ANDERSON SERANGOON JUNIOR COLLEGE

2022 JC 2 PRELIMINARY EXAMINATION SOLUTIONS WITH MARKERS COMMENTS

NAME:__________________________ (   ) **CLASS:** 22 / ____

CHEMISTRY **9729/02**

Paper 2 Structured Questions

14 September 2022

2 hours

READ THESE INSTRUCTIONS FIRST

Please look through the marks scheme and pay attention to the comments from markers. As you read, take note of:

- What are your misconceptions?
- What are common errors to avoid?
- How should you improve next time?

Do pay attention as your tutor go through in class and be proactive in asking questions. If you do not ask now, then when?

Remember the power of tiny gains and be a little better every day!

1 **(a)** **(i)**

- Ca has more filled principal quantum shells than Mg.
- Nuclear charge and shielding effect of Ca are higher
- Outermost electrons are of Ca further from the nucleus. [1]
- Less energy is required to overcome the weaker electrostatic forces of attraction between the nucleus and the electron to be removed for Ca.
- Second ionisation energies of Ca is lower than that of Mg. [1]

Comments:
This is a simple comparison of IE down the group. Although it is about the 2nd IE, the electron to be removed is from the same orbital as that of the 1st IE for both Ca and Mg.

Students commonly missed out:
- *electron to be removed from Ca is further away from the nucleus*
- *electrostatic forces of attraction is between the nucleus and the electron removed*

Other error:
- *spelled "principal" wrongly as "principle"*
- *thought that Ca has more valence shells than Mg when there should be only one valence shell for both Ca and Mg.*
- *wrote that the 2nd IE of Ca is higher when the values of ionisation energies can be found in the Data Booklet.*

(ii)

Thermal stability: $CaCO_3 > ZnCO_3 > MgCO_3$
Zn, Ca and Mg have the same cationic charge of +2
Ionic radius of Ca^{2+}: 0.099 nm
Ionic radius of Mg^{2+}: 0.065 nm
Ionic radius of Zn^{2+}: 0.074 nm

Ionic radius: $Ca^{2+} > Zn^{2+} > Mg^{2+}$ [1] with quoted values
Charge density (q/r): $Ca^{2+} < Zn^{2+} < Mg^{2+}$
[1]
Hence, polarising power of cation, ease of distortion of anion and weakening of C-O bond increases in the same order. [1]

Comments:
Many students were not able to use the ionic radius of the 3 cations to relate to the charge density, polarising power etc. Instead, some incorrectly quoted E^o values or atomic radius which have NEVER been used to explain thermal stability of carbonates!
Several students also missed out key words like the electron cloud of CO_3^{2-} was distorted to a greater extent or the C-O bond is weakened to a greater extent etc.
Some students spelled "extent" wrongly as "extend" in their answer.

(b) **(i)** $[Be(H_2O)_4]^{2+} + H_2O \rightleftharpoons [Be(H_2O)_3(OH)]^{+} + H_3O^{+}$
OR
$[Be(H_2O)_4]^{2+} \rightleftharpoons [Be(H_2O)_3(OH)]^{+} + H^{+}$ [1]

Comments:
Many students missed out the information from the qns that Be forms a complex ion $[Be(H_2O)_4]^{2+}$ and thus couldn't write the equation for the hydrolysis of this ion.

(ii)

$BeO(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + H_2O(l)$ [1]

$BeO(s) + 2NaOH(aq) + H_2O(l) \longrightarrow Na_2[Be(OH)_4](aq)$ [1]

(Also accept: $BeO(s) + NaOH(aq) + H_2O(l) \longrightarrow Na[Be(OH)_3](aq)$)

Comments:
Many students thought beryllium oxide is Be_2O_3 without realizing that Be is in Group 2 and not Group 13 like Al. They also couldn't balance the equation.

(iii) Be^{2+} has a high charge size of 2+ and a small ionic radius, giving rise to high charge density and hence high polarising power. It distorts the electron cloud of Cl^- anion to a great extent. The extent of sharing of electrons between the two nuclei is so great that $BeCl_2$ exhibits covalent character.[1]

Comments:
Many students wrote answers like Be is covalent thus not ionic, Be and Cl has similar electronegativity etc that are not accepted.

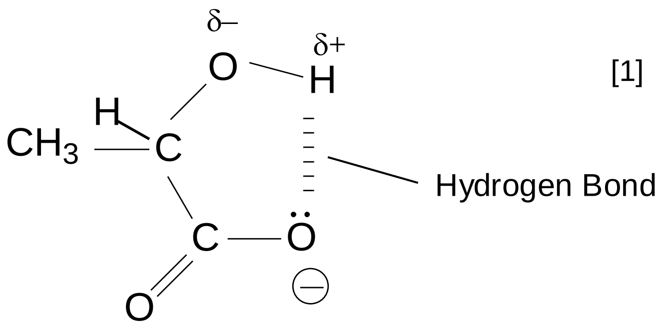
(iv) There is an increase in number of bond pairs around the central Be atoms (increase from 2 to 3)

To minimise repulsion (and maximise stability), the 3 bond pairs are arranged as far apart as possible, giving rise to a change in shape from linear to trigonal planar and a smaller (or decrease in) bond angle.

Comments:
Some students forgot to indicate the number of bond pairs around Be or did not state that the bond pairs are arranged as far apart as possible to minimise repulsion.
Students should be specific in their answer and shouldn't refer to bond pairs only as "electron pairs" as "electron pairs" can mean lone pairs too!
Many students incorrectly thought there is a lone pair on Be or thought that the lone pair of electrons on Cl that is used to form the dative bond is considered a lone pair around Be.

[Total: 10]

2 (a) (i)



[1]

Comments:
Common mistakes include:
- *Missing dipoles, lone pairs, labels*
- *Drawing of lactic acid instead of lactate*
- *Hydrogen bonding to the wrong H or O (remember that only H bonded to O,N or F can be used for Hydrogen bonding!)*
- *Drew intermolecular hydrogen bonding (between two ions) instead of intramolecular hydrogen bonding (within one ion) as required by question*
- *Missing atoms and bonds*

(ii)
- For lactate ion, **intramolecular hydrogen bonding** formed between the ionised –CO_2^- group and –OH group which results in the **greater stability** of the conjugate base/lactate ion compared to the ethanoate ion.
- Lactic acid is a stronger acid with **larger K_a value.** [1]

Comments:
Common mistakes include:
- *Explanations involving solubility*
- *Explanations about a second dissociation*
- *Acidity considerations not involving intramolecular H-Bonding despite the qualifier word "Hence"*
- *Answered in terms of pK_a*
- *Incorrectly related higher acidity to lower Ka*

(b) (i) *Since **n = 2**,*

$$E = E^{\ominus} - \left(\frac{0.0592}{2}\right)\log_{10}\frac{[NADH]}{[NAD^+]}$$

$$(-0.350) = (-0.320) - \left(\frac{0.0592}{2}\right)\log_{10}\frac{[NADH]}{[NAD^+]}$$

$$\log_{10}\frac{[NADH]}{[NAD^+]} = 1.01$$

$$\frac{[NADH]}{[NAD^+]} = \mathbf{10.3}$$ **[1]** (3 s.f.)

Comments:
Common mistakes include:
- *Using ln instead of lg*
- *Incomplete calculations*

(ii) % of $NAD^+ = \dfrac{1}{(10.3+1)}$ x 100%

= **8.85 %** **[1]**

Comments: Poorly done. Many students cannot properly compute the percentage.

(iii) $CH_3COCO_2^- + 2H^+ + 2e^- \rightleftharpoons CH_3CH(OH)CO_2^-$ **[1]**

$E^\ominus_{cell}$ at pH 7 = $E^\ominus_{red} - E^\ominus_{ox}$

$+0.135 = E^\ominus_{red} - (-0.320)$

$E^\ominus_{red} = -0.185$V **[1]**

Comments:
Very poorly done. Students are supposed to use the overall equation to deduce the reduction half-equation for pyruvate. This can be done by subtracting the oxidation half-equation involving NAD+/NADH from the overall reaction equation.

overall: $CH_3COCO_2^- + NADH + H^+ \rightarrow CH_3CH(OH)CO_2^- + NAD^+$ $\quad E^\ominus_{cell} = +0.135$ *V*
oxidation: $NADH \rightarrow NAD^+ + H^+ + 2e^-$
The reduction half-equation is hence as shown below after balancing the particles and charges: $CH_3COCO_2^- + \mathbf{2}\,H^+ + \mathbf{2}\,e^- \rightleftharpoons CH_3CH(OH)CO_2^-$

(iv) ΔG at pH 7 = $-nFE^\ominus_{cell}$

$= -2\,(96500)\,(+0.135)$

$= -26\,055$ J mol^{-1}

= **$-26\,100$ J mol^{-1}** (3 s.f.) **[1]**

Comments: Very poorly done. Many students either used the wrong E_{cell} *or used the wrong number of mole of electrons transferred or simply misremembered the equation.*

(c) **(i)** The amount of heat **evolved** when **one mole** of **lactic acid** in its **standard state** is **completely burned** in **excess oxygen** under standard conditions of **298 K and 1 bar**.

[1] correct definition with key words/points

Comments: Key words such as 'standard state', 'completely' and 'excess' are frequently missing.
Students should specify the substance as 'lactic acid'.

(ii) $\Delta H_c^\ominus = [3(-393.5) + 3(-285.8)] - (-483.2)$

$= -1554.7$ kJ mol^{-1}

= $\underline{\mathbf{-1550\ kJ\ mol^{-1}}}$ (3 s.f.) **[1]** (correct value and units)

Comments: Students did not take into account the mole ratio of the products CO_2 *and* H_2O*. Students are reminded to leave their answers to 3 sf.*

(iii) $CH_3CH(OH)CO_2H(l) + 3O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(l)$

Heat absorbed for bond breaking
= 2 BE(C–C) + 4 BE(C–H) + 2 BE(C–O) + 2BE(O–H) + BE(C=O) + 3 BE(O=O)
= 2(350) + 4(410) + 2(360) + 2(460) + (740) + 3(496)
= **6208 kJ mol^{-1}**

Heat released on bond formation
= 6 BE(C=O) + 6BE(O–H)
= 6(805) + 6(460)
= **7590 kJ mol^{-1}**

[1] working

$\Delta H_c^{\ominus}$ = (+6208) + (−7590)
= **−1382 kJ mol^{-1} [1]**

Comments:
Common mistakes observed:
- *ΔH is the sum of bonds **broken in reactants** – sum of bonds **formed in products***
- *C-C bonds and O=O bonds in reactants not taken into account.*
- *Counting the number of bonds in reactants and/or products wrongly*
- *Using wrong bond energy values for C=O and O=O*
- *Including ΔH_f values in calculation*

(iv) In **c(iii)** calculations, bond energies used are defined for gaseous compounds. However, in **c(ii)**, lactic acid and water are not gaseous in their standard state.

[1] show understanding that calculations involving bond energies are for gaseous substances.

*Comments: Many students were not aware that that bond energy of a covalent bond is the average amount of heat absorbed to break one mole of that particular covalent bond in a particular compound in the **gaseous state**.*

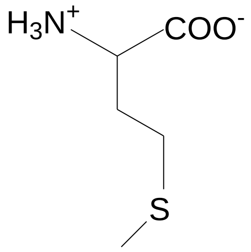
[Total: 12]

3 (a) (i) $[H^+] = \sqrt{10^{-2.28} \times 0.15} = 0.0281 \text{ mol dm}^{-3}$

pH = – lg 0.0281 = **1.55 [1]**

Comments: This question was done well. Only a small minority did not attempt the question or used the given concentration directly to calculate pH, incorrectly treating methionine as a strong acid.

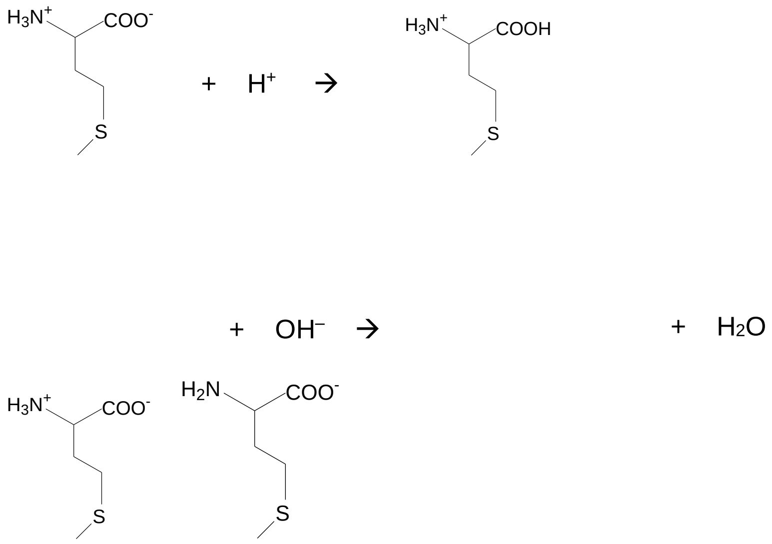
(ii)



[1]

Comments: Most students drew the correct structure. A zwitterion is a species that has both positive and negative charges but overall no net charge.

(iii)



[1] for each equation

> *Comments:*
> *Many students gave the correct equations. Common error was to leave out water as the product for the equation where OH⁻ was added. Those who represented the structure of methionine other than how it was given in the question, often wrote incorrect structures with missing atoms.*

(iv) The zwitterion is amphoteric and can act as both acid and base.

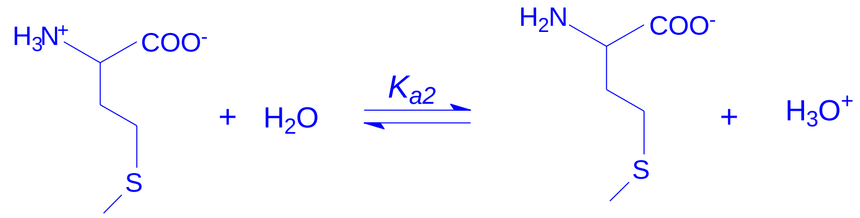
$pK_{b1} = 14 – 2.28 = 11.72$
$K_{b1} = 10^{–11.72} = 1.905 \times 10^{–12}$ [1]

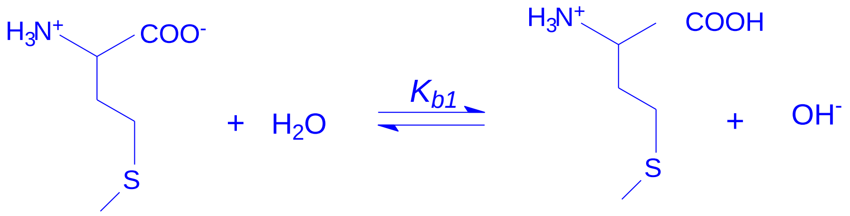
$pK_{a2} = 9.21$
$K_{a2} = 10^{–9.21} = 6.166 \times 10^{–10}$

Since $K_a(–NH_3^+) > K_b(–COO^–)$, the solution will be acidic. [1]

1 mark for calculating K_b and using the correct K_a for comparison
1 mark for correct conclusion of pH based on comparison

> *Comments:*
> *This proved to be a difficult question.*
> *At first equivalence point, only the zwitterion is present. Both the acidic group ($–NH_3^+$) and a basic group ($–COO^–$) can undergo hydrolysis to give H_3O^+ or $OH^–$ respectively. The pH of the resulting solution then depends on which hydrolysis reaction occurs to a greater extent. This can be determined by comparing which value, K_{b1} (calculated from K_{a1}) or K_{a2} is larger.*





Students can also refer to the Acid-Base Equilibria Tutorial Q16 for a similar question.

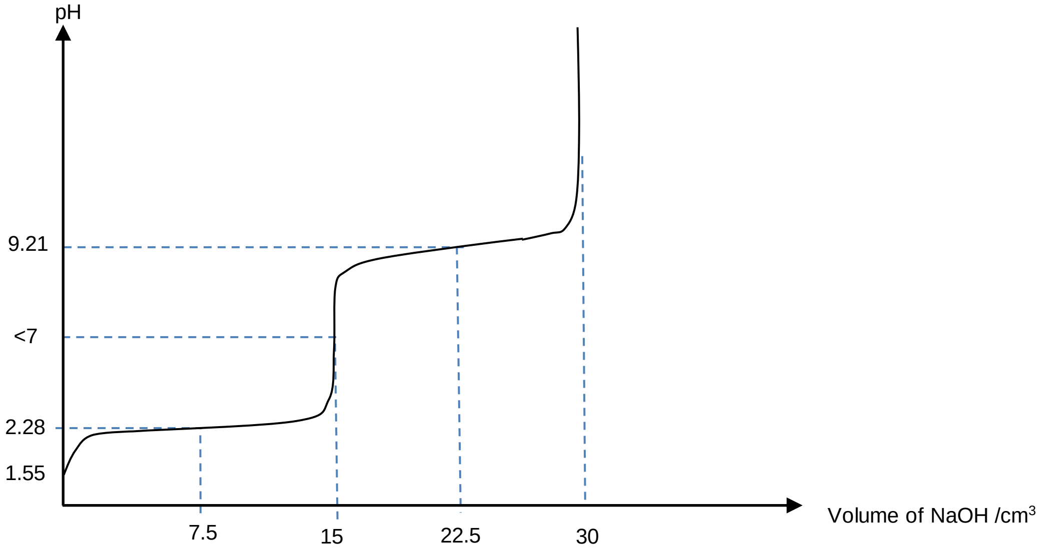
Common misconceptions:

- *Many students know that at first equivalence point, the zwitterion is present. However, they then wrongly concluded that since an acidic group (–NH_3^+) and a basic group (–COO^-) are present, the pH is then equal to 7.*
- *Others looked at the volumes and concentrations of methionine and NaOH given in the question to conclude that there was no limiting reagent / excess acid or base so the resulting solution would be neutral.*
- *A handful assumed that the hydrolysis of the –NH_3^+ group occurred to a greater extent but did not provide explanation and were not given full credit.*

(v) At 7.5 cm^3, 1st maximum buffering capacity point
pH = pK_{a1} = 2.28

At 15 cm^3, 1st equivalence point, pH = 5.22 or 5.75 [check part (iv)]

At 22.5 cm^3, 2nd maximum buffering capacity point
pH = pK_{a2} = 9.21



[1] labelled axes and correct shape of graph with the flattening at the buffer regions
[1] labelled points (0, 1.55), (7.5, 2.28), (15, <7) and (22.5, 9.21)

Comments:
Many students were able to draw an appropriate sketch, though quite a number did not show a sharp increase in pH initially when NaOH was first added. Many did not label all the required values on their graph. The volumes where pH = pK_a were often missing.

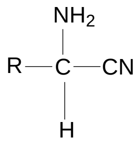
(vi) **Methyl orange**. [1]

Comments:
*Most students suggested a suitable indicator, based on the pH proposed in part **(iv)**.*

(b) **(i)** Step 1: Nucleophilic addition [1]
Step 2: Elimination (of H_2O) [1]

Comments:
Common wrong answers for Step 2 are condensation/hydrolysis/reduction.
The technique here is to compare the difference in molecular formulae of reactant and product of step 2 (there is loss of 2H and 1O, hence elimination of 1 H_2O).
Students must INDICATE clearly the step in which each answer is for!

(ii)

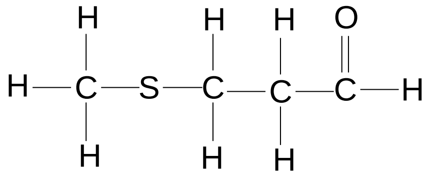


$R-CH(NH_2)-CN$

[1]

Comments:
Students often carelessly omitted the 2 in-NH_2. Students must work backwards from step 4 to see that the reagents suggest that of hydrolysis (of -CN group). So the -NH_2 group must be present in compound G.

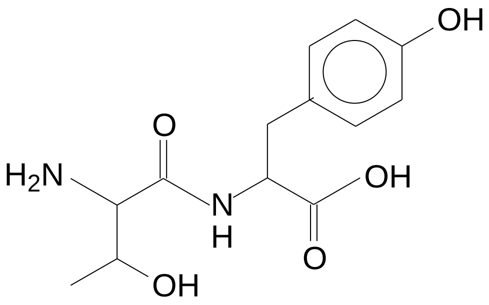
(iii)



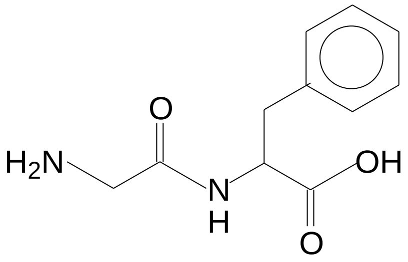
[1] for correct displayed structure

Comments:
*Most students who arrived at the correct structure were careless to have overlooked the keywords '**<u>displayed formula</u>**' in the question. There is a handful of students who thought that there were 2 S-H bonds. Remember that in writing the skeletal formula, only C-H and C-C bonds are abbreviated. A molecule that contains a S-H will still have the bond shown in the skeletal formula.*

(c)

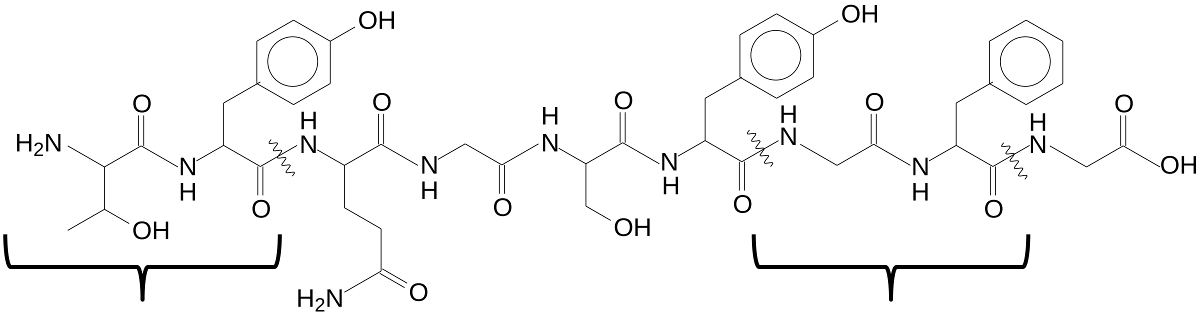


[1]



[1]

Comments:
Students need to know that a ***dipeptide*** *is* ***a molecule that consists of two amino acids joined together by a peptide bond****.*
To solve this question, you need to follow the instructions “hydrolyses the peptide bond on the carboxyl side of a residue that contains an aromatic ring”.
1) identify the aromatic ring in the R group (side chain) and
2) cleave at the C-O amide bond on the carboxyl side in response to the pattern given
3) look for fragments with 2 amino acids joined together (see below).



gives dipeptide fragment

gives dipeptide fragment

[Total: 15]

4 (a) (i) CH_3CCl_2COOH has **one more electron-withdrawing** group than $CH_3CHClCOOH$ and hence exerts **stronger electron-withdrawing effect** on the **carboxylate anion**, $CH_3CCl_2COO^-$. [1]

The **negative charge** on the anion becomes **more dispersed** and the anion is more stabilised. The **dissociation** of the acid, CH_3CCl_2COOH, to release H^+ ions is **more favoured**.

Hence, CH_3CCl_2COOH is a stronger acid with lower pK_a value.[1]

Comments:

Most students only mention the presence of more electron withdrawing groups resulting in greater dispersal of negative charge and did not include the ***stronger electron-withdrawing effect*** *and* ***dissociation of acid to release*** H^+ *ions.*

Wrong *concepts/phrasing of answers include:*

- *mistaken Cl as electron-donating group.*
- *mention 'greater dissociation of* H^+*' which is incorrect; it should be 'dissociation of acid to release* H^+*'.*

(ii) 4.00 (actual value) accept values of x larger than 2.80.

The electron-withdrawing group of CH_2ClCH_2COOH is **further** away from the carboxylate group than that in $CH_3CHClCOOH$ and hence exerts **weaker electron-withdrawing effect** on the **carboxylate anion**, $CH_2ClCH_2COO^-$.

The **negative charge** on the anion becomes **less dispersed** and the anion is less stabilised. The **dissociation** of the acid, CH_2ClCH_2COOH, to release H^+ ions is **less favoured**. [1]

Comments:

Most answers were able to correct relate greater distance of the electron-withdrawing group to the lower extent of dispersal of the negative charge. Weaker answers identified other irrelavant factors to explain the difference in acidity.

(iii)

$$K_c = \frac{[CH_3CHClCOO^-][CH_3CCl_2COOH]}{[CH_3CHClCOOH][CH_3CCl_2COO^-]}$$

$$= \frac{[H^+][CH_3CHClCOO^-][CH_3CCl_2COOH]}{[CH_3CHClCOOH][CH_3CCl_2COO^-][H^+]}$$

$$= \frac{\mathrm{Ka(CH_3CHClCOOH)}}{\mathrm{Ka(CH_3CCl_2COOH)}} \quad [1]$$

$$= \frac{10^{-2.80}}{10^{-1.74}}$$

= 0.08709

= 0.0871 (to 3sf) [1]

Comments:

Weak answers did not convert pK_a *to* K_a *before substitution and/or gave wrong* K_a *expression.*

Try the following as Additional Practice!

An equilibrium is set up at 25°C between acetic acid and dimethylamine as shown.

$$CH_3COOH\,(aq) + (CH_3)_2NH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + (CH_3)_2NH_2^+(aq)$$

$K_a(CH_3COOH) = 1.8 \times 10^{-5}$ mol dm^{-3}

$K_a((CH_3)_2NH_2^+) = 1.85 \times 10^{-11}$ mol dm^{-3}

Use the K_a values of the two acids to calculate K_c for the above equilibrium at 25°C.

[2]

Solution

$$K_a(CH_3COOH) = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K_a({(CH_3)_2NH_2}^+) = \frac{[(CH_3)_2NH][H^+]}{[{(CH_3)_2NH_2}^+]}$$

$$K_c = \frac{[CH_3COO^-][{(CH_3)_2NH_2}^+]}{[CH_3COOH][(CH_3)_2NH]}$$

$= \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \times \frac{[{(CH_3)_2NH_2}^+]}{[(CH_3)_2NH][H^+]}$

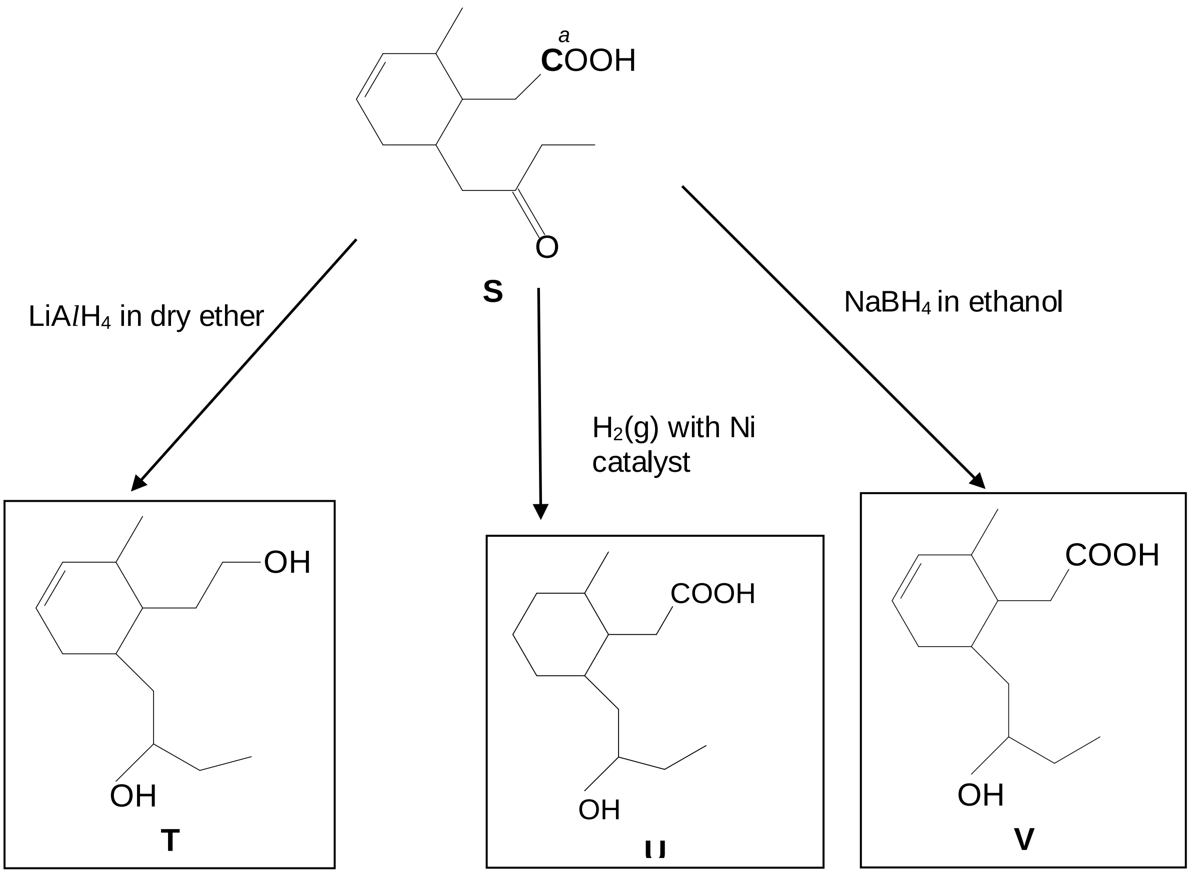
$= \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \div \frac{[(CH_3)_2NH][H^+]}{[{(CH_3)_2NH_2}^+]}$ [1] for this step or both K_a expressions

$= K_a(CH_3COOH) \div K_a({(CH_3)_2NH_2}^+)$

$= 1.8 \times 10^{-5} \div 1.85 \times 10^{-11}$

= **$\underline{9.73 \times 10^5}$** [1]

(b) (i)



1 mark for each structure

(ii) **Alkene** is not reduced by $LiAlH_4$. **Alkenes are not electron deficient** and **do not attract/react with nucleophiles such as H^-** from $LiAlH_4$.
Or **Alkenes** are **electron rich** and **do not react with nucleophiles such as H^-**. [1]

Comments:
For part (i)

- *Most students were unable to correctly identify the functional groups that were reduced by the respective reducing agents and drew the incorrect products.*
- *$LiAlH_4$ is a strong reducing agent and can reduce nitriles, carbonyls, carboxylic acids, esters and amides but not alkenes.*
- *H_2(g) with Ni catalyst can reduce alkenes, carbonyls and nitriles.*
- *$NaBH_4$ can only reduce carbonyls.*

For part (ii)

- *Weak answers identified the wrong functional group with wrong reasons or correct functional group with no/wrong reasons.*

(iii) Oxidation number of C^a in **S** = + 3
Oxidation number of C^a in **T** = -1
Change in oxidation number = **-4 (or from +3 to -1)** [1] with working

Comments:
*Most students were unable to determine the correct oxidation number of **C^a** in S and T. Students are advised to draw out the atoms surrounding **C^a** to be able to better assign the oxidation numbers.*

[Total: 10]

5 **(a)** **(i)** rate = $k_f[Cl_2]$ [1]

$k_f[Cl_2] = k_r[Cl\bullet]^2$
$[Cl\bullet] = \sqrt{}(k_f[Cl_2]/k_r)$ [1]

> *Comments:*
> *Most students were able to obtain the correct rate equation. However, some did not use the information that "rates of the forward and reverse reactions in step 1 are equal" to equate the forward and reverse rate equations and write an expression for $Cl\bullet$ radicals.*

(ii) rate = $k_2[Cl\bullet][CH_4]$ [1]

> *Comments: Most students got this correct. Careless ones did not use the correct rate constant as stated on the equation for step 2 in the question.*

(iii) rate = $k_2[Cl\bullet][CH_4]$
rate = $k_2\sqrt{}(k_f[Cl_2]/k_r)[CH_4]$
= $k[Cl_2]^{1/2}[CH_4]$ [1]

Order of reaction with respect to $[Cl_2]$ is ½.
Order of reaction with respect to $[CH_4]$ is 1.
The overall order of reaction is 1.5. [1]

> *Comments:*
> *Several students were clearly confused when they saw that the order of reaction with respect to $[Cl_2]$ is ½. They either changed their working and gave a different rate equation or concluded that the order with respect to $[Cl_2]$ is 1 or 2 instead. Please note that ½ order is common for reactions involving radicals.*

(b) **(i)** Bond energy of $Cl–Cl$ bond = 244 kJ mol^{-1}

Amount of energy to break one $Cl–Cl$ bond = $\frac{244\times1000}{6.02\times10^{23}}$ = 4.053×10^{-19} [1]

Using $E = \frac{hc}{\lambda}$,

$\lambda = \frac{hc}{E} = \frac{6.63\times10^{-34}\times3\times10^{8}}{4.053\times10^{-19}}$ = 4.907×10^{-7} m = 490.7×10^{-9} m = <u>**491 nm**</u> [1]

> *Comments:*
> *Many students did not understand the instructions in the question to find wavelength of light to break **<u>one</u>** bond and did not divide the bond energy by Avogadro's number. As such, many substituted the value of E as 244000 J instead and were penalized 1 mark. It also affected their ability to solve (ii) as the answer did not fall into the range of wavelengths provided.*

(ii) Blue/Violet [1]

> *Comments: Despite being unable to solve for the correct wavelength in **(i)**, some students were able to identify that blue/violet light were required for the reaction, possibly because they remember the FRS conditions is uv light. It is good to see students drawing links to relevant prior knowledge for solving questions!*

(iii) Br–Br bond is weaker than C*l*–C*l* bond.
Less energy is required to break the Br–Br bond in the initiation step.
Hence yellow light with a longer wavelength and lower energy, is adequate. [1]

Comments:
As this question has a "hence", its intention is to relate to the answer in (ii).
Since blue light is required to break the Cl-Cl bond while yellow light can be used for bromination, the difference in colour required is due to the ***difference in strength of bonds*** *and hence* ***different energy*** *and* ***wavelength of light*** *required to break the bonds. All 3 points must be present for complete explanation.*

6:1:2:3 [1]

(c) **(i)** *Comments:*
Majority were able to state the ratio of products successfully. However, some students were still unable to recognise skeletal structures, particularly for structure A. The most common error is to state the proportion of A as 3 instead of 6. These students probably did not realise that monosubstitution of either one of the **TWO** -CH_3 groups attached to the same carbon will give product A.

(ii)

Ratio of monochlorinated products	**A**	**:**	**B**	**:**	**C**	**:**	**D**	
Based on number of H	6	:	1	:	2	:	3	
	×		×		×		×	
Based on relative rate	1	:	5	:	3	:	1	
Combined ratio	6	:	5	:	6	:	3	[1]

Ratio of monobrominated products	**A**	**:**	**B**	**:**	**C**	**:**	**D**	
Based on number of H	6	:	1	:	2	:	3	
	×		×		×		×	
Based on relative rate	1	:	1600	:	80	:	1	
Combined ratio	6	:	1600	:	160	:	3	[1]

Comments:
Most students who were able to answer (i) correctly had no problem in (ii). These students were able to deduce that A, B, C and D are obtained by substitution of a primary H, tertiary H, secondary H and primary H respectively.
As the ratio of products were already stated in the question, it was rather obvious that the ratio can be obtained by taking into account the probability of substitution (from ratio in (i)) and the relative rate of substituting each type of hydrogen by each halogen.

(iii) Bromine is a better choice as it forms larger proportion of the required mono-brominated intermediate (2-bromo-2-methylbutane) and hence gives a better yield of the product. /

OR

The ratios show larger proportion of the tertiary halogenoalkane (or product B) will be formed when bromine is used instead of chlorine, resulting in a better yield of the tertiary alcohol. [1]

Answer must include:
larger proportion/fraction/ratio of the required mono-brominated intermediate AND
higher yield of desired product / lower proportion of unwanted side products formed due to substitution at other H atoms.

Also accept explanation that:
Chlorine is a less desired choice as there is little difference in the proportion of 2-chloro-2-methylbutane compared to the rest of the mono-chlorinated products and this leads to low yield of 2-methylbutan-2-ol.

Comments:
Majority were able to identify the correct halogen to use from the relative rates of substitution given or the calculated ratio of products.
Some students were not clear in explaining their choice, often not specifying the identity of the intermediate halogenoalkane that gives the final alcohol. Mark is not given to unclear explanations.

(d) **(i)** $\Delta H^{\ominus} = \Delta H_f^{\ominus}(\text{product}) - 2\Delta H_f^{\ominus}(\text{reactant})$
$= -167 - 2(103)$
$= -373$ kJ mol^{-1} [1]

Comments:
Most students successfully calculated the enthalpy change by using an energy cycle or the formula as shown.
However, some students incorrectly took $\Delta H_f^{\ominus}$(reactant) to subtract $\Delta H_f^{\ominus}$(product), while some carelessly omitted the coefficient "2" for $\Delta H_f^{\ominus}$(reactant) to account for the 2 mol of $\bullet C_3H_7(g)$ radicals.

(ii) <u>$\Delta H^{\theta} < 0$</u> as propyl free radical reacts to <u>form a C–C bond, releasing heat energy and thus it is an exothermic reaction.</u> [1]
<u>$\Delta S^{\theta} < 0$</u> as there is <u>one less gaseous product</u> than reactant (<u>$\Delta n = -1$), there are less ways to distribute particles and energies.</u> There is <u>decrease in disorderliness/the system gets more ordered</u> and thus <u>entropy change is negative</u>. [1]

Comments:
This question was quite badly done despite it being similar to a tutorial question. Students did not seem to understand the question. Students should note that "molecular level" usually refers to the specific changes observed in a chemical equation.
Some answers attempted to explain what a negative ΔH^{θ} and a negative ΔS^{θ} means rather than explaining why the termination reaction cause these changes to be negative, which includes a discussion of the C-C bond formation (for negative ΔH^{θ}) and the decrease in number of gaseous molecules (for negative ΔS^{θ}). A common omission in the explanation of the negative ΔS^{θ} is the concept of 'less ways to distribute particles and energies.' This is needed for a complete explanation.

(iii) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
$= -373 - 298(-0.190)$
$= -316$ kJ mol^{-1} [1]

As temperature increases, the <u>**$-T\Delta S$ becomes more positive**</u> and hence <u>**ΔG becomes less negative**</u>. The reaction is <u>**less spontaneous**</u> at temperatures above 298 K. [1]

Comments:
- *Though majority of the students recalled the formula for this calculation, many carelessly forgot to change both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ to the same units.*
- *In explaining the effect of increasing temperature on the spontaneity, many answers still vaguely refer to increase Δ**G** rather than a positive change. It has to be emphasized again that when referring to changes of Δ**G**, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ it is only clear to use 'negative/positive' changes and not 'increase/decrease' as these quantities has a sign.*

- *Some answers omitted the impact on the* ***$-T\Delta S$*** *term in the explanation, and mark is not given for incomplete explanation.*

[Total: 18]

6 **(a)** **(i)** $I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ $E^\ominus = +0.54$ V

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

$E_{cell}^\ominus = E_{red}^\ominus - E_{ox}^\ominus = +2.01 - (+0.54) =$ **$+1.47$ V**

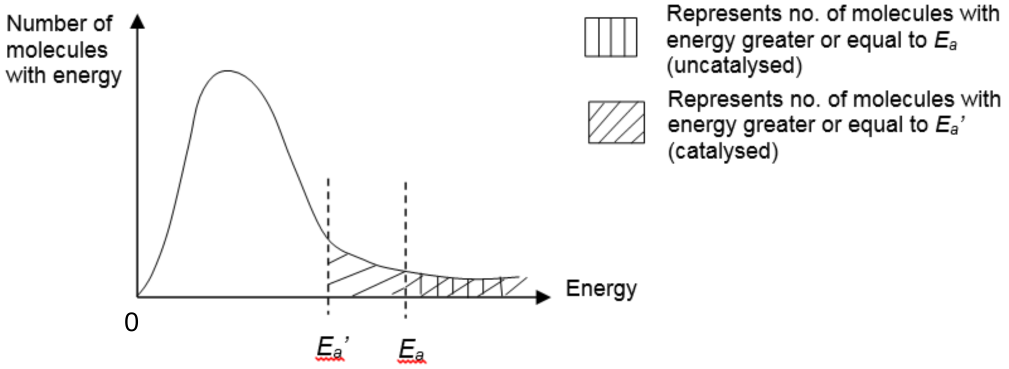
Since the **$E_{cell}^\ominus > 0$**, reaction is **feasible.**

Comments:
It is insufficient to only calculate the $E_{cell}^\ominus$ value; one must explain the significance of the positive $E_{cell}^\ominus$ value.

(ii) This is due to **electrostatic repulsion between two negatively charged ions** resulting in **high activation energy**. [1]

Comments:
Answer must mention the high activation energy involved in reaction between the two negatively-charged species.

(iii)



[1] for diagram

- A catalyst **speeds up the rate** of a reaction by providing an alternative reaction pathway which has **lower activation energy**. [1]
- As shown on the diagram, the **number of reactant molecules with energy greater or equal to the lowered activation energy** (E_a') will **increase**.
- This results in an increase in the frequency of **effective collisions**. [1]
- Hence, the **rate of reaction increases**.

Comments:

- *To be awarded the mark for the diagram, the following must be included:*
  - *(1) axes correctly labelled,*
  - *(2) correct shape of plot (starts at origin and tapering off at (but not touching) the x-axis) and*
  - *(3) a legend to explain the significance of the area under the graphs and to clearly label the activation energies of both uncatalyzed and catalyzed areas under the respective plot.*

- *The explanation must mention how the catalyst lowers the activation energy of the reaction, which is by providing an alternate pathway with lower activation energy.*

- *Correct answer must show understanding that when the reactants should possess energies* ***greater than or equal to*** *the lowered activation energy before they can effectively collide with one another, resulting in a reaction.*

(iv) As the 3d subshell of Fe^{2+} ion is close in energy to the 4s subshell, more electrons can be lost from the 3d subshell to form ions of higher oxidations states with similar stability. Interconversion between +2 and higher oxidation states of Fe can readily occur by losing and re-gaining the 3d electron. As a result, Fe(II) ion can act as a homogeneous catalyst. [1]

Ca^{2+}, however, is the only ion of stable oxidation state for calcium. Removing inner 3p electron(s) from Ca^{2+} to form calcium ions of higher oxidation states involves large amount of energy. Hence, Ca^{2+} cannot easily form ions of higher oxidation states and thus cannot act as a homogeneous catalyst. [1]

Comments:

- *The interconversion of different oxidation states of the catalyst ions in homogeneous catalysis is key. So, answer to this question need to be specific in explaining why Fe(II) ion is able to easily change to higher oxidation states and then back to +2 oxidation state.*
- *Hence, a general discussion on iron metal has partially filled orbitals and exhibiting variable oxidation states is not precise. (on this point, note that it is incorrect to say Fe(II) ion has variable oxidation states. Fe(II) is just one of the many oxidation states iron displays).*
- *Many also fail to point out the calcium(II) is the only stable oxidation state shown by calcium.*
- *Sadly, a significant number showed confusion between homogeneous catalysis and heterogeneous catalysis. They gave an incorrect discussion of heterogeneous catalysis where reactants forming weak temporary bonds on the surface of the catalyst.*

(b) **(i)** **X**: green **Y**: violet/purple
[1] for both colours

Comments:
A common mistake was identifying the complexes instead of describing the colours.

(ii) The d-orbital splitting in **Y** is larger. [1]
Y absorbs yellow light at a shorter wavelength, which corresponds to a higher amount of energy. [1]

Comments:

- *Many were confused with colour absorbed and complementary colour observed. Hence, instead of explaining the relative size of d-orbital splitting in terms of the* ***absorbed*** *red and yellow colours, a significant number discussed the splitting incorrectly in terms of the complementary green and violet/purple colours observed.*
- *Many students showed their lack of understanding of question and incorrectly attempted to calculate the size of the d-orbital splitting.*

[Total: 10]