

**ANDERSON SERANGOON JUNIOR COLLEGE****2022 JC 2 PRELIMINARY EXAMINATION SOLUTIONS**

NAME: \_\_\_\_\_ (    )

CLASS: 22 / \_\_\_\_\_

**CHEMISTRY**

Paper 1 Multiple Choice

**9729/01****21 September 2022****1 hour**

Additional Materials:     Multiple Choice Answer Sheet  
   Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Please look through the marks scheme and understand the concepts tested in each question.

Do pay attention as the tutor go through selected questions in lecture.

If you still have further questions, you may check with your tutor at your own time.  
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 Ans: D

Statement A is incorrect. Electrons has a larger  $e/m$  ratio and hence will be deflected to a larger extent than protons.

Statement C is incorrect. Electron beam should be deflected towards the positively charged plate.

Statement B is incorrect and D is correct. Proton beam travels in a parabolic path towards the negatively charged plate.

2 Ans: C

There is a large increase in the 7<sup>th</sup> to 8<sup>th</sup> ionisation energy. This means that the 8<sup>th</sup> electron is removed from the inner principal quantum shell and element D is from Group 17. Its valence configuration will be  $ns^2np^5$ . Hence the 5<sup>th</sup> electron is from the p subshell and 6<sup>th</sup> electron is from the s subshell.

While it is possible that D is fluorine (i.e. in Period 2), it cannot be conclusively inferred from the data given as element D may have more than 9 electrons. However, if the 10<sup>th</sup> I.E. is given, we can conclude that D is not fluorine in Period 2.

3 Ans: D

1: C-Cl bond is polar and there are 2 Cl bonds in molecule I, thus it is more polar than molecule II.

2: The dipole moments associated with the polar C-Cl bond is canceled out in the trans molecule. Thus, the cis isomer is more polar.

3: The dipole moments associated with the polar C-Cl bond is canceled out in the trans molecule. Thus, molecule I is more polar.

4: C-F bond is more polar than C-Cl bond. Thus, molecule I is more polar.

4 Ans: A

E has simple molecular structure with low m.p because little amount of energy is needed to overcome the weak intermolecular forces of attraction. It is unable to conduct electricity in any state due to absence of mobile charge carriers.

F has giant ionic lattice structure with high m.p because large amount of energy is needed to overcome the strong electrostatic forces of attraction between the oppositely charged ions. It conducts electricity in aqueous and molten state due to the presence of mobile ions.

G has giant metallic lattice structure with high m.p because large amount of energy is needed to overcome the strong metallic bonds. It conducts electricity in solid and molten state due to the presence of delocalised electrons.

H is SiO<sub>2</sub>. It has giant molecular structure with high m.p because large amount of energy is needed to overcome the strong and extensive covalent bonds between the atoms. It cannot conduct electricity in solid state because there is no mobile charge carriers.

3

5 Ans: D

Gas J deviates more than gas K from ideality and hence have stronger intermolecular forces of attraction.

A: O<sub>2</sub> has a greater electron cloud size and has greater ease of distortion of electron cloud. Hence it has stronger instantaneous dipole-induced dipole interactions between O<sub>2</sub> molecules and should deviate more.

B: HI has a greater electron cloud size and has greater ease of distortion of electron cloud. Hence it has stronger instantaneous dipole-induced dipole interactions between HI molecules and should deviate more. HI should be gas J.

C: H<sub>2</sub>O has stronger intermolecular hydrogen bonds and should deviate more.

D: HBr is polar and F<sub>2</sub> is non-polar. Hence, HBr has stronger permanent-dipole induced dipole interactions and deviate more.

6 Ans: C

$$pV = nRT$$

$$V = \frac{nRT}{p}$$

$$V = \frac{\frac{m}{Mr}RT}{p}$$

Since R, mass, pressure and temperature are constant, volume is proportional to  $\frac{1}{Mr}$

	NH <sub>3</sub>	CH <sub>3</sub> Cl	CH <sub>2</sub> Cl <sub>2</sub>	HCOOH
Mr	17	50.5	85	46

7 Ans: B

$$\text{Lattice energy} \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$$

Cationic charge: Mg<sup>2+</sup> > Na<sup>+</sup>

Anionic charge: O<sup>2-</sup> > Cl<sup>-</sup>

Cationic radius: Mg<sup>2+</sup> < Na<sup>+</sup>

Magnitude of lattice energy: MgO > MgCl<sub>2</sub> > NaCl

8 Answer: B

During vapourisation, molecules need to overcome intermolecular forces of attraction to move further apart to convert to gaseous states.

Atomisation is to convert molecules into atoms and that would need to break strong covalent bonds within molecules instead.

## 9 Answer: B

comparing expt I and II, when [sucrose] increased 1.5 times, the initial rate increased by 1.5 times. Since rate of reaction is directly proportional to [sucrose], order of reaction wrt sucrose is 1.

comparing expt I and III, when [HCl] is tripled, the initial rate tripled. Since the rate of reaction is directly proportional to [HCl], order of reaction wrt HCl is 1.

$$\text{rate} = k [\text{HCl}] [\text{sucrose}]$$

$$\text{rate} = k' [\text{sucrose}]$$

where  $k' = k [\text{HCl}]$  ∴ HCl is a catalyst and its concentration remains constant

Since the half-life of expt I is 3.0 s and

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k [\text{HCl}]_I} = 3.0 \text{ s for 1}^{\text{st}} \text{ order reaction wrt sucrose,}$$

expt II Since [HCl] is constant, half-life for expt II will remain as 3.0 s.

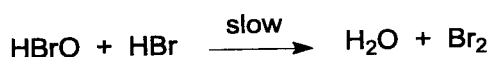
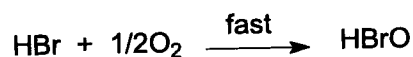
expt III As [HCl] is tripled, half-life for expt III will be 1.0 s

$$(t_{1/2} \text{ for expt III} = \frac{\ln 2}{k [\text{HCl}]_{III}} = \frac{\ln 2}{k(3[\text{HCl}]_I)} = \frac{1}{3} \left( \frac{\ln 2}{k [\text{HCl}]_I} \right) = \frac{1}{3} (3.0) = \underline{1.0 \text{ s}})$$

## 10 Answer: C

The rate equation / order of reaction of a reaction can be derived from the stoichiometric coefficients of the species involved in the slow step, including preceding fast step(s).

- 1 is consistent. 1 mol of  $\text{H}_2\text{O}_2$  reacts with 1 mol of  $\text{I}^-$  in the slow step (r.d.s.), which is also the first step. Hence the rate equation is as shown.
- 2 is inconsistent. Correct rate equation should be  $\text{rate} = k_2 [\text{H}_2]$  since only 1 mol of  $\text{H}_2$  is involved in the slow step.
- 3 is consistent. As the slow step is not the first step, you need to consider the preceding fast step. Based on the elementary step,  $\text{rate} = k_3 [\text{HBrO}] [\text{HBr}]$   
However, HBrO is an intermediate and its concentration is dependent on the reaction between HBr and  $\text{O}_2$  so you need to include this in the rate equation.  
Shortcut for consideration: If the intermediate is the ONLY product formed in the preceding fast step, you can just change its stoichiometric coefficient to be the same as that in the slow step. Similarly, multiply by the same factor for the reactants in the fast step. In this case, the mechanism can be rewritten as



$$\begin{aligned} \text{Hence the rate equation is } \text{rate} &= k_3 [\text{HBr}] [\text{HBrO}] \\ &= k_3' [\text{HBr}] [\text{HBr}] [\text{O}_2]^{1/2} \\ &= k_3' [\text{HBr}]^2 [\text{O}_2]^{1/2} \end{aligned}$$

11 Answer: D

Since this is a first order reaction based on the rate constant units, only the half-life remains constant.

Option A: Rate should decrease as the pressure of reactant decreases.

Option B: The total pressure should increase as the volume remains constant but more gas products are formed.

Option C: The rate constant is different without the use of gold as reaction rate will decrease.

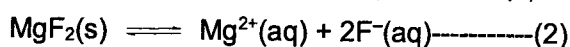
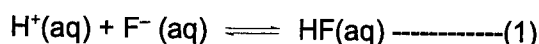
12 Answer: D

Options 2 and 3 are incorrect.

Option 2: Decreasing the partial pressure of nitrogen will decrease the rate of reaction even though the POE will eventually shift to the left.

Option 3: Adding a catalyst should affect the rate constant since it increases the rate of reaction without concentration change.

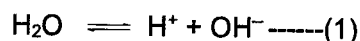
13 Answer: D



Towards lower pH as  $[\text{H}^+]$  increases, POE for equation (1) shifts right. This results in a decrease in  $[\text{F}^-]$  in equation (2).

By LCP, POE for equation (2) shifts right to increase  $[\text{F}^-]$ , thus increasing the solubility of  $\text{MgF}_2$ .

14 Answer: C



$$K_w = [\text{H}^+][\text{OH}^-]$$

When temperature increases,  $K_w$  increases, indicating POE for (1) shifts right to absorb additional heat. Thus the ionization of water is endothermic.

As POE shifts right,  $[\text{H}^+]$  and  $[\text{OH}^-]$  increases to the same amount.

$K_w$  at 10 °C is lower than  $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .  $[\text{H}^+]$  at 10°C will be less than  $\sqrt{(1 \times 10^{-14})}$ , pH will be higher than at 25 °C.

## 15 Answer: D

**Statement 1 is incorrect** as the lone pair is NOT delocalised; the lone pair is localised on the sp hybridised N atom of the nitrile group. Furthermore, the strength of the C-N bond does not impact the availability of the lone pair for donation to a proton.

**Statement 2 is correct.** Observing the nitrile is neutral, while the amine is basic indicates that the lone pair on the N of nitrile is not available for donation to a proton. This is due to the sp hybridised state of N in nitrile has higher s character than the sp<sup>3</sup> hybridised state of N in amine. This results in stronger attraction of the nucleus on the lone pair, making it less available to accept proton.

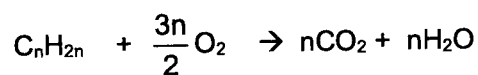
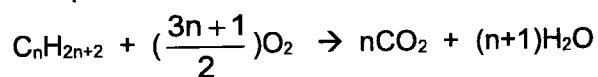
**Statement 3 is incorrect.** The **size** of the alkyl group does **not** affect the extent of electron donating effects significantly.

You may have thought that statement 3 is correct because of what you read in the Hydroxy Compounds lecture notes pg 25. However, please note that the difference in electron donating effect between alkyl groups of different sizes is insignificant (in fact you will only see very slight difference in pK<sub>a</sub> values of ethanoic acid vs propanoic acid) and it has never been mentioned as a reason to significantly impact basicity of organic compounds such that one compound is basic while the other is neutral.

If you are interested to read up more, you may see this website that is related to our syllabus: <https://www.chemguide.co.uk/basicorg/acidbase/acids.html>

## 16 Answer: A

Complete combustion of an aliphatic alkane and an alkene can be represented by:



At 298 K, H<sub>2</sub>O is a liquid. The same volume of CO<sub>2</sub> would be produced for both combustions.

D is incorrect.

Directly proportional means the ratio of C to O<sub>2</sub> should be a constant value that does not change as the number of C atoms increase.

It is hence not directly proportional for combustion of alkane because the ratio does not remain constant.

value of n	coefficient of O <sub>2</sub>	ratio (n:coefficient of O <sub>2</sub> )
1	2	1:2
2	3.5	1:1.75
3	5	1:1.67

## 17 Answer: C (1 only)

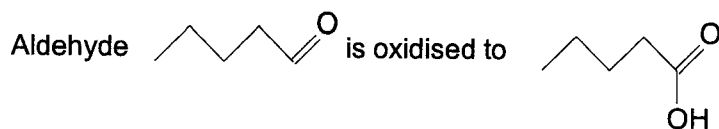
**L** is the cis isomer, **M** is the trans isomer. There is restricted rotation about the C-C due to presence of the cyclic structure.

**L** is not optically active as it has an internal plane of symmetry (meso compound). **M** is optically active as it has two chiral centres but no plane of symmetry.

Thus, **L** and **M** are not a pair of enantiomers and will not form a racemic mixture.

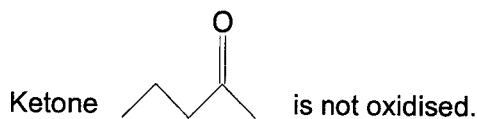
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18 Answer: A

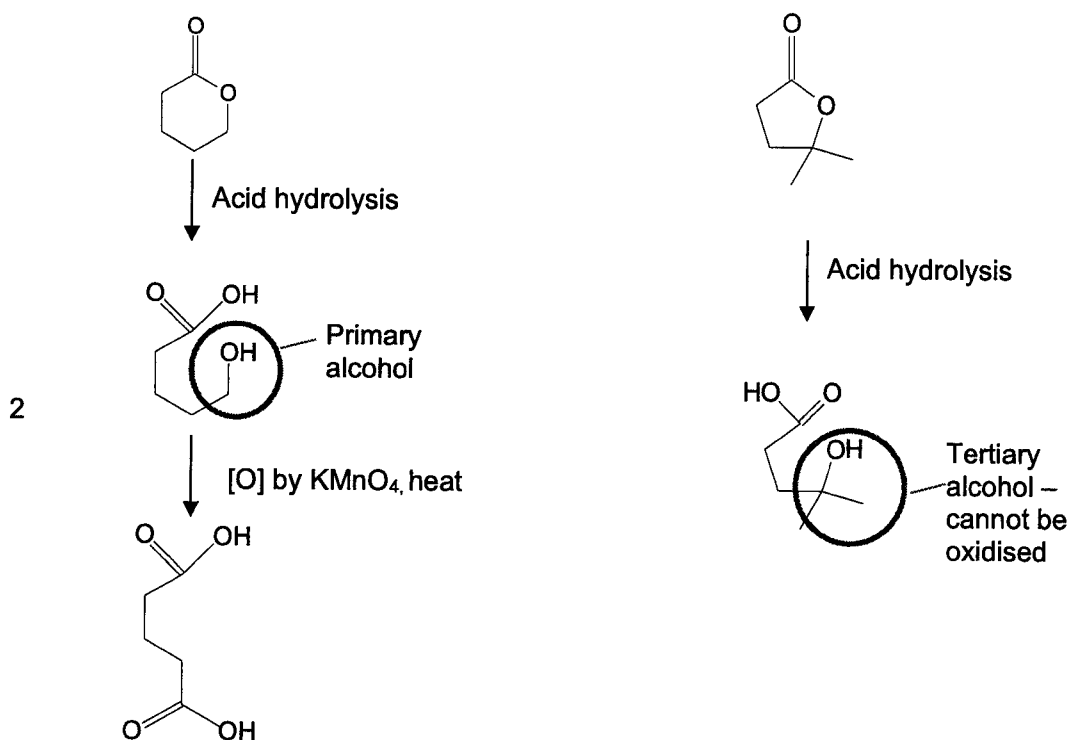


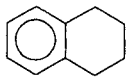
Observation: purple  $\text{KMnO}_4$  is decolourised.

1



Observation: purple  $\text{KMnO}_4$  remains.

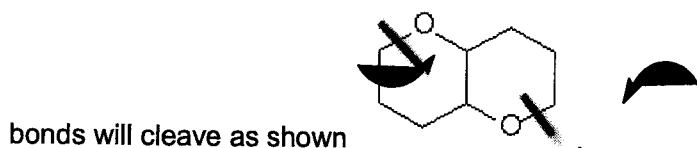


3 The arene,  undergoes side-chain oxidation, thus decolourises  $\text{KMnO}_4$ , while the cycloalkane will not be oxidised.

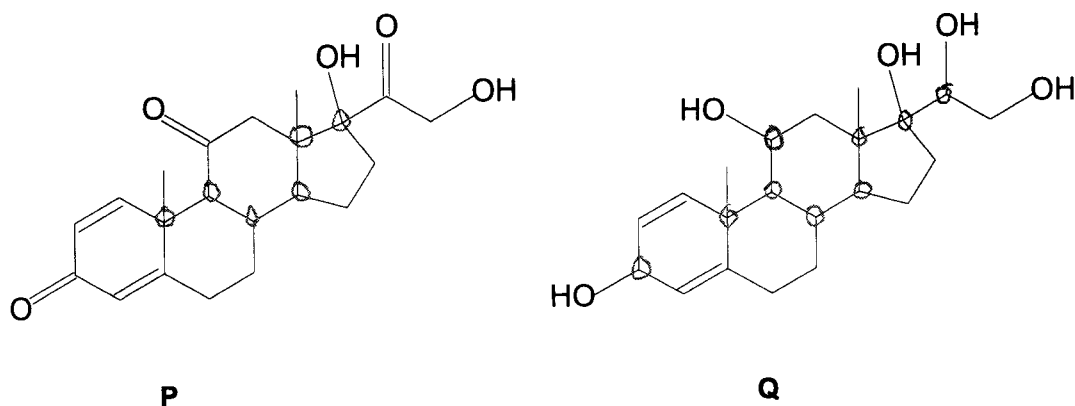
19 Answer: B

This question can be solved either by pattern recognition or using the info on the mechanism it undergoes ( $\text{S}_{\text{N}}2$ ).

$\text{I}^-$  will attack the electron deficient carbon with less steric hindrance ( $\text{S}_{\text{N}}2$ ) and hence the C–O



20 Answer: B



21 Answer: A

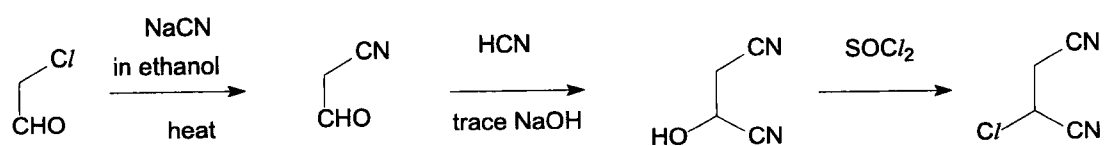
Option 1:  $(\text{CH}_3)_2\text{NH}$  is more basic than  $\text{CH}_3\text{NH}_2$  as it has more electron donating alkyl group, increasing the availability of the lone pair to accept proton.

Option 2:  $\text{CH}_3\text{COCH}_2\text{NH}_2$  (amine) is basic while  $\text{CH}_3\text{CH}_2\text{CONH}_2$  (amide) is neutral.

Option 3:  $\text{C}_6\text{H}_5\text{OH}$  is a weaker acid than  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ , hence its conjugate base ( $\text{C}_6\text{H}_5\text{O}^-$ ) is a stronger base than  $\text{C}_6\text{H}_5\text{CO}_2^-$ .

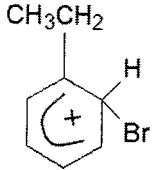
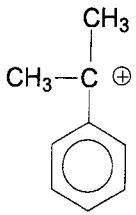
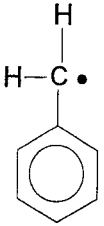
22 Answer: A

K is an aldehyde and reduces  $\text{Ag}(\text{NH}_3)_2^+$  to Ag metal which appears as a black solid.





23 Answer: B

Reactive C	Option 1	Option 2	Option 3
Mechanism	Electrophilic substitution	S <sub>N</sub> 1 mechanism	Free radical substitution
Before reaction	Trigonal planar	Tetrahedral	Tetrahedral
Intermediate	 Tetrahedral	 Trigonal planar	 Trigonal planar (note that alkyl radicals are sp <sup>2</sup> hybridised)

24 Answer: D

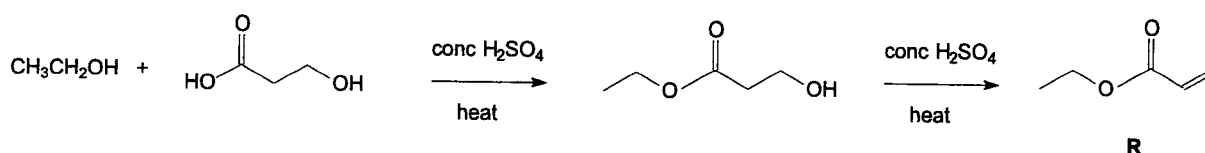
Addition reaction will involve breaking a  $\pi$  bond of the benzene, hence disrupting the continuous  $\pi$  electron cloud and destroying the resonance stability of the benzene ring.

25 Answer: D

Question tests the concept of formation of ester from heating an alcohol and a carboxylic acid in the presence of concentrated H<sub>2</sub>SO<sub>4</sub>. However, as concentrated H<sub>2</sub>SO<sub>4</sub> is a dehydrating agent, elimination of water can also occur.

Option 1: Reacting ethanol with P will not yield R.

Option 2: Ethanol reacts with P as shown:



By-product, CH<sub>3</sub>CH<sub>2</sub>OCOCH(OH)CH<sub>3</sub> shown, cannot be obtained.

Option 3: Two CH<sub>3</sub>CH(OH)CO<sub>2</sub>H molecules can undergo ester formation to yield the by-product cyclic ester shown.

26 Answer: D

Si is a semiconductor which can only give rise to delocalised electrons at high temperatures.

SiCl<sub>4</sub>(l) has a simple molecular structure hence is a non-conductor of electricity.



## 27 Answer: C

1 is wrong – this is a precipitation reaction between  $\text{Fe}^{3+}$  and  $\text{Fe}(\text{CN})_6^{4-}$ , there is no redox reaction occurring as OS of Fe does not change  
 2 is correct –  $\text{CN}^-$  ligands from  $\text{K}_3\text{Fe}(\text{CN})_6$  displaces  $\text{H}_2\text{O}$  ligands from  $\text{FeCl}_2$  and in turn produces Prussian blue,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , via precipitation  
 3 is correct – Prussian blue is an insoluble pigment (blue ppt) and the resultant solution is  $\text{KCl}$  which is a colourless solution

## 28 Answer: C

$\text{Ag}^+$  would be colourless as it has a fully filled 4d subshell  
 $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10})$   
 It is in the same group (group 11) as copper and hence  $\text{Ag}^+$  would have a similar valence d subshell electronic configuration as  $\text{Cu}^+$

## 29 Answer: B

$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$   $E^\ominus = -2.38\text{V}$  ( $E^\ominus$  less positive, [O] occurs at this half-cell)  
 → anode (negative terminal)

$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$   $E^\ominus = +0.77\text{V}$  ( $E^\ominus$  more positive, [R] occurs at this half-cell)  
 → cathode (positive terminal)

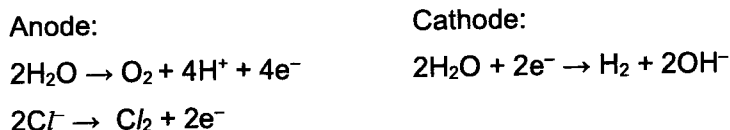
B is correct. Size of solid electrode has no effect on the reactions in both half-cell.  
 C is incorrect. Addition of water dilutes the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions equally, equilibrium position does not shift.  
 D is not true. Pressure is not a factor as there are no gaseous species involved in the electrochemical cell.

## 30 Answer: C

Since seawater is assumed to be dilute aqueous  $\text{NaCl}$  and with reference to the  $E^\ominus$  values for the oxidation of  $\text{H}_2\text{O}$  and  $\text{Cl}^-$  at the anode, and for the reduction of  $\text{H}_2\text{O}$  and  $\text{Na}^+$  at the cathode, it can be deduced that  $\text{H}_2\text{O}$  would undergo oxidation at the anode and reduction at the cathode.

Hence from 0 h to 90 h,  $[\text{Cl}^-]$  is increasing due to  $\text{H}_2\text{O}$  reacting away.

From 90 h onwards,  $[\text{Cl}^-]$  is decreasing. This suggests that the aqueous  $\text{NaCl}$  solution is now concentrated enough that  $\text{Cl}^-$  is preferentially oxidised (ie, brine).



Option A is correct

Option B is correct as the graph shows a linear increase in  $[\text{Cl}^-]$

Option D is correct as at 20 h,  $\text{H}^+$  is a product at the anode and  $\text{OH}^-$  is a product at the cathode

Option C is wrong as at 60 h,  $\text{H}_2\text{O}$  would undergo oxidation at the anode and reduction at the cathode, but given the same current supplied for the 60 h of electrolysis, there would be twice the volume of  $\text{H}_2$  produced compared to  $\text{O}_2$  as seen by the electrons transferred from both anode-cathode half-equations above.

**ANDERSON SERANGOON JUNIOR COLLEGE****ASR**  
JUNIOR COLLEGE**2022 JC 2 PRELIMINARY EXAMINATION SOLUTIONS  
WITH MARKERS COMMENTS****NAME:** \_\_\_\_\_ (      )**CLASS:** 22 / \_\_\_\_\_**CHEMISTRY**

Paper 2 Structured Questions

**9729/02****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 2<sup>nd</sup> IE, the electron to be removed is from the same orbital as that of the 1<sup>st</sup> 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 2<sup>nd</sup> IE of Ca is higher when the values of ionisation energies can be found in the Data Booklet.*

(ii)

Thermal stability:  $\text{CaCO}_3 > \text{ZnCO}_3 > \text{MgCO}_3$   
 Zn, Ca and Mg have the same cationic charge of +2  
 Ionic radius of  $\text{Ca}^{2+}$ : 0.099 nm  
 Ionic radius of  $\text{Mg}^{2+}$ : 0.065 nm  
 Ionic radius of  $\text{Zn}^{2+}$ : 0.074 nm

[1]

Ionic radius:  $\text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}$  [1] with quoted values

Charge density (q/r):  $\text{Ca}^{2+} < \text{Zn}^{2+} < \text{Mg}^{2+}$

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  $E^\ominus$  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  $\text{CO}_3^{2-}$  was distorted to a greater extent or the C-O bond is weakened to a greater extent etc.*

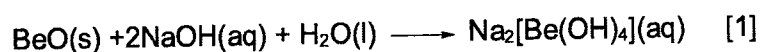
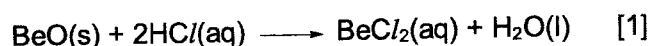
*Some students spelled "extent" wrongly as "extend" in their answer.*

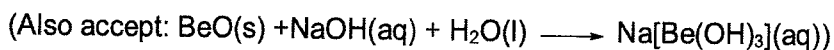
- (b) (i)  $[\text{Be}(\text{H}_2\text{O})_4]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Be}(\text{H}_2\text{O})_3(\text{OH})]^+ + \text{H}_3\text{O}^+$   
 OR  
 $[\text{Be}(\text{H}_2\text{O})_4]^{2+} \rightleftharpoons [\text{Be}(\text{H}_2\text{O})_3(\text{OH})]^+ + \text{H}^+$  [1]

**Comments:**

*Many students missed out the information from the qns that Be forms a complex ion  $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$  and thus couldn't write the equation for the hydrolysis of this ion.*

(ii)





*Comments:*

*Many students thought beryllium oxide is  $\text{Be}_2\text{O}_3$  without realizing that Be is in Group 2 and not Group 13 like Al. They also couldn't balance the equation.*

- (iii)  $\text{Be}^{2+}$  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  $\text{Cl}^-$  anion to a great extent. The extent of sharing of electrons between the two nuclei is so great that  $\text{BeCl}_2$  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)

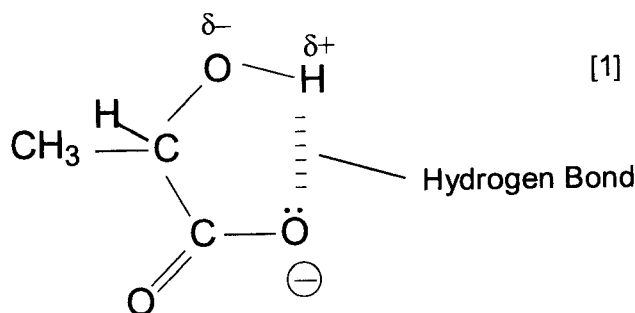
To minimise repulsion (and maximise stability), the 3 bond pairs are arranged as far apart as possible, giving rise to a change in shape from linear to trigonal planar and a smaller (or decrease in) bond angle.

*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)



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  $\text{CO}_2^-$  group and  $\text{OH}$  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  $K_a$

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

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

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

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

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

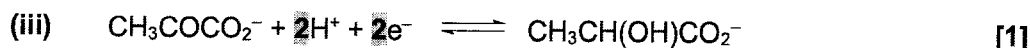
Comments:

Common mistakes include:

- Using  $\ln$  instead of  $\lg$
- Incomplete calculations

$$\begin{aligned} \text{(ii)} \quad \% \text{ of NAD}^+ &= \frac{1}{(10.3+1)} \times 100\% \\ &= 8.85\% \end{aligned} \quad [1]$$

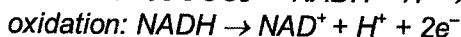
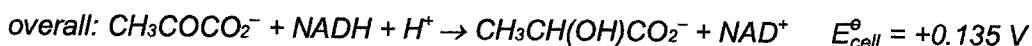
Comments: Poorly done. Many students cannot properly compute the percentage.



$$\begin{aligned} E_{\text{cell}}^{\circ} \text{ at pH 7} &= E_{\text{red}}^{\circ} - E_{\text{ox}}^{\circ} \\ +0.135 &= E_{\text{red}}^{\circ} - (-0.320) \\ E_{\text{red}}^{\circ} &= -0.185\text{V} \quad [1] \end{aligned}$$

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<sup>+</sup>/NADH from the overall reaction equation.



The reduction half-equation is hence as shown below after balancing the particles and charges:  $\text{CH}_3\text{COCO}_2^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-$

$$\begin{aligned} \text{(iv)} \quad \Delta G \text{ at pH 7} &= -nFE_{\text{cell}}^{\circ} \\ &= -2(96500)(+0.135) \\ &= -26\,055 \text{ J mol}^{-1} \\ &= -26\,100 \text{ J mol}^{-1} \text{ (3 s.f.)} \quad [1] \end{aligned}$$

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

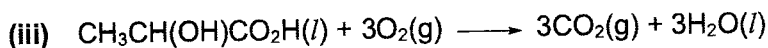
- (c) (i) The amount of heat evolved when one mole of lactic acid in its standard state is completely burned in excess oxygen under standard conditions of 298 K and 1 bar.

[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'.

$$\begin{aligned} \text{(ii)} \quad \Delta H_{\text{c}}^{\circ} &= [3(-393.5) + 3(-285.8)] - (-483.2) \\ &= -1554.7 \text{ kJ mol}^{-1} \\ &= -1550 \text{ kJ mol}^{-1} \text{ (3 s.f.)} \quad [1] \text{ (correct value and units)} \end{aligned}$$

Comments: Students did not take into account the mole ratio of the products CO<sub>2</sub> and H<sub>2</sub>O. Students are reminded to leave their answers to 3 sf.



Heat absorbed for bond breaking

$$\begin{aligned} &= 2 \text{BE}(\text{C}-\text{C}) + 4 \text{BE}(\text{C}-\text{H}) + 2 \text{BE}(\text{C}-\text{O}) + 2\text{BE}(\text{O}-\text{H}) + \text{BE}(\text{C}=\text{O}) + 3 \text{BE}(\text{O}=\text{O}) \\ &= 2(350) + 4(410) + 2(360) + 2(460) + (740) + 3(496) \\ &= \mathbf{6208 \text{ kJ mol}^{-1}} \end{aligned}$$

Heat released on bond formation

$$\begin{aligned} &= 6 \text{BE}(\text{C}=\text{O}) + 6\text{BE}(\text{O}-\text{H}) \\ &= 6(805) + 6(460) \\ &= \mathbf{7590 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta H_c^\ominus &= (+6208) + (-7590) \\ &= \mathbf{-1382 \text{ kJ mol}^{-1} [1]} \end{aligned}$$

[1]  
working

Comments:

Common mistakes observed:

- $\Delta H$  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  $\Delta H_f$  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.

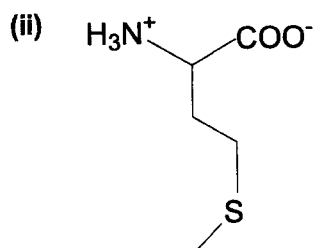
Comments: Many students were not aware that that bond energy of a covalent bond is the average amount of heat absorbed to break one mole of that particular covalent bond in a particular compound in the **gaseous state**.

[Total: 12]

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

$\text{pH} = -\lg 0.0281 = \mathbf{1.55 [1]}$

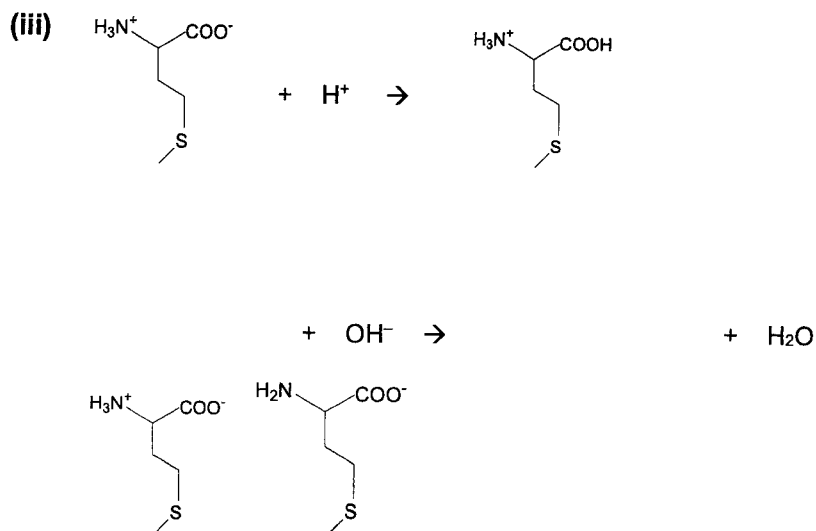
Comments: This question was done well. Only a small minority did not attempt the question or used the given concentration directly to calculate pH, incorrectly treating methionine as a strong acid.



[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.





[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  $\text{OH}^-$  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.

$$\begin{aligned}
 \text{p}K_{b1} &= 14 - 2.28 = 11.72 \\
 K_{b1} &= 10^{-11.72} = 1.905 \times 10^{-12} \quad [1]
 \end{aligned}$$

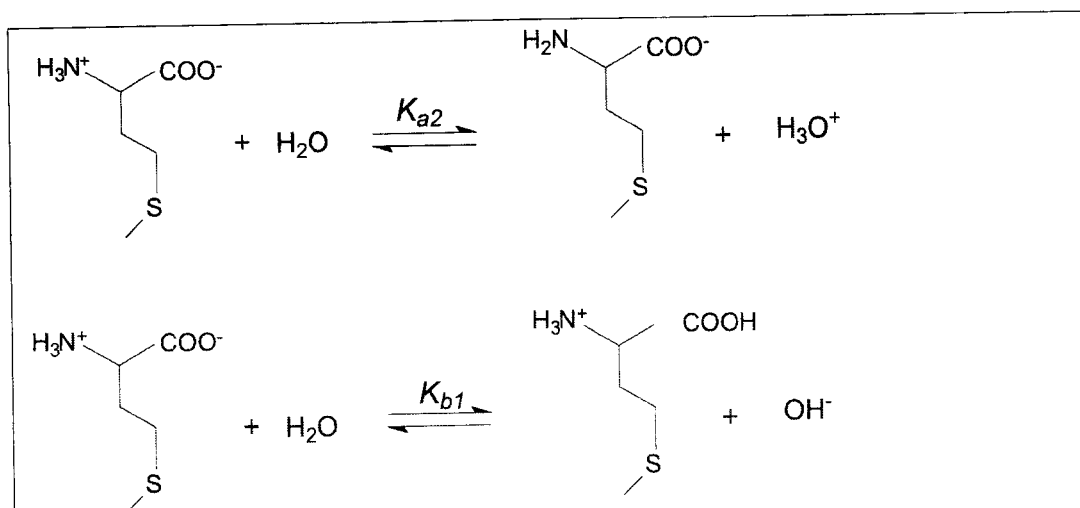
$$\begin{aligned}
 \text{p}K_{a2} &= 9.21 \\
 K_{a2} &= 10^{-9.21} = 6.166 \times 10^{-10}
 \end{aligned}$$

Since  $K_a(-\text{NH}_3^+) > K_b(-\text{COO}^-)$ , 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 ( $-\text{NH}_3^+$ ) and a basic group ( $-\text{COO}^-$ ) can undergo hydrolysis to give  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  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.

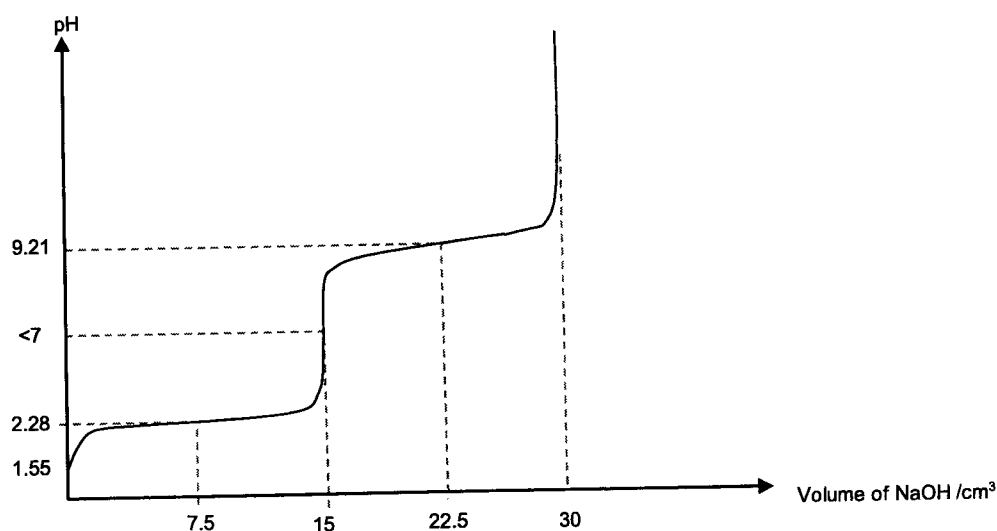
Common misconceptions:

- Many students know that at first equivalence point, the zwitterion is present. However, they then wrongly concluded that since an acidic group ( $-\text{NH}_3^+$ ) and a basic group ( $-\text{COO}^-$ ) 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  $-\text{NH}_3^+$  group occurred to a greater extent but did not provide explanation and were not given full credit.

(v) At  $7.5 \text{ cm}^3$ , 1<sup>st</sup> maximum buffering capacity point  
 $\text{pH} = \text{p}K_{a1} = 2.28$

At  $15 \text{ cm}^3$ , 1<sup>st</sup> equivalence point,  $\text{pH} = 5.22$  or  $5.75$  [check part (iv)]

At  $22.5 \text{ cm}^3$ , 2<sup>nd</sup> maximum buffering capacity point  
 $\text{pH} = \text{p}K_{a2} = 9.21$



[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, <math><7</math>) 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  $\text{pH} = \text{pK}_a$  were often missing.*

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

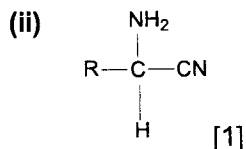
*Comments:*

*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<sub>2</sub>O) [1]

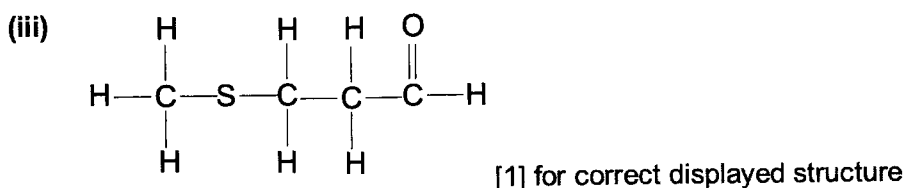
*Comments:*

*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<sub>2</sub>O). Students must INDICATE clearly the step in which each answer is for!*



*Comments:*

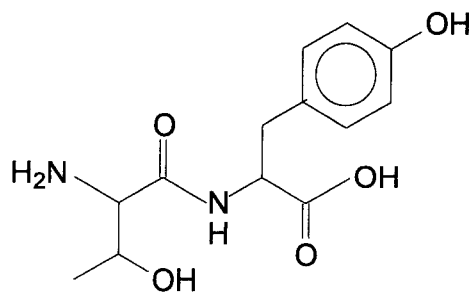
*Students often carelessly omitted the 2 in -NH<sub>2</sub>. Students must work backwards from step 4 to see that the reagents suggest that of hydrolysis (of -CN group). So the -NH<sub>2</sub> group must be present in compound G.*



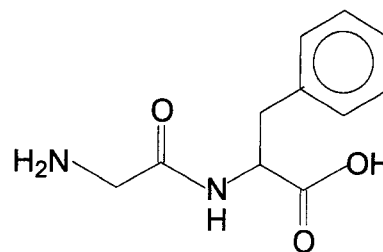
*Comments:*

*Most students who arrived at the correct structure were careless to have overlooked the keywords '**displayed formula**' 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:**

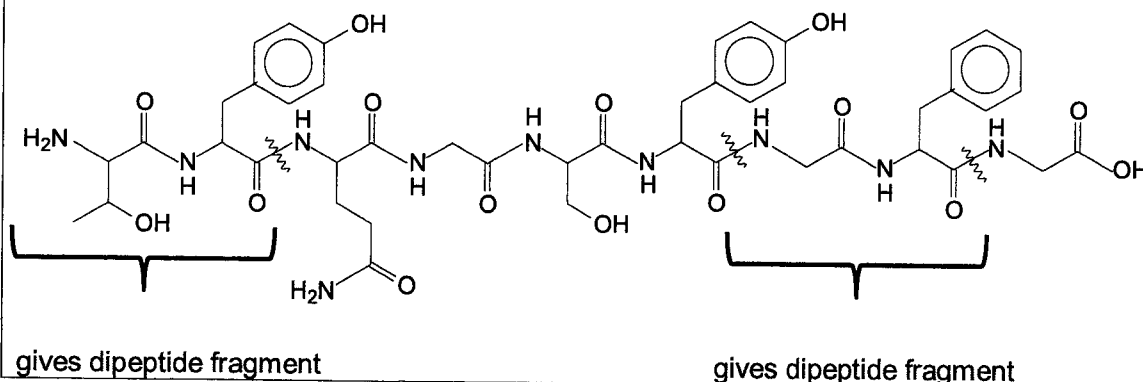
Students need to know that a **dipeptide** is a molecule that consists of two amino acids joined together by a peptide bond.

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).



[Total: 15]

- 4 (a) (i)  $\text{CH}_3\text{CCl}_2\text{COOH}$  has **one more electron-withdrawing** group than  $\text{CH}_3\text{CHClCOOH}$  and hence exerts **stronger electron-withdrawing effect** on the **carboxylate anion**,  $\text{CH}_3\text{CCl}_2\text{COO}^-$ . [1]  
 The **negative charge** on the anion becomes **more dispersed** and the anion is more stabilised. The **dissociation** of the acid,  $\text{CH}_3\text{CCl}_2\text{COOH}$ , to release  $\text{H}^+$  ions is **more favoured**.  
 Hence,  $\text{CH}_3\text{CCl}_2\text{COOH}$  is a stronger acid with lower  $\text{p}K_a$  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  $\text{H}^+$**  ions.*

*Wrong concepts/phrasing of answers include:*

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

- (ii) 4.00 (actual value) accept values of x larger than 2.80.  
 The electron-withdrawing group of  $\text{CH}_2\text{ClCH}_2\text{COOH}$  is **further** away from the carboxylate group than that in  $\text{CH}_3\text{CHClCOOH}$  and hence exerts **weaker electron-withdrawing effect** on the **carboxylate anion**,  $\text{CH}_2\text{ClCH}_2\text{COO}^-$ .  
 The **negative charge** on the anion becomes **less dispersed** and the anion is less stabilised. The **dissociation** of the acid,  $\text{CH}_2\text{ClCH}_2\text{COOH}$ , to release  $\text{H}^+$  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 irrelevant factors to explain the difference in acidity.*

$$\begin{aligned}
 \text{(iii)} \quad K_c &= \frac{[\text{CH}_3\text{CHClCOO}^-][\text{CH}_3\text{CCl}_2\text{COOH}]}{[\text{CH}_3\text{CHClCOOH}][\text{CH}_3\text{CCl}_2\text{COO}^-]} \\
 &= \frac{[\text{H}^+][\text{CH}_3\text{CHClCOO}^-][\text{CH}_3\text{CCl}_2\text{COOH}]}{[\text{CH}_3\text{CHClCOOH}][\text{CH}_3\text{CCl}_2\text{COO}^-][\text{H}^+]} \\
 &= \frac{K_a(\text{CH}_3\text{CHClCOOH})}{K_a(\text{CH}_3\text{CCl}_2\text{COOH})} \quad [1] \\
 &= \frac{10^{-2.80}}{10^{-1.74}} \\
 &= 0.08709 \\
 &= 0.0871 \text{ (to 3sf)} \quad [1]
 \end{aligned}$$

*Comments:*

*Weak answers did not convert  $\text{p}K_a$  to  $K_a$  before substitution and/or gave wrong  $K_a$  expression.*

Try the following as Additional Practice!

An equilibrium is set up at  $25^\circ\text{C}$  between acetic acid and dimethylamine as shown.



$$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

$$K_a((\text{CH}_3)_2\text{NH}_2^+) = 1.85 \times 10^{-11} \text{ mol dm}^{-3}$$

Use the  $K_a$  values of the two acids to calculate  $K_c$  for the above equilibrium at  $25^\circ\text{C}$ .

[2]

Solution

$$K_a(\text{CH}_3\text{COOH}) = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$K_a(\text{CH}_3)_2\text{NH}_2^+ = \frac{[(\text{CH}_3)_2\text{NH}][\text{H}^+]}{[(\text{CH}_3)_2\text{NH}_2^+]}$$

$$K_c = \frac{[\text{CH}_3\text{COO}^-][(\text{CH}_3)_2\text{NH}_2^+]}{[\text{CH}_3\text{COOH}][(\text{CH}_3)_2\text{NH}]}$$

$$= \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \times \frac{[(\text{CH}_3)_2\text{NH}_2^+]}{[(\text{CH}_3)_2\text{NH}][\text{H}^+]}$$

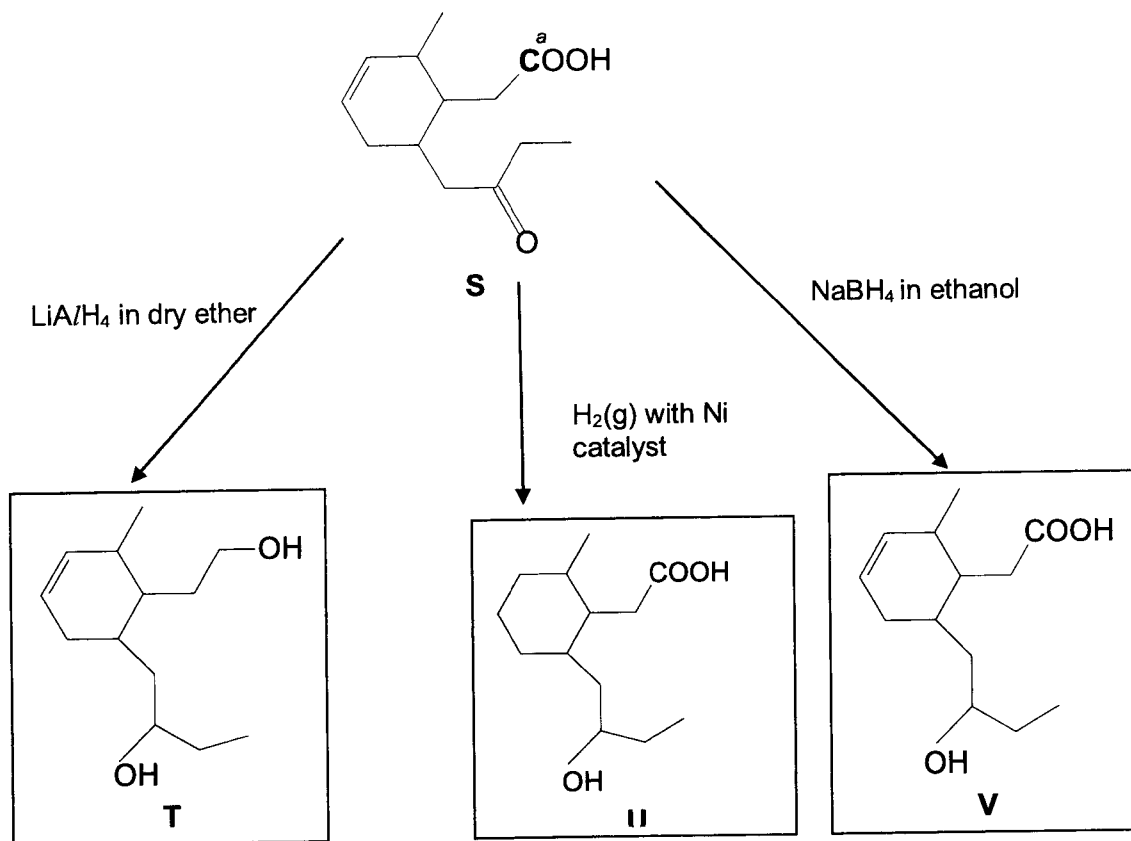
$$= \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \div \frac{[(\text{CH}_3)_2\text{NH}][\text{H}^+]}{[(\text{CH}_3)_2\text{NH}_2^+]} \quad [1] \text{ for this step or both } K_a \text{ expressions}$$

$$= K_a(\text{CH}_3\text{COOH}) \div K_a(\text{CH}_3)_2\text{NH}_2^+$$

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

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

(b) (i)



1 mark for each structure

- (ii) **Alkene** is not reduced by LiAlH<sub>4</sub>. **Alkenes are not electron deficient** and **do not attract/react with nucleophiles such as H<sup>-</sup>** from LiAlH<sub>4</sub>.  
 Or **Alkenes** are **electron rich** and **do not react with nucleophiles such as H<sup>-</sup>**. [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<sub>4</sub> is a strong reducing agent and can reduce nitriles, carbonyls, carboxylic acids, esters and amides but not alkenes.
- H<sub>2</sub>(g) with Ni catalyst can reduce alkenes, carbonyls and nitriles.
- NaBH<sub>4</sub> 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<sup>a</sup> in **S** = + 3  
 Oxidation number of C<sup>a</sup> 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<sup>a</sup> in **S** and **T**. Students are advised to draw out the atoms surrounding C<sup>a</sup> to be able to better assign the oxidation numbers.

[Total: 10]



5 (a) (i) rate =  $k_f[\text{Cl}_2]$  [1]

$$k_f[\text{Cl}_2] = k_r[\text{Cl}\cdot]^2$$

$$[\text{Cl}\cdot] = \sqrt{(k_f[\text{Cl}_2]/k_r)} \quad [1]$$

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• radicals.

(ii) rate =  $k_2[\text{Cl}\cdot][\text{CH}_4]$  [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 =  $k_2[\text{Cl}\cdot][\text{CH}_4]$   
 rate =  $k_2\sqrt{(k_f[\text{Cl}_2]/k_r)}[\text{CH}_4]$   
 =  $k[\text{Cl}_2]^{1/2}[\text{CH}_4]$  [1]

Order of reaction with respect to  $[\text{Cl}_2]$  is  $\frac{1}{2}$ .  
 Order of reaction with respect to  $[\text{CH}_4]$  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  $[\text{Cl}_2]$  is  $\frac{1}{2}$ . They either changed their working and gave a different rate equation or concluded that the order with respect to  $[\text{Cl}_2]$  is 1 or 2 instead. Please note that  $\frac{1}{2}$  order is common for reactions involving radicals.

(b) (i) Bond energy of Cl-Cl bond = 244 kJ mol<sup>-1</sup>

$$\text{Amount of energy to break one Cl-Cl bond} = \frac{244 \times 1000}{6.02 \times 10^{23}} = 4.053 \times 10^{-19} \quad [1]$$

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

$$\lambda = \frac{hc}{E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{4.053 \times 10^{-19}} = 4.907 \times 10^{-7} \text{ m} = 490.7 \times 10^{-9} \text{ m} = \underline{491 \text{ nm}} \quad [1]$$

Comments:

Many students did not understand the instructions in the question to find wavelength of light to break one 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 Cl-Cl 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<sub>3</sub> groups attached to the same carbon will give product A.

(ii) Ratio of monochlorinated products	<b>A</b>	:	<b>B</b>	:	<b>C</b>	:	<b>D</b>	
Based on number of H	6	:	1	:	2	:	3	
	x		x		x		x	
Based on relative rate	1	:	5	:	3	:	1	
Combined ratio	6	:	5	:	6	:	3	[1]
Ratio of monobrominated products	<b>A</b>	:	<b>B</b>	:	<b>C</b>	:	<b>D</b>	
Based on number of H	6	:	1	:	2	:	3	
	x		x		x		x	
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 monobrominated 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)  $\Delta H^\ominus = \Delta H^\ominus(\text{product}) - 2\Delta H^\ominus(\text{reactant})$   
 $= -167 - 2(103)$   
 $= -373 \text{ kJ mol}^{-1}$  [1]

Comments:

Most students successfully calculated the enthalpy change by using an energy cycle or the formula as shown.

However, some students incorrectly took  $\Delta H^\ominus(\text{reactant})$  to subtract  $\Delta H^\ominus(\text{product})$ , while some carelessly omitted the coefficient "2" for  $\Delta H^\ominus(\text{reactant})$  to account for the 2 mol of  $\bullet\text{C}_3\text{H}_7(\text{g})$  radicals.

- (ii)  $\Delta H^\ominus < 0$  as propyl free radical reacts to form a C–C bond, releasing heat energy and thus it is an exothermic reaction. [1]  
 $\Delta S^\ominus < 0$  as there is one less gaseous product than reactant ( $\Delta n = -1$ ), there are less ways to distribute particles and energies. There is decrease in disorderliness/the system gets more ordered and thus entropy change is negative. [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  $\Delta H^\ominus$  and a negative  $\Delta S^\ominus$  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  $\Delta H^\ominus$ ) and the decrease in number of gaseous molecules (for negative  $\Delta S^\ominus$ ). A common omission in the explanation of the negative  $\Delta S^\ominus$  is the concept of 'less ways to distribute particles and energies.' This is needed for a complete explanation.

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

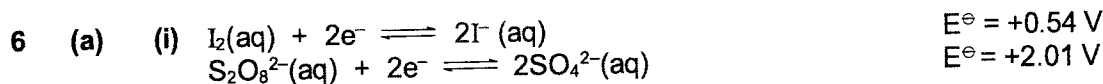
As temperature increases, the  $-T\Delta S$  becomes more positive and hence  $\Delta G$  becomes less negative. The reaction is less spontaneous at temperatures above 298 K. [1]

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  $\Delta G$  rather than a positive change. It has to be emphasized again that when referring to changes of  $\Delta G$ ,  $\Delta H^\ominus$  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]



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

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

**Comments:**

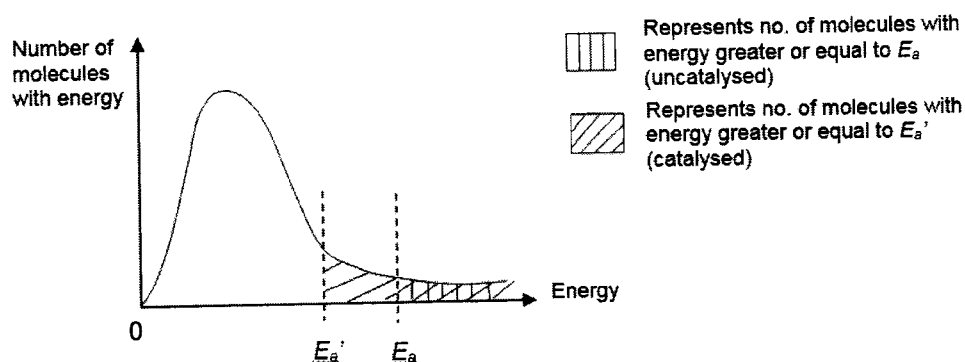
It is insufficient to only calculate the  $E_{\text{cell}}^\ominus$  value; one must explain the significance of the positive  $E_{\text{cell}}^\ominus$  value.

- (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:
  - axes correctly labelled,
  - correct shape of plot (starts at origin and tapering off at (but not touching) the x-axis) and
  - 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.





**ANDERSON SERANGOON JUNIOR COLLEGE****ASR 2022 JC 2 PRELIMINARY EXAMINATION SOLUTIONS  
WITH MARKERS COMMENTS**

NAME: \_\_\_\_\_ (      )

CLASS: 22 / \_\_\_\_\_

**CHEMISTRY****9729/03**

Paper 3 Free Response Questions

**16 September 2022****2 hours**

Candidates answer on the Question Paper.

Additional Materials:      Data Booklet

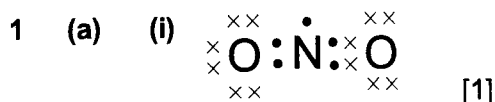
**READ THESE INSTRUCTIONS FIRST**

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!



(ii) bent,  $sp^2$  [1]

*Comments:*

(i) Many students did not know that in some molecules (eg  $\text{NO}_2$ ), the **total number of valence electrons is an odd number**. You can easily check by summing the total number of valence electrons before drawing the dot-and-cross diagram. In this case  $\text{NO}_2$  has  $5+6+6=17$  valence electrons. This means that there will be at least one unpaired electron in the molecule! You can see this in your Chemical Bonding lecture notes, Pg 20 for more example and details.



is incorrect as there are 9 electrons around N. N, in period 2, CANNOT expand octet. It will only have a maximum of 8 electrons.

(ii) In counting the number of bond pairs, each double bond or dative bond is counted as one bond pair. One lone electron is also counted as one lone pair as it also exerts repulsion, though less than a full 2-electron lone pair. This concept has been covered in our JC1 Chemical Bonding tutorial question 8!

When writing the hybridisation state such as  $sp^2$ , 'sp' is written in small letters and '2' is written in superscript (raised).

(iii) Bond length is the distance between the nuclei of the two atoms in the bond. [1]

(iv) The 2p orbital of N overlaps with the 2p orbital of the singly bonded O atom allows the lone pair of electrons on the O atom to be delocalised into the N=O bond. [1]

As a result, both the N–O bonds have partial double bond character. And the observed bond length is intermediate between a single and double bond. [1]

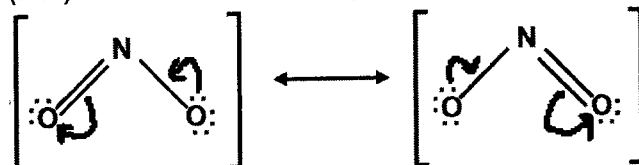
- Mention delocalization of electron pair of O into the N=O bond
- Leading to partial double bond character

*Comments:*

(iii) The words 'nuclei' and 'bond' are often missing.

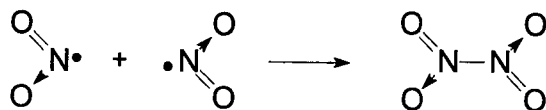
(iv) Many students attempted to explain the difference in bond length/bond strength of N=O and N–O instead of answering to the question on why the N–O in  $\text{NO}_2$  is intermediate between a single and double bond.

(FYI) Delocalisation of lone pair on O in N=O bond:





- (b) (i) Energy is released as a N-N covalent bond is formed using the single unpaired electron of each of the N atoms of two NO<sub>2</sub> radicals, thus forming N<sub>2</sub>O<sub>4</sub>.

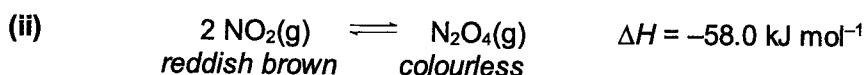


[1] mention energy released due to bond formation between 2 N atoms or it is N-N bond.

*Comments:*

Common misconceptions observed:

- N of one NO<sub>2</sub> radical forms a bond with O of another NO<sub>2</sub> radical
- The bond formed between N of one NO<sub>2</sub> radical and N of another NO<sub>2</sub> radical is dative
- Energy is absorbed during bond formation



As temperature increases from 273K, POE shifts to the left to decrease the temperature by absorbing the excess heat, favouring the endothermic reaction. } [1]

This POE shift is accompanied by increase in number of gaseous particles (2 vs 1), which contributes to increase in pressure. Hence the gradual increase in pressure as observed. } [1]

At temperature T, N<sub>2</sub>O<sub>4</sub>(g) has completely converted to NO<sub>2</sub> molecules. As temperature increases from T, the number of moles of NO<sub>2</sub> molecules does not change further. The pressure of the gaseous sample then increases proportionally with increase in temperature. } [1]

*Comments:*

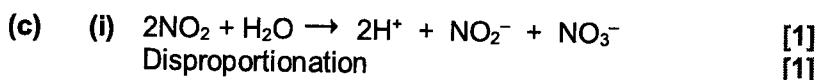
Some students did not apply the concept of Le Chatelier's Principle to the reversible reaction to explain the increase in pressure from 273 K to T K. It is insufficient to just write that position of equilibrium shifts left. The full explanation as above should be given in your answer.

Students did not realise that at temperature T, all the N<sub>2</sub>O<sub>4</sub> molecules has been converted to NO<sub>2</sub> molecules. The position of equilibrium lies fully to the right then and there is no further increase in the amount of gas particles

- (iii) Observation:  
 light brown/yellow gaseous mixture becomes darker brown, OR [1]  
 the colour of the gaseous mixture becomes darker brown

*Comments:*

*This part is well-done. As the question is about noting visible changes to the system, answers which discussed about the change to the gradient (or shape) of the graph or the pressure of the container were not accepted.*



**Comments**

While students showed confidence in cancelling out common terms to arrive at the correct equation, many incorrectly stated the equation as simply redox. Disproportionation is a more specific answer to this context as the same element (N) is both reduced and oxidised.

- (ii) TEA: catalyst as it is reacted/consumed in Step II and regenerated in Step IV. [1]  
 A: intermediate as it is produced/formed in in Step III and reacted in Step IV. [1]

State role + reason

**Comments:**

Good effort there in including the details of both species observed in the specific steps of the mechanism in relation to the roles.

Answers which explained that they have identified catalyst as it is chemically unchanged after the reaction or intermediate as it does not appear in the overall equation are not given credit as these answers do not clearly explain how the answer was derived based on the mechanism.

Ambiguous answers such as Stage II or Step 2 were accepted this time even though they differ from the labelling used by the question. Please be more mindful in A levels.

- (iii)  $(\text{HOCH}_2\text{CH}_2)_3\text{NH}^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{HOCH}_2\text{CH}_2)_3\text{N}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

$$\text{p}K_a = 14 - 6.23 = 7.77$$

$$\therefore K_a = 10^{-7.77} = 1.70 \times 10^{-8} \text{ mol dm}^{-3}$$

$$[\text{H}_3\text{O}^+] = \sqrt{(1.70 \times 10^{-8})(6.00 \times 10^{-2})}$$

$$= 3.19 \times 10^{-5} \text{ mol dm}^{-3} \quad [1]$$

$$\text{pH} = -\log(3.19 \times 10^{-5})$$

$$= 4.50 \quad [1]$$

**Comments:**

This question was badly done. Many students tried to solve in terms of  $K_b$  which will not work as F is an (conjugate) acid. Students should have solved in terms of  $K_a$  for this weak acid. Many students fumbled in this question evidently from their weird assumptions such as  $[\text{OH}] = [\text{F}]$  or  $[\text{F}] = [\text{TEA}]$ .

- (iv)

$$[\text{NO}_2]_{\text{av}} = \frac{(4.13 \times 10^{-3})(7.1 \times 10^{-2})}{(0.91 \times 10^{-4})(1.56 \times 10^{-5})(10 \times 24 \times 60 \times 60)}$$

$$= \underline{0.239 \mu\text{g m}^{-3}} \quad [1] \text{ for correct answer}$$

Since the  $[\text{NO}_2]_{\text{av}}$  is below / less than / does not exceed  $25 \mu\text{g m}^{-3}$ , the quality of air in terms of  $\text{NO}_2$  level is good / satisfactory / acceptable. [1] allow ecf

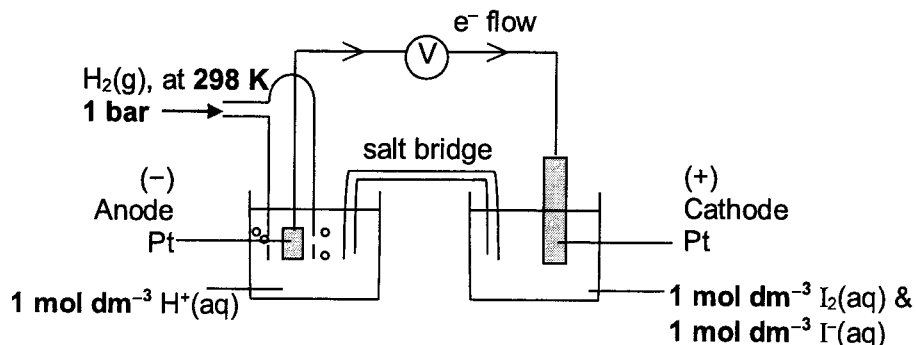
(accept words to the same effect)

**Comments:**

A handful of students struggled with the unit conversion from  $\text{cm}^2$  to  $\text{m}^2$ . Others who did not obtain full credit for this part often left out the basis on their comment on air quality.

[Total: 18]

2 (a) (i)



Category	Following must be correctly drawn and/or labelled. Any item missing/incorrect in each category will have the mark deducted.	Marks
1	Complete set of apparatus including: <ul style="list-style-type: none"> <li>• two separate half-cells (of which one is the Standard Hydrogen Electrode)</li> <li>• salt bridge</li> <li>• voltmeter</li> <li>• electrodes</li> </ul>	1
2	<ul style="list-style-type: none"> <li>• half-cells reactants</li> <li>• conditions (concentration of solutions, temperature, pressure)</li> <li>• choice of electrode material (usually Pt)</li> </ul>	1
3	<ul style="list-style-type: none"> <li>• direction of electron flow</li> <li>• label of cathode/anode</li> <li>• polarity of electrode</li> </ul>	1

where mistakes were made across the last two categories, only 1 out of the 2 marks was deducted if only one of the conditions was missing/incorrect in Category 2 and only one of the components in Category 3 is incorrect.

**Comments:**

*Almost all students attempted this question. The distinction is clear between students who revised and spent time remembering the set-up versus those who had very sketchy understanding. This is a giveaway 3 marks (almost the same as Electrochemistry tutorial question 3c) yet more than half lost it to carelessness or lack of effort.*

*The following components were commonly missed out by students:*

- Salt bridge
- labelling of temperature 298 K
- labelling of polarity of electrodes

*The following were often wrongly labelled by students:*

- labelling the electrode in  $I_2/I^-$  half-cell as  $I_2(s)$ . Iodine is NOT an electrical conductor! You cannot use it as an electrode!
- labelling temperature as 273 K. Common sense would have told you that water is frozen at 273 K. How do you even carry out the experiment with frozen ions?
- using  $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  without realising that that makes  $2 \text{ mol dm}^{-3} \text{ H}^+$  solution.
- Polarity of electrodes. This is electrochemical cell. The oxidation half-cell (anode) will produce electrons, resulting in build-up of negative charge on the electrode. The polarity is different from the anode in electrolytic cell!
- The worst mistakes did not include any SHE in the set-up at all and/or did not draw 2 separate half-cells.

- (ii)  $I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq) \quad E^\ominus = +0.54 \text{ V}$
- **$Ag^+$  will react with  $I^-$  to form a (yellow) precipitate ( $AgI$ ), so  $[I^-]$  decreases**
  - **Position of equilibrium shifts right to increase  $[I^-]$  [1] for both points including the above equilibrium**
  - Reduction reaction is favoured.  $E_{I_2/I^-}^\ominus$  becomes **more positive**, hence,  $E_{cell}^\ominus$  becomes **more positive** [1]

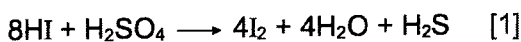
*Comments:*

*The question mentioned that "a few drops" of silver nitrate is added. Note that with such small amount added, it is not possible for the added silver or nitrate ions to be preferentially discharged since their concentration will be VERY LOW! As such, the reduction potential values given in the Data Booklet are not applicable since these ions have concentrations well below  $1 \text{ mol dm}^{-3}$ .*

*In fact, it is more common that when questions involve asking about addition of small amount of another reagent into a half-cell, it usually requires you to identify the component of the half-cell that reacts and how POE will shift.*

*Be more aware of the question types and answers required.*

- (b) O.N of iodine increased from -1 to 0  
O.N. of S decreased from +6 to -2. [1]



*Comments:*

*This is generally well done.*

*Students frequently missed out the oxidation states of sulfur. Others had problem balancing the equation. Please note that electrons should not appear in overall redox equation!*

- (c) (i)  $n(S_2O_3^{2-}) = \frac{21.85}{1000} \times 0.010 = 2.185 \times 10^{-4} \text{ mol}$
- $n(I_3^-)_{25\text{cm}^3} = 0.5 \times 2.185 \times 10^{-4} = 1.0925 \times 10^{-4} \text{ mol}$
- $I_3^- \equiv I_2$

$$[I_2(aq)] = \frac{1.0925 \times 10^{-4}}{\frac{25}{1000}} = 0.00437 \text{ mol dm}^{-3} \quad [1]$$

$$K_{pc} = \frac{[I_2(\text{organic solvent})]}{[I_2(aq)]}$$

$$93.8 = \frac{[I_2(\text{organic solvent})]}{0.00437}$$

$$[I_2(\text{organic solvent})] = 0.4099 \text{ mol dm}^{-3} [1]$$

$$n(I_2(\text{organic solvent})) = 0.4099 \times 15/1000 = 0.006148 \text{ mol}$$

$$\text{mass}(I_2(\text{organic solvent})) = 0.006148 \times (126.9 \times 2) = 1.56 \text{ g} [1]$$

*Comments:*

*Poorly done.*

*Students frequently got confused and assumed that the total volume is  $65\text{cm}^3$  but that would not be possible because it forms two separate layers.*

- (ii) Layer A (cyclohexane): Purple [1]  
 Layer B (water): Yellow / Yellow-Brown / Brown [1]

*Comments:*

*Poorly done. Colours of iodine in both aqueous and organic mediums are found in the data booklet. Many students mistaken that layer B is the organic layer although the question mentioned that water is denser of the two.*

- (iii) Iodine is non-polar and is able to form only intermolecular instantaneous dipole-induced dipole (id-id) interactions with cyclohexane and with water. The energy released is sufficient to overcome the id-id interactions between cyclohexane molecules and between iodine molecules but insufficient to overcome stronger intermolecular hydrogen bonds in water. [1]

*Comments:*

*Poorly done. Most students only identified that non-polar solutes can better dissolve in non-polar solvents. Poorer responses incorrectly identified the intermolecular forces of attraction or did not identify any at all.*

- (d) (i) O.S. of C = 0 [1]

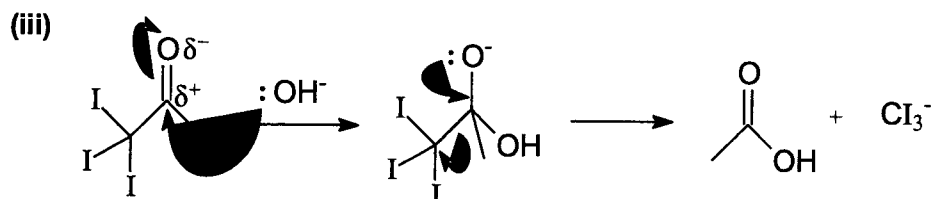
*Comments:*

*Poorly done. The carbon atom is bonded to two other carbon atoms with the same electronegativity. C is more electronegative than H and less electronegative than O, hence the oxidation state is 0.*

- (ii)  $2\text{OH}^- + \text{I}_2 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 \rightarrow 2\text{I}^- + 2\text{H}_2\text{O} + \text{CH}_3\text{COCH}_3$  [1]

*Comments:*

*Poorly done. Question has mentioned that propan-2-ol is oxidised to propanone via an alkaline medium.*



[1]: partial charges on carbonyl group, lone pair on hydroxide and curly arrows for first step

[1]: curly arrows, lone pair and charge on alkoxide, and generation of  $\text{CI}_3^-$

*Comments:*

*Poorly done. Many students are unclear as to how the electrons are supposed to move and are not precise with the placement of the arrows.*

*Further thinking question: Suggest why  $\text{CI}_3^-$  is considered a good leaving group.*

*Answer: It is a stable anion as the negative charge on carbon is dispersed by the three electron withdrawing iodine atoms.*

OR

*The negative charge is dispersed over a large anion, thereby stabilising  $\text{CI}_3^-$ .*

## (iv) Acid-base reaction [1]

**Comments:**

*Not well done. Candidates fail to recognise that ethanoic acid lost a  $H^+$  to  $Cl_3^-$  to form the products and thus is an acid-base reaction. Incorrect type of reaction such as nucleophilic substitution were proposed instead. Misconception that acid-base reaction is equal to neutralisation. Neutralisation is when an acid and a base react to form water and a salt and involves the combination of  $H^+$  ions and  $OH^-$  ions to generate water.*

(v) Ethanoyl chloride hydrolyses in water to produce  $HCl$ , which would react with the hydroxide ions required in Stages 3 and 4.

OR

Ethanoyl chloride hydrolyses in water to form ethanoic acid and is then unable to be oxidised further.

OR

$Cl^-$  is a much better leaving group than  $Cl_3^-$  in stage 3 and hence will not form  $CHI_3$  eventually.

1 mark for any reason above

**Comments:**

*Poorly attempted or not attempted. Poor answers often mention about the absence of the  $RCOCH_3$  structure in acyl chloride and thus unable to give a positive test. Wrong concepts such as the carbonyl carbon being bonded to an electronegative atom and is electron deficient, hence susceptible to nucleophilic substitution reaction were also often mentioned.*

[Total: 19]

- 3 (a) Add aq NaOH to each compound and heat.  
Cool the mixture and then add excess dilute HNO<sub>3</sub>.  
Add aq AgNO<sub>3</sub> and observe the colour of the ppt formed.

[1] for procedure

C<sub>2</sub>H<sub>5</sub>Cl – white ppt

C<sub>2</sub>H<sub>5</sub>Br – cream ppt

C<sub>2</sub>H<sub>5</sub>I – yellow ppt

[1] for correct colour of ppt

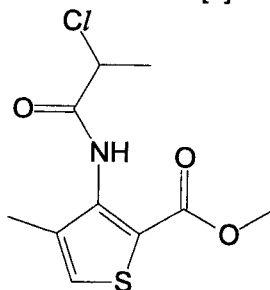
Note:

- annotate but not penalise if student chooses to indicate difference in rate of ppt formation.
- 'Cool' not marking point
- Do not accept "warm with ethanolic AgNO<sub>3</sub> and observe the colour of the ppt formed" because question said to use NaOH(aq).

**Comments:**

Most candidates know that aq NaOH and aq AgNO<sub>3</sub> were used but some missed out mentioning 'heat' and addition of 'HNO<sub>3</sub>' which are part of the procedure needed. Most candidates were also able to give the correct colour of the respective ppt expected. Poor answers include using the wrong chemicals or not mentioning the test as well as wrong colours of the ppt.

- (b) (i) **Structure of K** [1]



**step 2 reagent:** CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> [1]

**Comments:**

Candidates who are familiar with their organic reactions were able to give the correct structure of K and reagent in step 2. Some candidates fail to recognise that a propylamine is used in step 2 and wrongly proposed NH<sub>3</sub>.

- (ii) Cl atom of the acyl chloride (COCl) is more reactive/more readily substituted as it is bonded to a highly electron-deficient carbon/greater partial positive charge carbon which is attached to two strongly electronegative atoms, Cl and O as compared to only one electronegative Cl in the case for the C-Cl carbon. [1]

**Comments:**

Not well done and there were mixed up of concepts. Some candidates fail to recognise that the Cl atom of the acyl chloride is more reactive and even tried to apply acidity concepts to this question.

- (iii) N is less electronegative than O, lone pair of N is more readily delocalised into the carbonyl C=O group.

AND

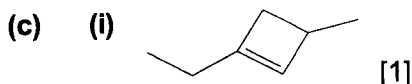
Thus the carbonyl carbon is less electron-deficient OR C-N bond in the amide has greater partial double bond character due to resonance,

and less susceptible to nucleophilic attack. [1]

Also accept inductive reason.

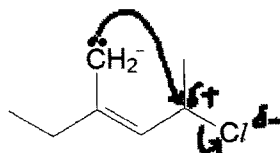
**Comments:**

*Not well done. Many candidates were not able to recognise that the differences in the rate of hydrolysis is due to carbon in ester being more electron deficient as it is bonded to the more electronegative oxygen. Wrong concepts such as acidity was again applied to this question.*



**Comments:**

*This question can be solved successfully if students have read the information given and applying their concept of nucleophilic substitution. The lone pair on the carbon anion would be the nucleophile to form the bond with the partial positive carbon of C-Cl bond, and hence displacing the Cl atom and forming compound G.*



*Most students were able to draw a cyclobutene ring structure with the ethyl side chain. However, some have placed the methyl side chain at the wrong position. There were some answers showing presence of Cl atom in G despite the molecular formula given.*



1 mark for arrow correctly shown on either structure

**Comments:**

*The resonance forms given in this question shows the delocalisation of the  $\pi$  electrons. Most students were able to draw a correct direction of the curly arrow to show the movement of the pair of  $\pi$  electrons though they are reminded to pay attention to where arrows should originate or end to show breaking and formation of bonds.*

*Students who drew the curly arrow from the positive charge clearly shows no understanding of what the curly arrow represents in organic mechanism. Some incorrect answers even showed a half arrow which represents movement of a single electron. Students may revisit a similar question in N2020 Paper 3 Q3(a)(i).*



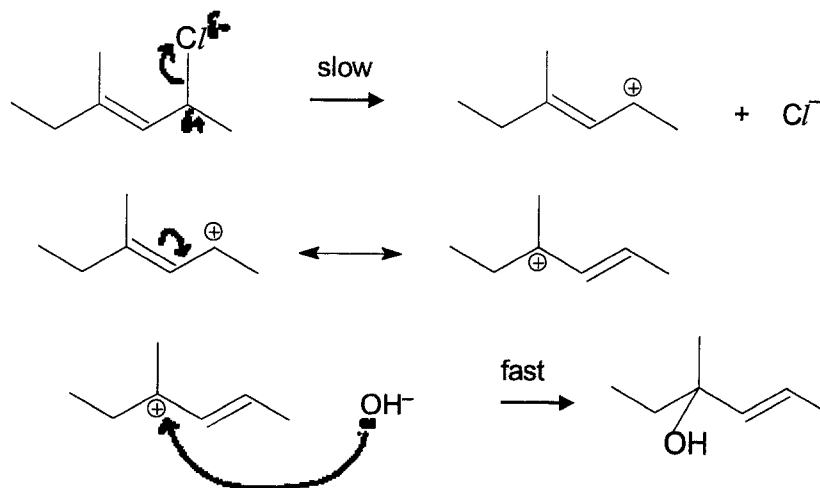
- (iii) The mechanism is  $S_N1$ . [1]

Reason (not required): A racemic mixture **H** is formed from the single enantiomer **E**, suggesting that the reaction occurs via a carbocation intermediate.

*Comments:*

Majority of the students were able to deduce the correct mechanism based on the evidence of the formation of a racemic mixture from the single enantiomer **E**. The recognized convention to write  $S_N1$  is with the capitalized 'N' as subscript, and not 'Sn1' as many students have carelessly written.

- (iv)  $S_N1$  mechanism



[1] for correct first slow step (including curly arrow, partial charges on C-Cl bond and formation of the correct carbocation and chloride anion.)

[1] for resonance structures of intermediates

[1] for correct fast step (curly arrow from lone pair of Nu: to the positive charge of the tertiary carbocation, correct structure of product.)

*Comments:*

Many students find this application question challenging.

Some students showed an understanding of the  $S_N1$  mechanism, showing correct Step 1 but the carbocation in Step 3 (and hence the product) was incorrect as they did not apply the concept of resonance of the allylic carbocation for Step 2.

The question has hinted to reference to information given in (c)(ii). To get full credit, answers must show the resonance of the allylic carbocation. Partial credit was given to some who attempted and managed to get Step 1 correct. Many answers which would have been correct for Step 1 omitted the chloride anion. No credit was given for this omission.

A handful of students drew an incorrect structure with an extra carbon (showing two -  $CH_3$  groups) after the substitution of Cl in Step 1. These students are advised to check their understanding of skeletal structures again.

- (v) Nucleophile,  $OH^-$ , uses its lone pair of electrons to attack the electron-deficient carbon 180° away from the departing halogen atom, Cl. Hence there is an inversion of configuration at the reactive carbon. [1]

*Comments:*

This question is a textbook concept but students were careless in their explanations. The answer must clearly explain:

- which atom the nucleophile would attack,
- the direction that it approaches this atom, and

- the idea of a leaving group.

Some answers incorrectly identified the carbon being attacked as the 'carbocation' which is not present in a  $S_N2$  mechanism. A careless mention of 'attack from the back' is not sufficient.

(d) (i) Words to a similar effect:

- availability of lone pair on the N atom in the amine product that allows further nucleophilic substitution in the presence of excess RX.

Suggested answer:

In the presence of excess  $C_2H_5Br$ , ammonia forms the primary amine product ( $C_2H_5NH_2$ ) which has a lone pair on the N atom which can also act as nucleophile to attack another molecule of  $C_2H_5Br$  via further nucleophilic substitution. Further substitutions of the secondary amine and subsequent tertiary amine products occur due to the availability of the lone pair on the N atom until the QAC is formed, where there is no lone pair on the N atom to act as nucleophile for further substitution.

Comments:

This question tests on the understanding of further nucleophilic substitution which students have encountered in the topic of Halogenoalkanes.

Many students were not too clear how the reaction occurs, often mistaken the nucleophile in further substitutions to be  $NH_3$ , rather than the amine product from the first substitution.

Some answers gave lengthy explanations of the electron donating alkyl groups which made better nucleophiles but failed to clearly identify the **availability of lone pair of electrons in the amine products** that act as nucleophile to justify **WHY** further substitution can even occur.

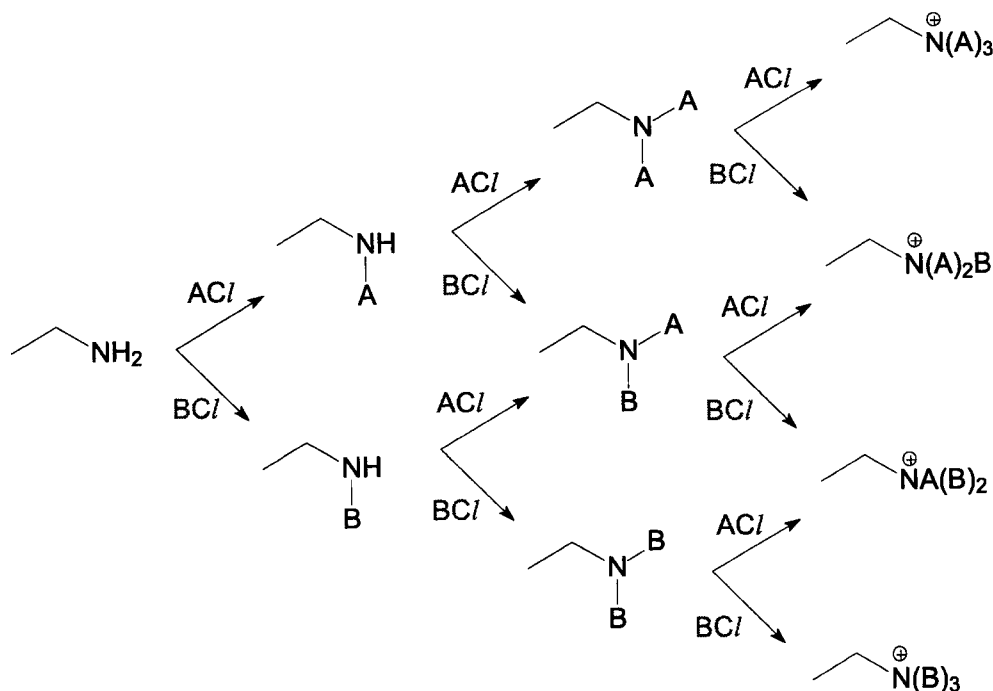
(ii) 4

Thinking process:

Let A be butyl group, B be benzyl

3 further substitutions of either A or B can occur on N atom of ethylamine.

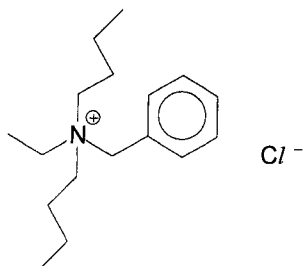
The following combinations are possible: AAA, AAB, ABB, BBB



Comments:

This seemingly easy question on the concept of further substitution proved challenging for many students. Students may use the above suggested thinking process to help deduce the possible products.

(iii)

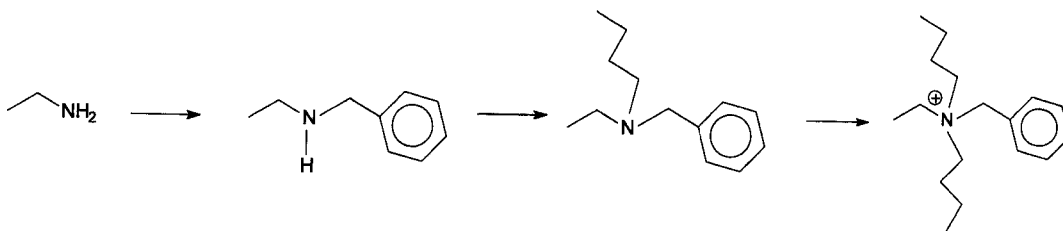


[1] for correct compound

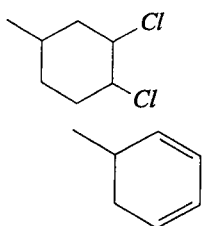
[1] for correct skeletal formula

Comments:

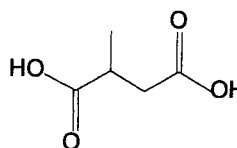
Poorly attempted with only a handful got the right answer. The correct QAC of  $\text{CH}_3\text{CH}_2\text{NH}_2$  can be formed as shown.



(e)



L



M

N

[1] for each structure

Information	Type of reaction	Deduction
L is a chlorocycloalkane, $\text{C}_7\text{H}_{12}\text{Cl}_2$	-	(L has a ring structure)
Heating L with ethanolic KOH, compound M, $\text{C}_7\text{H}_{10}$ , is formed as the only product.	Elimination [✓]	Elimination of 2 HCl from L indicates M contains two alkene groups C=C. [✓]
Treating with hot acidified $\text{KMnO}_4$ , M forms an optically active compound N,	Strong oxidation/Oxidative cleavage of alkene[✓]	• Loss of 2 carbons shows both alkene groups in M is oxidized to form two $\text{CO}_2$ and N upon strong

$C_5H_8O_4$ , as the only organic product		oxidation. [✓] • <b>N</b> contains a <u>chiral carbon</u> . [✓]
<b>N</b> does not react with 2,4-DNPH but liberates $CO_2$ from $Na_2CO_3(aq)$ .	<u>Acid-base</u> (reaction with $Na_2CO_3$ ) [✓]	• No reaction with 2,4-DNPH shows <b>N</b> has <u>no ketone group</u> (alkene in <b>M</b> does not have $R',RC=$ structure). [✓] • Reaction with $Na_2CO_3$ shows <b>N</b> contains carboxylic acid, its formula with 4 O atoms suggests <u>two <math>CO_2H</math></u> , present. [✓]

7 to 8 points – 3 marks

5 to 6 points – 2 marks

2 to 4 points – 1 mark

#### Thinking process

Since there are 2  $-CO_2H$  group in **N**, the remaining 3 C atoms connecting the dioic acid can be straight or branched chain ( $-CH_2-CH_2-CH_2-$  vs  $-CH(CH_3)-CH_2-$ ). In order for **N** to be optically active, the 3 C atoms have to be branched to get a chiral C. Hence **N** must be  $HO_2CCH(CH_3)CH_2CO_2H$ .

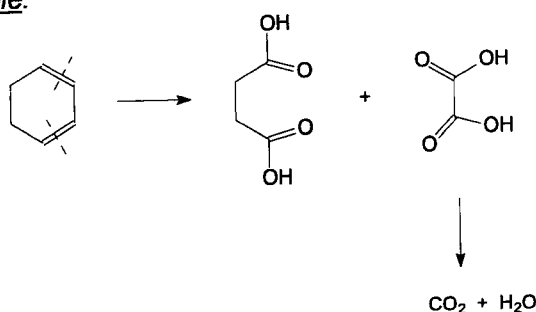
#### Comments:

Common mistakes include:

1. Overlooked the fact that **L** is a saturated cyclic compound and incorrectly deduced an aliphatic (open) chain with double bonds for **L**.
2. Did not accurately conclude from the molecular formula that two HCl molecules are eliminated from **L** to form two  $C=C$  bonds in **M** (a diene).
3. Did not realize that the fact that **M** is the only elimination product formed would imply that there is only one way to remove the two HCl molecules from **L**. So, the two Cl atoms are adjacent to each other on **L** as there will be more than one possible **N** if Cl are placed apart.
4. Read the question wrongly as **M** is optically active instead of **N**.
5. Did not highlight that the oxidation using acidified  $KMnO_4$  as strong oxidation or oxidative cleavage.
6. Did not show understanding that oxidative cleavage of a cyclic diene will produce 2 aliphatic open chain compounds. Many incorrectly deduced that there are terminal alkene groups present in **M**.

Note: The two aliphatic compounds formed are either ketones or compounds, cannot be aldehydes.

#### Example:



7. Not many noted that oxidative cleavage of M formed only one product N implied that the other oxidised compound is  $\text{CO}_2$ . Based on (6), it is  $\text{H}_2\text{CO}_2\text{H}$  ethanedioic acid which undergoes further oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .
8. Although many correctly deduced that N has chiral carbon, they did not use this knowledge to write the structure of N. Also, many did not make use of the molecular formula to conclude that N is a chiral, 5-carbon dicarboxylic acid.

Overall, the question was poorly done. To improve, students must practice more structural elucidation questions to sharpen their thinking skills. All are advised to revise the different organic chemistry mechanisms thoroughly so the type of reactions mentioned in such questions can be identified correctly.

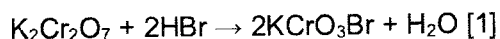
[Total: 23]

4 (a) (i)

	K	Cr	Br	O
No. of moles	$\frac{17.9}{39.1} = 0.4578$	$\frac{23.7}{52} = 0.4558$	$\frac{36.5}{79.9} = 0.4568$	$\frac{21.9}{16} = 1.369$
Simplest ratio	1	1	1	3

Empirical formula of **A** =  $\text{KCrO}_3\text{Br}$  (accept  $\text{KCrBrO}_3$ ) [1]

mass of empirical formula = 219.0  
therefore,  $n=1$

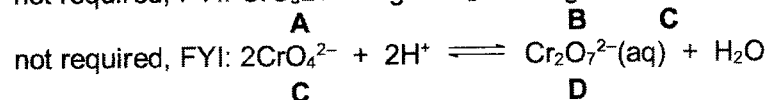


*Comments:*

*The method shown in the answer is especially useful if the question is asking to state the empirical formula, followed by the formula of A (also note that it is not molecular formula as A is not a molecule).*

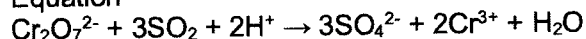
- (ii) Cream coloured ppt is **B** is silver bromide,  $\text{AgBr}$   
Yellow solution **C** contains  $\text{CrO}_4^{2-}$  (ignore cation if stated)  
Orange solution **D** contains  $\text{Cr}_2\text{O}_7^{2-}$   
**E**,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (accept  $\text{Cr}^{3+}$ )  
[2] 1 mark for any two unknowns **B, C, D, E**

not required, FYI:  $\text{CrO}_3\text{Br}^- + \text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{AgBr} + \text{CrO}_4^{2-} + 2\text{H}^+$

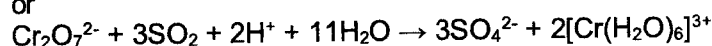


**D** undergoes redox reaction with  $\text{SO}_2$  to form **E** [1]

Equation



or



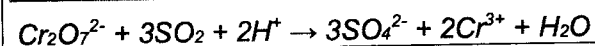
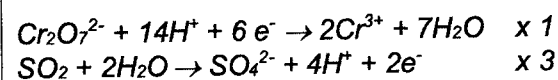
[1] type of reaction for the formation of solution **E** from solution **D**  
[1] balanced equation

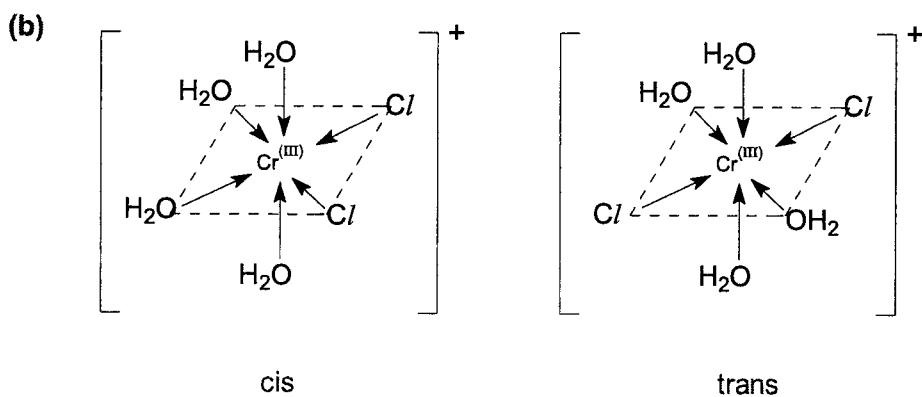
*Comments:*

*Many students wrote "reduction" without any indication if it is **D** or **E** or  $\text{SO}_2$  that was reduced. Some students incorrectly wrote it as **D** is reduced from **E**.*

*As for the balanced equation, do remember there should not be any electrons appearing on either side of the arrow.*

*The 2 half equations can be obtained from the Data Booklet:*



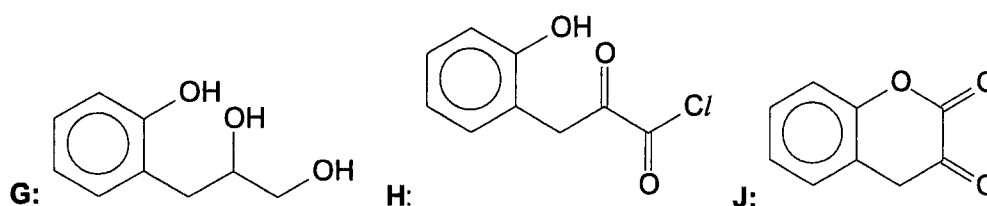


[1] for each isomer

**Comments:**

Many students did not draw the octahedral shape and hence could not show how the cis and trans isomer will look like. They also forgot to include the "III" on Cr, or the charge outside the square bracket, or the arrows were drawn pointing towards the ligands which is incorrect. Some students wrote the negative charge on the Cl even though there was an overall charge already indicated outside the square brackets.

(c) (i)

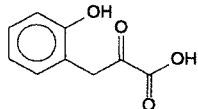


1 mark each

**Comments:**

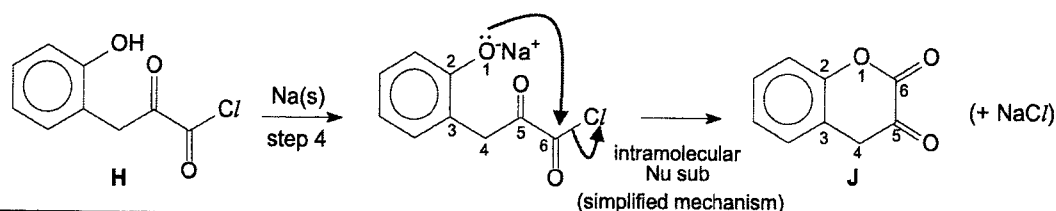
Most students could draw the structures for G and H, but could not determine the structure of J.

To work out the structure for G, we observe that the molecular formula in step 1 increased by 2H and 2O atoms (from  $C_9H_{10}O$  to  $C_9H_{12}O_3$ ) so likely the alkene group has undergone mild oxidation to form a diol (2 -OH groups added). Looking at the product of step 2 also shows that the alkene group is no longer present, and in place of the alkene, a ketone and a carboxylic acid are formed. Oxidation of the secondary and primary alcohols in G will give these two functional groups. Only the carboxylic



acid group in reacts with anhydrous  $PCl_5$  to form the acid chloride in H. Phenol group does not react with  $PCl_5$  as the C-O bond of the phenol group has partial double bond character due to resonance and do not participate in nucleophilic substitution reactions.

Addition of Na(s) causes a redox reaction with the phenol group in H, to form a phenoxide ion (a stronger nucleophile than phenol), which then undergoes intramolecular nucleophilic acyl substitution reaction with the acid chloride group, forming cyclic compound J.



- (ii) Step 1:  $\text{KMnO}_4$ , dilute  $\text{H}_2\text{SO}_4$ , cold [1]  
 Step 2:  $\text{K}_2\text{Cr}_2\text{O}_7$ , dilute  $\text{H}_2\text{SO}_4$ , heat under reflux [1] (cannot accept  $\text{KMnO}_4$ )  
 Step 3:  $\text{NaBH}_4$  (in methanol/ethanol), r.t./  $\text{H}_2$  with Ni, heat /  $\text{H}_2$  with Pd/Pt, r.t.p.[1]

**Comments:**

Many students could give the correct reagent and condition for step1 but had more trouble with steps 2 and 3.

**Common errors:**

**Step 1**

Use  $\text{K}_2\text{Cr}_2\text{O}_7$ . Alkenes can only be oxidised by  $\text{KMnO}_4$   
 Use heat under reflux instead of cold for mild oxidation

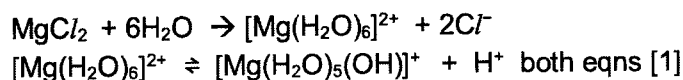
**Step 2**

Use  $\text{KMnO}_4$ . Note that the presence of benzylic hydrogen in G will cause side-chain oxidation to occur.

**Step 3**

Using  $\text{LiAlH}_4$ . The ester group present in J will be reduced by  $\text{LiAlH}_4$ .

- (d) (i) Due to the small cationic size and a large positive charge, and hence a high charge density of  $\text{Mg}^{2+}$ . After dissolving, the hydrated magnesium ion undergoes slight hydrolysis[1] to form a slightly acidic solution of pH 6.



**Comments:**

Many students could explain the pH value in terms of the hydrolysis of  $\text{Mg}^{2+}$  but fewer students explained hydrolysis occurred due to the high charge density of  $\text{Mg}^{2+}$ . Quite a number of students wrote an incorrect equation where both  $\text{Mg}(\text{OH})_2$  or  $\text{MgO}$  and  $\text{HCl}$  were formed as products together.

- (ii)  $n\text{MgCl}_2 = \frac{1}{2} \times n\text{NaOH} = \frac{1}{2} \left( \frac{20}{1000} \times 1.00 \right) = 0.0100 \text{ mol}$   
 $[\text{MgCl}_2] = \frac{1000}{50} \times 0.0100 = 0.200 \text{ mol dm}^{-3}$  [1]

**Comments:**

Most students who attempted scored the mark here. Most common errors were to use the wrong volume of  $\text{NaOH}$  or the wrong mole ratio ( $n\text{MgCl}_2 = n\text{NaOH}$ ) for calculations.

- (iii)  $\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2 \text{ [1]}$$

**Comments:**

Most students scored the mark here, though a few wrote the expression wrongly in terms of soluble  $\text{MgCl}_2$  instead. A handful also wrote the  $K_c$  expression for the reaction of  $\text{MgCl}_2$  with  $\text{NaOH}$  as the answer.



(iv) pH = 9 when 10 cm<sup>3</sup> of NaOH was added

$$[\text{OH}^-] = 10^{-(14-9)} = 1.00 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{Mg}^{2+}] = \frac{1}{2} (0.200) = 0.100 \text{ mol dm}^{-3} \text{ both conc [1]}$$

$$K_{sp} = (0.100)(1.00 \times 10^{-5})^2 = 1.00 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9} \text{ [1] for correct value.}$$

*Comments:*

*This question was poorly done.*

*Students need to be able to see the similarities in the typical acid-base titration graph that they are familiar with and apply to this new context (e.g. in this graph, at 20 cm<sup>3</sup> of NaOH, all the MgCl<sub>2</sub> has been reacted away similar to equivalence point in acid-base graph).*

*To find the K<sub>sp</sub> value, we need to use the information given in the question including the information from Fig 4.2.*

*When 10 cm<sup>3</sup> of NaOH was added,*

- *the [Mg<sup>2+</sup>(aq)] halved as some Mg<sup>2+</sup>(aq) is precipitated as Mg(OH)<sub>2</sub>.*
- *the pH of the solution is 9 (from Fig. 4.2) due to the [OH<sup>-</sup>] present from the equilibrium: Mg(OH)<sub>2</sub>(s) ⇌ Mg<sup>2+</sup>(aq) + 2OH<sup>-</sup>(aq)---eqm 1*

*Common errors:*

- *Halving the [Mg<sup>2+</sup>] calculated from (d)(ii) and using mole ratio to determine [OH<sup>-</sup>]. This method is not valid since [Mg<sup>2+</sup>(aq)] present in the solution comes from both the MgCl<sub>2</sub> remaining and the Mg<sup>2+</sup>(aq) from the eqm 1.*
- *Finding the [OH<sup>-</sup>] in the solution by taking nNaOH added / total volume. This method is incorrect as the 10 cm<sup>3</sup> of NaOH added is the limiting reagent and would have all reacted to form Mg(OH)<sub>2</sub>. So the amount of OH<sup>-</sup> present is due to partial solubility of the Mg(OH)<sub>2</sub> formed.*
- *Incorrectly reading the graph or taking pH = 9 to be pOH to calculate [OH<sup>-</sup>].*

[Total: 20]

- 5 (a) NaCl dissolves in water but will not hydrolyse in it thus forming a neutral solution of pH 7.  
 $\text{NaCl (s)} + \text{aq} \rightarrow \text{Na}^+ (\text{aq}) + \text{Cl}^- (\text{aq})$  (no need to write this equation)

$\text{SiCl}_4$  undergoes complete hydrolysis in water to produce very acidic solutions of pH 1–2.  
 $\text{SiCl}_4 (\text{l}) + 4 \text{H}_2\text{O} (\text{l}) \rightarrow \text{SiO}_2 \cdot 2\text{H}_2\text{O} (\text{s}) + 4 \text{HCl} (\text{aq})$

correct equation for  $\text{SiCl}_4$  [1]  
 both correct pH [1]  
 both descriptions [1]

*Comments:*

*Most students were clear that NaCl only undergoes hydration (that is dissolves) in water to form a neutral solution. A handful however thought that NaCl in water formed both NaOH and HCl, that is why the solution is neutral!*

*The complete hydrolysis of  $\text{SiCl}_4$  is familiar to many, and strong students explained the presence of empty low-lying 3d orbitals in Si which can accept the lone pair of electrons from water for hydrolysis to occur (not required to explain). A few students, though, gave incorrect explanations about the high charge density of  $\text{Si}^{4+}$ , wrote equations involving the hydration of covalent  $\text{SiCl}_4$  to form ions or wrongly stated that  $\text{SiCl}_4$  was insoluble in water so pH = 7.*

*The terms 'dissociate' and 'hydrolysis' are not the same.  
 dissociate – separation of ions (similar to hydration)  
 hydrolysis – breaking of a covalent bond in a molecule using water*

- (b) (i) 3  $\sigma$  bonds and 4  $\pi$  bonds [1]  
 $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}$

*Comments:*

*Most students answered this question correctly. Drawing out the structure of cyanogen will help students to see the 3  $\sigma$  bonds (1 in each  $\text{C} \equiv \text{N}$  bond and in the C-C bond) as well as the 4  $\pi$  bonds (2 in each  $\text{C} \equiv \text{N}$  bond).*

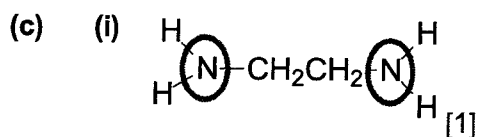
- (ii) Step 1:  $\text{Br}_2(\text{l})$  or  $\text{Cl}_2(\text{g})$  in  $\text{CCl}_4$  [1]  
 Step 2: (Excess)  $\text{NH}_3$  in ethanol, heat in sealed tube [1]

intermediate:  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl} / \text{Br}-\text{CH}_2-\text{CH}_2-\text{Br}$  [1]

*Comments:*

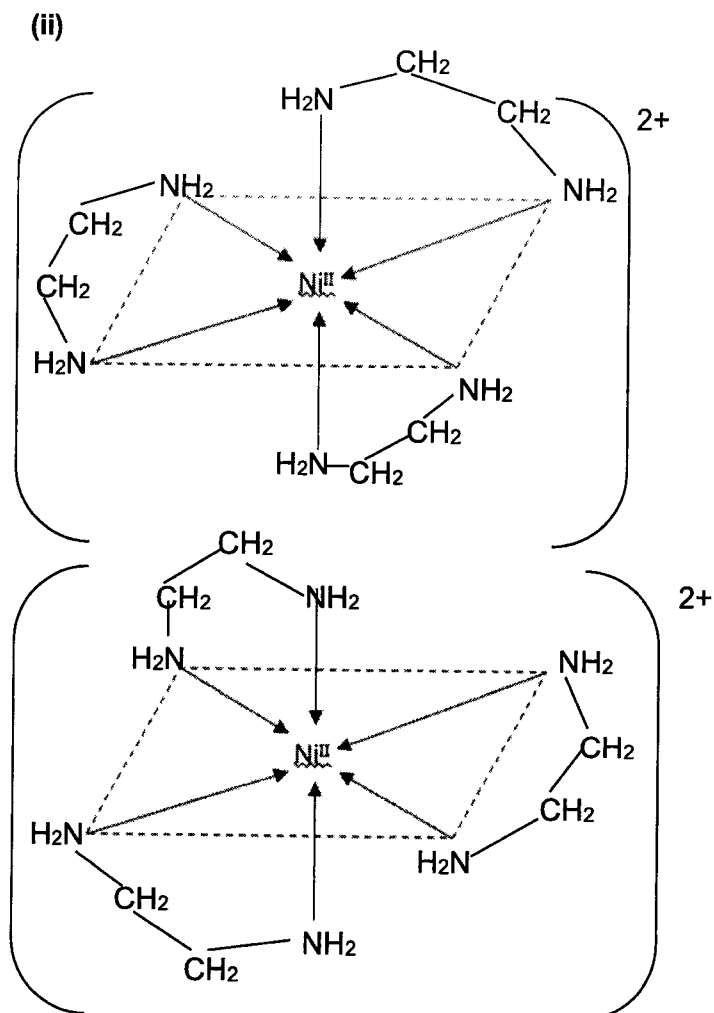
*Students recognised that they should carry out electrophilic addition of halogen on ethene, then substitute the added groups with  $-\text{NH}_2$  groups to form ethylenediamine. Many students chose to form a diol by carrying out mild oxidation of ethene but did not realise that there is no reaction for the conversion of alcohols to amines directly. Use of  $\text{Br}_2(\text{aq})$  for step 1 was not given credit as this would form a bromohydrin instead (Br and OH groups added across the  $\text{C}=\text{C}$ ).*

*Students must be more careful about including solvents like  $\text{CCl}_4$  and ethanol for the reagents and conditions. It is important in step 2 for the reaction mixture to be heated in a sealed tube (not under reflux) to prevent the escape of ammonia gas.*



Comments:

The formula for ethylenediamine is given in (b) but there were students who drew the structure wrongly.



[1] for either structure

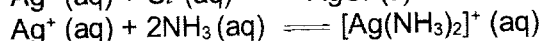
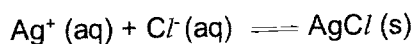
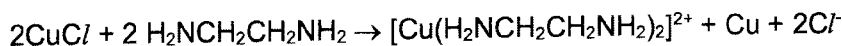
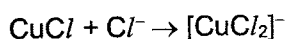
(iii) Enantiomerism [1]

1 mark for correct mirror image of the answer in (ii) shown.

Comments:

Students must understand from (i) that ethylenediamine is a bidentate ligand. Since there are 3 ethylenediamine ligands in  $[\text{Ni}(\text{en})_3]^{2+}$ , there will be 6 dative bonds formed and the complex will thus have an octahedral shape. Several students forgot to indicate the overall charge of the complex outside the square brackets.

- (iv) Q :  $[\text{CuCl}_2]^-$   
 R:  $[[\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$  (or  $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2$ )  
 S: Cu metal  
 T: AgCl

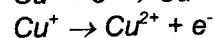
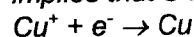


1 mark each for equations for each reaction  
 2 marks for the 4 unknowns Q, R, S, T

*Comments:*

As **Q** has a linear shape and contains Cu and Cl only, this implies that it is  $\text{CuCl}_2^-$  (2 dative bonds  $\Rightarrow$  linear shape)

As  $\text{CuCl}$  reacts with ethylenediamine to form a blue solution **R** and a pink solid **S**, this implies that **S** is  $\text{Cu}$  and a disproportionation reaction has occurred.



Since **R** contains only ethylenediamine and has a square planar shape, this implies that a complex between  $\text{Cu}^{2+}$  and ethylenediamine is formed. As ethylenediamine is a bidentate ligand and a square planar complex is formed, this implies that two ethylenediamine ligands formed 4 dative bonds to  $\text{Cu}^{2+}$ .

- (d) (i) The amount of heat absorbed or evolved when one mole of a solute is dissolved in an infinite volume of water under the standard conditions of 298 K and 1 bar. [1]

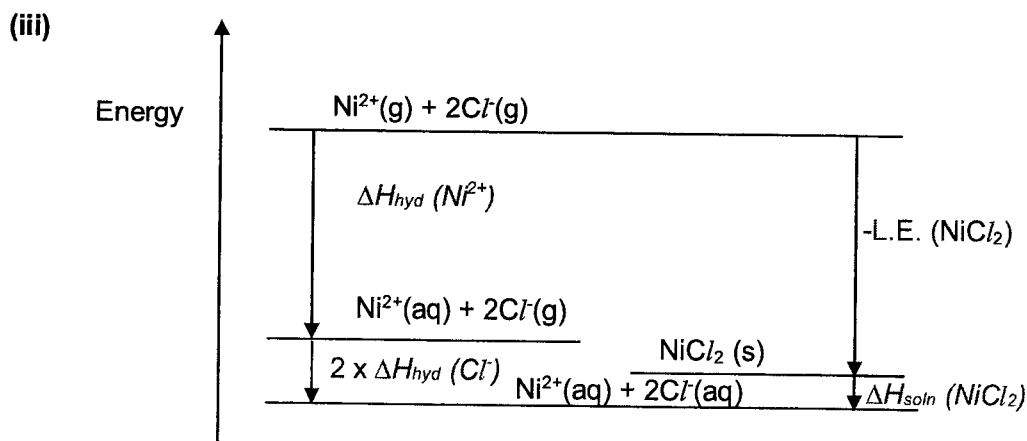
*Comments:*

The majority had problem remembering the full definition correctly.

- (ii)  $\Delta H_{\text{soln}} (\text{NiCl}_2) = -(-2753) + (-2096) + 2(-381) = -105 \text{ kJmol}^{-1}$   
 Correct value of  $\Delta H_{\text{soln}} (\text{NiCl}_2)$  [1]

*Comments:*

Most who attempted were unable to remember or apply the formula correctly. Note that  $\Delta H_{\text{soln}} = -LE + \Delta H_{\text{hyd}}$



Energy cycle [2]

- all energy changes present  
(any enthalpy change or energy level missing = 0 marks)

For complete energy cycles,

- balanced eqn
- correct direction of arrows
- state symbols
- correct labelling of energy changes

any component missing or made mistake deduct 1 mark

any three components missing or made mistakes deducts both marks

*Comments:*

*Construction of the energy level diagram proved challenging for those who are not familiar with the enthalpy change definitions.*

*Please note that direction of arrows should also be consistent with the sign of the enthalpy change. Arrows should point down if the enthalpy change is negative. Adjust the relative energy levels of the substances accordingly.*

[Total: 20]



1

## 2022 H2 Chemistry Prelim Paper 4 Marks Scheme with Markers' Comments

1 Determination of a value for an enthalpy change of solution

mass of capped bottle / weighing bottle and FA 1 / g	9.514
OR mass of capped bottle and residual FA 1	
OR mass of weighing bottle with residue	5.519
OR mass of weighing bottle after transfer / g	
mass of FA 1 used / transferred / g	3.995

3

(b)(iii)

$$T_{av} = \frac{(25 \times 31.2) + (50 \times 27.6)}{(25+50)} = 28.8 \text{ } ^\circ\text{C}$$

(b)(iv)

$$\begin{aligned} \text{heat change } (q_2) &= mc\Delta T \\ &= (25+50) \times 1.00 \times 4.18 \times (|28.1 - 28.8|) \\ &= 219.45 \text{ J} \end{aligned}$$

$$n(\text{NaHCO}_3) = \frac{50}{1000} \times 1.00 = 0.050 \text{ mol}$$

$$\begin{aligned} \Delta H_2 &= + \{(219.45 / 0.050)\} \times 2 \\ &= + 8778 \\ &= + 8780 \text{ J mol}^{-1} \text{ or } + 8.78 \text{ kJ mol}^{-1} \end{aligned}$$

Final answer to 3 s.f. and appropriate units for (b)(i), (b)(ii), (b)(iii), (b)(iv).

1  
1

Comments:

(b)(i): Instead of using the information given that the density of the solution is  $1.00 \text{ g cm}^{-3}$ , giving the mass,  $m$ , of solution as 25 g, many students made the mistake of adding the mass of the solid to 25. Some even made the mistake of using the mass of the solid rather than the mass of the solution. A few students were still making the mistake of adding '273' to temperature change.

(b)(ii): Most students were unable to score this mark. Common mistakes include:

- Did not realise that the value of  $\{(q_1) / n(\text{NaHCO}_3)\}$  gives the heat absorbed for only 1 mol of  $\text{NaHCO}_3$  used, while  $\Delta H_2$  is the enthalpy change of the reaction (per balanced equation) for 2 mol of  $\text{NaHCO}_3$ , hence the necessity to multiply by 2.
- Did not recognise the endothermic reaction (temperature dropped) and incorrectly giving a negative sign to  $\Delta H_2$ .
- Dividing the heat change by the  $M_r$  instead of the number of moles of solid used.
- Wasting time to determine the limiting reagent when it was given in the question stem that 'the sulfuric acid is in excess'. Students should read questions carefully to avoid unnecessary waste of time.

(b)(iii): Most students correctly calculated the average initial temperature using the formula given.

(b)(iv): Similar errors were made in this part as in (b)(ii). Another common error made here was in using the wrong volume of 25 or 50  $\text{cm}^3$  instead of the total volume of reaction mixture which is 75  $\text{cm}^3$ . Some students did not make use of the  $T_{av}$  they have correctly calculated to find  $\Delta T$ , not understanding the purpose of the calculation in (b)(iii).

1 Accuracy

$T_i / ^\circ\text{C}$	29.4
$T_m / ^\circ\text{C}$	21.0
$\Delta T / ^\circ\text{C}$	8.4

• May record data in a single table or have one table for mass and one table for temperature

[1]: correct headers and units.

[1]: mass readings to 3 d.p. and temperature readings to 1 d.p.

[1]: correctly determined maximum temperature change and mass of FA 1 used

Accuracy

2

Comments:

The majority of students presented their data clearly. It is more accurate to describe the mass after reweighing as 'mass of weighing bottle with residue' than to describe as 'mass of empty bottle' as there might not be complete transfer of all solids into the cup. It was disappointing that some students were still recording mass to 2 d.p. instead of 3 d.p., and surprisingly some students did not realise something must be amiss when the mass of the bottle they measured was less than 1.000 g! Students should have a judgement of the magnitude of the quantity they are measuring and make corrections if necessary.

Students could have used the notations ( $T_i$ ,  $T_m$ ,  $\Delta T$ ) given for the various temperatures measured in their tabulation instead of giving long descriptions. Descriptions of 'final' or 'maximum' temperature were not accepted as the temperature dropped in this experiment. Majority was able to score the accuracy marks.

(b)(i) Calculate heat change using result from 1(a)

1

$$\begin{aligned} \text{heat change } (q_1) &= mc\Delta T \\ &= (25 \times 1.00) \times 4.18 \times (\text{temp drop}) \\ &= \text{_____ J} \end{aligned}$$

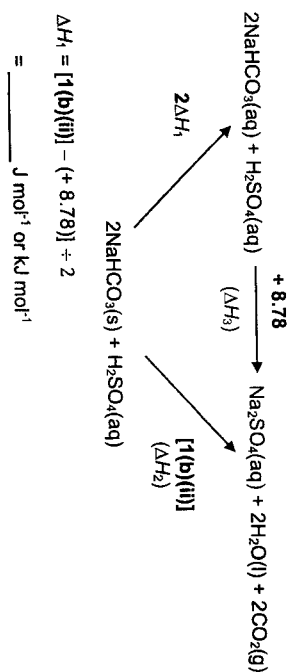
Ignore sign

$$\Delta H_2 = + \{(q_1) / n(\text{NaHCO}_3)\} \times 2$$

1

$$= + \text{_____ J mol}^{-1} \text{ or kJ mol}^{-1} \text{ with correct sign}$$

(c)



or  
 $\Delta H_1 = [x - (+8.78)] \div 2$

or  
 $\Delta H_1 = [x - y] \div 2$

[1]: correct application of Hess' Law  
 [1]: correct answer; awarded only if 1(b)(ii) and 1(b)(iv) applied correctly

**Comments:**  
 Many students attempted this part using the most straightforward method of drawing an energy cycle.  
 However, many were not careful in balancing the species in the cycle and not multiplying  $\Delta H_1$  by 2, leading to an incorrect value for the calculated  $\Delta H_1$ .  
 Students need to revisit their concepts in Energetics especially on the definition of the various enthalpy changes and application of Hess' Law.

[Total: 14]

2

To determine the order of reaction with respect to the concentration of iodine in the iodination of propanone reaction

Mark

(a)

Correct header with units  
 Include for transfer time, in min and s for each entry

t	t <sub>d</sub> / min	initial burette reading / cm <sup>3</sup>	final burette reading / cm <sup>3</sup>	Volume of FA 6 / cm <sup>3</sup>
4 min 18 s	4.0	0.00	17.40	17.40
8 min 2 s	8.0	18.00	34.20	16.20
12 min 0 s	12.0	30.00	44.90	14.90
16 min 0 s	16.0	0.00	13.70	13.70
20 min 0 s	20.0	14.00	26.40	12.40

Records all

- volumes to 0.05 cm<sup>3</sup>
- transfer time, t, to consistent precision, i.e. nearest s
- correctly calculates decimal values of t<sub>d</sub> and records to 1 d.p.

5 sets of titration results and 1 aliquot is taken at between 3.5 min to 5 min and student chooses well-spaced values of time of transfer, where the longest time  $\leq 20$  min

1

**Comments:**

- Some students did not follow instructions to reflect the recording of data to the appropriate significant figures/decimal places or units.
- Many wrote the units for time incorrectly as mins or sec, or did not leave t<sub>d</sub> as 1 decimal place.
- The maximum time taken should not exceed 20 min and the 5 readings taken should be well-spaced from 4 to 20 min.
- A number of students also forgot to include t as part of the table and thus lost marks for recording.

(b)(i)

Axes correct way round + correct labels + scale + units the scale must be chosen so that the y intercept would fall within the scale range; and, that the plotted points occupy at least half the graph grid in the x direction (including x = 0) and the plotted points and the y intercept together occupy at least half the graph grid in the y direction.

1

Plotting – within  $\pm 1/2$  small square. Check all points; put ticks if correct.

1

Graph line is straight and is the best-fit line with a fair scatter of points either side of the line.

1

Accuracy

1

**Comments:**  
 As the volume of FA 6 at t<sub>d</sub> = 0.00 min is required, you should clearly indicate the coordinates of the y-intercept on the graph.  
 Since the question does not need you to find the x-intercept from the graph, it is unnecessary to include y=0. Students who did this usually ended up with a scale that does not fulfill the requirement for the plotted points to occupy at least half the graph grid in both x and y directions.  
 Please show the scale/division for every 10 small boxes to avoid plotting wrongly and also for the ease of reference by the marker.

1



As the reaction is between  $I_2$  and  $CH_3COCH_3$ , the amount of  $I_2$  will be decreasing during the reaction, thus the graph of volume of  $S_2O_3^{2-}$  used against time should be a decreasing graph.

- (b)(ii) order with respect to  $[I_2]$ : zero  
 explanation: the graph line is straight OR gradient of the graph is constant, so no change in rate as  $[I_2]$  decreases.  
 Do not allow this mark if the graph line is not straight.

Comments:  
 Many students wrongly thought that the order with respect to  $[I_2]$  was one upon obtaining a straight-line graph. Students will need to know that gradient of a concentration-time graph is rate. Since the rate did not change as the  $[I_2]$  drop, reaction is zero order with respect to  $[I_2]$ .

- (b)(iii) Clear indication of correct co-ordinates from graph (read to  $\pm 1/2$  small square) and triangle drawn should be at least half the number of grids in x & y direction of the line drawn.

gradient correctly calculated  
 Do not award this mark if coordinates, or volume and time values not given or if graph not straight line.

Comments:  
 The 2 points used for the calculation of gradient must be far apart (i.e. gradient triangle should be large) to minimise percentage error.

- (b)(iv) Line correctly extrapolated to meet y-axis.  
 and  $V_{max}$  correctly read from intercept to within  $\pm 1/2$  small square

$nS_2O_3^{2-} = V_{max} \times 10^{-3} \times 0.0100 = a$  mol  
 $nI_2$  (in  $10 \text{ cm}^3$ ) =  $1/2 a$  mol  
 $nI_2$  (in  $100 \text{ cm}^3$  of reaction mixture / in  $50 \text{ cm}^3$  of FA 5) =  $(1/2 a) \times 10 = b$  mol  
 $[I_2]$  in FA 5 =  $b \times 1000/50 \text{ mol dm}^{-3}$

Comments:  
 Most students made the mistake of not scaling up to find  $nI_2$  in  $100 \text{ cm}^3$  of reaction mixture. This is a sampling method in which samples of  $10 \text{ cm}^3$  are pipetted from the  $100 \text{ cm}^3$  reaction mixture for titration.

- (b)(v) Correctly calculates  $t_{max} = V_{max} / |\text{gradient}| = V_{max} / b(\text{iii})$

Comments:  
 Also accepted the  $y=mx+c$  method.

- (c)

rate =  $k[CH_3COCH_3][H^+]$   
 Rate units =  $\text{mol dm}^{-3} \text{ s}^{-1}$ , allow  $\text{mol dm}^{-3} \text{ min}^{-1}$   
 allow ecf if student deduces order with respect to iodine to be other than zero

Comments:  
 Many students did not include the order with reaction wrt  $H^+$  though it was already mentioned in the question that it is first order wrt to both propanone and  $H^+$ . Many students also fail to give the correct units for rate and wrote down the units for  $k$  instead.

- (d)

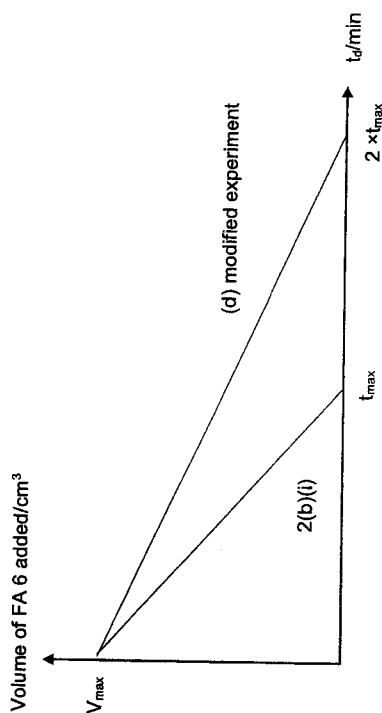


Fig. 2.2

- Marking point for sketch: Same shape of line as in 2(b)(i) + starts at same point + new line gradient is about  $1/2$  that of original.

Explanation:

(new graph starts at the same volume as initially the amount of iodine is the same.)  
 As reaction is 1st order with respect to  $[CH_3COCH_3]$ , when  $[CH_3COCH_3]$  is halved,

- the rate of reaction (which is the gradient of the graph) is also halved.
- or
- so  $t_{max} = 2 \times$  original as twice the amount of time is needed to complete the reaction at half the original rate.

Comments:

- Most of the students are unable to relate the first order reaction with respect to propanone to the effect on rate when its concentration is halved.
- In addition, they did not realize that the initial volume of FA6 used should remain the same as amount of iodine is the same.
- Question asked for labelled graph so there should be clear indication on the graph on the points of consideration to show the change in the gradient such as  $t_{max}$  and  $2t_{max}$ .

- (e)(i) FA 7 helps to quench the reaction by removing H<sup>+</sup>. Omission of it will result in the further reaction of the iodine with propanone, causing the value to be lower than expected.

Comments:

- Many students mention FA7 'stops' the reaction which is technically not correct because quenching means to slow down the reaction till the rate is close to zero. Therefore, it is preferred that students use the word 'quench' for such question. Students also did not mention how the reaction was quenched by the removal of H<sup>+</sup> which should have been mentioned together.
- 'The value is lower than expected' is preferred over 'the value decreases' because the former makes comparison between what is obtained versus what we expect.

- (e)(ii) The temperature will decrease/drop/fall/become lower. The reaction between NaHCO<sub>3</sub>(aq) and H<sub>2</sub>SO<sub>4</sub>(aq) is endothermic (from question 1).

Comments:

Most students were unable to relate the quenching reaction of FA7 to remove H<sup>+</sup> to the reaction in question and information in table 1.1. The results in table 1.1 showed a decrease in temperature which means an endothermic reaction had taken place. Most of them jumped to the conclusion that it is an exothermic reaction because neutralisation has taken place.

- (f)(i) It acts as a catalyst, consumed/reacted in step 1 and regenerated in step 3 and hence its concentration remains unchanged.

Comments:

A number of students failed to recognise that H<sup>+</sup> is a catalyst and did not explicitly mention the evidence on the steps that it is consumed and regenerated. Some of them even think that it is a nucleophile/electrophile.

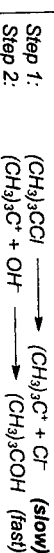
- (f)(ii) step 3 [accept step 1]

Comments:

Many students are unable to relate the rate equation to the correct slow step.

In general, there are 3 main cases which you will be asked to infer the rate equation from mechanisms. Read on below to see which is the correct case for this question.

Case 1: slow step is 1<sup>st</sup> step



In this case, Rate = k [(CH<sub>3</sub>)<sub>3</sub>CCl]

We simply need to check the coefficient of the reactant to determine the order wrt the reactant.

Case 2: slow step is not 1<sup>st</sup> step AND product formed in preceding steps are used up in subsequent steps



The rate equation for the rate-determining step (i.e. slow step) is: rate = k [N<sub>2</sub>O<sub>2</sub>][O<sub>2</sub>].

However, N<sub>2</sub>O<sub>2</sub> is an intermediate and should not appear in the rate equation.

Therefore, we must eliminate [N<sub>2</sub>O<sub>2</sub>] from the rate equation.

To do so, we express [N<sub>2</sub>O<sub>2</sub>] in terms of [reactants] from the first step.

The rate equation for the overall third order reaction will be: **rate = k [NO]<sup>2</sup> [O<sub>2</sub>]**

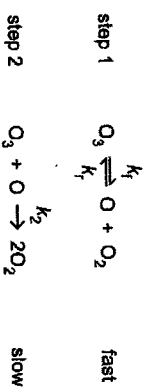
\*\*This question of this practical exam belongs to Case 2 and not Case 1!\*\*

WHY?

The first two steps of the reaction are not slow step as they are both at equilibrium, showing that both forward and reverse reactions occur readily and likely not to have high activation energy. Furthermore, the first 2 steps do not have repulsion of like charges or breaking of strong bonds to give high E<sub>a</sub>. The 3<sup>rd</sup> step is most likely the slow step since it involves breaking a stronger C-H sigma bond and forming a weaker pi bond.

Since the reactant of the 3<sup>rd</sup> slow step is formed from the preceding 2 steps as the only product, we can express the [reactant] in the 3<sup>rd</sup> step in terms of those in the preceding 2 steps. This hence gives us the rate equation in terms of propanone and acid only, which is in line with what we found in this experiment.

Case 3: slow step is not 1<sup>st</sup> step AND not all product formed in preceding steps are used up  
We see this example in N2021 Paper 3 Qn 3c.



Since the 2<sup>nd</sup> step is the slow step, we must represent the concentration of the O intermediate in terms of the reactants and products in the preceding step.

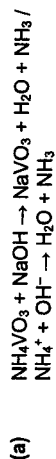
Notice that at higher concentration of oxygen, it causes the POE of step 1 to shift to the left. This slows down the overall reaction as the O intermediate required for the second slow step will be present in lower concentration.

This is in line with the negative order of reaction observed for O<sub>2</sub> in the overall rate equation: rate = k [O<sub>3</sub>]<sup>2</sup>[O<sub>2</sub>]<sup>-1</sup>

Such substances with negative order of reaction are called inhibitors in chemistry.

[Total: 21]

3 Investigation of the chemistry of some vanadium ions



gas turns (moist) red litmus blue and confirms  $\text{NH}_3$  evolved

*Comments:*  
 Generally well done. Some students however, incorrectly mentioned about the production of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) instead of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ .

	tests	observations
(i)	Using a 50 cm <sup>3</sup> measuring cylinder, measure about 10 cm <sup>3</sup> of FA 8 into a 250 cm <sup>3</sup> beaker.  Using the same measuring cylinder, measure about 40 cm <sup>3</sup> of FA 3 to the same beaker.  The resulting solution obtained is solution W, which will be used in 3(b)(ii) and 3(c).	colourless solution turns yellow on acidification [✓]
(ii)	Transfer about 30 cm <sup>3</sup> of solution W into a 100 cm <sup>3</sup> conical flask, using the same measuring cylinder used in 3(b)(i).  Using a spatula, slowly add all the FA 9 provided, a small spatula measure each time, into the conical flask. Swirl after each addition.  You may then leave the mixture to stand, swirling the flask from time to time and observe the solution until no further changes are seen.	1. effervescence/bubbles formed [✓] 2. solution turns blue [✓] 3. then green/turquoise/blue-green/grey-blue [✓] 4. then lilac/purple/mauve [✓]  Marks allocated as follows: 4 - 5[✓] = 2 2 - 3[✓] = 1 0 - 1[✓] = 0

While you are waiting, continue with test 3(c).

*Comments:*

Some pointers to take note.

- Gas evolved ≠ effervescence (you technically cannot see gas evolved, what you see are bubbles which is effervescence)
- There are 5 observation points in 3(b) – and the observations ought to be in sequence

(c)

tests	observations
Transfer about 10 cm <sup>3</sup> of solution W into a boiling tube using the same measuring cylinder used in 3(b)(i).  Add all the tin powder in the weighing bottle into the boiling tube and shake the mixture.  Gently warm the boiling tube. You should not allow the mixture in the boiling tube to boil or heat to dryness.  To view the colour of the solution clearly, you may find it necessary, from time to time, to allow the tin to settle.  Observe the mixture until no further changes are seen.	1. blue solution formed [✓]; 2. then green/turquoise/blue-green/grey-blue final solution [✓].  Both [✓] for 1 mark

*Comments:*

Once again, the two observation points here ought to be in sequence. Many students mistakenly thought that the colour arises due to colored ppt formed. However, should you follow the instructions of the test to allow for time for the solid tin to settle, you would be able to see that the solution is the one responsible for the colours, not the solid.

(d)(i)

tests	observations
1 To about 1 cm depth of FA 10 in a test-tube, add aqueous sodium hydroxide until no further changes are observed.	White ppt soluble in excess [1]
2 To about 1 cm depth of FA 10 in a test-tube, add aqueous ammonia until no further changes are observed.	White ppt soluble in excess [1]

Zinc

(d)(ii)

$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2$  (also accept  $\rightleftharpoons$  to be in line with the POE shift to explain why the salt dissolves)



*Comments:*

Generally well done for d(i).

Students should note that d(ii) has to be Zn(s) only, as the question specifically mentioned on page 13 of the question paper that FA9 is a metal.

$\text{Zn}^{2+}$  is a metal cation and hence should students give that answer, it would be assumed that students are referring to FA10, instead of FA9 as required by the

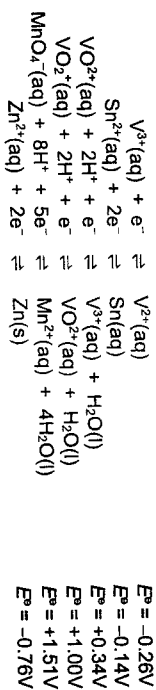
question.

d(ii) is poorly done. The relevant equations have been covered in Experiment 12 and can also be found in the Inorganic QA notes.

One way to remember is by relating to what you have learnt from similar observation for  $\text{Cu}^{2+}$ . When ammonia is added, the formation of ppt is due to the metal hydroxide formed. The ppt is soluble in excess ammonia as a complex is formed with ammonia ligands.

[Total: 9]

Extension question:  
Relevant half-equations and standard electrode potential data are given below.



Can you explain why a series of colours is observed when Zn and Sn were added to the vanadate solution and which species is responsible for each of the colour observed?

## Planning

- (a) Minimum mass of  $\text{Ca}(\text{CO}_3)_2$  required =  $6.2 \times 10^{-3} \times 389.9 \times \frac{100}{1000} = 0.242 \text{ g}$

Comments:  
Most students were able to score here.  
Those who got it wrong often mistook solubility for solubility product.

## (b)

### Suggested plan

1. Measure 100.0 cm<sup>3</sup> of deionised water using a 100.0 cm<sup>3</sup> measuring cylinder and add it to a 250 cm<sup>3</sup> conical flask. Place the conical flask in a thermostatically-controlled water bath at 20 °C. Place a thermometer into the flask to monitor the temperature of the water.
2. Using an electronic weighing balance, weigh about 1.0 g of  $\text{Ca}(\text{CO}_3)_2$  in a weighing bottle. Add some  $\text{Ca}(\text{CO}_3)_2$  solid to the deionised water in the conical flask. Stir the mixture continuously with a glass rod. Continue adding  $\text{Ca}(\text{CO}_3)_2$  with stirring, until some undissolved solid remains. Allow the mixture to stand for 1 hour to reach equilibrium.
3. Filter the mixture to obtain the saturated solution by using dry filter paper and dry filter funnel into a dry conical flask placed in a thermostatically controlled water bath at 20 °C, so that the filtrate is collected at 20 °C.
4. Fill a burette with  $\text{Na}_2\text{S}_2\text{O}_3$ .
5. Pipette 25.0 cm<sup>3</sup> of the filtrate from step 3 into a 250 cm<sup>3</sup> conical flask.
6. Use a measuring cylinder to add about 10 cm<sup>3</sup> of  $\text{H}_2\text{SO}_4$  to the same conical flask.
7. Use another measuring cylinder to add about 10 cm<sup>3</sup> of KI to the same conical flask. The solution turns brown.
8. Run  $\text{Na}_2\text{S}_2\text{O}_3$  from the burette into the conical flask until a pale-yellow solution is obtained.
9. Using a dropper, add 5 drops of starch solution to the conical flask. Continue adding  $\text{Na}_2\text{S}_2\text{O}_3$  until the blue-black colour just disappears. Record your titration results.
10. Repeat titration until consistent titration results within 0.10 cm<sup>3</sup> of each other are obtained.

1

3

(c)(i)  $K_{sp}$  of  $\text{Ca}(\text{IO}_3)_2 = [\text{Ca}^{2+}] [\text{IO}_3^-]^2$

Amount of  $\text{S}_2\text{O}_3^{2-}$  ions =  $0.100 \times V = 0.1V$  mol

Amount of  $\text{I}_2$  reacted =  $\left(\frac{1}{2}\right) (0.1V) = 0.05V$  mol

Amount of  $\text{IO}_3^-$  ions in  $25.0 \text{ cm}^3$  of filtrate =  $\left(\frac{1}{2}\right)(0.05V)$

=  $0.016667V$  mol [1]

Amount of  $\text{IO}_3^-$  ions in  $100 \text{ cm}^3$  of saturated solution =  $\left(\frac{100.0}{25.0}\right)(0.016667V) = 0.066667V$  mol

Amount of  $\text{Ca}^{2+}$  ions in  $100 \text{ cm}^3$  of saturated solution =  $\left(\frac{1}{2}\right) (0.066667V) = 0.033333V$  mol

$K_{sp}$  of  $\text{Ca}(\text{IO}_3)_2 = [\text{Ca}^{2+}] [\text{IO}_3^-]^2$

$K_{sp}$  of  $\text{Ca}(\text{IO}_3)_2 = \left(\frac{0.033333V}{0.100}\right) \left(\frac{0.066667V}{0.100}\right)^2$  [1] for concentrations of both ions

=  $0.148V^3 \text{ mol}^3 \text{ dm}^{-9}$  [1] with correct simplified expression

OR

Amount of  $\text{IO}_3^-$  ions in  $25.0 \text{ cm}^3$  of filtrate =  $\left(\frac{1}{2}\right)(0.05V)$

=  $\left(\frac{1}{60}\right)V$  mol [1]

$[\text{IO}_3^-] = \left(\frac{1000}{25.0}\right) \left(\frac{1}{60}\right)V = \left(\frac{2}{3}\right)V \text{ mol dm}^{-3}$

$[\text{Ca}^{2+}] = \left(\frac{1}{2}\right) \left(\frac{2}{3}\right)V = \left(\frac{1}{3}\right)V \text{ mol dm}^{-3}$  [1] for concentrations of both ions

$K_{sp}$  of  $\text{Ca}(\text{IO}_3)_2 = \left(\frac{1}{3}V\right) \left(\frac{2}{3}V\right)^2$

=  $\left(\frac{4}{27}\right)V^3 \text{ mol}^3 \text{ dm}^{-9}$  [1] with correct simplified expression

Answers in word may be accepted but there must be clear indications of how the stoichiometry is applied in the working, not just quote mole ratio in the reaction equations.

Comments:

(c)(i) was generally well done. A few answers forgot to write " $K_{sp}$ " in their expression or forgot the charges of the ions.

Solving for concentration of the ions is the most challenging part of (c)(ii).

Quite a number of students forgot that the titration was performed only on  $25 \text{ cm}^3$  of the filtrate and instead calculated as though  $V \text{ dm}^3$  of sodium thiosulfate is used to react with the entire  $100 \text{ cm}^3$  filtrate.

Students who chose to add  $\text{H}_2\text{SO}_4$  before pipetting a portion out for titration also encountered greater difficulty in performing calculations as they had to factor in that the pipetted solution is diluted and not the original saturated salt solution.

marks	description
1	<p>prepare saturated solution of <math>\text{Ca}(\text{IO}_3)_2</math> in <math>100 \text{ cm}^3</math> deionised water by adding excess <math>\text{Ca}(\text{IO}_3)_2</math> (at least <math>0.250 \text{ g}</math>)</p> <ul style="list-style-type: none"> <li>masses smaller than <math>0.250 \text{ g}</math> were not accepted as the uncertainty involved in using the weighing balance affects the 3<sup>rd</sup> decimal place and may not allow us to accurately ensure <math>&gt;0.242 \text{ g}</math> of <math>\text{Ca}(\text{IO}_3)_2</math> solid has been used.</li> </ul>
1	<p>maintain constant temperature (use of water bath and thermometer)</p> <ul style="list-style-type: none"> <li>many students forgot the use of the thermometer to check that the temperature of the saturated solution is maintained the same as that of the water bath during the entire equilibration process.</li> <li>This checking should ideally be done BEFORE the 1 hour to establish equilibrium so that the equilibrium is established under the correct temperature.</li> </ul>
1	<p>filtration: dry filter paper, funnel, conical flask (or beaker)</p> <ul style="list-style-type: none"> <li>few students remembered the use of dry apparatus to prevent additional water added that will dilute the saturated solution, causing the position of equilibrium to be affected.</li> </ul>
1	<p>titration procedure to determine the concentration of dissolved <math>\text{IO}_3^-</math>: pipette a portion (<math>25 \text{ cm}^3</math>), add <math>\text{H}^+</math> and <math>\text{I}^-</math> (<math>10 \text{ cm}^3</math>) before titration, describe end-point colour change</p> <ul style="list-style-type: none"> <li>As the phrasing in question is subject to different interpretations, addition of acid can be done to the bulk saturated solution or after pipetting. However, adding acid after pipetting will make subsequent calculations in (c)(ii) easier.</li> <li>Answers that took portions of filtrate less than <math>25 \text{ cm}^3</math> and top up to <math>25 \text{ cm}^3</math> for "acidified solution of the filtrate" were also accepted.</li> </ul>
1	<p>apparatus (for preparation of saturated solution and titration)</p> <ul style="list-style-type: none"> <li>measuring cylinders for the volumes of deionised water, sulfuric acid and potassium iodide</li> <li><math>10</math> or <math>25 \text{ cm}^3</math> pipette to ensure that equal portions of filtrate were drawn out for titration. Measuring cylinder is not accepted for this as there is greater error in volume measurement using measuring cylinder, leading to inconsistent portions and titration results may not be consistent.</li> <li>burette for titration</li> <li>conical flasks for preparation of saturated solution and titration</li> </ul>
1	<p>ensure reliability of results.</p> <ol style="list-style-type: none"> <li>to equilibrate for at least 1 hour,</li> <li>add starch indicator to make the end-point colour change more visible and</li> <li>repeat titration until titre volumes are within <math>\pm 0.10 \text{ cm}^3</math> of each other.</li> </ol>

Comments:

It was great to see the vast majority attempting this part.

Most students were able to give reasonably sound plans though a few confused it with the experiment in Question 2 and started to describe plans involving timed intervals.

See the breakdown of marks scheme below and points to note:

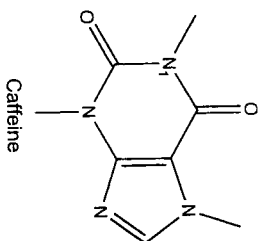




3

- 4 In which of the following sequences are the species quoted in order of decreasing boiling points?
- RbCl, KCl
  - HF, HCl
  - K, Ca
  - CO, CO<sub>2</sub>

- 5 People drink beverages containing caffeine to relieve or prevent drowsiness and to improve cognitive performance.



Which statement about caffeine is true?

- Caffeine molecule has a planar structure.
- The  $\pi$  bond in C=C is formed by sideways overlap of 2p orbitals.
- The nitrogen atom in caffeine, N<sub>1</sub> is basic.
- There are 16 sigma bonds in a caffeine molecule.

- 6 Which of the following substances conduct electricity due to delocalised electrons?

- Graphite
- Solid magnesium
- Molten sodium chloride

- 1 only
- 1 and 2 only
- 2 and 3 only
- 1, 2 and 3

4

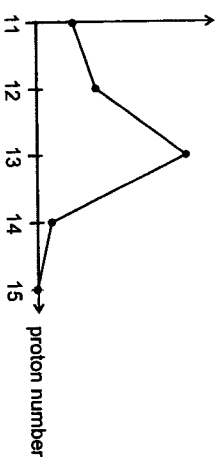
- 7 Which of the following statements is **Incorrect**?

- When methane gas is subjected to low pressure, it liquefies.
- Tyre pressure readings are higher on a hot day.
- The boiling point of water is lower than 100°C at a higher altitude.
- The density of an ideal gas at constant pressure is inversely proportional to the temperature.

- 8 For the oxides of Period 3 elements (Na to P), which property decreases from Na<sub>2</sub>O to P<sub>4</sub>O<sub>10</sub>?

- melting point
- covalent character
- pH when mixed with water
- solubility in aqueous alkali

- 9 The following graph shows how a property of the elements in Period 3, from Na to P, or their compounds, varies with proton number.



What property is shown by the graph?

- ionisation energies of elements
- melting point of element
- pH of aqueous chloride
- electrical conductivity of element

- 10 Use of *Data Booklet* is relevant to this question.

The  $\Delta G^\circ_{\text{solution}}$  and  $\Delta S^\circ_{\text{solution}}$  for silver chloride, AgCl are +55.6 kJ mol<sup>-1</sup> and +33.2 J mol<sup>-1</sup> K<sup>-1</sup> respectively.

What is the standard enthalpy change ( $\Delta H^\circ$ ) when 287 g of AgCl is precipitated under the same conditions?

- +65.5 kJ
- 65.5 kJ
- +131 kJ
- 131 kJ



5

- 11 The rate equation for a reaction between **A** and **B** is given by: rate =  $k[A]$   
Which of the following statements about the reaction is true?

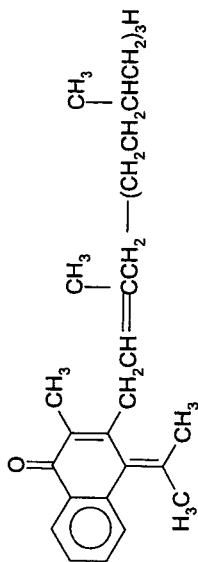
- A** is involved in the rate-determining step in the reaction mechanism.
- The rate constant,  $k$ , increases with increasing concentration of **A**.
- A graph of rate against  $[A]$  gives a straight line that passes through the origin.

- A** 1, 2 and 3    **B** 1 and 3 only    **C** 2 only    **D** 1 only

- 12 What is the pH of the final solution when  $V$  cm<sup>3</sup> of dilute nitric acid of pH 2.0 is mixed with  $V$  cm<sup>3</sup> of dilute nitric acid of pH 4.0 followed by the addition of  $2V$  cm<sup>3</sup> of water?

- A** 2.3    **B** 2.6    **C** 3.0    **D** 3.6

- 13 Compound **K** is a yellow viscous oil found in plants. It has the following structure.



What is the total number of stereoisomers for compound **K**?

- A** 4    **B** 8    **C** 16    **D** 32

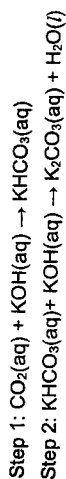
- 14 In the free radical substitution reaction of methane,  $\text{CH}_4$ , one of the side-products formed is ethane,  $\text{C}_2\text{H}_6$ , which is formed when two  $\bullet\text{CH}_3$  radicals combine. Upon careful heating, a sample of butane,  $\text{C}_4\text{H}_{10}$ , reacted with chlorine gas in a free radical substitution reaction to give only mono-substituted products.

How many possible organic side-products would be obtained in this reaction when the radicals produced combine with each other?

- A** 2    **B** 3    **C** 4    **D** 5

6

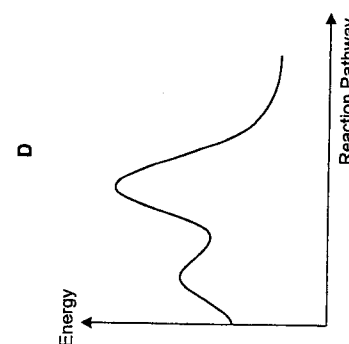
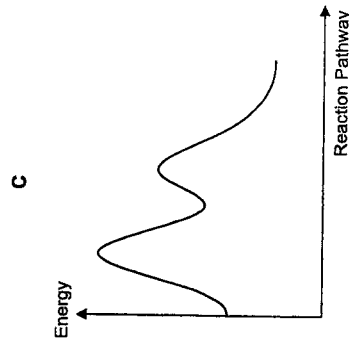
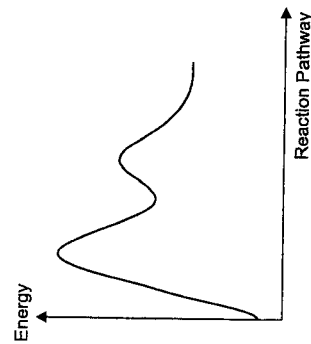
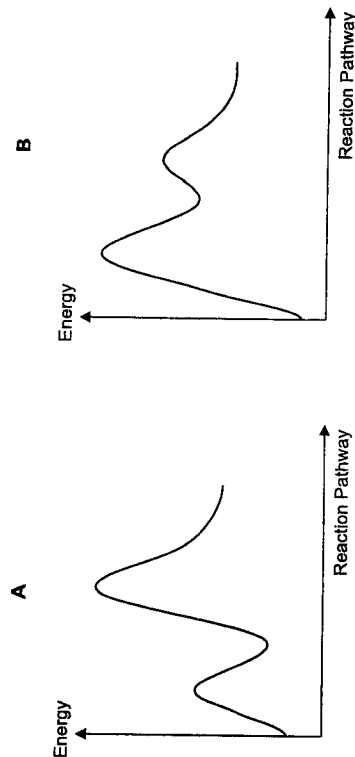
- 15 The reaction between carbon dioxide and potassium hydroxide is exothermic. The proposed two-step mechanism of the reaction is shown below:



Experiments were carried out to study the rate of the reaction above.

Experiment Number	Initial concentration of $\text{CO}_2$ / mol dm <sup>-3</sup>	Initial concentration of $\text{KOH}$ / mol dm <sup>-3</sup>	Initial reaction rate / mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.2	0.2	0.0034
2	0.4	0.2	0.0068
3	0.2	0.1	0.0017

Which of the following graphs most likely describes the energy profile of the reaction above?

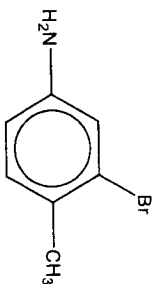


16 Aqueous bromine can react with propene in the presence of concentrated potassium nitrate solution.

Which of the following is the major product formed in the reaction?

- A  $\text{CH}_3\text{CHBrCH}_2\text{ONO}_2$   
 B  $\text{CH}_3\text{CHBrCH}_2\text{Br}$   
 C  $\text{CH}_3\text{CHBrCH}_2\text{OH}$   
 D  $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{Br}$

17 Which synthetic route is most likely to lead to the most successful synthesis of the following product from benzene?



- A nitration, bromination, alkylation, reduction  
 B nitration, bromination, reduction, alkylation  
 C nitration, alkylation, reduction, bromination  
 D alkylation, bromination, nitration, reduction

18 A few drops of 1-chlorobutane, 1-bromobutane, 1-iodobutane were placed separately into three test-tubes each, containing 1.0 cm<sup>3</sup> of aqueous silver nitrate at 60 °C.

A hydrolysis reaction occurred. (X is the halogen atom)



Which of the following would be the best explanation for the rate of the reaction?

- A The bond energy of C-X bond decreases from C-Cl to C-I.  
 B The bond polarity of C-X bond decreases from C-Cl to C-I.  
 C The electron deficiency of the carbon atom bonded to X decreases from C-Cl to C-I.  
 D The solubility of AgX decreases from AgCl to AgI.

19 Concentrated ammonia was heated in a sealed tube with excess bromoethane. Which of the following product will **not** be formed?

- A  $\text{C}_4\text{H}_{10}\text{N}$   
 B  $\text{C}_4\text{H}_{11}\text{N}$   
 C  $\text{C}_6\text{H}_{15}\text{N}$   
 D  $\text{C}_8\text{H}_{20}\text{NBr}$

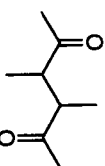
20 An alcohol **A** with molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  is oxidised by acidified potassium dichromate(VI) under certain conditions to give **B**. The following shows some properties of **B**:

- 1 **B** does not produce a yellow precipitate with aqueous alkaline iodine.  
 2 **B** gives a brick-red precipitate when reacted with Fehling's solution.

How many isomers of alcohol **A** could result in the observations for **B**?

- A 1                      B 2                      C 3                      D 4

21 Compound **Z** shown below is an intermediate used to generate pyrolys which are essential to the production of many different chemicals in the pharmaceutical industry.



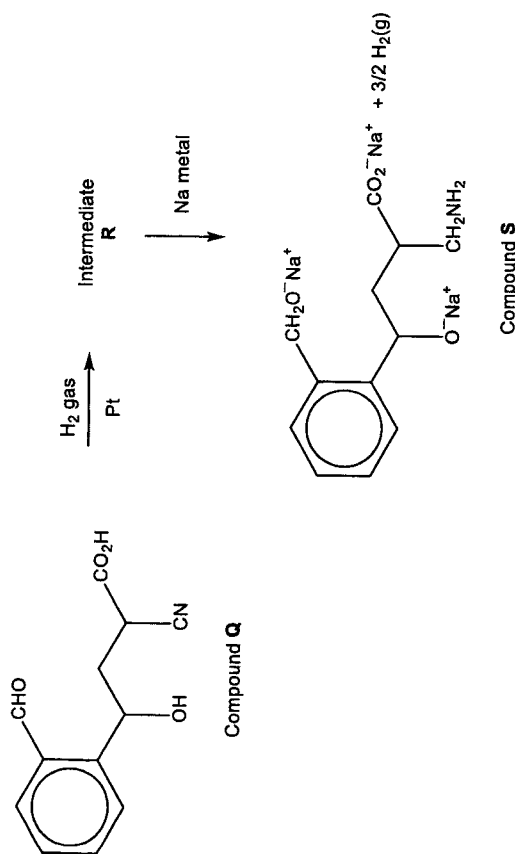
compound **Z**

Which sentence is correct for compound **Z**?

- A It produces a silver mirror with Tollen's reagent.  
 B It decolourises acidified potassium manganate(VII).  
 C It produces a yellow precipitate with aqueous alkaline iodine.  
 D It does not produce an orange precipitate with 2,4-dinitrophenylhydrazine.

9

- 22 Compound **S** can be obtained via the following 2-step synthesis from compound **Q**.

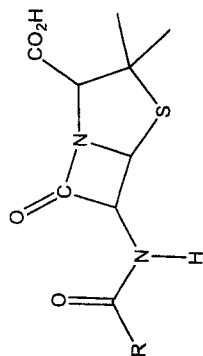


If 96 dm<sup>3</sup> of hydrogen gas was reacted with **one mole** of compound **Q**, followed by the addition of sodium metal at room temperature and pressure, what is the final gas volume when the reaction was completed? (Given  $V_m = 24 \text{ dm}^3 \text{ mol}^{-1}$  at r.t.p.)

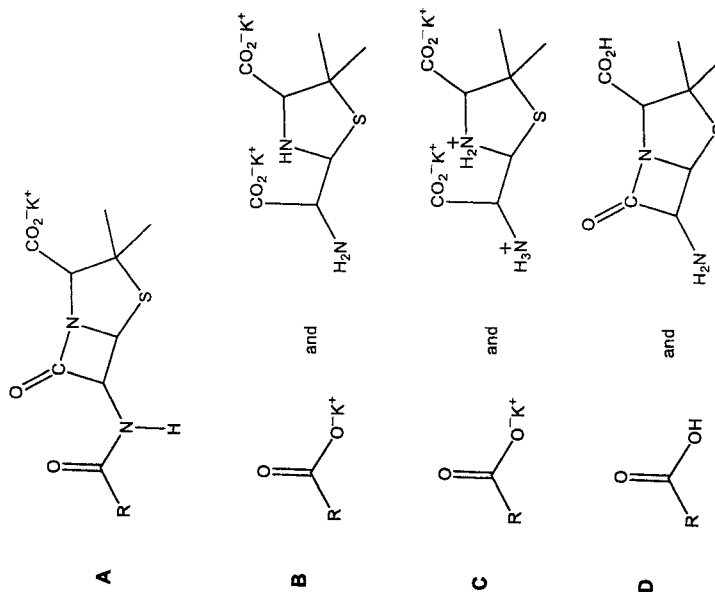
- A** Gas volume decreases by 36 dm<sup>3</sup>.  
**B** Gas volume decreases by 60 dm<sup>3</sup>.  
**C** Gas volume increases by 36 dm<sup>3</sup>.  
**D** No change in gas volume.

10

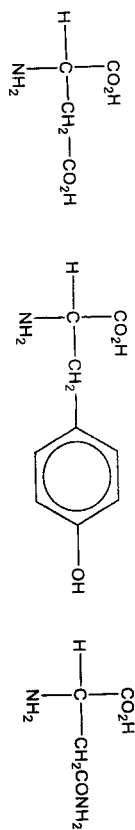
- 23 Penicillin is an antibiotic commonly used to treat a number of bacterial infections. The general structure of a penicillin molecule is given below.



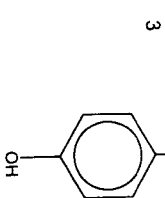
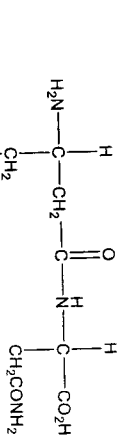
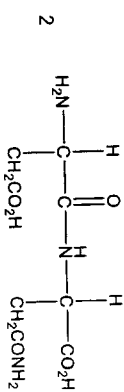
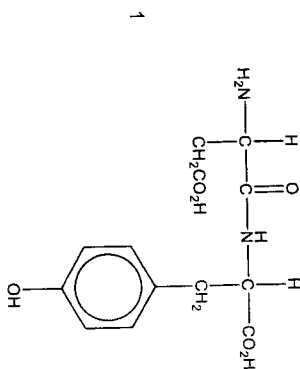
What are the products formed when penicillin is boiled with excess aqueous potassium hydroxide?



- 24 The following shows the structures of three amino acids.

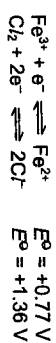


Which of the following represent the dipeptides formed from these amino acids?



- A 1, 2 and 3  
 B 1 and 2  
 C 1 and 3  
 D 2 only

- 25 Two electrode potentials are given.



Which species is the strongest reducing agent?

- A  $\text{Fe}^{3+}$       B  $\text{Fe}^{2+}$       C  $\text{Cl}_2$       D  $\text{Cl}^{-}$

- 26 Use of the Data Booklet is relevant to this question.

An electrochemical cell is set up using a  $\text{Fe}^{2+}(\text{aq})|\text{Fe}(\text{s})$  half-cell and a  $\text{VO}_2^{+}(\text{aq})|\text{VO}^{2+}(\text{aq})|\text{Pt}(\text{s})$  half-cell.

Which of the following gives a correct effect on the  $E_{\text{cell}}$  and a correct explanation for the effect when each of the changes is made to the cell separately?

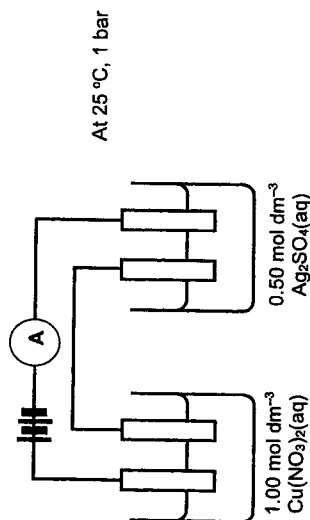
- |   | effect on $E_{\text{cell}}$ | explanation  |
|---|-----------------------------|--|
| 1 add KCN(aq) to the $\text{Fe}^{2+}(\text{aq}) \text{Fe}(\text{s})$ half-cell                          | increases                   | concentration of $\text{Fe}^{2+}(\text{aq})$ decreases |
| 2 add water to the $\text{VO}_2^{+}(\text{aq}) \text{VO}^{2+}(\text{aq}) \text{Pt}(\text{s})$ half-cell | decreases                   | concentration of water increases                       |
| 3 increase temperature of the $\text{Fe}^{2+}(\text{aq}) \text{Fe}(\text{s})$ half-cell                 | no change                   | temperature change does not affect $E_{\text{cell}}$   |

- A 1, 2 and 3      B 1 and 2      C 2 and 3      D 1 only

13

27 Use of the Data Booklet is relevant to this question.

Using inert electrodes, a current was passed through two beakers containing aqueous silver sulfate and aqueous copper(II) nitrate, connected in series under standard conditions.



What is the ratio of the mass of silver to copper deposited after the current was passed for  $t$  minutes?

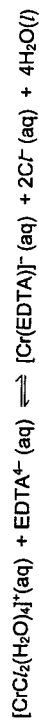
- A 0.59      B 0.85  
C 1.70      D 3.40

28 A current of 10 A is passed for 150 minutes through molten aluminium oxide using inert electrodes.

What will be the approximate volume of gas liberated, measured at s.t.p.?

- A 0.089 dm<sup>3</sup>      B 5.3 dm<sup>3</sup>      C 5.6 dm<sup>3</sup>      D 11.2 dm<sup>3</sup>

29 EDTA<sup>4-</sup>(aq) solution is added dropwise until in excess to a solution of [CrC<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup>. The equilibrium constant for this reaction is greater than 1 and the equation for the reaction is as shown below.



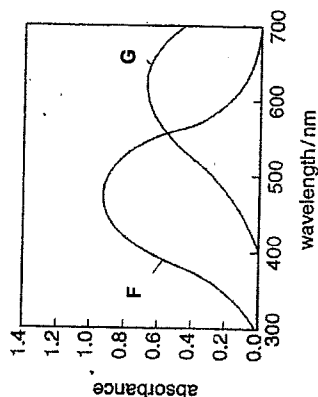
Which one of the following statements about the above reaction is correct?

- A There is no change in colour of the solution after addition of EDTA<sup>4-</sup>.  
B [Cr(EDTA)]<sup>-</sup> is a less stable complex ion than [CrC<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup>.  
C Both [Cr(EDTA)]<sup>-</sup> and [CrC<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> are octahedral complexes.  
D The above is a redox reaction.

14

30 The absorbance of a solution at a particular wavelength is proportional to the concentration of ion responsible for the absorption.

The visible spectra of solutions of two transition metal complexes **F** and **G** are shown in the diagram below. Both complexes contain the same transition metal ion.



Given that energy is inversely proportional to wavelength and the visible region of the electromagnetic spectrum is as follows:

violet	blue	green	yellow	orange	red
400		500	600	700	
Wavelength (nm)					

Which of following statements can be deduced from the spectra?

- 1 Complex **F** is likely to be red while complex **G** is likely to be blue.  
2 The energy gap in complex **F** is greater than that in complex **G**.  
3 The  $K_c$  value for the formation of complex **F** is higher than the  $K_c$  value for formation of complex **G**.
- A 1, 2 and 3 are correct  
B 1 and 2 only are correct  
C 2 and 3 only are correct  
D 1 only is correct

END OF PAPER

