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CENTRE NUMBER	S					NDEX IUMBER				

**CHEMISTRY** 

9729/03

Paper 3 Free Response

11 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

### **READ THESE INSTRUCTIONS FIRST**

Write your name, CT group, centre number and index number on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO NOT WRITE ON ANY BARCODES.

Answer all questions in the spaces provided in the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

### Section A

Answer all questions.

### Section B

Answer one question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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.

No. of sheets of writing paper submitted (write 0 if none)	er
For Examiner's Use	
1	/ 20
2	/ 19
3	/ 21
Circle your option below	<del></del> .
4/5	/ 20
Deductions (s.f.)	
Deductions (units)	
Deductions (structures)	<del></del> .
Total	/ 80

#### Section A

Answer all questions in this section.

1 (a) Like Group 2 carbonates, Group 2 nitrates also undergo thermal decomposition according to the following equation:

$$M(NO_3)_2(s) \to MO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$$
  $\Delta H > 0$ 

- (i) Draw a dot-and-cross diagram showing the bonding in Mg(NO<sub>3</sub>)<sub>2</sub>, clearly indicating any co-ordinate bonds it contains. [2]
- (ii) Explain why the temperature for thermal decomposition of Group 2 nitrates increases down the group. [2]
- (iii) Deduce, with reasoning, the sign of the entropy change of the reaction. Hence, suggest why high temperature is needed for thermal decomposition to take place. [2]
- (iv) Using Table 1.1 and data from the *Data Booklet*, draw a Born-Haber cycle to calculate a value for the lattice energy of MgO. Show your working.

1st electron affinity of oxygen

2<sup>nd</sup> electron affinity of oxygen

Table 1.1

Z electron annity of oxygen			4
standard enthalpy change of atomisa	tion of Mg(s)	+148	
standard enthalpy change of formation	n of MgO(s)	-602	
			[4]
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ΔH<sup>e</sup> / kJ mol<sup>-1</sup> –142

+844

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(b)	Desc for ar	ribe the reactions, if any, of the oxides MgO, $Al_2O_3$ and $P_4O_{10}$ with water. Write equations by reaction and state the pH of the resultant mixtures. [3]
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(c)		e presence of $AlCl_3$ , methylbenzene can undergo electrophilic substitution with halogens chlorine.
	(i)	Explain why A/C/ <sub>3</sub> can act as a Lewis acid. [1]
	(ii)	Draw the structures of the major organic products formed in the electrophilic substitution reaction between methylbenzene and chlorine.
	(iii)	Write a balanced equation for the reaction between methylbenzene and hot acidified potassium manganate(VII). Use [O] to represent the oxidising agent. [1]
	read	halogen is changed to iodine, electrophilic substitution of methylbenzene occurs much less ily. To increase its reactivity, reagents like iodine monochloride, $ICI$ , in the presence of $AICI_3$ used instead.
	(iv)	Explain why $ICl$ is more reactive in the electrophilic substitution of methylbenzene compared to $I_2$ . [1]
	(v)	Draw the mechanism of the reaction between methylbenzene and ICl, showing the formation of the electrophile and any intermediates. Use curly arrows to indicate the movement of electron pairs, and show any relevant lone pairs. [3]

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2	(a)		ribe and explain the difference in reactivity of alkenes and carbonyl compounds toward cophilic reagents.	is 2]
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	(b)	race	ne pharmaceutical industry, understanding optical activity and addressing the effects mic mixtures is crucial in drug development.  Explain why a racemic mixture is optically inactive.	[2]
		(ii)	With reference to a reaction involving a suitable alkene or carbonyl compound of yo choice, explain why a racemic mixture is obtained in the reaction.  Give the organic compound and reagents used, and draw structures to illustrate the tyl of stereoisomerism present in the product mixture.	
		(iii)	Stereoisomers of a drug such as ibuprofen often have different pharmacological activities Suggest a reason for why this is so.	es. [1]
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(c) Fig. 2.1 shows the reaction of compound A with hot concentrated hydroiodic acid.

Fig. 2.1

(i) Suggest the type of reaction that occurs during this reaction.

[1]

(ii) Give the systematic name for B.

[1]

(iii) C and D are constitutional isomers of B. The three compounds may be distinguished via a two-step procedure.

- I. In step 1, the three compounds are heated separately with acidified potassium dichromate(VI). State what would be observed for each compound.
- II. The organic products formed from positive tests in step 1 are isolated for a further test in step 2. Suggest a reagent, other than 2,4-dinitrophenylhydrazine, that can be used to distinguish these products, and state the observations for each compound. [3]

(iv)	Phenol can be converted to phenyl ethanoate via a two-step process. State the reac required for each step of this process.	tant [2]
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(d) Fig. 2.2 shows a synthetic scheme for the conversion of compound E to compounds G and H. In E, the R group could be at positions 2, 3 or 4 relative to the -OH group on the benzene ring.

Fig. 2.2

- (i) Draw the structure of the organic product formed when compound **G** is reacted with 2,4-dinitrophenylhydrazine. [1]
- (ii) In step 1 of Fig. 2.2, the relative molecular mass of E changes from 178.0 to 335.8 in F, the major product of the reaction.
   Deduce, with reasoning, the position of the R group relative to the –OH group in E. [1]
- (iii) Based on your answer to (d)(ii) and the following information, suggest the structures of F and H, both of which contain brominated benzene rings.
  - G and H are the only carbon-containing products formed when F undergoes sidechain oxidation in step 2
  - one mole of H produces one mole of hydrogen gas on complete reaction with sodium metal

F gives orange precipitate with 2,4-dinitrophenylhydrazine	[2]
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3	(a)	Expla	ain why transition metal complexes are often coloured.	[3]
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	4.		Otata the plantagic configuration of chromium	[1]
	(b)	(i)	5	
		(ii)	Explain why chromium can exhibit a number of different oxidation states in its compound	us. [1]
			,	

(c)	air, t adde	ack oxide CrO, dissolves readily in dilute acid to form a sky blue solution <b>A</b> . When left in the the solution changes to a green solution <b>B</b> . When a small amount of sodium hydroxide is set to <b>B</b> , a grey green precipitate <b>C</b> is formed. Upon the addition of excess sodium hydroxide, mplex $[Cr(OH)_6]^{3-}$ is formed which reacts with $H_2O_2$ to form a yellow solution, $CrO_4^{2-}$ .							
	(i)	Give the formula of the unknown chromium-co	ontaining species present in A, B, and C.	[3]					
	(ii)	What type of reaction occurs when CrO <sub>4</sub> <sup>2-</sup> is t	formed from [Cr(OH) <sub>6</sub> ] <sup>3-</sup> ?	[1]					
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(d)	In an	acidic medium, chromium(VI) exists as Cr <sub>2</sub> O <sub>7</sub> <sup>2</sup>	<del>-</del> .						
	(i)	not exist.	[1]						
	(ii)	In aqueous solution, Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> exists in equilibri	aqueous solution, Cr₂O <sub>7</sub> ²⁻ exists in equilibrium with CrO₄²⁻ as shown below.						
		$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 0$	2CrO₄²⁻(aq) + 2H⁺(aq)						
		orange	vellow						
		Describe the observation when an aqueous so your reasoning.	lution of Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> is diluted with water. Expl	lain [2]					
	(iii)	With the aid of E <sup>o</sup> values from the <i>Data Booki</i> is bubbled into acidified K₂Cr₂O <sub>7</sub> (aq). Write an	et, explain why a reaction occurs when S equation for this reaction.						
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(e)	An a	ydrated salt <b>E</b> ( $M_r$ = 399.7) contains 13.0 % of Cr, 27.0 % of H <sub>2</sub> O and 60.0 % of Br baqueous solution containing 0.400 g of <b>E</b> immediately gives 0.188 g of cream property treated with aqueous silver nitrate.	y mass. ecipitate
	(i)	Calculate the mole ratio of Cr: H₂O: Br in the hydrated salt <b>E</b> .	[1]
	(ii)	Identify the cream precipitate and hence, determine the formula of the octahedral cation in the hydrated salt E.	complex [3]
	(iii)	Given that the complex ion in E has a net dipole moment, draw the structure of this ion, showing clearly how the ligands are arranged around chromium.	complex [1]
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concer	namber used in ntrated sulfuric a ne <i>Data Booklet</i> ,	cid, whereas l	ead is only	be made of superficially	steel as attacked.	iron rapidly With the aid	dissolves in l of <i>E</i> <sup>o</sup> values [2]
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#### Section B

Answer one question from this section.

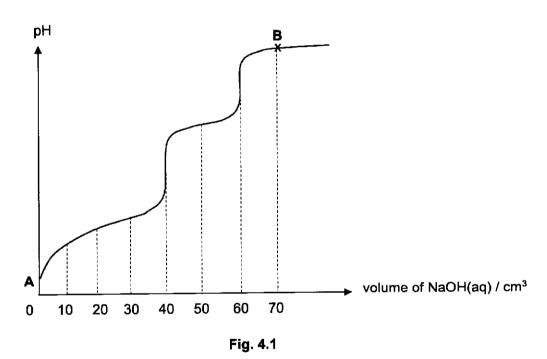
4 (a) The structure of glutamic acid is shown below.

$$_{\text{HO}}$$
  $_{\text{NH}_{2}}$   $_{\text{OH}}$ 

glutamic acid

There are three  $pK_a$  values associated with glutamic acid: 2.19, 4.25 and 9.67.

A 10.0 cm<sup>3</sup> sample of the *fully protonated* form of glutamic acid is titrated against 0.100 mol dm<sup>-3</sup> NaOH(aq). The titration curve is shown in Fig. 4.1.



(i) Define  $pK_a$ . [1]

(ii) When 60 cm<sup>3</sup> of NaOH is added, all three acidic groups are deprotonated. Calculate the concentration of glutamic acid in the given sample. [1]

(iii) Calculate the pH of glutamic acid at point A. [2]

(iv) Draw the zwitterion of glutamic acid. [1]

(v) The isoelectric point (pI) is the pH where the amino acid exists primarily as the zwitterion.

On the titration curve in Fig. 4.1, mark the point at which this occurs, with a cross. [1]

(vi) Calculate the pH at point B. [2]

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(b) Table 4.1 gives the structures and pI values of three different amino acids.

Table 4.1

amino acid	HO OH OH ONH <sub>2</sub> asp	O OH NH <sub>2</sub> ala	H <sub>2</sub> N OH NH <sub>2</sub>
pI	2.77	6.00	9.74

(i)	Draw the structure of the tripeptide asp-ala-lys. The left-most end of the peptide	lide should be
1.7	a free -NH <sub>2</sub> group, while the right-most end is a free -CO <sub>2</sub> H group.	[2]

(ii) A mixture of the three amino acids in Table 4.1 can be separated via a process known as electrophoresis.

The amino acid mixture is placed in the centre of a strip of filter paper soaked in a buffer solution of pH 6.00 as shown in Fig. 4.2. Two electrodes are then placed in contact with the edges of the filter paper.

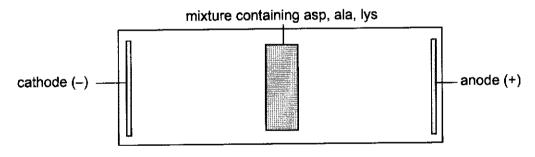
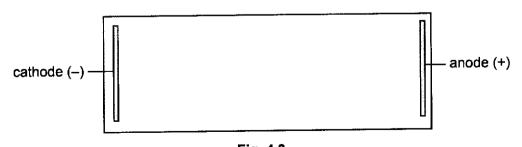


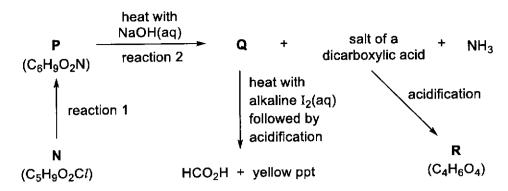
Fig. 4.2

By considering the net charge on the predominant form of each amino acid at pH 6.00, label the positions of the three amino acids at the end of the experiment **on Fig. 4.3**. [2]



(c)	Describe and explain the relative basicities of ethylamine, diethylamine and triethylamine in the gaseous state.

(d) Consider the reaction scheme below.



(i) By considering the change in molecular formulae of **N** to **P**, suggest the reagents and conditions for reaction 1. [1]

Compound P does not rotate plane-polarised light and is insoluble in both dilute

(ii) State the type of reaction for reaction 2.

[1]

(iii) Suggest the structure of Q.

(iv)

[1]

hydro structi	ures of	acid Pano	and a	aqueo	us s	sodium							Sugges	[2]
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5 The Sabatier reaction is the catalytic reduction of carbon dioxide to produce methane.

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g)$$

(a)	6.87	mol of $CO_2(g)$ was reacted with 4.00 mol of $H_2(g)$ in a sealed vessel with a volume dm <sup>3</sup> . The reaction mixture was allowed to reach <i>dynamic equilibrium</i> at a pressure bar and a temperature of 500 °C.	of
	(i)	Explain what is meant by the term dynamic equilibrium.	[1]
	(ii)	Using the ideal gas equation, calculate the total number of moles of gas present equilibrium.	at [2]
	(iii)	Hence, determine the partial pressures of each of the individual gases at equilibrium.	[3]
	(iv)	Write an expression for the equilibrium constant $K_p$ , for the Sabatier reaction, includunits.	ling [2]
	(v)	Calculate the value of $K_p$ at 500 °C.	[1]
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(b)	In the	e Sabatier reaction, the proportion of products at equilibrium decreases as temperature ases.
	(i)	Deduce whether the Sabatier reaction is endothermic or exothermic. Explain your reasoning. [1]
	(ii)	Sketch the graph of the $K_p$ value against temperature. [1]
	(iii)	How would the $K_p$ value change if the total pressure decreases? Explain your answer. [1]

(C)	to coal-fired power plants.	[1]

(d) In recent years, there has been breakthroughs in producing methane-oxygen fuel cells that require lower operating temperatures, by changing the catalyst used at the anode. An example of a methane-oxygen fuel cell is shown in Fig. 5.1 below.

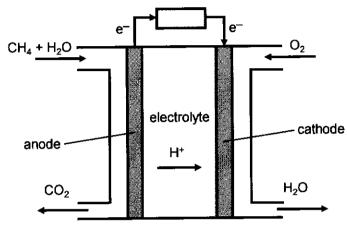


Fig. 5.1

The half-equations for the reactions at the anode and cathode are given by equations 1 and 2 respectively:

equation 1 
$$CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^- \qquad \Delta G^{e_1} = +131.2 \text{ kJ mol}^{-1}$$

equation 2 
$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

The overall equation of the reaction in the fuel cell is given by equation 3:

equation 3 
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

- (i) Use relevant data from the *Data Booklet* to calculate the standard Gibbs free energy change,  $\Delta G^{\circ}_{2}$ , for the reaction in equation 2. [2]
- (ii) Hence, determine the standard Gibbs free energy change, ΔG°3, for the reaction in equation 3, and E°cell for the methane-oxygen fuel cell. ΔG° can be used in the same manner as ΔH° in a Hess' law cycle but E° cannot.
  [2]

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(e) The Sabatier reaction and the methane-oxygen fuel cell both require the use of transition metals as heterogeneous catalysts.

Transition metal compounds can also act as homogeneous catalysts. For instance, the catalytic role of Fe $^{2+}$  in the reaction between I<sup>-</sup> and S $_2$ O $_8$ <sup>2-</sup> is well-known.

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

Using relevant data from the <i>Data Booklet</i> , suggest a transition metal cation, other than Fe <sup>2+</sup> or Fe <sup>3+</sup> , that can catalyse this reaction. Include relevant chemical equations and calculations to support your answer.
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# Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.
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# HWA CHONG INSTITUTION 2024 C2 H2 CHEMISTRY PRELIMINARY EXAMINATION SUGGESTED SOLUTIONS

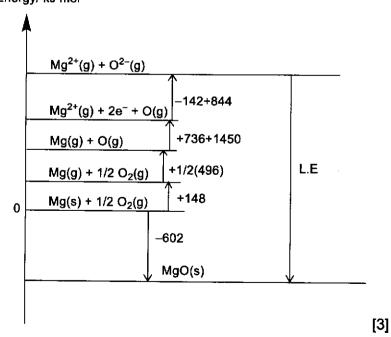
### Paper 3

- (ii) [0.5] for each point
  - Down the group, <u>cationic radius increases</u>, and <u>charge remains the</u> same.
  - Charge density of the cation decreases
  - Electron cloud of the anion is less polarized and the (N-O) covalent bonds are weakened to a smaller extent going down the group
  - More energy required to break these bonds hence temperature increases
- (iii) Number of moles of gaseous products increases as reaction takes place, entropy change is positive. [1]

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

Since  $\Delta H$  is positive, for  $\Delta G$  to be negative and reaction to be spontaneous, the <u>magnitude of  $T\Delta S$  needs to be greater than  $\Delta H$ </u>. Hence, high temperature is needed. [1]

(iv) Energy/ kJ mol<sup>-1</sup>



 $-602 = + 148 + \frac{1}{2}(496) + 736 + 1450 - 142 + 844 + L.E$ 

2024 HCI C2 H2 Chemistry Prelims / Paper 3

L.E =  $-3886 \text{ kJ mol}^{-1} = -3890 \text{ kJ mol}^{-1} (3 \text{ s.f.}) [1] (ecf based on energy cycle drawn)$ 

(b) MgO dissolves sparingly with water / has limited solubility in water. pH = 9 [0.5]

MgO + 
$$H_2O \rightarrow Mg(OH)_2$$
  
Mg(OH)<sub>2</sub>  $\rightleftharpoons Mg^{2+} + 2OH^-$  [0.5]

 $Al_2O_3$  does not react with water [0.5]. pH = 7 [0.5]

 $P_4O_{10}$  reacts violently with water to give an acidic solution. pH = 2 [0.5]

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 [0.5]$$

- (c) (i) AlCl<sub>3</sub> is electron deficient and can accept a pair of electrons. [1]
  - (ii) [0.5] for each product

(iv) Chlorine atom is more electronegative than iodine atom, the I-Cl bond is polar and  $\underline{I}$  atom in  $\underline{ICl}$  is more electron deficient as compared to the iodine atom in  $\underline{Icl}$ .

**OR** 

There is a partial positive charge on the I atom.

(v) [1] for each step

$$I-Cl + AlCl_3 \rightarrow I^+ + AlCl_4^-$$

2 (a) Alkenes <u>do not react/are unreactive</u> with nucleophiles [0.5] as C-H and C=C bonds are <u>non-polar</u> so there is <u>no electron deficient site</u> for nucleophilic attack

OR due to their electron rich  $\pi$  cloud/C=C bond which tends to repel nucleophiles [0.5]

Carbonyl compounds <u>react</u> with nucleophiles [0.5] due to the presence of <u>polar C=O bond/electronegative O</u> which causes the <u>C=O carbon to be electron deficient</u>. [0.5]

(b) (i) A racemic mixture contains equimolar amounts of two enantiomers. [1]

<u>Each enantiomer</u> in a racemic mixture <u>rotates plane-polarised light by the same magnitude in opposite directions</u>, [1] hence there is no net rotation of the plane-polarised light.

(ii) [1]: Choice of an alkene reaction that produces a carbocation intermediate, e.g. alkene + HCl / HBr / H2O / Cl2 / Br2 OR Choice of a carbonyl compound with a suitable nucleophile, e.g. HCN (in trace KCN)

[1]: Explain why racemic mixture is obtained:

- 0.5m (trigonal) planar geometry <u>about positively charged carbon</u> of the carbocation intermediate (for alkene reaction) or <u>C=O carbon</u> (for carbonyl reaction);
- 0.5m <u>equal probability</u> of attack from <u>top and bottom of the plane</u> by the nucleophile

[1]: Correct products drawn as a <u>pair of enantiomers</u>, with tetrahedral geometry about chiral carbon and use of <u>wedge/dash bonds</u> to illustrate 3D structure – mark is lost if there is no chiral carbon at all, or if products are drawn wrongly for the proposed reaction

Sample answer: presented in written prose

A carbocation intermediate with (trigonal) <u>planar geometry about the positively charged carbon</u> is formed. Br could <u>attack from top or bottom of the plane with equal probability</u> to produce equal concentrations of both enantiomers / a racemic mixture.

# Sample answer: presented using diagram and annotations

Organic compound and reagents used: CH<sub>3</sub>CHO, HCN in trace KCN

- (iii) Stereoisomers of a drug have <u>different arrangement of atoms in 3D space</u> (different 3D conformation) [0.5], and would hence have different binding properties to <u>chiral binding sites</u> in the body, e.g. enzymes, receptors [0.5]
- (c) (i) (nucleophilic) substitution [1]
  - (ii) 5-iodopentan-1-ol or 5-iodo-1-pentanol [1]
  - (iii) Orange K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> turns green for **B** & **C** [0.5] K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> remains orange for **D** [0.5]

Possible answers for step 2:

Reagent [1]	Product of <b>B</b> observations [0.5]	Product of <b>C</b> observations [0.5]			
Na <sub>2</sub> CO <sub>3</sub> (aq)	Effervescence (of CO <sub>2</sub> (g))	No effervescence			
Na(s)	Effervescence (of H <sub>2</sub> (g))	No effervescence			
PCl <sub>5</sub> (s)	White fumes (of HCI(g))	No white fumes			

(iv) Step 1: Na(s) or NaOH(s) [1]

Step 2: ethanoyl chloride (CH3COCI) [1]

(ii) Two Br atoms have been incorporated in F [0.5]
R group must be at position 4 (or 2) relative to OH group to prevent tri-substitution of phenol when Br<sub>2</sub>(aq) is added. [0.5]

(iii) 
$$OH$$
  $Br$   $OH$   $Br$   $OH$   $Br$   $CO_2H$   $H$ 

[0.5]  $\times$  2 for correct side-chain of F and  $-CO_2H$  of H [0.5]  $\times$  2 for relative positions of Br and side-chain/CO<sub>2</sub>H in each compound, based on answer in (ii)

- In the <u>presence of ligands</u>/ In a ligand field
  - the degenerate d-orbitals split into two different energy levels with an energy gap, ΔE.
  - There are vacancies in the higher energy d orbitals/ Partially-filled d orbitals
  - The promotion of an electron from the lower to higher of these d orbitals
  - requires <u>absorption of radiation in the visible spectrum</u> corresponding to ΔE.
  - The colour seen is the complement of the absorbed colour.

6 points [3] 4 to 5 points [2] 2 to 3 points [1]

- (b) (i)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$  [1]
  - (ii) Cr can exhibit variable oxidation states due to the <u>close/similar in energy of the 3d and 4s electrons</u>. Hence, once the 4s electrons are removed (or used for bonding), some or all the 3d electrons may also be removed without requiring much more energy. [1]
- (c) (i) A:  $[Cr(H_2O)_6]^{2+}$  (accept  $Cr^{2+}(aq)$ , 1/2 if  $Cr^{2+}$ )
  B:  $[Cr(H_2O)_6]^{3+}$  (accept  $Cr^{3+}(aq)$ , 1/2 if  $Cr^{3+}$ )
  C:  $Cr(OH)_3$  /  $Cr(OH)_3(H_2O)_3$

[1 each, total 3 marks]

- (ii) [Cr(OH)<sub>6</sub>]<sup>3-</sup> undergoes <u>oxidation</u> to form CrO<sub>4</sub><sup>2-</sup> [1]
- (d) (i) <u>High ionisation energy</u> needed to remove <u>6</u> valence electrons **OR**

Cr<sup>6+</sup> has <u>high charge density/ high polarising power</u> and thus undergoes hydrolysis in water to form a polyatomic oxoanion [1]

- (ii) Dilution causes the <u>concentration</u> of <u>all</u> aqueous species to <u>decrease</u> (to the same extent). [1/2]
  - As there are more concentration terms of the right hand side of the equation, position of equilibrium shifts towards the right [1] to produce more CrO<sub>4</sub><sup>2-</sup>.

- Hence the (orange) solution becomes yellow. [1/2] (accept 'less orange') (to earn this ½ mark, need to mention either the eqm shifts right or more CrO<sub>4</sub><sup>2-</sup> is produced)
- (iii)  $E^{\circ}_{cell} = (+1.33) (+0.17) = +1.16 \text{ V} [1/2]$

Since  $E^{e}_{cell}$  is positive, the reaction is <u>spontaneous/reaction occurs</u>. [1/2] Solution changes colour from orange to green/  $Cr_2Or^{2-}$  is reduced to  $Cr^{3+}$ 

$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$
 [1]

(e)	(i)		Cr	H <sub>2</sub> O	Br	
		Mass in 100 g	13.0	27.0	60	
		No. of moles	0.25	1.5	0.75	
		Mole ratio	1	6	3	[1]
		Formula	-			

Working must be shown to earn the mark.

(ii) Cream precipitate: AgBr [1]

No. of moles of AgBr = 0.188 / (108 + 79.9) = 0.00100 mol No. of moles of E = 0.400 / 399.7 = 0.00100 mol **[both amts: 1]** 

No. of moles of Br<sup>-</sup> anion: No of moles of **E**1 : 1

Formula of complex cation in E: [Cr(H<sub>2</sub>O)<sub>4</sub>(Br)<sub>2</sub>]<sup>+</sup> [1]

(iii) 
$$\begin{bmatrix} H_2O \\ H_2O \end{bmatrix} \xrightarrow{Br} Br \\ H_2O \xrightarrow{Br} Br \end{bmatrix}$$
 [1]

(Octahedral; bond should be shown from O to Cr)

(e) 
$$E^{\circ} / V$$
  
 $Fe^{2+} + 2e \rightleftharpoons Fe$   $-0.44$   
 $Pb^{2+} + 2e \rightleftharpoons Pb$   $-0.13$ 

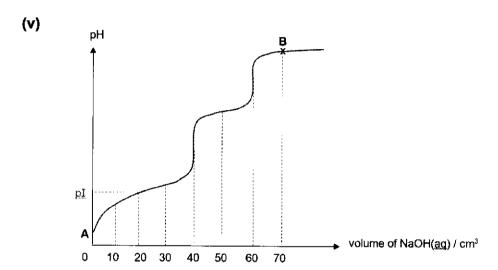
Quote E° values for Fe and Pb with relevant explanation [1]

 $E^{o}_{Fe2+/Fe}$  is more negative than  $E^{o}_{Pb2+/Pb}$ , Fe is more easily oxidised by concentrated sulfuric acid than Pb. Hence, Fe rapidly dissolves in concentrated sulfuric acid while Pb is only superficially attacked. [1]

4 (a) (i)  $pK_a = -\lg K_a$  (where  $K_a$  is acid dissociation constant for a weak acid with the expression  $K_a = [H^+][A^-]/[HA]$ ) [1]

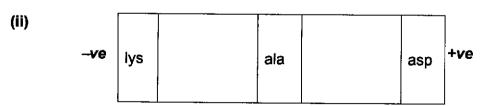
(ii) [glutamic acid] = 
$$(20 \times 0.10) / 10 = 0.200 \text{ mol dm}^{-3}$$
 [1]

(iii) 
$$pK_a = 2.19$$
,  $K_a = 10^{-2.19} = 6.456 \times 10^{-3}$   
 $6.456 \times 10^{-3} = x^2 \div (0.200 - x) \approx x^2 \div 0.200$  (assume  $x \ll 0.200$ )  $x = [H^+] = 0.0359$  mol dm<sup>-3</sup> [1] ecf from [HA] in (ii)  $pH = 1.44$  [1] ecf from [H<sup>+</sup>]



(vi) At point B, no. of moles of excess NaOH added =  $0.010 \times 0.100 = 1.00 \times 10^{-3}$  mol  $[OH^-] = 1.00 \times 10^{-3} / 0.080 = 0.0125$  mol dm<sup>-3</sup> [1] pOH = 1.903 pH = 12.1 [1] ecf from  $[OH^-]$  found

[1] for correct sequence of asp-ala-lys, 1m for correct structure



[1] correct amino acids moving to the respective –ve (lys) and +ve (asp) electrodes

[1] ala not moving

(c) Ethylamine has one alkyl group (or ethyl) attached to the N atom. Diethylamine and triethylamine has two alkyl groups and three alkyl groups attached to the N atom, respectively. [1] for comparing no. of alkyl groups and to state their electron donating property

An alkyl group is an electron-donating group that increases the electron density on the N atom, making the lone pair of electrons on N more available for protonation. [1] for describing the availability of lone pair on N to accept  $H^+$  / for protonation / to form dative bond to  $H^+$ 

Hence, basicity of triethylamine > diethylamine > ethylamine [1]

- (d) (i) Ethanolic KCN, heat [1]
  - (ii) (alkaline) hydrolysis [1]
  - (iii) Q: CH<sub>3</sub>CH<sub>2</sub>OH

[1]

(iv) O CN [1]

- 5 (a) (i) A dynamic equilibrium refers to a reversible reaction in a closed system in which the forward and reverse reactions are both taking place at the same rate resulting in no overall changes in concentrations. [1]
  - (ii) PV = nRT  $30 \times 10^5 \times 6.87 \times 10^{-3} = n(8.31)(773)$ n = 3.21 [2]

(iii)		CO <sub>2</sub> (g)	+	4H <sub>2</sub> (g)	1	CH₄(g)	+	2H₂O(g)
` '	I/ mol	1		4		0		0
	C/ mol	-x		-4x		+x		+2x
	E/ mol	1 – x		4 – 4x		X		2x

$$1 - x + 4 - 4x + x + 2x = 3.21$$

5 - 2x = 3.21

x = 0.895[1]

	CO <sub>2</sub> (g)	+	4H <sub>2</sub> (g)	1	CH <sub>4</sub> (g)	+	2H <sub>2</sub> O(g)
E/ mol	0.105		0.420		0.895		1.79
E/ bar	$\begin{array}{c} 0.105 \\ \hline 3.21 \\ =0.981 \end{array}$		$\frac{0.420}{3.21} \times 30$ =3.925		$\frac{0.895}{3.21} \times 30$ =8.354		1.79 3.21 × 30 =16.73

[1] for the amounts of each gas

[1] for partial pressures of each gas (with units)

(iv) 
$$K_p = \frac{(P_{CH_4})(P_{H_2O})^2}{(P_{CO_2})(P_{H_2})^4}$$

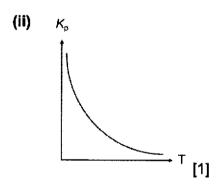
Units: bar -2

[1] for expression

[1] for units in any units of pressure

(v) 
$$K_p = \frac{(8.364)(16.73)^2}{(0.981)(3.925)^4} = 10.1 [1]$$

(b) (i) As temperature increases, the ratio of products to reactants decreases. This means that the <u>position of equilibrium shifted to the left</u> so as to absorb additional heat, hence the forward <u>reaction must be exothermic</u>. [1]



- (iii) No change. Pressure does not affect the value of  $\underline{K_p}$  OR  $\underline{K_p}$  only changes with temperature [1]
- Fuel cells have higher efficiency OR Fuel cells have good energy-to-mass ratio OR The hydrogen-oxygen fuel cell only produces water as a side product hence there is no pollution. [1]

(d) (i) 
$$\Delta G^{e_2} = -nFE^{e_2} = -(4)(96500)(+1.23) = -474.8 \text{ kJ mol}^{-1}$$

[1] for using +1.23

[1] for using formula correctly

(ii)  $\Delta G^{e_3} = \Delta G^{e_1} + 2(\Delta G^{e_2}) = -818.4 \text{ kJ mol}^{-1} [1] (OR use energy cycle as shown)$ 

$$\begin{array}{c} \Delta G^{\circ}{}_{3} \\ 8 H^{+}(aq) + 8 e^{-} + C H_{4}(g) + 2 O_{2}(g) \rightarrow C O_{2}(g) + 2 H_{2} O(l) + 8 H^{+}(aq) + 8 e^{-} \\ \\ 2 (\Delta G^{\circ}{}_{2}) & \Delta G^{\circ}{}_{1} \\ \\ C H_{4}(g) + 4 H_{2} O(l) \end{array}$$

$$E^{e_{cell}} = \Delta G^{e_3} \times 1000/(-8 \times 96500) = +1.06 \text{ V} [1]$$

(e) 
$$E^{\Theta}(I_2/I^-) = +0.54V$$
  $E^{\Theta}(S_2O_8^{2-}/SO_4^{2-}) = +2.01V$ 

Any TM ion can be chosen as long as the  $E^{\rm e}$  falls between those of  $E^{\rm e}(I_2/I^-)$  and  $E^{\rm e}(S_2O_8^{2-}/SO_4^{2-})$ .

$$2\text{Co}^{3+} + 2\text{I}^{-} \rightarrow 2\text{Co}^{2+} + \text{I}_{2}$$
  
 $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{red}} - E^{\ominus}_{\text{ox}} = +1.89 - (+0.54) = +1.35 \text{ V}$ 

$$2\text{Co}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Co}^{3+} + 2\text{SO}_4^{2-}$$
  
 $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{red}} - E^{\ominus}_{\text{ox}} = +2.01 - (+1.89) = +0.12 \text{ V}$ 

- [1] for correct TM ion
- [1] for two correct equations
- [1] for two correct  $E^{\dot{\Theta}_{\text{cell}}}$  calculated