



CANDIDATE
NAME

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INDEX
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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)	
For Examiner's Use	
1	/ 20
2	/ 19
3	/ 21
Circle your option below	
4 / 5	/ 20
Deductions (s.f.)	
Deductions (units)	
Deductions (structures)	
Total	/ 80

- 2 (a) Describe and explain the difference in reactivity of alkenes and carbonyl compounds towards nucleophilic reagents. [2]

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- (b) In the pharmaceutical industry, understanding optical activity and addressing the effects of racemic mixtures is crucial in drug development.

(i) Explain why a racemic mixture is optically inactive. [2]

(ii) With reference to a reaction involving a suitable alkene or carbonyl compound of your choice, explain why a racemic mixture is obtained in the reaction.
Give the organic compound and reagents used, and draw structures to illustrate the type of stereoisomerism present in the product mixture. [3]

(iii) Stereoisomers of a drug such as ibuprofen often have different pharmacological activities. Suggest a reason for why this is so. [1]

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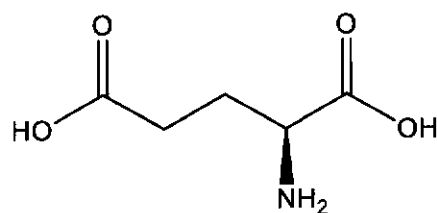
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Section B

Answer **one** question from this section.

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



glutamic acid

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

A 10.0 cm^3 sample of the *fully protonated* form of glutamic acid is titrated against $0.100 \text{ mol dm}^{-3} \text{ NaOH(aq)}$. The titration curve is shown in Fig. 4.1.

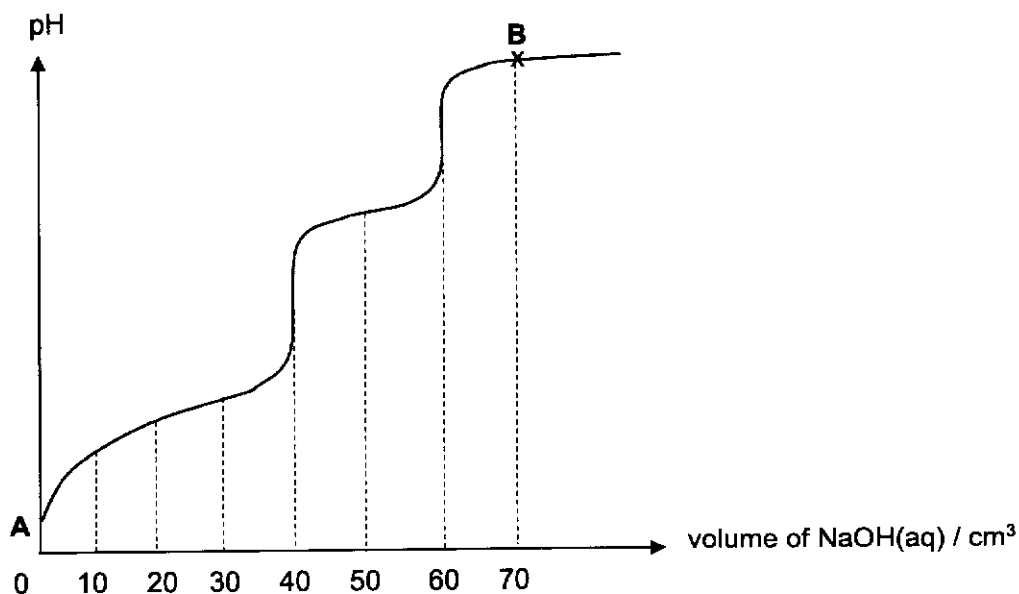
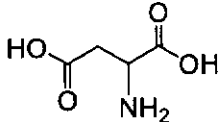
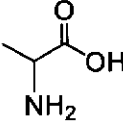
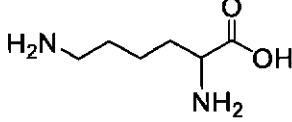


Fig. 4.1

- (i) Define pK_a . [1]
- (ii) When 60 cm^3 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]

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

Table 4.1

amino acid			
pI	2.77	6.00	9.74

- (i) Draw the structure of the tripeptide asp-ala-lys. The left-most end of the peptide should be a free -NH_2 group, while the right-most end is a free $\text{-CO}_2\text{H}$ group. [2]

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- (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.

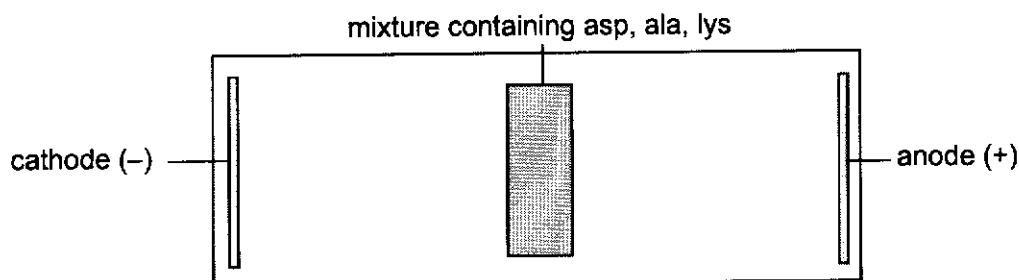


Fig. 4.2

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]

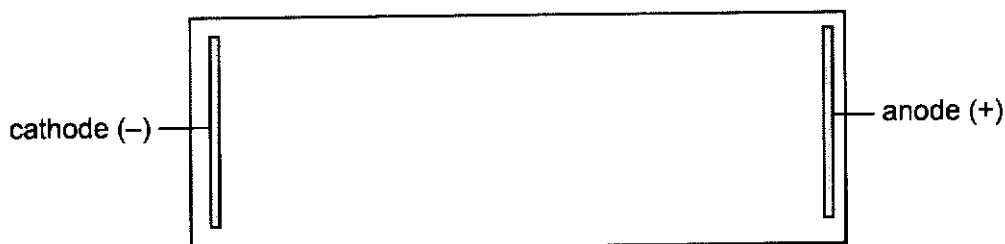


Fig. 4.3

- (c) State an advantage of using the hydrogen-oxygen fuel cell to generate electricity as compared to coal-fired power plants. [1]

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- (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.

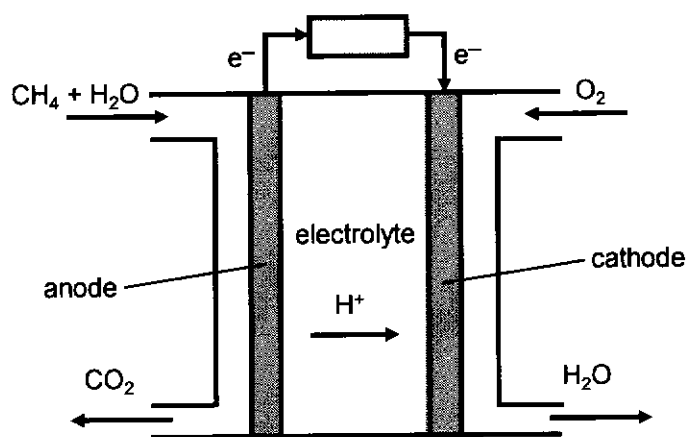
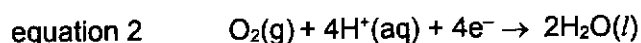
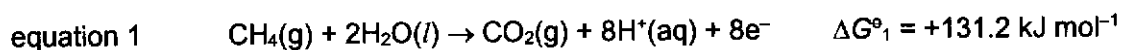
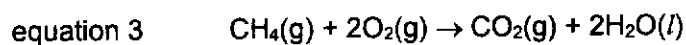


Fig. 5.1

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



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



- (i) Use relevant data from the *Data Booklet* to calculate the standard Gibbs free energy change, ΔG^\ominus_2 , for the reaction in equation 2. [2]
- (ii) Hence, determine the standard Gibbs free energy change, ΔG^\ominus_3 , for the reaction in equation 3, and E^\ominus_{cell} for the methane-oxygen fuel cell. ΔG^\ominus can be used in the same manner as ΔH^\ominus in a Hess' law cycle but E^\ominus cannot. [2]

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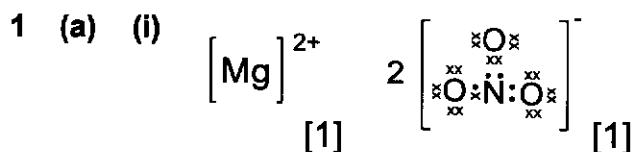
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HWA CHONG INSTITUTION
2024 C2 H2 CHEMISTRY PRELIMINARY EXAMINATION
SUGGESTED SOLUTIONS

Paper 3



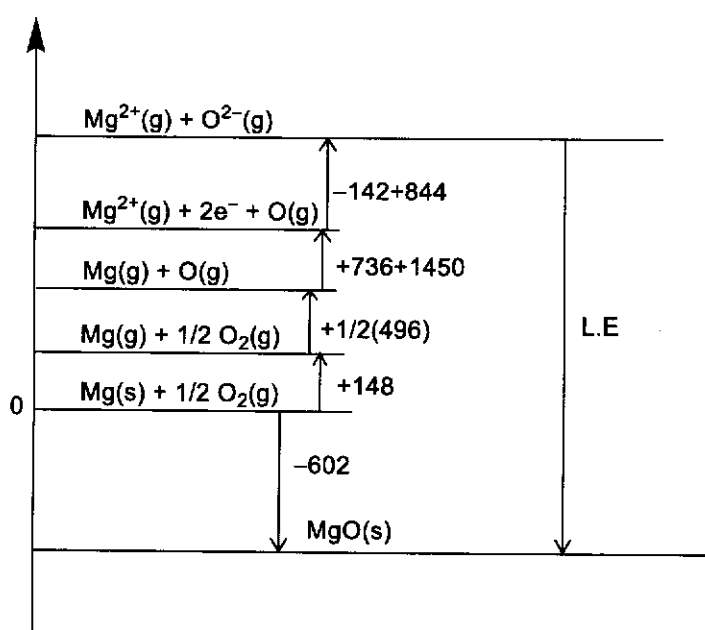
- (ii) [0.5] for each point
- Down the group, cationic radius increases, and charge remains the same.
 - Charge density of the cation decreases
 - Electron cloud of the anion is less polarized and the (N-O) covalent bonds are weakened to a smaller extent going down the group
 - More energy required to 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 ΔH is positive, for ΔG to be negative and reaction to be spontaneous, the magnitude of $T\Delta S$ needs to be greater than ΔH . Hence, high temperature is needed. [1]

- (iv) Energy/ kJ mol^{-1}

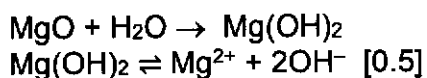


[3]

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

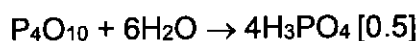
L.E = $-3886 \text{ kJ mol}^{-1} = -3890 \text{ kJ mol}^{-1}$ (3 s.f.) [1] (ecf based on energy cycle drawn)

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



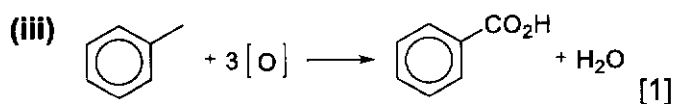
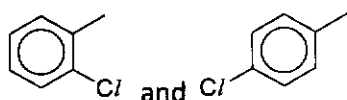
Al₂O₃ does not react with water [0.5]. pH = 7 [0.5]

P₄O₁₀ reacts violently with water to give an acidic solution. pH = 2 [0.5]



- (c) (i) AlCl₃ is electron deficient and can accept a pair of electrons. [1]

- (ii) [0.5] for each product

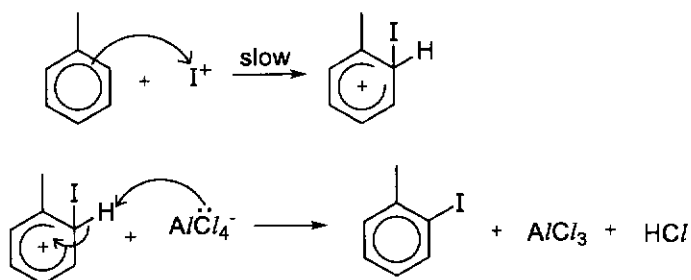
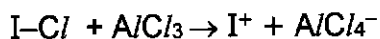


- (iv) Chlorine atom is more electronegative than iodine atom, the I-Cl bond is polar and I atom in ICl is more electron deficient as compared to the iodine atom in I₂.

OR

There is a partial positive charge on the I atom.

- (v) [1] for each step



- 2 (a) Alkenes do not react/are unreactive with nucleophiles [0.5] as C-H and C=C bonds are non-polar so there is no electron deficient site for nucleophilic attack
OR due to their electron rich π cloud/C=C bond which tends to repel nucleophiles [0.5]

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

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

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

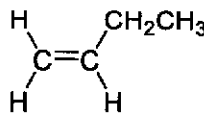
- (ii) [1]: Choice of an alkene reaction that produces a carbocation intermediate, e.g. alkene + HCl / HBr / H₂O / Cl₂ / Br₂ OR
Choice of a carbonyl compound with a suitable nucleophile, e.g. HCN (in trace KCN)

[1]: Explain why racemic mixture is obtained:

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

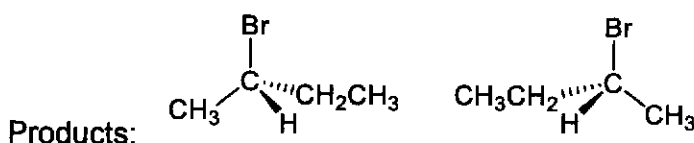
[1]: Correct products drawn as a pair of enantiomers, with tetrahedral geometry about chiral carbon and use of wedge/dash bonds to illustrate 3D structure – mark is lost if there is no chiral carbon at all, or if products are drawn wrongly for the proposed reaction

Sample answer: presented in written prose



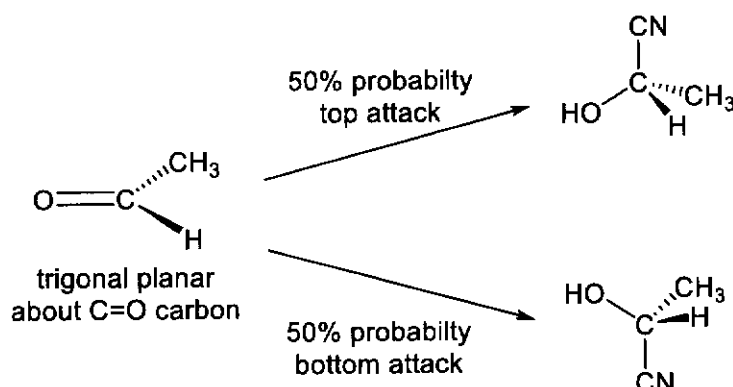
Organic compound and reagents used: _____, HBr

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



Sample answer: presented using diagram and annotations

Organic compound and reagents used: CH₃CHO, HCN in trace KCN



(iii) Stereoisomers of a drug have different arrangement of atoms in 3D space (different 3D conformation) [0.5], and would hence have different binding properties to chiral binding sites in the body, e.g. enzymes, receptors [0.5]

(c) (i) (nucleophilic) substitution [1]

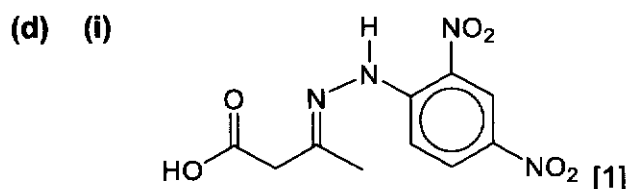
(ii) 5-iodopentan-1-ol or 5-iodo-1-pentanol [1]

(iii) Orange K₂Cr₂O₇ turns green for **B** & **C** [0.5]
K₂Cr₂O₇ remains orange for **D** [0.5]

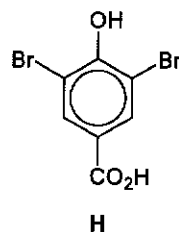
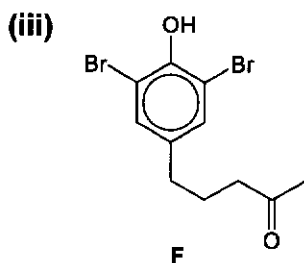
Possible answers for step 2:

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

(iv) Step 1: Na(s) or NaOH(s) [1]
Step 2: ethanoyl chloride (CH₃COCl) [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 Br₂(aq) is added. [0.5]



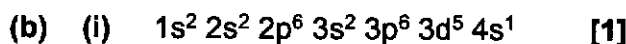
[0.5] × 2 for correct side-chain of **F** and $-\text{CO}_2\text{H}$ of **H**
 [0.5] × 2 for relative positions of Br and side-chain/ CO_2H in each compound, based on answer in (ii)

- 3 (a)
- In the presence of ligands/ 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 absorption of radiation in the visible spectrum 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]



- (ii) Cr can exhibit variable oxidation states due to the close/similar in energy of the 3d and 4s electrons. 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: $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (accept $\text{Cr}^{2+}(\text{aq})$, 1/2 if Cr^{2+})
 B: $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (accept $\text{Cr}^{3+}(\text{aq})$, 1/2 if Cr^{3+})
 C: $\text{Cr}(\text{OH})_3$ / $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$

[1 each, total 3 marks]

- (ii) $[\text{Cr}(\text{OH})_6]^{3-}$ undergoes oxidation to form CrO_4^{2-} [1]

- (d) (i) High ionisation energy needed to remove 6 valence electrons **OR**

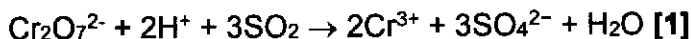
Cr^{6+} has high charge density/ high polarising power and thus undergoes hydrolysis in water to form a polyatomic oxoanion [1]

- (ii)
- Dilution causes the concentration of all aqueous species to decrease (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_4^{2-} .

- 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 CrO₄²⁻ is produced)

(iii) $E^{\circ}_{\text{cell}} = (+1.33) - (+0.17) = +1.16 \text{ V}$ **[1/2]**

Since E°_{cell} is positive, the reaction is spontaneous/ reaction occurs. **[1/2]**
 Solution changes colour from orange to green/ Cr₂O₇²⁻ is reduced to Cr³⁺



(e) (i)

	Cr	H ₂ 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	Cr(H ₂ O) ₆ (Br) ₃			

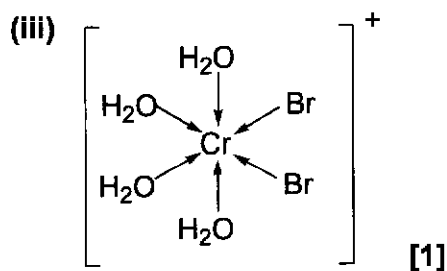
Working must be shown to earn the mark.

(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⁻ anion : No of moles of E
 1 : 1

Formula of complex cation in E: [Cr(H₂O)₄(Br)₂]⁺ **[1]**



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

(e)

	$\frac{E^{\circ}}{V}$
$\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}$	-0.44
$\text{Pb}^{2+} + 2\text{e} \rightleftharpoons \text{Pb}$	-0.13

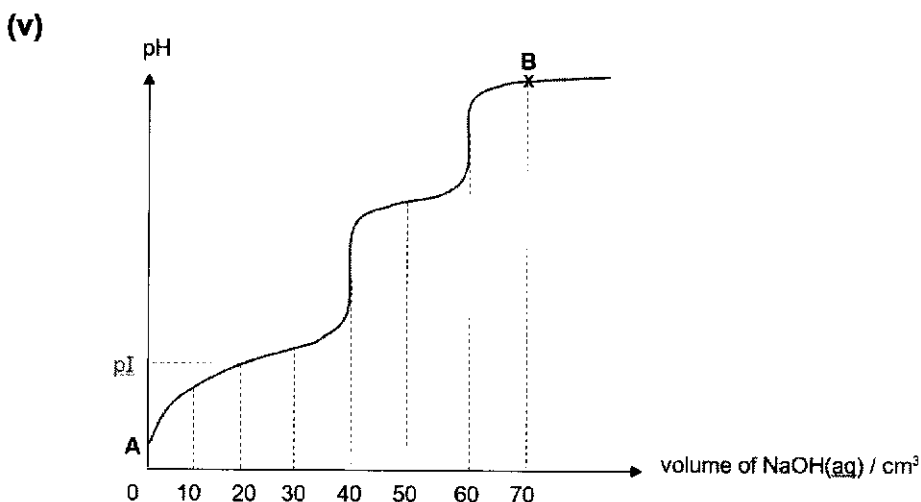
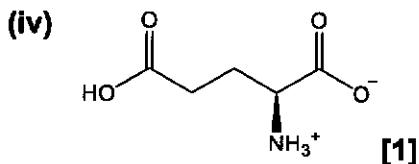
Quote E° values for Fe and Pb with relevant explanation **[1]**

$E^{\circ}_{\text{Fe}^{2+}/\text{Fe}}$ is more negative than $E^{\circ}_{\text{Pb}^{2+}/\text{Pb}}$, 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]**

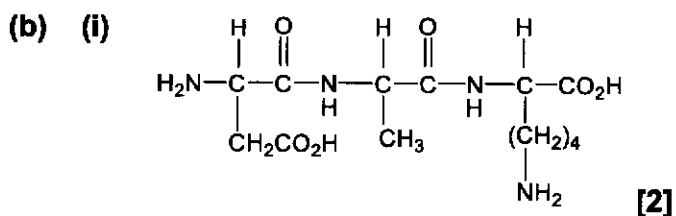
4 (a) (i) $\text{p}K_{\text{a}} = -\lg K_{\text{a}}$ (where K_{a} is acid dissociation constant for a weak acid with the expression $K_{\text{a}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$) **[1]**

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

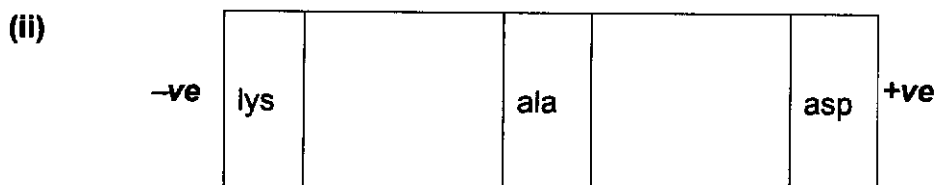
(iii) $\text{p}K_a = 2.19$, $K_a = 10^{-2.19} = 6.456 \times 10^{-3}$
 $6.456 \times 10^{-3} = x^2 + (0.200 - x) \approx x^2 + 0.200$ (assume $x \ll 0.200$)
 $x = [\text{H}^+] = 0.0359 \text{ mol dm}^{-3}$ [1] ecf from [HA] in (ii)
 $\text{pH} = 1.44$ [1] ecf from $[\text{H}^+]$



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

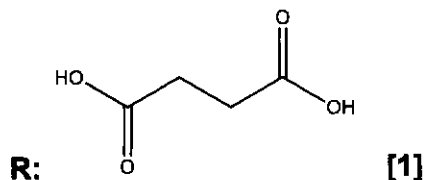
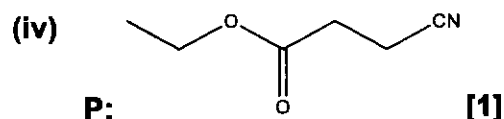
[1] for describing the availability of lone pair on N to accept H^+ / for protonation / to form dative bond to H^+

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

- (d) (i) Ethanolic KCN, heat [1]

(ii) (alkaline) hydrolysis [1]

(iii) Q: CH_3CH_2OH [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)

	$CO_2(g)$	+	$4H_2(g)$	\rightleftharpoons	$CH_4(g)$	+	$2H_2O(g)$
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 ₂ (g)	+	4H ₂ (g)	⇌	CH ₄ (g)	+	2H ₂ O(g)
E/ mol	0.105		0.420		0.895		1.79
E/ bar	$\frac{0.105}{3.21} \times 30$ =0.981		$\frac{0.420}{3.21} \times 30$ =3.925		$\frac{0.895}{3.21} \times 30$ =8.354		$\frac{1.79}{3.21} \times 30$ =16.73

[1] for the amounts of each gas

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

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

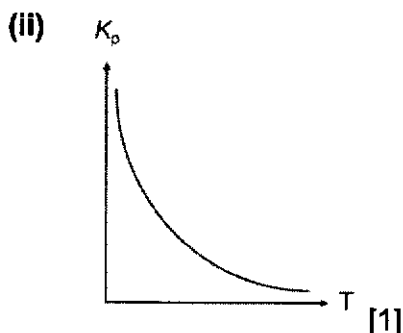
Units: bar⁻²

[1] for expression

[1] for units in any units of pressure

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

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



- (iii) No change. Pressure does not affect the value of K_p OR K_p only changes with temperature [1]

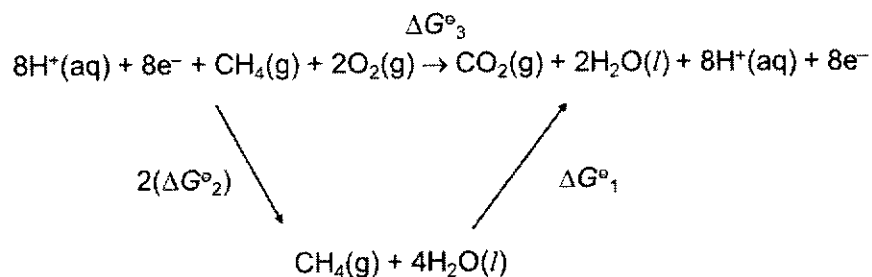
- (c) Fuel cells have higher efficiency OR Fuel cells have good energy-to-mass ratio OR The hydrogen-oxygen fuel cell only produces water as a side product hence there is no pollution. [1]

(d) (i) $\Delta G^\circ_2 = -nFE^\circ_2 = -(4)(96500)(+1.23) = -474.8 \text{ kJ mol}^{-1}$

[1] for using +1.23

[1] for using formula correctly

(ii) $\Delta G^\circ_3 = \Delta G^\circ_1 + 2(\Delta G^\circ_2) = -818.4 \text{ kJ mol}^{-1}$ [1] (OR use energy cycle as shown)

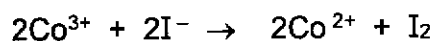


$$E^\ominus_{\text{cell}} = \Delta G^\ominus_3 \times 1000 / (-8 \times 96500) = +1.06 \text{ V [1]}$$

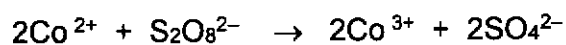
(e) $E^\ominus(\text{I}_2/\text{I}^-) = +0.54\text{V}$ $E^\ominus(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}) = +2.01\text{V}$

Any TM ion can be chosen as long as the E^\ominus falls between those of $E^\ominus(\text{I}_2/\text{I}^-)$ and $E^\ominus(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-})$.

E.g. Mn^{3+} , Mn^{2+} , Co^{3+} , Co^{2+} , VO_2^+ , VO^{2+}



$$E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{ox}} = +1.89 - (+0.54) = +1.35 \text{ V}$$



$$E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{ox}} = +2.01 - (+1.89) = +0.12 \text{ V}$$

[1] for correct TM ion

[1] for two correct equations

[1] for two correct E^\ominus_{cell} calculated