2011 NJC Prelim H2 Chemistry Paper 2 Solutions

1

(a) $Mg(OH)_2$ is not soluble in water therefore ΔH cannot be determined directly. [1]

(b)

(i) $Mg(OH)_2\,(s) + 2HCl\,(aq) \rightarrow MgCl_2\,(aq) + 2\,H_2O\,(l) \quad \Delta H < 0$ [1]

Comments:

- Thermochemical eqn must be accompanied with the associated enthalpy change, indicating whether it is endo or exo when there is no ambiguity.
- Pls note that this is enthalpy change of reaction, not enthalpy change of neutralization. It defines the heat released when 1 mole of $Mg(OH)_2$ and 2 moles of HCl are reacted together, it is NOT heat released when 1 mole of water is formed.

(ii)

Amt of $Mg(OH)_2$ = 1.17/ (24.3 + 17.0 x 2) = 0.02007 mol

Amt of HCl = 50/1000 x 2.0 = 0.100 mol

0.02007mol of $Mg(OH)_2$ needs 0.04 mol of HCl for reaction, therefore $Mg(OH)_2$ is limiting.

Heat released by reaction = heat absorbed by solution

$$30000 \times 0.02007 = 50 \times 4.18 \times \Delta T$$
$$\Delta T = 2.9\,^{o}C$$

Amt of solid $Mg(OH)_2$ not suitable as ΔT is not within 5-10 ^{o}C.

Comments:

- To judge whether the quantities of reagent used is suitable, you must prove whether the data you are collecting from this quantities used is of suitable range. For energetics, the data you are collecting is change in temperature and it must be of this range: $5^{o}C < \Delta T < 10^{o}C$
- This calculation actually leads you to preliminary consideration of more suitable working quantities of the reagents.
- First of all recognize that the solid $Mg(OH)_2$ being the limiting agent is the one that determines the amt of heat released from reaction.
- Therefore the easiest method to increase ΔT it to use (i) more solid $Mg(OH)_2$ or (ii) use half the volume of HCl solution.
- Method (ii) is rejected as half the volume of 50 cm^3 HCl causes the depth of solution to be too shallow, thus not able to cover the bulb of thermometer to ensure reliability of results.
- For method (i), it is logical for students to use multiple of 1.17 g of $Mg(OH)_2$ so that ΔT is also the same multiple of 2.9 ^{o}C. However, students must make sure that the increase in mass of solid $Mg(OH)_2$ used cannot cause amt of $Mg(OH)_2$ to be in

excess of the amt of HCl present as the linear relationship between mass of $Mg(OH)_2$ used and ΔT is no longer linear. This is because when HCl becomes limiting, it will be the regent that determines the magnitude of ΔT.

- For example, a student suggesting triple amt of solid $Mg(OH)_2$ will expect ΔT to be 3 x 2.9 = 8.7 °C. Student has failed to realize that HCl has become the limiting agent and the temp expected is no longer 8.7°C. Do you know what will be the ΔT instead?

(iii)

1. **Use double the mass of $Mg(OH)_2$ solid so that ΔT is doubled to become 5.8 °C and dil HCl is still present in excess.**

2. Weigh accurately about 2.34 g of $Mg(OH)_2$ using a weighing bottle.

   Pls do not tap the weighing bottle to ensure complete transfer of solid and this will result in more heat exchange between the reaction and the environment, this is why there is a need to measure the weighing bottle again to calculate the actual mass transfer.

   Pls do not suggest rinsing the remaining solid into the cup as it will cause the same problem of increasing heat exchange between reaction and environment and it will also add extra volume to the reaction mixture and the calculation to determine enthalpy change is affected.

3. Using a 50 ml measuring cylinder, measure 50 cm^3 of HCl into a styrofoam cup supported in beaker.

4. Measure initial temperature of HCl.

5. Add solid $Mg(OH)_2$ into the styrofoam cup, ***taking care to replace the lid immediately***.

6. ***Stir (stirring should be done continuously so that reaction can be completed within the shortest time possible so that heat exchange with the environment is minimized.***) with thermometer and measure the **highest temperature reached/** ***final constant temp attained (a final constant temp indicates that the reaction is completed).***

7. Weigh mass of weighing bottle and residual solid and calculate the actual mass transfer.

8. Wash the styrofoam cup and dry it thoroughly before the next experiment.

9. Repeat expt till ΔT/ m is within 5% difference.
   (Solid reactant is limiting, therefore ΔT/m is used to check consistency between different sets of experiments as the mass of solid reactant transferred to HCl solution for each expt may not be exactly the same.)

Comments:

A1 *"taking care to replace the lid immediately", "Stir* with thermometer" *and* "measure the *highest temp attained" are steps taken to ensure ΔT measured for this expt is reliable. (heat exchange with the environment is kept to minimal therefore result is reliable)*

A2 However, student may choose to monitor temp change with time and it is in general divided into three segments. (i) before addition of 2nd reagent (ii) during the reaction (iii) when reaction mixture starts to cool down. The extrapolation from the cooling curve and its intersection with the time you start the reaction determines the actual ΔT as heat exchange with environment is already taken into account. This will also ensure reliability of ΔT. This will also mean that step 4, 5 and 6 of the above procedure will be replaced with those underlined above.

B1 Some students suggested adding solid reactant to the Styrofoam cup followed by addition of HCl solution. It is actually alright if the student has measured the initial temp of the HCl acid before it is added to the solid $Mg(OH)_2$ in the styrofoam cup. However some students only started measuring the initial temp when HCl is added to solid $Mg(OH)_2$ in the styrofoam cup, this is wrong as reaction has already started and results will become unreliable.

B2 In fact, addition of solid to solution is a better method than the reverse. This is because tipping the solid into the solution is much faster than adding a big volume of solution into the Styrofoam cup. This is crucial as the longer you need to transfer the second reactant, the more heat exchange can take place between the reaction mixture and the environment.

[5]

(c) Given the following data, show how the enthalpy change of reaction between solid $Mg(OH)_2$ and hydrochloric acid can be determined accurately.

	Expt
Mass of weighing bottle and solid sample/g	a
Mass of weighing bottle and residual solid /g	b
Initial temp of 50.0 cm^3 of hydrochloric acid	T_1
Final constant temp of hydrochloric acid	$T_2 > T_1$

Heat released from reaction is absorbed by solution, therefore it should be 50 cm^3 of HCl solution.
Since it's a dilute solution, its density is similar to water, mass of 50 cm^3 HCl solution = 50.0 x 1gcm^{-3} = 50 g

-ve or +ve sign of enthalpy change is important as it will affect the calculation for the unknown enthalpy later.

$$\Delta H = -\frac{\enclose{circle}{50}\times 4.18\times(T_2-T_1)}{a-b\Big/(24.3+34.0)}$$

$$= -\frac{209(T_2-T_1)\times 58.3}{a-b}$$

$$= \enclose{circle}{-}12185\frac{(T_2-T_1)}{a-b}$$

[1]

1 (d)

$$\begin{tikzcd}
2HCl\,(aq) + Mg(OH)_2\,(s) + aq \arrow[r] \arrow[dr, "\Delta H \text{ from part (c)}"'] & Mg^{2+}\,(aq) + 2OH^-\,(aq) + 2\,HCl\,(aq) \arrow[d, "2 \times \Delta H_1"] \\
 & MgCl_2\,(aq) + 2\,H_2O\,(l)
\end{tikzcd}$$

$\Delta H_{solution} = \Delta H(c) - 2 \times \Delta H_1$

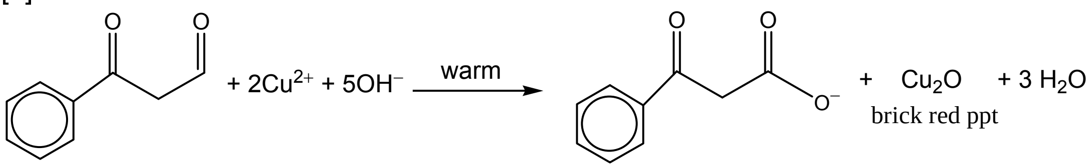
[2]

(e) Wear gloves to avoid direct contact with HCl as it is of high concentration.

[1]

2 **(a)** Reddish brown/ brick red ppt formed. [1]

[1]

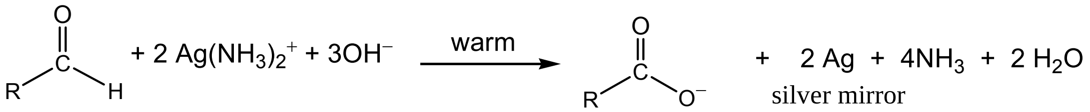


Comments:

Warming with Fehling's solution (alkaline solution of Cu^{2+} complex) is to test for aliphatic aldehydes.

Many students cannot balance the equation. A number wrote copper(II) oxide instead of copper(I) oxide. In writing the equation, first write out the reagents and products, ensure that the atoms and charges are balanced.

Warming with Tollen's reagent (ammonical solution of $Ag(NH_3)_2^+$ complex) is to test for aldehydes.



2 **(b)** **(i)** Reaction **I** : Hydrazine, N_2H_4, $H_2N\text{-}NH_2$

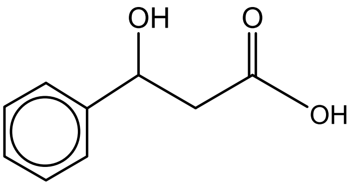
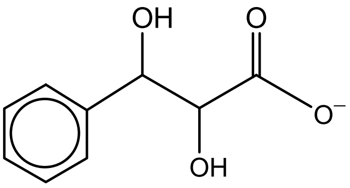
Reaction **II** : PBr_3 or $SOBr_2$ or red phosphorus, Br_2, heat

Comments:

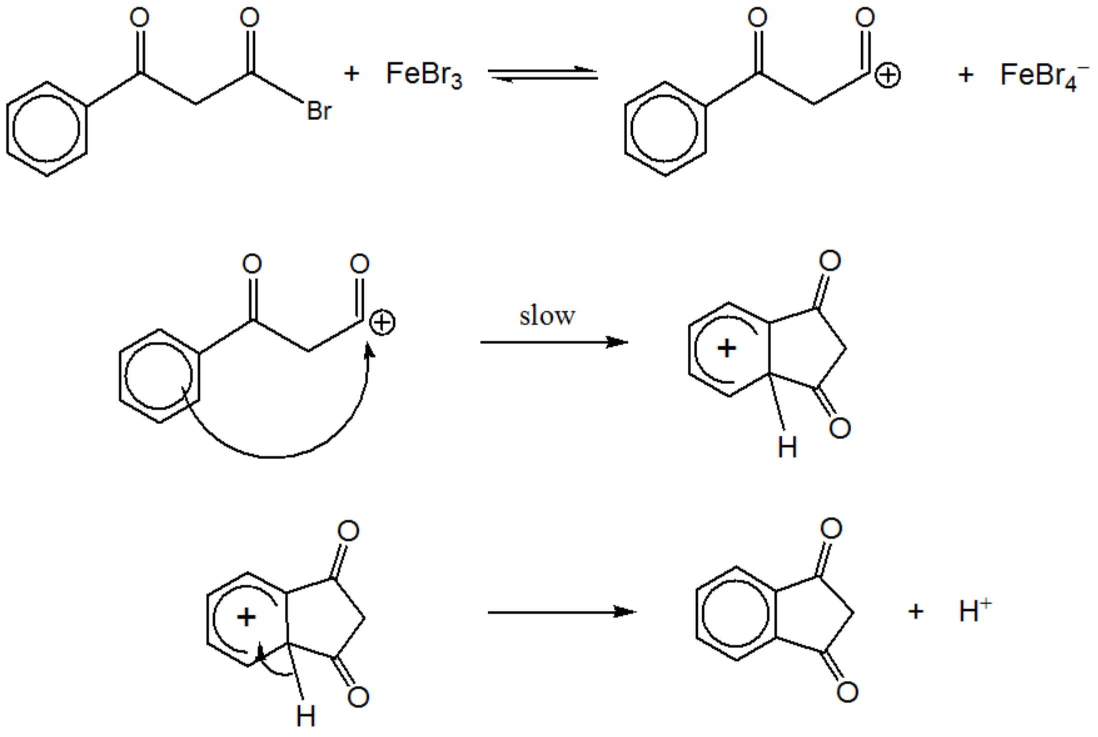
KBr, conc. H_2SO_4, heat to produce HBr is not acceptable.
HBr cannot react with RCOOH as HBr is also an acid.

PBr_3 and $SOBr_2$ have to be anhydrous.
If water is present, it will hydrolyse the acyl bromide back into the carboxylic acid immediately. Hence the medium cannot be aqueous.

2 **(b)** **(ii)**

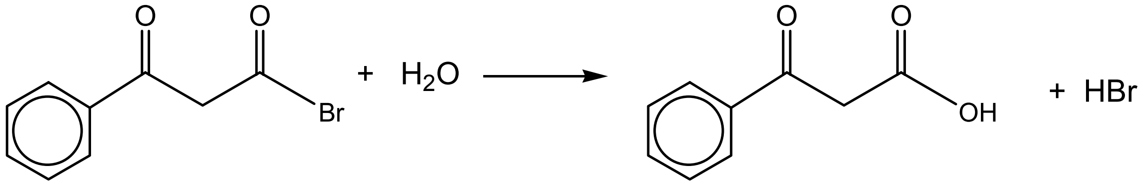
E	**G**
 [1]	 [1]
Comments: NaBH$_4$ in methanol is a weak reducing agent, it cannot reduce RCOOH to alcohol. It can only reduce carbonyl groups to alcohol. Only LiAlH$_4$ in dry ether can reduce RCOOH.	Comments: Many forgot that **G** is formed in an alkaline medium, and drew the protonated structured for **G**.

2 (iii)
b Electrophilic substitution



$FeBr_4^- \quad + \quad H^+ \longrightarrow FeBr_3 \quad + \quad HBr$

2 (c) (i)



$Br^- (aq) \quad + \quad Ag^+ (aq) \longrightarrow AgBr(s)$

Cream ppt

To show that cream ppt is AgBr, state symbols or words must be included.

2 c (ii) The lone pair on Br is delocalized with the pi electrons on the adjacent C=C bond/ p-orbital on Br overlaps with the pi-orbitals of adjacent C=C bond/ resonance,
→ strengthening the C-Br bond in **H**/ resulting in partial double bond character in C-Br bond in **H**. [1]

C-Br bond in H is not easily broken,
→ no free Br^- ions available to react with Ag^+ to form AgBr, cream ppt. [1]

Other possible reasons:

1. Extra resonance stability for **H** due to extended conjugation/ delocalization of electrons from benzene ring, C=O, C=C, oxygen atom of –OH group to Br. Hence **H** will not undergo nucleophilic substitution even with heating as the activation energy is very high.

2. The lone pair on the oxygen atom of –OH group is delocalized into the C=C pi electron cloud. This decreases the partial positive charge on the carbon atom next to Br, hence **H** is less susceptible towards nucleophilic substitution.

Comments:
The question is asking for **H** only, not **C**.
Your answer should focus on **H** only.
No marks are allocated for compound **C**.

3. (a)(i) beta-pleated sheet/ β-pleated sheet\
alpha-helix/α-helix

Common Mistakes:

Mistakes are mostly found in the naming of beta-pleated sheet where students wrote Beta-plated sheet/ Beta-pleated structures.

(a)(ii) Haemoglobin is a quaternary protein structure made up of
-2α and 2β subunits. Each subunit has a **heam group containing Fe^{2+}.**
-held by **R-group/side chain interactions** such as **ionic bonds, van der waals forces, disulphide bonds/linkages and hydrogen bonding**.

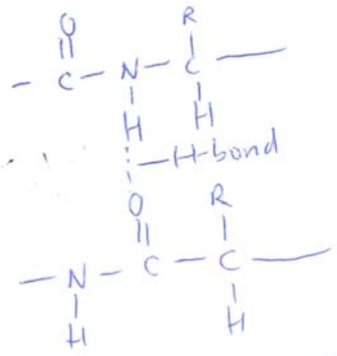
Common mistakes:
Most students failed to answer the question with reference to haemoglobin or failed to specify the presence of heam group for each subunit. There are misconceptions that the 4 subunits share 1 haem group.

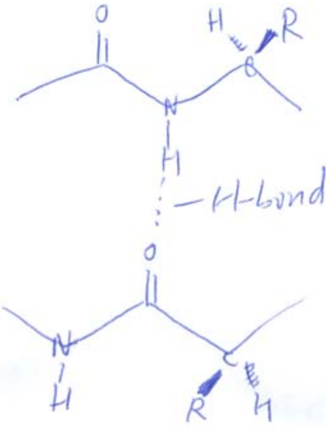
Students also failed to specify R-group/side chain interactions, and some wrote disulphide linkages as dilsulphate linkages/ disulfate linkages, disulphite linkages/ disulfite linkages.

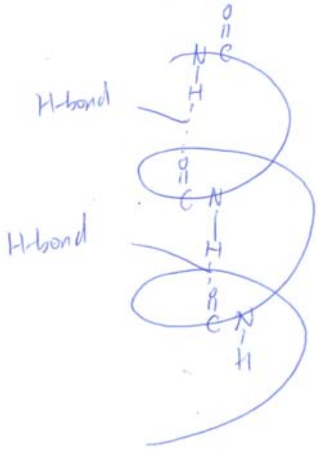
Note: sulfite/sulphite represents SO_3^{2-}, sulfate/ sulphate represents SO_4^{2-}

(a)(iii) Students need only to show the hydrogen bonding formed between N-H and C=O between 2 peptide bonds. At least 1 amino acid unit must be shown.

Accepted answers: (any one of the structures)



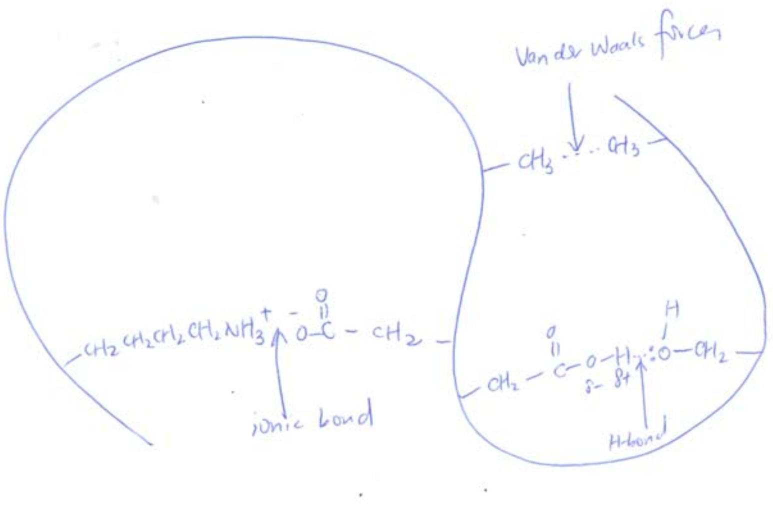




Common mistakes:
Students did not label Hydrogen bonding or has shown other side chain interactions which are not responsible for holding the secondary structures together.

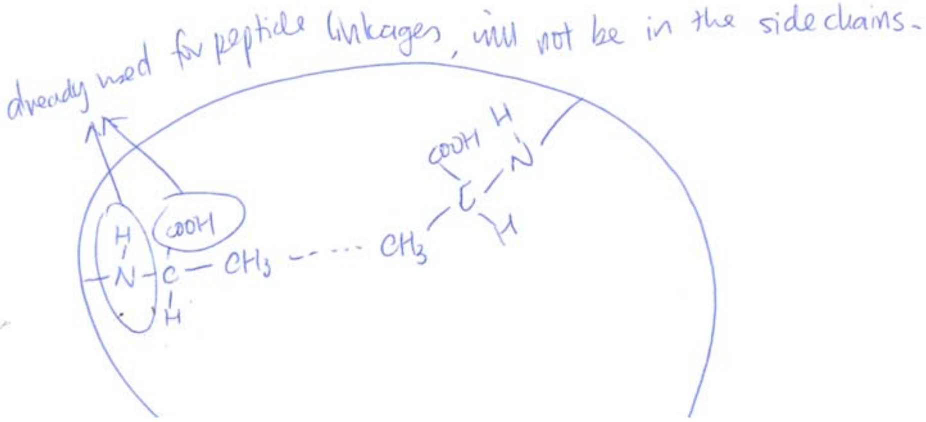
3 (b)(i) Possible interactions in maintaining the structures are ionic bond, hydrogen bonds and van der Waal's forces. Use only the R groups (found in bracket) for the interactions

i.e. For $NH_2CH(CH_3)COOH$, R group is $-CH_3$



Common mistakes:
1. Side chain interactions are shown without polypeptide backbone.

2. Hydrogen bonding bonds formed between $-NH_2$ and $-COOH$. When $-NH_2$ and $-COOH$ are close together, neutralization will occur and $-NH_3^+$ and $-COO^-$ will be formed instead.
3. Even after drawing the back bones, the $-NH_2$ and $-COOH$ is still shown. $-NH_2$ and $-COOH$ of the amino acids will not be present as they will be involved in formation of amide linkages.

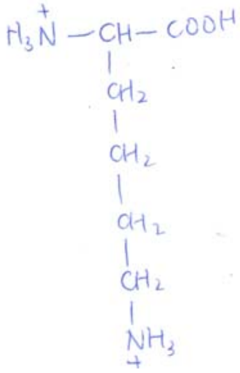


4. Not the whole R group is shown for the interaction.

5. $-CH_2CH_2CH_2NH_2$ is a polar group and will not form van der Waals forces with $-CH_3$.

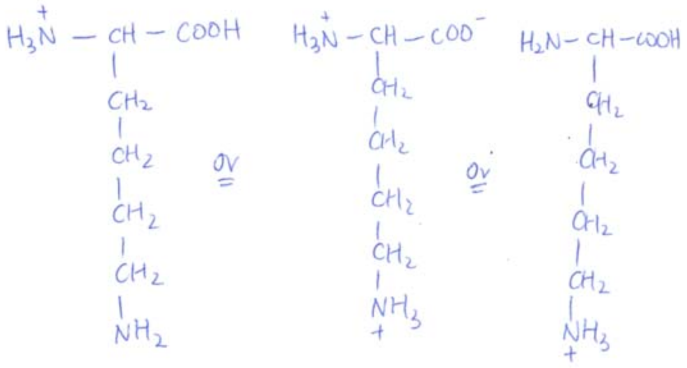
3 (b) (ii)

pH 1:



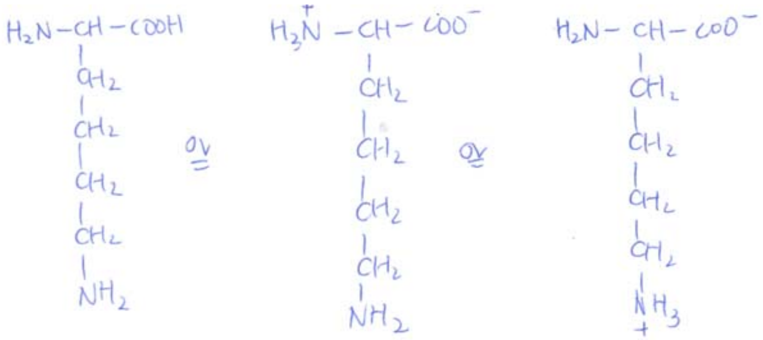
$H_3\overset{+}{N}-CH(CH_2CH_2CH_2CH_2\overset{+}{N}H_3)-COOH$

pH 5:



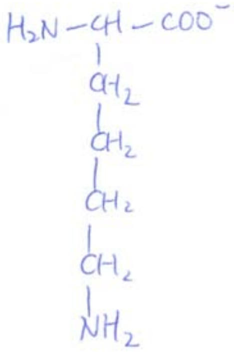
$H_3\overset{+}{N}-CH(CH_2CH_2CH_2CH_2NH_2)-COOH$ or $H_3\overset{+}{N}-CH(CH_2CH_2CH_2CH_2\overset{+}{N}H_3)-COO^-$ or $H_2N-CH(CH_2CH_2CH_2CH_2\overset{+}{N}H_3)-COOH$

pH 9:



$H_2N-CH(COOH)-CH_2-CH_2-CH_2-CH_2-NH_2$ or $H_2\overset{+}{N}-CH(COO^-)-CH_2-CH_2-CH_2-CH_2-NH_2$ or $H_2N-CH(COO^-)-CH_2-CH_2-CH_2-CH_2-NH_3^+$

pH 13:



$H_2N-CH(COO^-)-CH_2-CH_2-CH_2-CH_2-NH_2$

3 (c) Show stacking as working

Val-Val-Ala
Ala-Val-Val-Val-Ala
Ala-Glu
Glu-Gly-Asp-Phe
Trp-Ala-Val

Polypeptide chain is: Trp-Ala-Val-Val-Val-Ala-Glu-Gly-Asp-Phe

4 (a) (i) $NO_2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$
$2NO + O_2 \rightarrow 2NO_2$

(ii) NO_2 is a catalyst as it is regenerated.

(b) Both SeO_2 and SO_2 have 2 bond pairs and 1 lone pair.
Se has 1 more principal quantum shell than S and has a bigger lone pair region which forces the bond pairs closer together, leading the smaller bond angle in SeO_2.

OR

Se is less electronegative than S and hence the electrons in Se=O bonds are further away from Se. The bond pairs around Se experiences less repulsion and can come closer together, hence the bond angle is smaller.

4 (c) (i) (I) Partial Pressure of O_2(g) = 110-32-35 = 43

$$K_p = \frac{\left(p_{SO_3}\right)^2}{\left(p_{SO_3}\right)^2 p_{O_2}} = \frac{(35)^2}{(32)^2(43)} = 0.0278 \text{ kPa}^{-1} = 2.78 \times 10^{-5} \text{ Pa}^{-1}$$

Common mistakes:
Careless in subtraction and conversion from kPa^{-1} to Pa^{-1}.
Wrong units such as atm^{-1} and missing units.

Comments:
You can leave your answer in kPa^{-1}, there is no need to change to Pa^{-1}.

(II)

$$pV = nRT$$

$$p_{SO_2} V_{total} = n_{SO_2} RT$$

$$(32\times10^3)V_{total} = (20.5)(8.31)(27+273)$$

$$V_{total} = 1.60 \text{ m}^3$$

Or

$$p_{SO_2} = \frac{n_{SO_2}}{n_{total}} p_{total}$$

$$32 = \frac{20.5}{n_{total}} 110$$

$$n_{total} = 70.46 \text{ mol}$$

$$p_{total} V_{total} = n_{total} RT$$

$$(110\times10^3)V_{total} = (70.46)(8.31)(27+273)$$

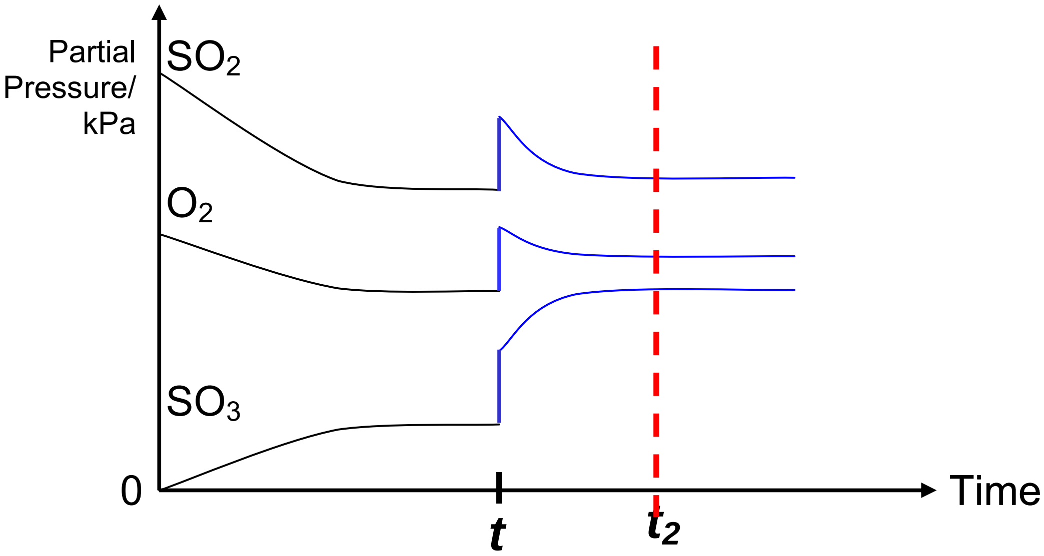
$$V_{total} = 1.60 \text{ m}^3$$

Comments:
Partial pressure is the pressure that one component of a mixture of gases would exert if it were alone in a container. Hence using p_{SO_2} will allow you to determine the total volume of the system as volume occupied by each of the 3 gases is the same.

(**III**) No change in position of equilibrium.
The catalyst *increases the rate of the forward reaction and the backward rate of reaction by the* ***same extent*****,** hence allowing the equilibrium position to be reached faster but there will not be any change in equilibrium position.

Comments:
Many students did not score for the explanation for no change in position of equilibrium.

4 c (ii)



Comments:

When volume of the system is compressed the at time **t**, total pressure of system increased, i.e. partial pressures of all gases increased.

To ***partially offset*** the increase in total pressure, the eqm shifts right to favour the side with less moles of gas. Hence SO_3 increases (by 2x amt) while O_2 decreases (by x amt) and SO_2 decreases (by 2x amt) according to stiochoimetry ratio until new eqm is reached at $\mathbf{t_2}$.

Decrease in pSO_2 and pO_2 cannot drop beyond the original partial pressure as the system is at a higher total pressure.

4 c (iii) Mr of H_2SO_4 = 98.1

Amt of H_2SO_4 in 1 × 10^6 tonnes = $\frac{1\times10^6\times10^3\times10^3}{98.1}$ = 1.019×10^{10} mol [1]

Since conversion is 100%,
Mass of S required = $1.019 \times 10^{10} \times 32.1$
= 3.27×10^{11} g
or 3.27×10^{8} kg or 3.27×10^{5} tonnes [1]

Common mistakes:
Careless in conversion from *tonnes* to *grams*.

5 (a) **L**: $Mg(OH)_2$

Reaction between Mg metal and steam produces MgO because reaction condition must be at least 100°C, this provides sufficient energy to cause hydroxide ion to decompose to form MgO. However, in this reaction, NaOH is added at r.t.p. $Mg(OH)_2$ will be formed as thermal decomposition cannot take place.

M: $BaSO_4$
N: $Cr(OH)_6^{3-}$

H_2O_2 causes color change, there are two reasons why transition compounds undergo color change (i) ligand displacement (ii) redox reaction.
Check E^o values to check for possible redox reaction.
E^o_{red} of H_2O_2 = 1.77 while E^o_{ox} of Cr^{3+} = -1.33 V,
hence E^o_{cell} = 1.77 – 1.33 > 0

$\therefore H_2O_2$ and Cr^{3+} can undergo redox therefore color change observed is most probably due to redox..

P: CrO_4^{2-}
Q: $Cr_2O_7^{2-}$
R: CH_3COOH

Step 6 is a familiar reaction placed in an unfamiliar context. Orange to green shows reduction of dichromate ion to chromium ions, therefore oxidation of ethanol occurs.

5(b) Cr_2O_3exhibits amphoteric property as Cr_2O_3 is an ionic compound with significant covalent character in its oxide.

Comments

- Read question: "Cr_2O_3 can also react with aq H_2SO_4 to form a soluble salt". From this statement, the question is highlighting the acid base property, and the word "also" highlighted amphoteric property.
- Recall from Chemical Periodicity that acid-base property of an oxide depends on the nature of bonds formed. For e.g. a covalent oxide exhibits acidic properties therefore can react with base. An ionic oxide exhibits basic property, therefore can react with acid. Therefore an oxide with ionic bonds with significant covalent character, it will exhibit amphoteric property.
- Acid base reaction is not a redox reaction, therefore discussion of the ability of Cr to undergo variable oxidation states is totally irrelevant.
- The presence of partially filled d orbitals in Cr is also totally irrelevant as this is not a heterolytic catalysis context.

5(c) To ensure all Cr_2O_3 in the residue forms the soluble complex and can be removed from $Mg(OH)_2$ residue via filtration as filtrate.
Washed with deionised water to rinse down the soluble ions on the surface of the residue e.g. NaOH, soluble chromium complex.

- Identify species that are being reacted away at each stage and highlight how this ensure purity of $Mg(OH)_2$ obtained.
- **Paper 2** focus on ***data analysis***, therefore your answer should make explicit reference to the data available.
- Addition of excess NaOH to the residue IS NOT to ensure complete precipitation of Mg^{2+} as this purpose is better served when excess NaOH is added to the solid mixture containing Cr_2O_3 and $MgSO_4$ in step 1.

5 (d) E^o_{red} of $Cr_2O_7^{2-}/ Cr^{3+}$ = +1.33V
E^o_{ox} of ethanol = – 0.65 V
E^o_{cell} = 0.68 V > 0, E^o_{cell} value is a positive value, therefore reaction is feasible.

- Some students discuss this question as if they are given a $Cr_2O_7^{2-}/Cr^{3+}$ half cell vs R/ethanol half cell. Therefore they went on to compare their E^o_{red} value to judge which reactant undergoes reduction, which reactant undergoes oxidation. This is totally irrelevant as the question gives you only part of the half cell ⇒ only $Cr_2O_7^{2-}$ and ethanol are present, therefore $Cr_2O_7^{2-}$ can ONLY undergo reduction and ethanol ONLY undergo oxidation. To prove whether this redox reaction can take place, calculate E^o_{cell}.
- Some students successfully calculated E^o_{cell} value but failed to discuss the significance of this value. Students should proceed to comment that it is a positive value, therefore reaction between $Cr_2O_7^{2-}$ and ethanol is feasible.
- A few students uses Cl_2 to oxidize ethanol without realizing that they are only given Cl^-, no Cl_2.

5 (e) To provide heat energy to overcome the strong covalent bonds present in organic compound.

- Please read the context of the question carefully. If this is an extension from part (d), e.g. a subpart (ii) of part (d) where E cell in subpart (i) shows that reaction is feasible but can only take place at elevated temp then the reason is due to kinetics therefore discussion of input of energy necessary to overcome high Ea will be a sufficient answer.
- However for this question, it appears as a new part (e) and it emphasizes the fact that it is only necessary for step 6, therefore students should observe that it is the only reaction that involves organic compound, therefore answer should focus on the energy needed to cleave covalent bonds in ethanol.

5(f) (i) Water undergoes more extensive hydrogen bonding than ethanol, therefore more energy required to overcome stronger hydrogen bonding between water molecules than between ethanol.
On the other hand, O-H bond in **R** is more polar due to additional electron withdrawing effect from the second oxygen, attraction for lone pair on neighbouring molecule is thus stronger, hence more energy required to vaporize **R** than water.

OR

CH_3COOH has higher molecular mass, therefore temporary dipole induced dipole is stronger which outweighs the effect of a more extensive hydrogen bonding bonding between H_2O molecules, therefore more energy required to vaporize **R**.

5 (f) (ii) Through (fractional) distillation, collecting the distillate at 120°C. (118 – 122 °C)

5 (f) (iii) To remove all traces of moisture from the liquid compound **R** isolated from fractional distillation.

- Notice that part (f) consist of three subparts, therefore should read these subparts together to see the relatedness between different parts, how one part leads to the other.

- Part (i) emphasizes differences in b.pt of these three compounds, therefore this property should be made use of to isolate pure compound **R**.

- Do note that the synthesis of ethanoic acid from ethanol occurs with less than 100% yield, therefore at the end of reaction, reaction mixture will contain unreacted ethanol, the newly formed ethanoic acid and H_2O (due to aq reagents added) and inorganic products such as Cr^{3+}, SO_4^{2-} ions. Hence to isolate ethanoic acid **R**, have to carry out fractional distillation.

- Some students suggested that they will distill off ethanol and water first since they are more volatile (of lower boiling point), leaving R behind without realizing that it will be mixed with inorganic products Cr^{3+} and SO_4^{2-} ions. Therefore distillation must continue and they should collect the distillate, ethanoic acid **R** at a temp around 120 °C to isolate it from the remaining inorganic products Cr^{3+} and SO_4^{2-} ions.

- Distillate collected at 120°C will contain traces of moisture, therefore anhydrous $CaCl_2$ is needed to absorb moisture. Solid hydrated $CaCl_2$ will be obtained after the absorption of moisture from the organic layer, it is then filtered away to isolate pure ethanoic acid **R**.

- Some students suggested adding anhydrous $CaCl_2$ directly to the reaction mixture (without any distillation) containing ethanol, water and compound **R** to absorb both water and ethanol, thus leaving pure ethanoic acid **R** behind, this is wrong. The addition of anhydrous $CaCl_2$ can only remove traces of water not when there is large amt of water. When water is present in large excess, $CaCl_2$ will dissolve in it instead, causing more impurities to be present instead.

- Some students attempted to use chemical reaction to isolate ethanoic acid **R**, e.g. react acid R with NaOH to form a salt soluble in aq layer without realizing that it will be mixed together with the inorganic products.

- Some students attempted to use a separatory funnel to isolate ethanoic acid **R** thinking that the ethanol, ethanoic acid and H_2O are immiscible with each other. This is not true therefore this method fails.