| Cambridge International AS & A Level | Cambridge International Examinations Cambridge International Advanced Subsidiary and Advanced Level |
|--|--|
| CANDIDATE NAME | |

| | | | - | |
|------------------|--|--|------|---------------|
| CENTRE NUMBER | | | CANE | DIDATE BER |
| | | | - | |

CHEMISTRY

Paper 4 A Level Structured Questions

9701/43 October/November 2018 2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in. Write in dark blue or black pen. You may use an HB pencil for any diagrams or graphs. Do not use staples, paper clips, glue or correction fluid. DO **NOT** WRITE IN ANY BARCODES.

Answer all questions.

Electronic calculators may be used. You may lose marks if you do not show your working or if you do not use appropriate units. A Data Booklet is provided.

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

This document consists of **20** printed pages.



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

1 (a) An aldehyde, an alkane and a carboxylic acid, all of similar volatility, are mixed together. The mixture is then analysed in a gas chromatograph.

The gas chromatogram produced is shown.



The separation of the compounds depends on their relative solubilities in the stationary phase. The stationary phase is a liquid alcohol.

(i) Complete the table to suggest which compound in the mixture is responsible for each peak X, Y and Z. Explain your answer by reference to the intermolecular forces of the compounds.

| peak | organic compound | explanation |
|------|---------------------|-------------|
| x | | |
| Y | | |
| z | | |

(ii) A student calculates the areas underneath the three peaks in the chromatogram.

| peak | X | Y | Z |
|----------------------|----|----|----|
| area/mm ² | 19 | 32 | 47 |

The area underneath each peak is proportional to the mass of the respective compound.

Calculate the percentage **by mass** in the original mixture of the compound responsible for peak **Z**.

% of mixture responsible for peak **Z** =[1]

(b) (i) The mass spectrum of a halogenoalkane containing one chlorine atom **or** bromine atom will show an additional peak at M+2.

State the isotopes of chlorine and bromine responsible for M+2 peaks.

chlorine bromine

(ii) The mass spectrum of bromochloromethane, CH_2BrCl , has a molecular ion peak, M, at an m/e value of 128. It also has M+2 and M+4 peaks.

Suggest the identity of the molecular ions that give rise to these peaks.

M peak M+2 peak

M+4 peak

[2]

[1]

(c) Halogenoalkanes can be formed from the reaction of an alkene with a hydrogen halide.Methylpropene reacts with hydrogen bromide to form 2-bromo-2-methylpropane.



methylpropene

2-bromo-2-methylpropane

[3]

(i) Draw the mechanism of this reaction. Include all relevant curly arrows, dipoles and charges.

(ii) 1-bromo-2-methylpropane is also formed in this reaction.

Explain why 2-bromo-2-methylpropane will be the **major** product in this reaction.

......[1]

(d) (i) Explain what is meant by the term *partition coefficient*, $K_{partition}$.

- (ii) The partition coefficient of organic compound **H** between dichloromethane and water is 4.75.
 - 2.50 g of compound **H** was dissolved in water and made up to 100 cm³ in a volumetric flask.
 - 50 cm³ of this aqueous solution were shaken with 10 cm³ of dichloromethane.

Calculate the mass of compound **H** that was extracted into the dichloromethane.

mass of compound H extracted = g [2]

[Total: 14]

6

2 (a) Ethanedioate ions, $C_2O_4^{2-}$, are bidentate ligands.

Explain what is meant by the term *ligand*.

.....[1]

(b) $Cr^{3+}(aq)$ and $C_2O_4^{2-}(aq)$ ions form the complex ion $[Cr(C_2O_4)_2(H_2O)_2]^-$.

Draw **two** stereoisomers of this complex ion.



- (c) The solubility of calcium ethanedioate, CaC_2O_4 , is 6.65×10^{-3} g dm⁻³ at 298 K.
 - (i) Write an expression for the solubility product, K_{sp} , of CaC₂O₄. Include its units.

 $K_{\rm sp}$ =

units =[2]

(ii) Calculate the numerical value of K_{sp} CaC₂O₄ at 298 K. Give your answer in **standard form** to **two** significant figures.

 $K_{sp} CaC_2O_4 =$ [2]

[Total: 7]

3 (a) Complete the table to show the total number of **unpaired** electrons in the 3d and 4s orbitals of each isolated gaseous atom.

| | number of unpaired electrons | | | | | | |
|----|-------------------------------------|--|--|--|--|--|--|
| | 3d 4s | | | | | | |
| Cr | | | | | | | |
| Mn | | | | | | | |
| Fe | | | | | | | |

[2]

(b) Solid potassium manganate(VII), $KMnO_4$, decomposes on heating to form manganese(IV) oxide, potassium manganate(VI) and a colourless gas.

Construct an equation for this reaction.

.....[2]

(c) Explain the origin of colour in transition element complexes.

 (d) The reaction scheme shows some reactions of $[Cu(H_2O)_6]^{2+}.$

| | $[Cu(H_2O)_6]^{2+} \xrightarrow[NaOH(aq)]{} precipitate A \xrightarrow[excess]{} solution of excess \\ NH_3(aq) \end{bmatrix}$ | В |
|----------------|--|-----|
| | $CuCO_{3}(s) \xrightarrow{reaction 4} solution of C$ | |
| (i) | Write the formulae of | |
| | precipitate A, | |
| | complex ion B , | |
| | compound C. | [3] |
| (ii) | Identify a suitable reagent for reaction 3. | |
| | | [1] |
| (iii) | Write an equation for reaction 4. | |
| | | [1] |
| (iv) | Describe two visual observations that would be made during reaction 4. | |
| | | [1] |
| | | [1] |
| (e) Pla | latin, $Pt(NH_3)_2Cl_2$, is a neutral complex of platinum(II). | |
| Exp | xplain why $Pt(NH_3)_2Cl_2$ has no charge. | |
| | | |
| | | [1] |

(f) (i) $Pt(NH_3)_2Cl_2$, displays *cis-trans* isomerism.

Draw the structure of *trans*-platin. State its shape and the C1–Pt–C1 bond angle.

| | shape Cl-Pt-Cl bond angle | [2] |
|------|---|-----|
| (ii) | Cis-platin is an effective anti-cancer drug. | |
| | Describe the action of <i>cis</i> -platin in this role. | |
| | | |
| | | |
| | | |
| | | [2] |

(g) The use of *cis*-platin can cause side effects so nedaplatin has been developed.

Nedaplatin can be synthesised from *cis*-platin, $Pt(NH_3)_2Cl_2$, by replacing the two chloride ion ligands with a **single** bidentate ligand as shown.

Suggest the structure for nedaplatin.



[Total: 19]

4 (a) The enthalpy change of solution, ΔH_{sol}^{e} , of the Group 2 sulfates becomes more endothermic down the group.

State and explain the trend in the solubility of the Group 2 sulfates down the group.

[3]

(b) (i) Write the expression for K_w , the ionic product of water.

*K*_w =

(ii) The numerical value of K_w increases with increasing temperature.

Place a tick (\checkmark) in the appropriate column in each row to show the effect of increasing the temperature of water on the pH and on the ratio [H⁺]:[OH⁻].

| effect of increasing temperature of water | decrease | stay the same | increase |
|---|----------|---------------|----------|
| рН | | | |
| ratio [H⁺]∶[OH⁻] | | | |

[2]

(c) An aqueous solution of sodium hydroxide has a pH of 13.25 at 298 K.

Calculate the concentration of this sodium hydroxide solution.

concentration = $mol dm^{-3}$ [2]

(d) Buffer solutions are used to regulate the pH of a solution to keep its pH value within a narrow range.

Write **two** equations to describe how hydrogencarbonate ions, HCO_3^- , and carbonic acid, H_2CO_3 , control the pH of blood.

| |
|---------|
| [2] |

- (e) The $K_{\rm a}$ for ethanoic acid is 1.75×10^{-5} mol dm⁻³ at 298 K.
 - (i) When ethanoic acid is dissolved in water, an equilibrium mixture containing two acid-base pairs is formed.

Write an equation for this equilibrium. In the boxes label each species acidic or basic to show its behaviour in this equilibrium.

| CH ₃ CO ₂ H | + | \rightleftharpoons | + | |
|-----------------------------------|---|--------------------------|-------|-----|
| | | | | |
| | | | | [2] |

(ii) A buffer solution was prepared by adding 30.0 cm³ of 0.25 mol dm⁻³ ethanoic acid, an excess, to 20.0 cm³ of 0.15 mol dm⁻³ sodium hydroxide.

Calculate the pH of the buffer solution formed at 298K. Give your answer to **one** decimal place.

pH = [4]

(f) Titration curves for two different acid-base reactions, **M** and **N**, are shown.



(i) Use the titration curve for reaction **M** to deduce the volume of acid added at the end-point for this titration.

(ii) The table shows some acid-base indicators.

| name of indicator | pH range of colour change |
|-------------------|---------------------------|
| malachite green | 0.2–1.8 |
| bromocresol green | 3.8–5.4 |
| bromothymol blue | 6.0–7.6 |
| thymolphthalein | 9.3–10.6 |

Name a suitable indicator for each of the acid-base titrations ${\bf M}$ and ${\bf N}.$ Explain your answers.

| reaction M | reaction N |
|-------------|------------|
| | |
| explanation | |
| | |
| | [2] |

[Total: 19]

5 (a) Polyhydroxyamide is a fire-resistant polyamide which is formed from the two monomers, F and G.



(i) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **F** and **G**.



[2]

(ii) Draw the repeat unit of polyhydroxyamide. The amide bond should be shown displayed.

[2]

(b) When poly(ethene) is formed from ethene, many bonds are broken and formed.

Place **one tick** (\checkmark) in **each row** of the table to indicate the types of bonds broken and formed in this process.

| | σ -bonds only | π -bonds only | both σ - and π -bonds |
|--------------|----------------------|-------------------|----------------------------------|
| bonds broken | | | |
| bonds formed | | | |

- (c) Addition polymers can be classified into two types.
 - homopolymer a polymer made up of the same monomer unit
 - copolymer a polymer made up of two or more different monomer units

The reaction of propene, $CH_3CH=CH_2$, with phenylethene, $C_6H_5CH=CH_2$, gives a copolymer.

Draw a length of the chain of this copolymer that contains one molecule of **each** monomer.

| (d) | (i) | Polyalkenes biodegrade very slowly. | |
|-----|------|---|--|
| | | Explain why by referring to the structures of the polymers. | |
| | | | |
| | | | |
| | | [1] | |
| | (ii) | Some polymers will degrade in the environment. | |
| | | Describe two processes by which this occurs. | |
| | | 1 | |
| | | 2 | |
| | | [2] | |

[Total: 11]

6 (a) Use the *Data Booklet* to draw the structure of the dipeptide val-lys. The peptide bond should be shown displayed.

[2]

(b) The isoelectric point is the pH at which an amino acid exists as a zwitterion. The isoelectric point of valine is 6.0 and of lysine is 9.8.

A mixture of the dipeptide, val-lys, and its two constituent amino acids, valine and lysine, was analysed by electrophoresis using a buffer at pH 6.0.

Draw and label **three** spots on the diagram of the electrophoresis paper to indicate the likely position of each of these three species after electrophoresis. Explain your answer.



[Total: 7]

7 (a) Chlorobenzene and phenol both show a lack of reactivity towards reactants that cause the breaking of the C–X bond (X = Cl or OH).

Explain why.

[3]

(b) When phenol is reacted with bromine dissolved in an inert solvent, two isomeric bromophenols, C_6H_4BrOH , are formed.

Suggest structures for these products. Name each compound.



name:

- $\underbrace{\underbrace{step 1}_{phenol} \underbrace{step 2}_{phenol} \underbrace{step 2}_{NaNO_2(aq)/HCl(aq)} \underbrace{step 3}_{NaNO_2(aq)/HCl(aq)} \underbrace{step 3}_{S^{\circ}C} \underbrace{step 4}_{K}$
- (c) A student suggested that phenol can be prepared from benzene by the method shown.

(i) Suggest reagents and conditions for each of the following steps.

| | step 1 | |
|-------|--|-----|
| | step 2 | |
| | step 4 | |
| | | [3] |
| (ii) | Deduce the structure for ${\bf K}$ and draw its structural formula in the box. | [1] |
| (iii) | Name the mechanism for step 1. | |
| | | [1] |

(iv) Write an equation for step 2. Use [H] for the reducing agent in this equation.

[1]

[Total: 11]

- 8 Entropy is a measure of the disorder of a system.
 - (a) Assume the entropy, S, for H_2O is zero at 0K.

Sketch a graph on the axes to show how the entropy changes for H_2O between 0 K and 300 K.



(b) Place one tick (\checkmark) in each row of the table to show the sign of the entropy changes, ΔS .

| | ΔS is negative | ΔS is positive |
|---------------------------|------------------------|------------------------|
| solid dissolving in water | | |
| water boiling to steam | | |

[1]

[2]

(c) The equation for a reaction that produces methanol is shown.

 $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$

Use relevant bond energies from the *Data Booklet* to calculate the enthalpy change, ΔH , for this gas phase reaction.

 $\Delta H = \dots kJ \, mol^{-1} [2]$

(d) At 298 K, both products of this reaction are liquid.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(I) + H_2O(I) \qquad \Delta H^{\circ} = -131 \text{ kJ mol}^{-1}$$

Standard entropies are shown in the table.

| substance | CO ₂ (g) | H ₂ (g) | CH ₃ OH(I) | H ₂ O(I) |
|---------------------------------------|---------------------|--------------------|-----------------------|---------------------|
| S°/JK ⁻¹ mol ⁻¹ | +214 | +131 | +127 | +70 |

(i) Calculate the standard entropy change, ΔS° , for this reaction.

 ΔS^{e} = J K⁻¹ mol⁻¹ [2]

(ii) Calculate the standard Gibbs free energy change, ΔG° , for this reaction at 298 K.

 ΔG° = kJ mol⁻¹ [2]

(iii) Predict the effect of increasing the temperature on the feasibility of this reaction.

.....[1]

(e) In a methanol-oxygen fuel cell, CH₃OH(I) and O₂(g) are in contact with two inert electrodes immersed in an acidic solution.

The half-equation for the reaction at the methanol electrode is shown.

 $CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^- E^\circ = -0.02V$

(i) Use the Data Booklet to write an equation for the overall cell reaction.

(ii) Use E° values to calculate the E°_{cell} for this reaction.

 $E_{\text{cell}}^{\bullet}$ = V [1]

[Total: 12]

Permission to reproduce items where third-party owned material protected by copyright is included has been sought and cleared where possible. Every reasonable effort has been made by the publisher (UCLES) to trace copyright holders, but if any items requiring clearance have unwittingly been included, the publisher will be pleased to make amends at the earliest possible opportunity.

To avoid the issue of disclosure of answer-related information to candidates, all copyright acknowledgements are reproduced online in the Cambridge International Examinations Copyright Acknowledgements Booklet. This is produced for each series of examinations and is freely available to download at www.cie.org.uk after the live examination series.

Cambridge International Examinations is part of the Cambridge Assessment Group. Cambridge Assessment is the brand name of University of Cambridge Local Examinations Syndicate (UCLES), which is itself a department of the University of Cambridge.