Paper 2

1 (a) (i) HC*l*: does not decompose even on strong heating

HBr: gives brown fumes of $Br_2(g)$ on strong heating

HI: gives large amounts of violet fumes of $I_2(g)$ when a red-hot rod is plunged into a jar of HI gas

Observation of brown & violet fumes for HBr and HI: **1m**

Description of trend in ease/rate/extent of decomposition: **1m**

1 (a) (ii) The thermal stabilities of these halides decrease in the order HC*l* > HBr > HI as the H-X bond strength/bond energy decreases in the same order, and less energy is needed to break the H-X bond. **[1]**

1 (b) (i) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ **[1]**
(Minus 0.5m for wrong or no state symbols, minus 0.5m if acid/base not written as a compound)

1 (b) (ii) $HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$ **[1]**
(Minus 0.5m for wrong or no state symbols, minus 0.5m if acid/base not written as a compound)

Acceptable alternatives:
$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ – provided this answer was not given in (b)(i)

1 (c) (i) From the pH, $[H^+] = 10^{-2.10} = 7.94 \times 10^{-3}$ mol dm^{-3} **[1]**

Since $[H^+] < [HF]$, HF does not dissociate fully to give H^+ ions and is a weak acid. **[1]**

OR
If HF is a strong acid, pH of a 0.100 mol dm^{-3} HF = –lg 0.100 = 1.00 **[1]**

Since the actual pH of HF is higher than if it were a strong acid, HF does not dissociate fully to give H^+ ions and is a weak acid. **[1]**

OR

Degree of dissociation, $\alpha = (10^{-2.10}) \div 0.100 = 0.0794$ **[1]**

Since the degree of dissociation is less than 1, HF does not dissociate fully to give H^+ ions and is a weak acid. **[1]**

1 (c) (ii) $K_a = (10^{-2.10})^2 \div (0.100 - 10^{-2.10}) = 6.85 \times 10^{-4}$ mol dm^{-3} **[1]**

1 (c) (iii) Both titration curves would show a decrease in pH as the acid is added.

OR

Both titration curves would show a sharp **drop** in pH when **12.50 cm^3** of the acid is added. [1]

1 (c) (iv) 1. The pH at equivalence point is more than 7 when HF is used but equal to 7 when HC*l* is used [•], as F^- is able to hydrolyse in water, but not Cl^- [•].

2. After equivalence point, the pH remains relatively constant/curve is more gentle or flatter when HF is used, while the pH drops more when HC*l* is used [•]. This is due to formation of a buffer solution consisting of F^- and excess HF after equivalence point but no buffer is formed for Cl^- and HC*l* [•].

3. When 50 cm^3 of the acid is added, pH of solution is lower when HC*l* is used [•] as HC*l* is a stronger acid which dissociates to give higher concentration of H^+ than HF of the same concentration [•].

0.5m for each description [•] and each corresponding explanation [•]

2 (a) $_{26}Fe$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
$_{26}Fe^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
$_{26}Fe^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Small jump from 6th to 7th IE, indicating 7th electron is removed from inner 3p subshell of Fe^{2+} / there are 6 electrons in the outer 3d subshell. Therefore x = 2.

[1] x = 2 & attempt to explain, e.g. only mention small jump from 6th to 7th IE but never interpret this jump **[1]** complete reasonable explanation

2 (b) (i) Diagram must include:

- Concentration of 1 mol dm^{-3} for all aqueous solutions (H^+, $C_4H_4O_6^{2-}$, HCO_2^-)
- 1 bar pressure for $CO_2(g)$, $H_2(g)$, 25 ^oC for set-up
- (Platinised) platinum electrodes / graphite electrode
- Salt bridge (no need to mention concentrated KNO_3) & Voltmeter (symbol V accepted) with external wires

[1x2] correct each half cell
[1] voltmeter and salt bridge

2 (b) (ii) Both reactants $S_2O_8^{2-}$ and $C_4H_4O_6^{2-}$ ions are **negatively charged, will repel [1/2]** each other, thus reaction is slow due to **high activation energy**. **[1/2]**

2 (b) (iii) <u>Step 1</u>

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $\quad E^\ominus = +2.01$ V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\ominus = +0.77$ V

Overall equation for step 1:

$S_2O_8^{2-} + 2\,Fe^{2+} \rightarrow 2SO_4^{2-} + 2\,Fe^{3+}$ **[1]**

$E^\ominus_{cell} = +2.01 - (+0.77) = +1.24$ V $> 0 \Rightarrow$ reaction is spontaneous **[1/2]**

<u>Step 2</u>

$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- = C_4H_4O_6^{2-} + 2H_2O$ $\quad E^\ominus = -1.02$ V

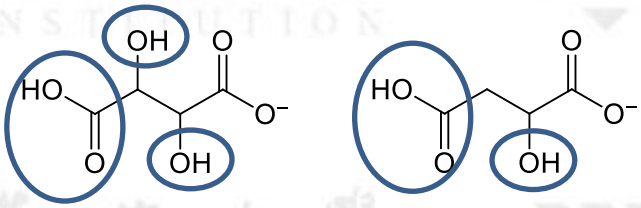
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\ominus = +0.77$V

Overall equation for step 2:

$6Fe^{3+} + C_4H_4O_6^{2-} + 2H_2O \rightarrow 6Fe^{2+} + 2CO_2 + 2HCO_2^- + 6H^+$ **[1]**

$E^\ominus_{cell} = +0.77 - (-1.02) = +1.79$ V $> 0 \Rightarrow$ reaction is spontaneous **[1/2]**

2 (c) Tartaric acid has a lower pK_{a1}.



(A) (B)

Conjugate based of tartaric acid (A) is more stable than that of malic acid (B).

The **negative charge on the carboxylate ion of A is dispersed to a larger extent [1]** due to the presence of **3 electron withdrawing groups** (2−OH and 1−CO_2H)/ **more electron withdrawing groups [1]**, vs only 2 electron withdrawing groups/ lesser withdrawing groups in **B**.

<u>OR</u>

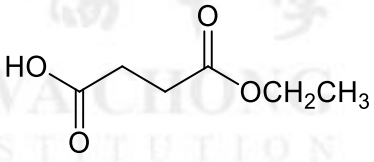
The **negative charge on the carboxylate ion of A is dispersed to a larger extent [1]** due to more electronegative atoms **[1]** helping to disperse the negative charge for **A**

[No marks for no explanation]

2 (d) (i) In Step I, the π bond of the unsaturated carbon in C=O is broken and a new C−O σ bond is formed **[1]**, suggesting that an addition reaction takes place.

In Step III, the C−OH_2^+ bond is broken and a C=O π bond is formed with an elimination of a H_2O molecule **[1]**, suggests elimination reaction takes place.

2 (d) (ii)



[1]

3 (a) (i)

	$PCl_5(g)$	=	$PCl_3(g)$	+	$Cl_2(g)$
Initial /mol	0.2		3.0		0
Change/mol	-0.05		+0.05		+0.05
Equi/mol	0.15		3.05		0.05

Total amount of gas = 0.15 + 0.05 + 3.05 = 3.25 mol **[1]**

3 (a) (ii) $P = nRT/V = 3.25 \times 8.31 \times 500 / 10 \times 10^{-3} = 1.3504 \times 10^6 = 1.35 \times 10^6$ Pa (3 s.f.) **[1]** ecf from (i)

3 (a) (iii) $P(PCl_5) = 0.15 \times 1.3504 \times 10^6 / 3.25 = 6.2326 \times 10^4$ Pa

$P(PCl_3) = 3.05 \times 1.3504 \times 10^6 / 3.25 = 1.2673 \times 10^6$ Pa

$P(Cl_2) = 0.05 \times 1.3504 \times 10^6 / 3.25 = 2.0775 \times 10^4$ Pa **[1]**

$K_p = (1.2673 \times 10^6) \times (2.0775 \times 10^4) / (6.2326 \times 10^4) = 4.22 \times 10^5$ Pa (3 s.f.) **[1]** ecf from (i) & (ii)

3 (a) (iv) When volume of container is decreased, <u>total pressure increases</u> hence <u>position of equilibrium shifts left</u> **[1]** so as to <u>favor production of fewer number of moles of gas</u> to offset the increase in pressure **[1].**

3 (a) (v) Since <u>value of K_p is large</u>, position of equilibrium is on the right side, implying that the reaction is <u>spontaneous</u>, the sign of ΔG_r would be negative. **[1]**

OR

Given that $\Delta G_r = -RT\ln K$ (and $K > 1$), therefore ΔG_r must be negative. **[1]**

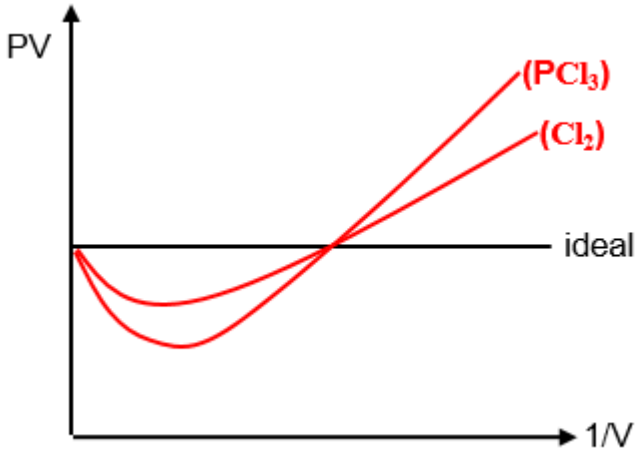
3 (a) (vi) No effect as adding a catalyst only changes the rate of both forward and backward reactions to the same extent, achieving equilibrium faster. It does not affect the amount of reactants and products produced. **[1]**

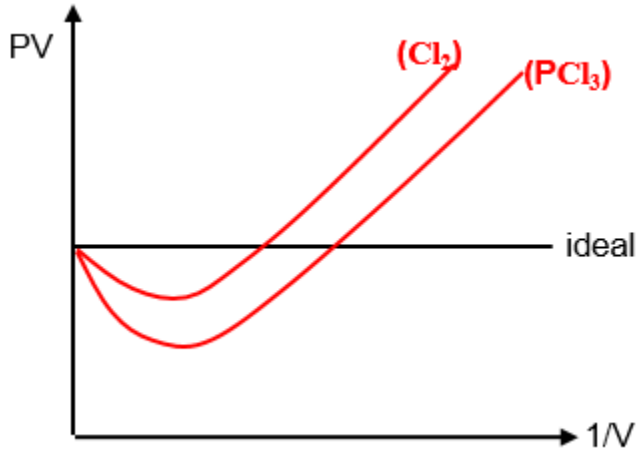
OR

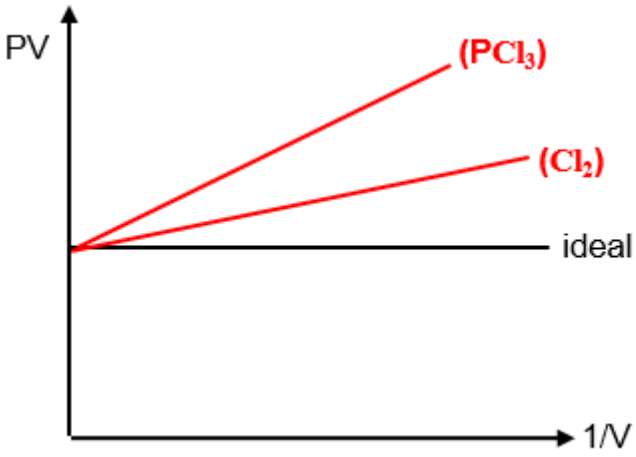
No effect as K_p is only affected by temperature. **[1]**

3 (a) (vii) Graphs that show that PCl_3 deviates more from ideality than Cl_2. **[1]**

Examples:





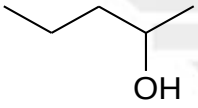


3 (a) (viii) The gases would behave <u>less ideally</u> at 300 K. **[1]**

At lower temperature of 300 K, the gas particles would have <u>lesser kinetic energy</u>. <u>Intermolecular forces (dispersion forces)</u> between gas molecules would be <u>more significant</u> in this case resulting in less ideal behaviour. **[1]**

3 (b) (i) Isomers with unbranched structure:

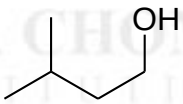
Pentan-1-ol



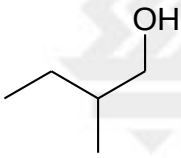
Pentan-2-ol

0.5m each for correct structure; 0.5m each for correct name

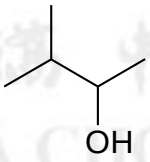
Isomers with branched structure (non-exhaustive):



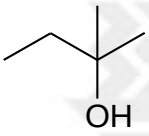
3-Methylbutan-1-ol



2-Methylbutan-1-ol



3-Methylbutan-2-ol



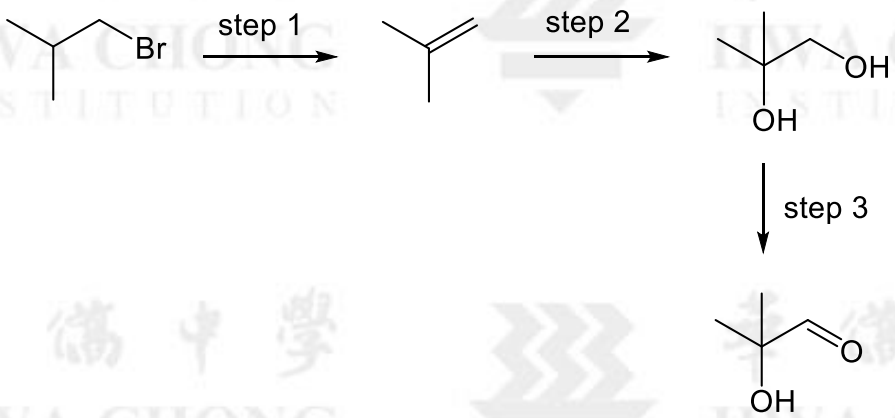
2-Methylbutan-2-ol

0.5m each for correct structure; 0.5m each for correct name

3 (b) (ii) $CH_3SO_3^-$ is the weaker base. **[1]**

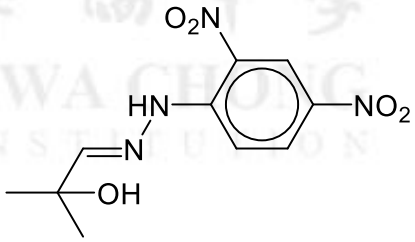
3 (b) (iii) $CH_3SO_3^-$ is more stable or (better leaving group) than OH^-, therefore **B** can undergo nucleophilic substitution more readily with CN^-. **[1]**

4 (a) (i)



Each structure **[1]** x 2
Step 1: Ethanolic KOH, heat **[1]**
Step 2: $KMnO_4(aq)$, $H_2SO_4(aq)$ or NaOH(aq), cold **[1]**
Step 3: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat with immediate distillation **[1]**

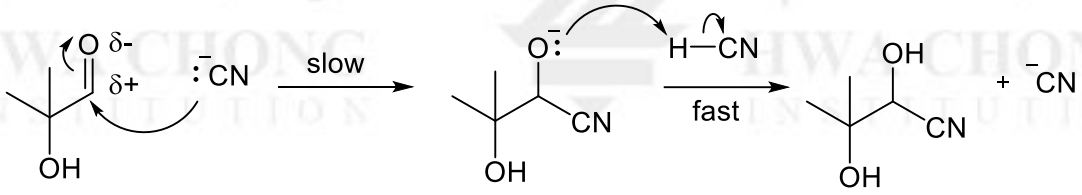
4 (a) (ii)



[1]

4 (b) (i) Nucleophilic addition **[1]**

$KCN \rightarrow K^+ + CN^-$



[1] x 2 for each step

4 (b) (ii) Electronic reason: The aldehyde has one electron-donating alkyl group while the ketone has two. **[0.5]** Hence, the carbonyl carbon of the aldehyde has a higher partial positive charge compared to that of the ketone, making it more susceptible towards nucleophilic attack. **[0.5]**

or

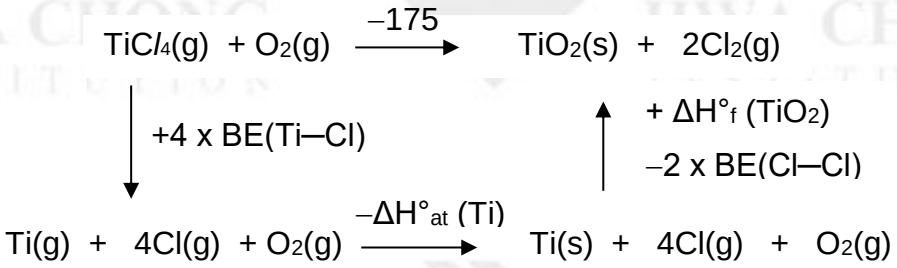
Steric reason: The presence of two relatively large substituents in the ketone group versus only one large substituent in the aldehyde group **[0.5]** means that attacking nucleophiles are able to approach the carbonyl carbon in the aldehyde with less steric hindrance. **[0.5]**

4 (c) (i) Tertiary halogenoalkanes are sterically hindered due to the presence of three alkyl groups **[0.5]**, hence it is hard for the nucleophile to attack the C-X bond. **[0.5]**

4 (c) (ii) Tertiary halogenoalkanes undergo unimolecular nucleophilic substitution (S_N1), where the nucleophile attacks the trigonal planar carbocation intermediate from both top and bottom with equal probability, forming a racemic mixture of the product. **[1]**

4 (c) (iii) Enantiomers have identical chemical properties except in their interactions with another chiral molecule, hence a chiral cation can promote the formation of one enantiomer but not the other spatially. **[1]** *Alternative answers to the effect were accepted.*

5 (a)

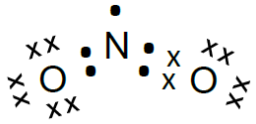


By Hess' Law,

$4 \times BE(Ti{-}Cl) = (-175) - (-939) - (-2 \times 244) - (-473)$
$= 1725$
$BE(Ti{-}Cl) = +431.3 \text{ kJ mol}^{-1}$

Correct equations and correct cycle [2]
Correct final answer [1]
Deduct 1 mark for any mistake, e.g. include extra O=O bond energy, arrow with wrong direction, energy term with wrong sign, incorrect multiples of energy terms like 4 x 244, etc.

5 (b) (i)



5 (b) (ii) Expected 120° / trigonal arrangement from VSEPR because of three electron groups. [1]
Or
Expected 118° because of two bond pairs and one lone pair.

However, the electron repulsion between unpaired electron and the single bond / double bond is weaker than that between a lone pair and bond pair, hence a larger bond angle than 120° / 118°. [1]

Allow for answers that make reference to 180° (expected of two bond pairs and no lone pair), and say that the unpaired electron makes the bond angle smaller than 180°.

5 (c) (i) $H_2O \rightarrow HO^{\bullet} + e^- + H^+$ (1) - given
$NO_2 + HO^{\bullet} \rightarrow HNO_3$ (2)
reject NO_2OH (does not follow convention of formulas)
$e^- + O_2 \rightarrow O_2^-$ (3)
$O_2^- + NO \rightarrow O_2NO^-$ (4) - Accept NO_3^-

$H_2O + NO_2 + NO + O_2 \rightarrow HNO_3 + H^+ + ONO_2^-$

Accept $H_2O + NO_2 + NO + O_2 \rightarrow 2HNO_3$

Three correct equations [2]; two correct equations, 1 mark

Correct overall equation [1]

Identify O_2 / oxygen gas (undergoes reduction) [1]

5 (c) (ii) Identifies HNO_3 and $HONO_2$ (from $H^+ + ONO_2^-$) as two different compounds with a reason that they have different structures / arrangement of atoms / N has different oxidation states [1].

5 (d) (i) From Expt 1 and 2: when P_{NO} is doubled, p_{H2} kept constant, the rate increases 4 times. Therefore, 2nd order wrt P_{NO}. [½]

From Expt 2 and 3: when P_{H2} is tripled, P_{NO} kept constant, the rate increases 3 times. Therefore, 1st order wrt P_{H2} [½]

Rate = $k (P_{NO})^2 P_{H2}$ [1]

5 (d) (ii) Calculate k:
From Expt 1: $k = 5.62 \times 10^{-6}$ kPa^{-2} s^{-1}

Correct numerical value [1]
Correct units [1]

5 (d) (iii) Since NO is in excess, p_{NO} is constant and the reaction is pseudo 1st order wrt p_{H2}.
Then Rate = $k' P_{H2}$ where $k' = k (P_{NO})^2$

$$t_{½} = \frac{\ln 2}{k'}$$

$$= \frac{\ln 2}{5.62 \times 10^{-6} \times 106^2}$$

$$= 10.98 \text{ s}$$

$$= 11.0 \text{ s} \quad \text{(3 sf)} \quad [1]$$

5 (d) (iv) Since Step 2 is the rate determining step,
then Rate = $k\, p_{N2O2}\, p_{H2}$ [1]

But $K_p = \frac{P_{N2O2}}{P_{NO}{}^2}$

$\therefore$ Rate = $k K_p (P_{NO})^2 p_{H2}$

$= k' (P_{NO})^2 p_{H2}$

which is consistent to the experimental rate equation. [1]

5 (e) (i) From $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$,

$$\Delta S^{\ominus} = \frac{\Delta H^{\emptyset} - \Delta G^{\emptyset}}{T}$$

$$= \frac{(+155.8)-(+112.5)}{298}$$

$$= + 0.1453 \text{ kJ mol}^{-1} \text{ K}^{-1} \quad [1]$$

$\Delta S^{\ominus}$ is positive because the reaction occurs with an increase in the no. of moles of gaseous molecules; so there are more ways to distribute the energies of the molecules. [1]

5 (e) (ii)

- Since $\Delta H^{\ominus}$ is positive and $\Delta S^{\ominus}$ is also positive, $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ will only be negative at high temperatures when the magnitude of $\Delta H^{\ominus}$ is smaller than the magnitude of $T\Delta S^{\ominus}$. Therefore the reaction is spontaneous only at high temperatures [1]
- Set $\Delta G^{\ominus} = 0$, then $T = \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}}$

$$= \frac{155.8 \times 10^3}{145.3}$$

$$= 1073 \text{ K } (800\ ^{o}\text{C}) \quad [1]$$

This is the minimum temperature for the reaction to be spontaneous.