $S_2O_3^{2-}$  ions are present in **P** as monodentate ligands. Define the term monodentate ligand. (i) (ii) Give the formula of **P**, including its charge. (b) When 1.0 mol dm<sup>-3</sup> NaCN(aq) is added to a solution of **P**, a mixture which includes a second linear complex, Q, is formed. In this mixture the concentration of Q is much greater than the concentration of P. Write an equation for the reaction that occurs when NaCN(aq) is added to a solution of P. (i) Suggest a reason why the concentration of Q is much greater than the concentration of P (ii) in the mixture. (iii) Name the type of reaction in which P forms Q.

6

- (c) Platinum forms a complex ion with the formula  $[Pt(CN)_2Cl_2]^{2-}$ . In this complex ion the carbon atom of each  $CN^-$  ligand bonds to the platinum ion. This complex shows stereoisomerism.
  - (i) There are only two isomers of this complex.

Draw structures of these two isomers in the boxes below.



- 7 Phenol,  $C_6H_5OH$ , is a weak acid.
  - (a) Phenol can be made from phenylamine,  $C_6H_5NH_2$ .

Give the reagents and conditions for this reaction.



(b) Phenol reacts with dilute aqueous nitric acid under room conditions to give a mixture of two isomeric products with molecular formula C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>.

Use the *Data Booklet* to draw the structural formulae of these two products in the boxes and name each product.



[2]

- (c) Phenol reacts with an excess of aqueous bromine.
  - (i) Draw and name the organic product of this reaction in the box.

name	

[2]

	(ii)	Describe <b>two</b> visual observations that can be made when plaqueous bromine.	nenol reacts with an excess of
		observation 1	
		observation 2	[1]
(d)	Wri	te an equation for a neutralisation reaction in which phenol b	ehaves as an acid.
			[1]
(e)	Wa	ter, phenol and ethanol can all behave as acids.	
		ce these three compounds in order of acidity, starting with th plain your answer.	e <b>most</b> acidic.
		most acidic	least acidic
			[3]

[Total: 11]

- 8 Benzene,  $C_6H_6$ , can be obtained from crude oil.
  - (a) Benzene reacts with bromine, in the presence of a suitable catalyst, forming bromobenzene as one product.
    - (i) Give the name or formula of the other product of this reaction.
      - ......[1]
    - (ii) In the presence of the catalyst, bromine can be considered to form the electrophile Br<sup>+</sup>.

Complete the mechanism by which benzene reacts with Br<sup>+</sup>, using curly arrows to show the movement of electron pairs.



- (iii) Name this mechanism.

(b) Benzene can be used as a starting material in the synthesis of cyclohexylmethanol,  $C_6H_{11}CH_2OH$ , as outlined below.



cyclohexylmethanol

(i) Identify a suitable reagent and a suitable catalyst for step 1.

reagent ..... catalyst .....[2]

(ii) Draw the structure of A.



[1]

(iii)	Identify suitable reagents for steps 3 and 4.
	step 3
	step 4
	[2]
(iv)	Deduce the number of peaks in the carbon-13 NMR spectrum of cyclohexylmethanol.
	[Total: 10]

**9** The proton NMR spectrum of compound **E** in the solvent  $CDCl_3$  is shown. The molecular formula of compound **E** is  $C_9H_{10}O_2$ .



- (a) Explain why  $CDCl_3$  is used as a solvent instead of  $CHCl_3$ .
- (b) Explain why TMS is added to give the small peak at chemical shift  $\delta$  = 0.
  - ......[1]

(c) Compound E is hydrolysed by hot NaOH(aq), giving two organic products only. One of these products is ethanol.

Name the functional group in compound **E** that is hydrolysed by hot NaOH(aq).

......[1]

(d) (i) Describe and explain the splitting patterns of the peaks at  $\delta$  = 1.4 and  $\delta$  = 4.3.

(ii) Each molecule of compound **E** contains five protons which give rise to the peaks between  $\delta$  = 7.0 and  $\delta$  = 8.5.

Identify the functional group in compound **E** which contains these protons.

[1	1]
----	----

(iii) Give the structural formula of compound **E**.

(e) The mass spectrum of compound E includes fragment ions with *m/e* values of 29 and 77.
Give the formulae of these fragment ions.
fragment ion with *m/e* = 29
fragment ion with *m/e* = 77

[Total: 9]

[1]

10 (a) The table shows three pairs of monomers that are capable of polymerisation.

Complete the table by identifying each type of polymerisation.

type of polymerisation

- (b) 2-aminopropanoic acid, CH<sub>3</sub>CH(NH<sub>2</sub>)CO<sub>2</sub>H, can polymerise under suitable conditions. No other monomer is involved in this reaction.
  - (i) Draw a section of the polymer chain formed including **three** monomer residues. Clearly identify **one** repeat unit on your diagram.

[3]

[2]

[1]

(ii) 2-aminopropanoic acid,  $CH_3CH(NH_2)CO_2H$ , exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of 2-aminopropanoic acid. State the type of stereoisomerism shown.

type of stereoisomerism .....

(c) The skeletal formula of compound W is shown.



When W is mixed with a second compound, called a hardener, a polymerisation reaction occurs, producing a non-solvent-based adhesive.

(i) Give the name of this type of non-solvent-based adhesive.

(ii) The hardener is a diamine. A diamine has an alkyl chain with two amine groups which are not bonded to the same carbon atom.

Draw the structural formula of a compound that would make a suitable hardener.

[1]

[Total: 8]

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