

HWA CHONG INSTITUTION 2024 C2 H2 CHEMISTRY PRELIMINARY EXAMINATION SUGGESTED SOLUTIONS

Paper 3

1 (a) (i)

$$\operatorname{Mg}^{2+} 2 \begin{bmatrix} \stackrel{\scriptscriptstyle \times O \times }{\underset{\scriptscriptstyle \times O}{\overset{\scriptscriptstyle \times \times}{\overset{\scriptstyle \times}{\overset{\scriptstyle \times \times}{\overset{\scriptstyle \times \times}{\overset{\scriptstyle \times}}{\overset{\scriptstyle \times}{\overset{\scriptstyle \times}{\overset{\scriptstyle \times}{\overset{\scriptstyle \times}{\overset{\scriptstyle \times}}{\overset{\scriptstyle \times}}{\overset{\scriptstyle \times}{\overset{\scriptstyle \times}}{\overset{\scriptstyle \times}{\overset{\scriptstyle \times}}{\overset{\scriptstyle \times}{\overset{\scriptstyle \times}}}}}}}}}}}}}}}}}}}}}}}}}}}}} } } }$$

(ii) [0.5] for each point

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

 $\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$

<u>Since ΔH is positive</u>, for ΔG to be negative and reaction to be spontaneous, the <u>magnitude of T ΔS needs to be greater than ΔH </u>. Hence, high temperature is needed. [1]

(iv) Energy/ kJ mol⁻¹



-602 = + 148+ ½(496) + 736 + 1450 - 142 + 844 + L.E 2024 HCI C2 H2 Chemistry Prelims / Paper 3

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

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

 $\begin{array}{l} \mathsf{MgO}+\mathsf{H_2O}\to \mathsf{Mg(OH)_2}\\ \mathsf{Mg(OH)_2}\rightleftharpoons \mathsf{Mg^{2+}+2OH^{-}} \ [0.5] \end{array}$

 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) AlCl₃ is electron deficient and can accept a pair of electrons. [1]
 - (ii) [0.5] for each product



- (iii) $(+ 3[0] \rightarrow (+ H_20)$
- (iv) Chlorine atom is more electronegative than iodine atom, the I-Cl bond is polar and <u>I atom in ICl is more electron deficient</u> as compared to the iodine atom in I₂.

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 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.

[1]: Choice of an alkene reaction that produces a carbocation intermediate, (ii) 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

 $\begin{array}{c} H \\ C = C \\ H \\ H \end{array}$

Organic compound and reagents used: H

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.

 $\begin{array}{c} \mathsf{Br} \\ \mathsf{H} \\ \mathsf{CH}_3 \\ \mathsf{H} \\ \mathsf{H} \\ \mathsf{CH}_2 \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{CH}_2 \\ \mathsf{CH}_3 \\$ Products:

Sample answer: presented using diagram and annotations

Organic compound and reagents used: CH₃CHO, 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 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	Product of C observations			
	[0.5]	[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 (CH₃COC*l*) [1]



(d)

 (ii) <u>Two Br</u> atoms have been incorporated in F [0.5] R group must be at <u>position 4 (or 2)</u> relative to OH group to <u>prevent</u> <u>tri-substitution</u> of phenol when Br₂(aq) is added. [0.5]



 $[0.5] \times 2$ for correct side-chain of **F** and $-CO_2H$ of **H** $[0.5] \times 2$ for relative positions of Br and side-chain/CO₂H in each compound, based on answer in (ii)

- 3 (a)
- In the presence of ligands/ In a ligand field
 - the degenerate d-orbitals <u>split into two different energy levels</u> with an energy gap, ΔE.
 - There are <u>vacancies in the higher energy d orbitals</u>/ 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 <u>complement</u> 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</u> <u>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) $[Cr(OH)_6]^{3-}$ undergoes <u>oxidation</u> to form CrO_4^{2-} [1]
- (d) (i) <u>High ionisation energy</u> needed to remove <u>6</u> valence electrons **OR**

Cr⁶⁺ has <u>high charge density/ high polarising power</u> and thus undergoes hydrolysis in water to form a polyatomic oxoanion **[1]**

- 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 CrO₄²⁻.

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

Since E°_{cell} is positive, the reaction is <u>spontaneous</u>/<u>reaction occurs</u>. **[1/2]** Solution changes colour from orange to green/ $Cr_2O_7^{2-}$ 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 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]

(iii) $\begin{bmatrix} H_2O \\ H_2O \\ H_2O \\ H_2O \\ H_2O \end{bmatrix}^+$ Br H_2O Br H_2O

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

(e)

 $E^{2^+} + 2e \rightleftharpoons Fe$ E° / V $Pb^{2^+} + 2e \rightleftharpoons Pb$ -0.13Quote E° values for Fe and Pb with relevant explanation [1]

<u> $E^{e}_{Fe2+/Fe}$ is more negative than $E^{e}_{Pb2+/Pb}$ </u>, 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⁻³ [1] ecf from [HA] in (ii) pH = 1.44 [1] ecf from [H⁺]





- (vi) At point B, no. of moles of excess NaOH added = 0.010 × 0.100 = 1.00 × 10⁻³ mol [OH⁻] = 1.00 × 10⁻³ / 0.080. = 0.0125 mol dm⁻³ [1] pOH = 1.903 pH = 12.1 [1] ecf from [OH⁻] found
- (b) (i) $H O H O H \\ | | | | | | | | \\ H_2N-C-C-C-N-C-C-N-C-CO_2H \\ | H | H | H | \\ CH_2CO_2H CH_3 (CH_2)_4 \\ | NH_2$ [2]

[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]



- 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)	1	CH ₄ (g)	+	2H ₂ O(g)
	l/ mol	1		4		0		0
	C/ mol	—x		-4x		+X		+2x
	E/ mol	1 – x		4 - 4x		Х		2x

1 - x + 4 - 4x + x + 2x = 3.21 5 - 2x = 3.21x = 0.895 [1]

	CO ₂ (g)	+	4H ₂ (g)	1	CH4(g)	+	2H ₂ O(g)
E/ mol	0.105		0.420		0.895		1.79
E/ bar	0.105		0.420		0.895		1.79 x 30
	3.21		3.21 ~ 30		3.21		3.21 ~ 30
	=0.981		=3.925		=8.354		=16.73

[1] for the amounts of each gas

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

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

Units: bar⁻² [1] for expression [1] for units in any units of pressure

(v)
$$K_{\rm p} = \frac{(8.364)(16.73)^2}{(0.981)(3.925)^4} = 10.1$$
 [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) <u>No change</u>. <u>Pressure does not affect</u> the value of $\underline{K_p}$ OR $\underline{K_p}$ 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)
$$\Delta G^{\Theta_2} = -nFE^{\Theta_2} = -(4)(96500)(+1.23) = -474.8 \text{ kJ mol}^{-1}$$

[1] for using +1.23[1] for using formula correctly

(ii) $\Delta G^{\Theta_3} = \Delta G^{\Theta_1} + 2(\Delta G^{\Theta_2}) = -818.4 \text{ kJ mol}^{-1} [1] (OR use energy cycle as shown)$





$$E^{\Theta}_{\text{cell}} = \Delta G^{\Theta}_3 \times 1000 / (-8 \times 96500) = +1.06 \text{ V} [1]$$

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

Any TM ion can be chosen as long as the E^{θ} falls between those of $E^{\theta}(I_2/I^-)$ and $E^{\theta}(S_2O_8^{2-}/SO_4^{2-})$. E.g. Mn³⁺, Mn²⁺, Co³⁺, Co²⁺, VO₂⁺, VO²⁺

 $2\text{Co}^{3+} + 2\text{I}^- \rightarrow 2\text{Co}^{2+} + \text{I}_2$ $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{red}} - E^{\ominus}_{\text{ox}} = +1.89 - (+0.54) = +1.35 \text{ V}$

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

[1] for correct TM ion

[1] for two correct equations

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