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]

[1]

Comments:

(i) Many students did not know that in some molecules (eg NO₂), the **total number of valence electrons is an <u>odd</u> number**. You can easily check by summing the total number of valence electrons before drawing the dot-and-cross diagram. In this case NO₂ 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 sp², 'sp' is written in small letters and '2' is written in superscript (raised).

- (iii) Bond length is the <u>distance</u> between the <u>nuclei of the two atoms</u> in the <u>bond</u>. [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, <u>both</u> the N–O bonds have <u>partial double bond character</u>. 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 NO_2 is intermediate between a single and double bond.

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



(b) (i) <u>Energy is released as a N-N covalent bond</u> is formed using the single unpaired electron of each of the <u>N atoms of two NO₂</u> radicals, thus forming N_2O_4 .



[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 NO₂ radical forms a bond with O of another NO₂ radical
- The bond formed between N of one NO_2 radical and N of another NO_2 radical is dative
- Energy is absorbed during bond formation

2

(ii)

 $2 \text{ NO}_2(g) \longrightarrow N_2O_4(g)$ $\Delta H = -58.0 \text{ kJ mol}^{-1}$ reddish brown colourless

As temperature increases from 273K, POE shifts to the <u>left</u> to decrease the temperature by <u>absorbing the excess heat</u>, favouring the <u>endothermic</u> reaction.

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

At temperature T, $N_2O_4(g)$ has completely converted to NO_2 molecules. As temperature increases from T, the number of moles of NO_2 molecules does not change further. The pressure of the gaseous sample then increases proportionally with increase in temperature.

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_2O_4 molecules has been converted to NO_2 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 <u>becomes darker brown</u>, OR [1] the colour of the gaseous mixture <u>becomes darker brown</u>

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.

[1]

[1]

(c) (i) $2NO_2 + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^-$ Disproportionation [1]

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: <u>catalyst</u> as it is <u>reacted/consumed in Step II</u> and <u>regenerated in Step IV</u>. [1]
 A: <u>intermediate</u> as it is <u>produced/formed in in Step III</u> and <u>reacted in Step IV</u>. [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) $(HOCH_2CH_2)_3NH^+(aq) + H_2O(l) \longrightarrow (HOCH_2CH_2)_3N(aq) + H_3O^+(aq)$

 $pK_{a} = 14 - 6.23 = 7.77$ $\therefore K_{a} = 10^{-7.77} = 1.70 \times 10^{-8} \text{ mol } dm^{-3}$ $[H_{3}O^{+}] = \sqrt{(1.70 \times 10^{-8})(6.00 \times 10^{-2})}$ $= 3.19 \times 10^{-5} \text{ mol } dm^{-3}$ $pH = -\log (3.19 \times 10^{-5})$ = 4.50[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 [OH] = [F] or [F] = [TEA].

(iv)

$$[NO_2]_{av} = \frac{(4.13 \times 10^{-3})(7.1 \times 10^{-2})}{(0.91 \times 10^{-4})(1.56 \times 10^{-5})(10 \times 24 \times 60 \times 60)}$$

= 0.239 µg m⁻³

[1] for correct answer

Since the $[NO_2]_{av}$ is <u>below / less than / does not exceed 25 µg m⁻³</u>, the quality of air in terms of NO₂ level is <u>good / satisfactory / acceptable.</u> [1] allow ecf

(accept words to the same effect)

Comments: A handful of students struggled with the unit conversion from cm^2 to 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]



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 l₂/l half-cell as l₂(s). lodine 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 mol dm⁻³ H₂SO₄ without realising that that makes 2 mol dm⁻³ 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) $I_2(aq) + 2e^- = 2I^-(aq)$ $E^{\Theta} = +0.54 V$
 - <u>Ag</u>⁺ will <u>react with I</u>⁻ to <u>form</u> a (yellow) <u>precipitate</u> (AgI) , so <u>[I⁻] decreases</u>
 - Position of equilibrium shifts right to increase [I⁻] [1] for both points including the above equilibrium
 - Reduction reaction is favoured. *E*^O_{I2/I⁻} becomes <u>more positive</u>, hence, *E*^O_{cell} becomes <u>more positive</u> [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 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]

 $8HI + H_2SO_4 \longrightarrow 4I_2 + 4H_2O + H_2S \quad [1]$

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)
$$n(S_2O_3^{2^-}) = \frac{21.85}{1000} \times 0.010 = 2.185 \times 10^{-4} \text{ mol}$$

 $n(I_3^-)_{25cm^3} = 0.5 \times 2.185 \times 10^{-4} = 1.0925 \times 10^{-4} \text{ mol}$
 $I_3^- \equiv I_2$
 $[I_2(aq)] = \frac{1.0925 \times 10^{-4}}{25/1000} = 0.00437 \text{ mol dm}^{-3}$ [1]
 $\mathcal{K}_{pc} = \frac{[I_2(\text{organic solvent})]}{[I_2(aq)]}$
 $93.8 = \frac{[I_2(\text{organic solvent})]}{0.00437}$
 $[I_2(\text{organic solvent})] = 0.4099 \text{ mol dm}^{-3}$ [1]
 $n(I_2(\text{organic solvent})) = 0.4099 \times 15/1000 = 0.006148 \text{ mol}$

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

Comments: Poorly done.

Students frequently got confused and assumed that the total volume is 65cm³ 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) <u>lodine is non-polar</u> and is able to form only <u>intermolecular instantaneous dipole-induced dipole (id-id) interactions</u> with cyclohexane and with water. The energy released is sufficient to overcome the <u>id-id interactions between cyclohexane</u> <u>molecules</u> and <u>between iodine molecules</u> but insufficient to overcome stronger <u>intermolecular hydrogen bonds in water</u>. [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) $2OH^- + I_2 + CH_3CH(OH)CH_3 \longrightarrow 2I^- + 2H_2O + CH_3COCH_3$ [1]

Comments:

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

(iii)



[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 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 CI₃⁻ 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 CI₃.

(iv) Acid-base reaction [1]

Comments:

Not well done. Candidates fail to recognise that ethanoic acid lost a H^+ to CI_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 HC*l*, 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 CI_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 RCOCH₃ 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 <u>aq NaOH</u> to each compound and <u>heat</u>.
 Cool the mixture and then add <u>excess dilute HNO₃</u>.
 Add <u>aq AgNO₃</u> and observe the colour of the ppt formed.

[1] for procedure

 C_2H_5Cl – white ppt C_2H_5Br – cream ppt C_2H_5I – 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 AgNO₃ and observe the colour of the ppt formed" because question said to use NaOH(aq).

Comments:

Most candidates know that aq NaOH and aq AgNO₃ were used but some missed out mentioning 'heat' and addition of 'HNO₃' 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: CH₃CH₂CH₂NH₂ [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_3 .

(ii) Cl atom of the acyl chloride (COCl) is more reactive/more readily substituted as it is bonded to a <u>highly electron-deficient carbon/greater partial positive charge carbon</u> which is attached to <u>two strongly electronegative</u> 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) <u>N is less electronegative</u> than O, <u>lone pair of N is **more** readily delocalised into the carbonyl C=O group</u>.

AND

Thus the <u>carbonyl carbon is **less** electron-deficient</u> OR <u>C-N bond in the amide has **greater** partial double bond character</u> 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.

(c)

(i)

[1]

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.

(ii)



1 mark for arrow correctly shown on either structure

Comments:

The resonance forms given in this question shows the delocalisation of the π electrons. Most students were able to draw a correct direction of the curly arrow to show the movement of the pair of π 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-C*l* 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 <u>attack the electron-deficient</u> <u>carbon 180° away from the departing halogen atom</u>, *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 <u>lone pair on the N atom in the amine product</u> that allows <u>further</u> <u>nucleophilic substitution</u> in the presence of excess RX.

Suggested answer:

In the presence of excess C_2H_5Br , ammonia forms the primary <u>amine product</u> $(C_2H_5NH_2)$ which has a <u>lone pair on the N atom which can also act as nucleophile to</u> attack another molecule of C_2H_5Br via further nucleophilic substitution. Further <u>substitutions</u> of the secondary amine and subsequent tertiary amine products <u>occur</u> due to the availability of the lone pair on the N atom <u>until</u> 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.



(e)





[1] for each structure

Information	Type of reaction	Deduction
L is a	-	(L has a ring structure)
chlorocycloalkane,		
$C_7H_{12}Cl_2$		
Heating L with	Elimination [1]	Elimination of <u>2 HCl</u> from L
ethanolic KOH,		indicates M contains two
compound M , C_7H_{10} , is		alkene groups C=C. $[]$
formed as the only		
product.		
Treating with hot	<u>Strong</u>	 Loss of 2 carbons shows
acidified KMnO ₄ , M	oxidation/Oxidative	both alkene groups in M is
forms an optically	cleavage of	oxidized to form two CO ₂
active compound N ,	<u>alkene[</u> √]	and N upon strong

Μ

$C_5H_8O_4$, as the only organic product		oxidation. $[]$ • N contains <u>a chiral</u> carbon. $[]$
N does not react with 2,4-DNPH but liberates CO ₂ from Na ₂ CO ₃ (aq).	<u>Acid-base</u> (reaction with Na₂CO₃) [√]	 No reaction with 2,4- DNPH shows N has no ketone group (alkene in M does not have R',RC= structure). [√] Reaction with Na₂CO₃ shows N contains carboxylic acid, its formula with 4 O atoms suggests two CO₂H, 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 (-CH₂-CH₂-CH₂- vs -CH(CH₃)-CH₂-). 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 HO₂CCH(CH₃)CH₂CO₂H.

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 <u>two HCl molecules</u> are eliminated from L to form <u>two C=C bonds</u> in M (a diene).
- 3. Did not realize that the fact that M is the <u>only elimination product</u> formed would imply that there is <u>only one way to remove the two HCI molecules</u> from L. So, the <u>two CI</u> <u>atoms are adjacent to each other on L</u> as there will be more than one possible N if CI 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 KMnO4 as <u>strong</u> oxidation or <u>oxidative cleavage</u>.
- 6. Did not show understanding that <u>oxidative cleavage of a cyclic diene</u> will <u>produce 2</u> <u>aliphatic open chain compounds</u>. Many incorrectly deduced that there are terminal alkene groups present in M.

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

Example:



- 7. Not many noted that oxidative cleavage of M formed <u>only one product N</u> implied that the other oxidised compound is <u>CO₂</u>. Based on (6), it is <u>H₂CO₂H ethanedioic acid</u> which undergoes further oxidation to CO₂ and H₂O.
- 8. Although many correctly deduced that <u>N has chiral carbon</u>, 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 <u>dicarboxylic acid</u>.

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	0
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 $\mathbf{A} = \text{KCrO}_3\text{Br} \left(\frac{\text{accept KCrBrO}_3}{\text{CrBrO}_3} \right)$ [1]

mass of empirical formula = 219.0 therefore, n=1

 $K_2Cr_2O_7 + 2HBr \rightarrow 2KCrO_3Br + H_2O$ [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, AgBr Yellow solution C contains CrO₄²⁻ (ignore cation if stated) Orange solution D contains Cr₂O₇²⁻
E, [Cr(H₂O)₆]³⁺ (accept Cr³⁺)
[2] 1 mark for any two unknowns B, C, D, E

not required, FYI: $CrO_3Br^- + Ag^+ + H_2O \rightarrow AgBr + CrO_4^{2-} + 2H^+$ **A** not required, FYI: $2CrO_4^{2-} + 2H^+ \implies Cr_2O_7^{2-}(aq) + H_2O$ **C D**

D undergoes <u>redox</u> reaction with SO₂ to form **E** [1] Equation $Cr_2O_7^{2^-} + 3SO_2 + 2H^+ \rightarrow 3SO_4^{2^-} + 2Cr^{3^+} + H_2O$ or $Cr_2O_7^{2^-} + 3SO_2 + 2H^+ + 11H_2O \rightarrow 3SO_4^{2^-} + 2[Cr(H_2O)_6]^{3^+}$

[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 SO₂ 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:

 $Cr_2O_7^{2^-} + 14H^+ + 6 e^- \rightarrow 2Cr^{3^+} + 7H_2O \quad x \ 1$ $SO_2 + 2H_2O \rightarrow SO_4^{2^-} + 4H^+ + 2e^- \qquad x \ 3$

 $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O_7^{3+}$



[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 CI 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 ^o reacts with anhydrous PCI₅ to form the acid chloride in H. Phenol group does not react with PCI₅ 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: KMnO₄, dilute H₂SO₄, cold [1] Step 2: K₂Cr₂O₇, dilute H₂SO₄, heat under reflux [1] (cannot accept KMnO₄) Step 3: NaBH₄ (in methanol/ethanol), r.t./ H₂ with Ni, heat / H₂ 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 $K_2Cr_2O_7$. Alkenes can only be oxidised by KMnO₄ Use heat under reflux instead of cold for mild oxidation

Step 2 Use KMnO₄. Note that the presence of benzylic hydrogen in G will cause side-chain oxidation to occur.

Step 3 Using LiAIH₄. The ester group present in J will be reduced by LiAIH₄.

(i) Due to the small cationic size and a large positive charge, and hence a high charge density of Mg²⁺. After dissolving, the hydrated magnesium ion undergoes slight hydrolysis[1] to form a slightly acidic solution of pH 6.

> $MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^{-}$ $[Mg(H_2O)_6]^{2+} \Rightarrow [Mg(H_2O)_5(OH)]^+ + H^+$ both eqns [1]

Comments:

Many students could explain the pH value in terms of the hydrolysis of Mg²⁺ but fewer students explained hydrolysis occurred due to the high charge density of Mg²⁺. Quite a number of students wrote an incorrect equation where both Mg(OH)2 or MgO and HCl were formed as products together.

(ii) nMgC $l_2 = \frac{1}{2} \times nNaOH = \frac{1}{2} \left(\frac{20}{1000} \times 1.00\right) = 0.0100 \text{ mol}$ $[MgCl_2] = \frac{1000}{50} \times 0.0100 = 0.200 \text{ mol dm}^{-3} [1]$

Comments:

Most students who attempted scored the mark here. Most common errors were to use the wrong volume of NaOH or the wrong mole ratio ($nMgCl_2 = nNaOH$) for calculations.

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

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

Comments:

Most students scored the mark here, though a few wrote the expression wrongly in terms of soluble MqCl₂ instead. A handful also wrote the K_c expression for the reaction of MgCl₂ with NaOH as the answer.

(d)

(iv) pH = 9 when 10 cm³ of NaOH was added

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

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

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

Comments:

This question was poorly done.

Students need to 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 cm³ of NaOH, all the MgCl₂ has been reacted away similar to equivalence point in acid-base graph).

To find the K_{sp} value, we need to use the information given in the question including the information from Fig 4.2.

When 10 cm³ of NaOH was added,

- the [Mg²⁺(aq)] halved as some Mg²⁺(aq) is precipitated as Mg(OH)₂.
- the pH of the solution is 9 (from Fig. 4.2) due to the [OH⁻] present from the equilibrium: Mg(OH)₂(s) ≠ Mg²⁺(aq) + 2OH⁻(aq)----eqm 1

Common errors:

- Halving the [Mg²⁺] calculated from (d)(ii) and using mole ratio to determine [OH⁻]. This method is not valid since [Mg²⁺(aq)] present in the solution comes from both the MgCl₂ remaining and the Mg²⁺(aq) from the eqm 1.
- Finding the [OH⁻] in the solution by taking nNaOH added / total volume. This method is incorrect as the 10 cm³ of NaOH added is the limiting reagent and would have all reacted to form Mg(OH)₂. So the amount of OH⁻ present is due to partial solubility of the Mg(OH)₂ formed.
- Incorrectly reading the graph or taking pH = 9 to be pOH to calculate $[OH^{-}]$.

[Total: 20]

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

> SiC l_4 undergoes <u>complete hydrolysis</u> in water to produce very acidic solutions of <u>pH 1–2</u>. SiC $l_4(l) + 4$ H₂O (l) \rightarrow SiO₂.2H₂O (s) + 4 HCl (aq)

correct equation for SiCl₄ [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 SiCl₄ 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 Si⁴⁺, wrote equations involving the hydration of covalent SiCl₄ to form ions or wrongly stated that SiCl₄ 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 σ bonds and 4 π bonds [1] N≡C-C≡N

Comments:

Most students answered this question correctly. Drawing out the structure of cyanogen will help students to see the 3 σ bonds (1 in each C=N bond and in the C-C bond) as well as the 4 π bonds (2 in each C=N bond).

(ii) Step 1: Br₂(I) or Cl₂(g) in CCl₄ [1]
 Step 2: (Excess) NH₃ in ethanol, heat in sealed tube [1]

intermediate: $Cl - CH_2 - CH_2 - Cl_1 / Br - CH_2 - CH_2 - Br_{[1]}$

Comments:

Students recognised that they should carry out electrophilic addition of halogen on ethene, then substitute the added groups with $-NH_2$ 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 $Br_2(aq)$ for step 1 was not given credit as this would form a bromohydrin instead (Br and OH groups added across the C=C).. Students must be more careful about including solvents like CCl₄ and ethanol for the

reagents must be more careful about including solvents like CCI₄ 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.

(c) (i) H
$$H^{-}CH_{2}CH_{2}N^{+}H^{-}$$

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 $[Ni(en)_3]^{2+}$, 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** : $[CuCl_2]^-$

R: $[(Cu(H_2NCH_2CH_2NH_2)_2]^{2+}(or Cu(H_2NCH_2CH_2NH_2)_2]Cl_2)$ **S**: Cu metal **T**: AgC*l*

 $CuCl + Cl^{-} \rightarrow [CuCl_2]^{-}$

 $2CuCl + 2 H_2NCH_2CH_2NH_2 \rightarrow [Cu(H_2NCH_2CH_2NH_2)_2]^{2+} + Cu + 2Cl^{2+}$

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 $CuCl_2^-$ (2 dative bonds \Rightarrow linear shape)

As CuCl reacts with ethylenediamine to form a blue solution **R** and a pink solid **S**, this implies that **S** is Cu and a disproportionation reaction has occurred. $Cu^+ + e^- \rightarrow Cu$ $Cu^+ \rightarrow Cu^{2^+} + e^-$

Since **R** contains only ethylenediamine and has a square planar shape, this implies that a complex between 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 Cu^{2+} .

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

Comments: The majority had problem remembering the full definition correctly.

(ii) $\Delta H_{soln} (NiCl_2) = -(-2753) + (-2096) + 2 (-381) = -105 \text{ kJmol}^{-1}$ Correct value of $\Delta H_{soln} (NiCl_2)$ [1]

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



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]