

CANDIDATE
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CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

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.

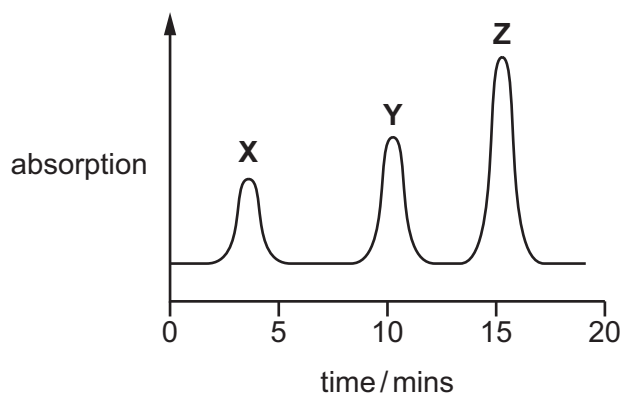
The number of marks is given in brackets [] at the end of each question or part question.

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		

[2]

- (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 [1]

- (ii) The mass spectrum of bromochloromethane, CH₂BrCl, 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

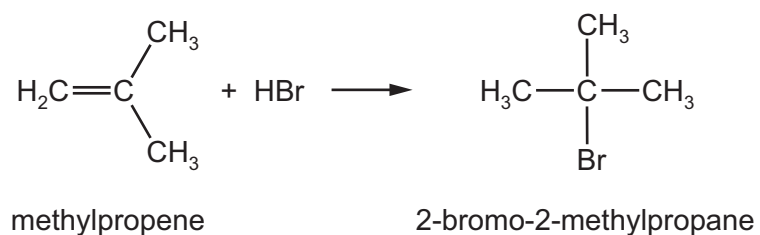
M+2 peak

M+4 peak

[2]

(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.



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

[3]

(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*, $K_{\text{partition}}$.

.....
.....
.....
..... [2]

(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]

- 2 (a) Ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, are bidentate ligands.

Explain what is meant by the term *ligand*.


.....

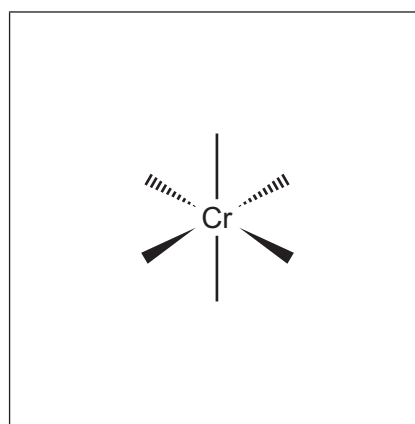
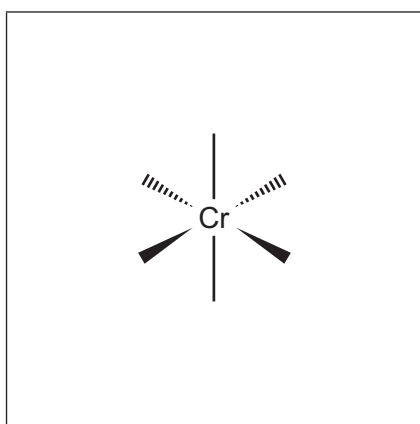
.....

..... [1]

- (b) $\text{Cr}^{3+}(\text{aq})$ and $\text{C}_2\text{O}_4^{2-}(\text{aq})$ ions form the complex ion $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$.

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

You may use  to represent $\text{C}_2\text{O}_4^{2-}$.



[2]

- (c) The solubility of calcium ethanedioate, CaC_2O_4 , is $6.65 \times 10^{-3} \text{ g dm}^{-3}$ at 298 K.

- (i) Write an expression for the solubility product, K_{sp} , of CaC_2O_4 . Include its units.

$$K_{\text{sp}} =$$

units =

[2]

- (ii) Calculate the numerical value of K_{sp} CaC_2O_4 at 298 K. Give your answer in **standard form** to **two** significant figures.

$$K_{\text{sp}} \text{ CaC}_2\text{O}_4 = \dots\dots\dots [2]$$

[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.

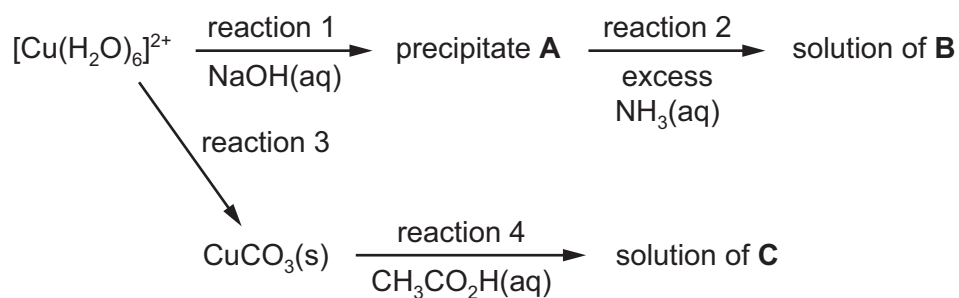
..... [2]

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

.....

 [3]

(d) The reaction scheme shows some reactions of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.



(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]

(e) Platin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, is a neutral complex of platinum(II).

Explain why $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ has no charge.

.....
 [1]

- (f) (i) $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, displays *cis-trans* isomerism.

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

shape Cl-Pt-Cl bond angle

[2]

- (ii) *Cis*-platin is an effective anti-cancer drug.

Describe the action of *cis*-platin in this role.

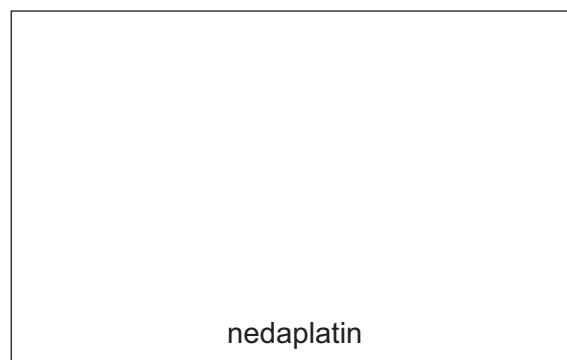
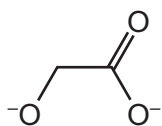
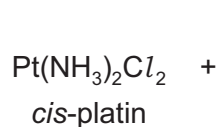
.....

[2]

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

Nedaplatin can be synthesised from *cis*-platin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, by replacing the two chloride ion ligands with a **single** bidentate ligand as shown.

Suggest the structure for nedaplatin.



[1]

[Total: 19]

- 4 (a) The enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$, 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.

$$K_w =$$

[1]

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

Place a tick (✓) in the appropriate column in each row to show the effect of increasing the temperature of water on the pH and on the ratio $[\text{H}^+]:[\text{OH}^-]$.

effect of increasing temperature of water	decrease	stay the same	increase
pH			
ratio $[\text{H}^+]:[\text{OH}^-]$			

[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.

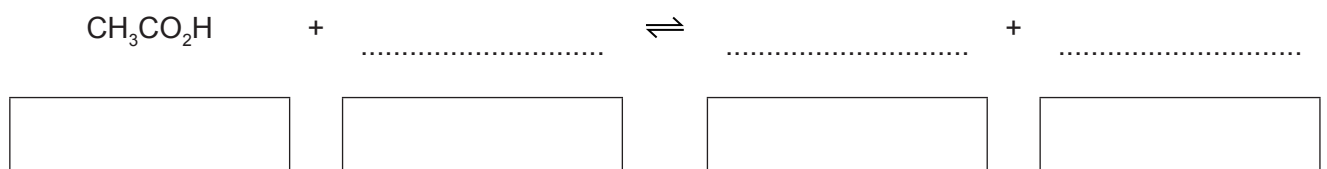
Write **two** equations to describe how hydrogencarbonate ions, HCO_3^- , and carbonic acid, H_2CO_3 , control the pH of blood.

.....
 [2]

- (e) The K_a for ethanoic acid is $1.75 \times 10^{-5} \text{ mol dm}^{-3}$ 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.



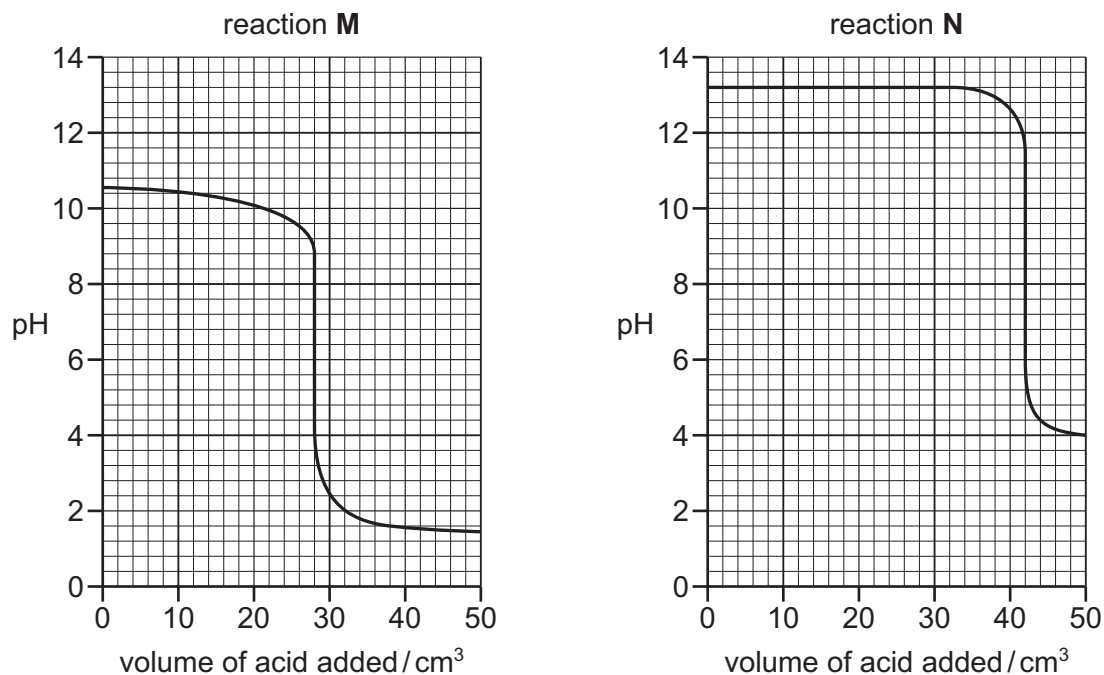
[2]

- (ii) A buffer solution was prepared by adding 30.0 cm^3 of 0.25 mol dm^{-3} ethanoic acid, an excess, to 20.0 cm^3 of 0.15 mol dm^{-3} sodium hydroxide.

Calculate the pH of the buffer solution formed at 298 K. 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.

volume of acid added at the end-point = cm³ [1]

(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 **M** and **N**. Explain your answers.

reaction **M** reaction **N**

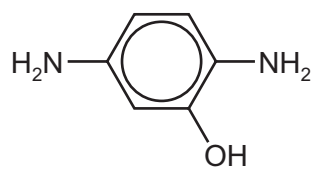
explanation

.....

[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**.

	number of peaks
F	
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** (✓) 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			

[2]

(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, $\text{CH}_3\text{CH}=\text{CH}_2$, with phenylethene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, gives a copolymer.

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

[2]

(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]

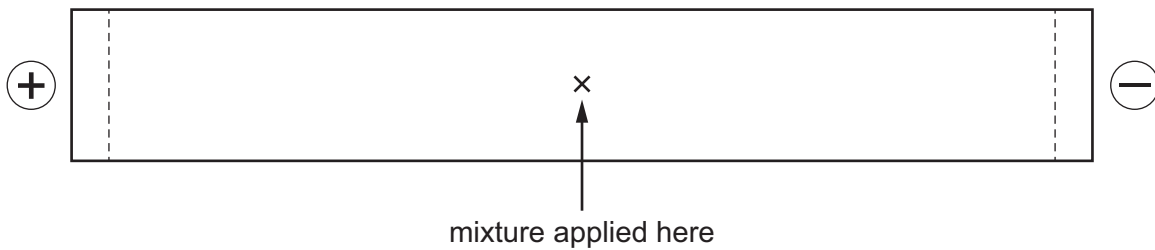
- 6 (a) Use the *Data Booklet* to draw the structure of the dipeptide val-lys. The peptide bond should be shown displayed.

[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.



explanation

.....

.....

[5]

[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.

.....

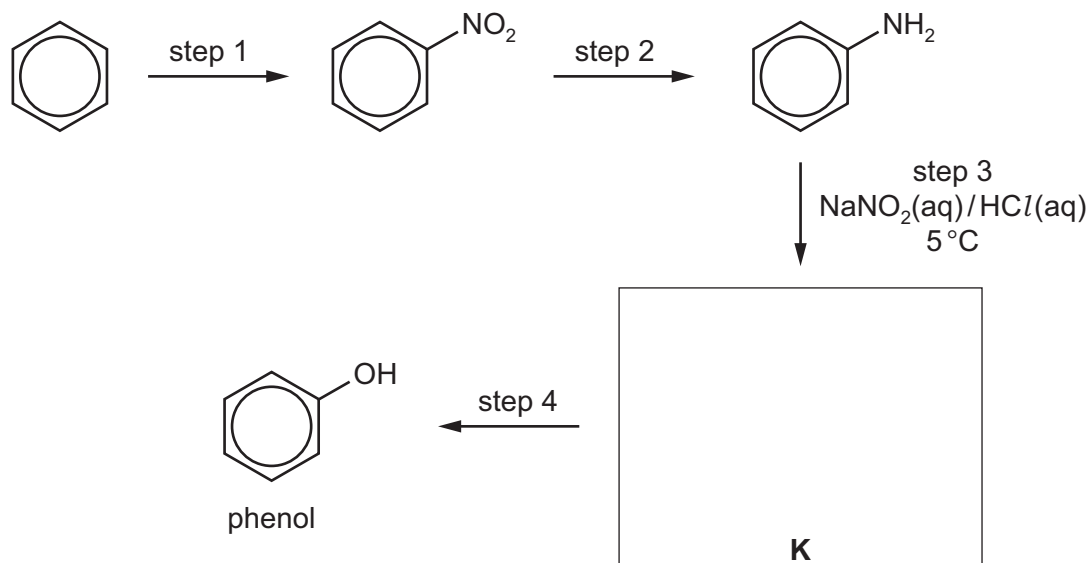
name:

.....

name:

[2]

(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 **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 $[\text{H}]$ for the reducing agent in this equation.

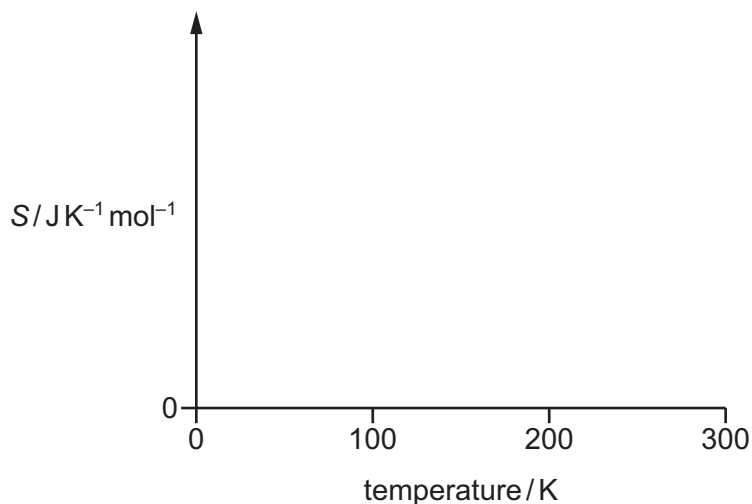
[1]

[Total: 11]

8 Entropy is a measure of the disorder of a system.

(a) Assume the entropy, S , for H_2O is zero at 0 K.

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



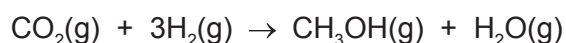
[2]

(b) Place **one tick** (✓) 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]

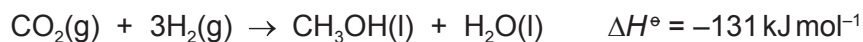
(c) The equation for a reaction that produces methanol is shown.



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

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

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



Standard entropies are shown in the table.

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

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

$$\Delta S^\circ = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [2]$$

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

$$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

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

.....
 [1]

- (e) In a methanol-oxygen fuel cell, $\text{CH}_3\text{OH}(\text{l})$ and $\text{O}_2(\text{g})$ are in contact with two inert electrodes immersed in an acidic solution.

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



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

.....

 [1]

- (ii) Use E^\ominus values to calculate the E^\ominus_{cell} for this reaction.

$$E^\ominus_{\text{cell}} = \dots\dots\dots \text{V} \quad [1]$$

[Total: 12]

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