

EUNOIA JUNIOR COLLEGE JC2 Preliminary Examination 2022 General Certificate of Education Advanced Level Higher 2

CANDIDATE NAME					
CIVICS GROUP	2	1	-	INDEX NUMBER	

# CHEMISTRY

Paper 2 Structured Questions

9729/02 15 September 2022 2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

# READ THESE INSTRUCTIONS FIRST

Write your name, civics group, index number on all the work you hand in.Write in dark blue or black pen.You may use an HB pencil for any diagrams or graphs.Do not use staples, paper clips, glue, or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use					
Paper 2					
1	/ 20				
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This document consists of **19** printed pages and **1** blank page.

- 1 The carbon family consists of the elements of Group 14. The elements at the top of the group, carbon to germanium, have very different properties from those at the bottom, tin and lead. For instance, Group 14 elements tend to adopt oxidation states of +4, whereas the heavier elements, such as tin and lead, exhibit the +2 oxidation state due to the inert pair effect.
  - (a) State the valence shell configuration of Group 14 elements.

ns<sup>2</sup> np<sup>2</sup> [1] Comments:

This is generally badly attempted. Many erroneous responses include electron in box diagram, +4, p4,  $s^2p^2$ .

(b) One of the contributing factors to the inert pair effect is the unexpected increase in the ionisation energies, after lead, down the group.

Explain why the 1<sup>st</sup> ionisation energies are expected to decrease down the group.

Down the group, nuclear charge increases and shielding effect increases. Valence

electrons are further away from the nucleus and this leads to decrease in

electrostatic forces of attraction between the nucleus and the valence electron...

Less energy needed to remove the valence electron, resulting in decrease in 1<sup>st</sup> I.E.

down the group. [2]

Comments:

Generally well done. Candidates were penalised for mistaking that nuclear charge remains unchanged due to same number of valence electrons instead of number of protons. Down the group, effective nuclear charge actually increases slightly down the group or remains approximately unchanged and does not really aid in the explanation for the decreasing 1<sup>st</sup> ionisation energies down the group. Hence, the emphasis is on the decreasing electrostatic forces of attraction between the nucleus and the valence electron being further away due to increasing number of shells of electrons.

- (c) Carbon forms carbide anion,  $C_2^{2-}$  in calcium carbide while silicon mostly forms Si<sup>4+</sup> ions.
  - (i) Draw the dot-and-cross diagram of the carbide anion,  $C_2^{2-}$ .

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Generally well done. Some responses were penalised for giving solely dots only or crosses only. Candidates were reminded the purpose of the use of dots and crosses is to distinguish the valence electrons from different atoms regardless if they are of the same element. Also, the use of the dots and crosses also differentiates the valence electrons of the carbon atoms from the additional electrons from the –2 charge.

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[1]

For Examiner's Use (ii) In a particular experimental set-up, a beam of <sup>28</sup>Si<sup>4+</sup> ions was deflected by an angle of +4.2°. Assuming an identical set of conditions, by what angle will the <sup>12</sup>C<sub>2</sub><sup>2-</sup> ions be deflected?

<sup>28</sup>Si<sup>4+</sup> whose 
$$\frac{q}{m} = \frac{+4}{28} = +\frac{1}{7}$$
 gives an angle of deflection,  $\theta$ , of +4.2°  
 $\theta = k \left(\frac{q}{m}\right) \Rightarrow +4.2^{\circ} = k \left(+\frac{1}{7}\right) \Rightarrow k = 29.4$   
For <sup>12</sup>C<sub>2</sub><sup>2-</sup> whose  $\frac{q}{m} = \frac{-2}{24} = -\frac{1}{12}$ ,  
angle of deflection,  $\theta = 29.4 \times \left(-\frac{1}{12}\right) = -2.45^{\circ}$ 

#### Comments:

Generally badly done. Many erroneous responses failed to recognise that there are 2, not just 1, carbon atoms in the  ${}^{12}C_2{}^{-2}$  ions. Omission of the negative sign is common. Candidates are reminded of the importance of the sign as it indicates the direction of the deflected beam of ions.

(d) Table 1.1 shows that the melting points of the elements of Group 14.

#### Table 1.1

element	С	Si	Ge	Sn	Pb
melting point / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each form a solid with the same type of structure. Using bonding and structure, suggest why the melting points of these elements decrease from carbon to germanium.

Carbon, silicon and germanium are of giant covalent structure. To melt these

elements, strong covalent bonds between the atoms have to be broken. From C to

Ge, the orbitals become bigger and more diffuse. The overlap of the orbitals

becomes less effective. Bond strength decreases and hence less energy is required

for melting. [2]

Generally well done. Common mistakes include omission of the bonding and structure, failure to recognise that germanium is of the same bonding and structure as carbon, silicon as stated in the question stem or mistaking carbon, silicon and germanium to be of giant metallic lattice structure. Another common mistake is that of breaking of ionic bonds or intermolecular instantaneous dipole-induced dipole interactions in the giant covalent structure. Several candidates also tried to replicate their response to Question 1(b) here failed to recognise that this question is on chemical bonding rather than atomic structure in Question 1(b).

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[1]

Comments:

(e) Carbon forms many allotropes such as graphite and diamond. Recent scientific research has found that replacing the graphite electrodes with graphene in lithium-ion batteries can extend battery life.

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(i) Graphene is a **single**, **one atom thick** layer of graphite. Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms within graphene.

Each carbon atom is **sp<sup>2</sup> hybridised**, and forms **3**  $\sigma$  **bonds via head-on overlap** 

**between sp<sup>2</sup> hybrid orbital** from an adjacent C atom. The  $\pi$  bond is formed

through sideways overlap of the unhybridised p orbitals from an adjacent C

atom. [2]

#### **Comments:**

Generally badly. Many candidates merely indicated that strong covalent bonds are formed between the hybridised orbitals without indicating sigma bonds are formed due to head-on overlapping of hybridised orbitals. Omission of the explanation of pi bonds being formed from side-on overlapping of the unhybridised p orbitals is common as candidates recognise that both sigma and pi bonds are formed between carbon atoms. Reference to the bond angles or the molecular shape with respect to the carbon atoms does not warrant any credit since this is not a requirement of the question.

(ii) Using your answer from (e)(i), explain why graphene can conduct electricity along the plane.

The remaining 2p electron on each carbon atom can delocalise along the

plane when a potential difference is applied.

#### **Comments:**

Generally well done. Candidates are reminded that terms such as lone pair of electrons are not acceptable here since the mobile carriers are the delocalised sole unpaired electrons in unhybridised 2p orbitals. Also, there is no 'sea' of delocalised electrons since there is no metallic bonding here.

(iii) State and explain how you would expect the bond strength of carbon-carbon bonds in graphene to differ when compared with that in diamond.

The carbon-carbon bond in graphene is **stronger** than that in diamond. This is

due to the presence of both  $\sigma$  and  $\pi$  bonds / partial double bond character in

the C-C bond in graphene, while there are only  $\sigma$  bonds present in

<u>diamond</u>..

Generally badly done. Most common mistake include inferring that diamond has stronger carbon-carbon bonds than graphite due to more extensive covalent bonds in diamond than graphite and absence of instantaneous dipole-induced dipole interactions without recognising that the question is asking for comparison of the bond strength of covalent carbon-carbon bond in the 2 allotropes of carbon. Responses that involve ring strain, comparison of bond angles in diamond and graphite are also not acceptable since ring strain is not main factor in affecting bond strength here.

(f) Diamond and graphite are allotropes of carbon. Fig. 1.1 gives the structure of diamond and graphite. Diamond is an important abrasive while graphite is used as a lubricant.



Fig. 1.1

(i) Explain why the sign of the entropy change for the conversion of diamond to graphite is positive.

There is greater disorderliness as the layers of graphite are loosely held by

weak instantantaneous dipole-induced dipole interactions as compared to

the carbon atoms being held in the 3-dimensional lattice in diamond. This results

in greater spread of energies and more ways to arrange the particles in

graphite compared to diamond. [2]

#### Comments:

Generally well done. The most common mistake is the omission of the description of the structure of diamond being more orderly, rigid or fixed due to the extensive network of covalent bonds between the carbon atoms in comparison with the relatively more disorderly state of graphite due to the mobility of the layers of carbon. The presence of mobile electrons can contribute to, but not the sole explanation for, the relatively more disorderly state in graphite. Many candidates also mistake the lower density or physical state of graphite being liquid while diamond is solid to be reason for the increased entropy. In addition, responses that make reference to energy absorbed during bond breaking in the conversion of diamond to graphite are penalised as it is evident that they are confused between the terms of <u>entropy change,  $\Delta S$ </u>, and <u>enthalpy change,  $\Delta H$ </u>.

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(ii) The standard enthalpy change of reaction for the conversion of diamond to graphite is exothermic. Explain whether the conversion of diamond to graphite is spontaneous at all temperatures.

Since <u>∆S > 0, –*T*∆S is always negative at all temperatures.</u>

and  $\Delta H < 0$  (given in question). Hence  $\Delta G = \Delta H - T \Delta S \Rightarrow \Delta G < 0$  is spontaneous

at all temperatures. [2]

### Comments:

Generally well done. The most common mistake is not recognising that temperature cannot fall before zero kelvins, not zero degrees Celsius when using  $\underline{\Delta}G = \underline{\Delta}H - T\underline{\Delta}S$ .

(iii) In daily life, we do not observe diamond converting to graphite readily. Explain why this is so.

Although the reaction is spontaneous, it has a high activation energy and it

takes place at a very slow rate. [1]

**Comments:** 

Generally well done. The most common mistakes include recognising that diamond has high melting point or many strong covalent bonds without making reference to how fast or slow the reaction is. Several candidates were also penalised for linking high covalent bond strength to being not energetically feasible rather than being slow reaction and therefore not <u>kinetically</u> favourable.

(g) A three-membered ring cycloalkane, C<sub>5</sub>H<sub>10</sub>, gives only two mono-brominated products with Br<sub>2</sub> under uv light. Only one of the two mono-brominated product is chiral. Give the structural formulae of the cycloalkane and the two mono-brominated products formed. State the ratio in which the two mono-brominated products will be formed.





Br

bromoalkane A bromoalkane B

[3]

ratio of the products A : B = 6 : 4 = 3 : 2

Generally well done. The two most commonly wrong cycloalkanes are as follows:



brominated products clearly were penalized. Other common mistakes include failure to read question carefully that a 3-membered ring cycloalkane was expected, not cyclopentane or an aliphatic alkane.

[Total: 20]

For

**2 (a)** The reaction of secondary halogenoalkanes with NaOH(aq) may be a first order or second order reaction.

0.0500 mol dm<sup>-3</sup> (C<sub>6</sub>H<sub>5</sub>)CHBrCH<sub>3</sub> was reacted with 2.00 mol dm<sup>-3</sup> NaOH(aq) at a constant temperature and the half-life is constant at 277 seconds.

- (i) Explain the meaning of the following terms:
  - order of reaction
  - half-life

The order of reaction with respect to a given reactant is the power to which the

concentration of that reactant is raised to in the rate equation.

The half-life of a reaction is the time taken for the concentration of a reactant

to decrease to half its initial value. [2]

This two definition questions are generally badly done. Candidates missed out key words important for defining the terms, or used the wrong terms, such as 'compound' or 'substance', instead of the correct term 'reactant'.

(ii) Although the half-life of the experimental study is constant, explain why the half-life of the reaction cannot be used to determine whether the reaction takes place via an  $S_N1$  or  $S_N2$  mechanism.

As [NaOH(aq)] is significantly higher than/ in large excess of [(C6H5)CHBrCH3],

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Use

[2]

the [NaOH(aq)] effectively remains constant such that the reaction would be

approximated as first-order kinetics/ would behave as a pseudo 1st order

reaction even if was 2<sup>nd</sup> order kinetics. Hence, it is not possible to differentiate

between  $S_N1$  (first-order kinetics) and  $S_N2$  (second-order kinetics) based on the

half-life of the experimental study. [1]

### **Comments:**

Generally well done. A very common misconception that arises from this question is that  $(C_6H_5)CHBrCH_3$  is a secondary halogenoalkane, hence it can react via  $S_N1$  or  $S_N2$  mechanism. However, this is not true as the question is with respect to the reaction stated in 2(a), where [NaOH] is in large excess, and reaction is a pseudo 1<sup>st</sup> order reaction.

(iii) Optically pure (C<sub>6</sub>H<sub>5</sub>)CHBrCH<sub>3</sub> reacts with NaOH via an S<sub>N</sub>1 mechanism. Describe the mechanism. In your answer, show any relevant charges, dipoles or lone pairs of electrons you consider important in the mechanism.



Many candidates made the following mistakes when drawing mechanism:

- no partial charges/ full charge
- wrong direction of arrow
- in the fast step, the tail of arrow is not at lone pair on O of OH, and head of arrow is not directly pointed at C with positive charge.
- Br<sup>-</sup> missing for slow step
- Missing slow/ fast steps labelling

**Comments:** 

(iv) Suggest, with reference to the mechanism in (a)(iii), why the product does not rotate plane polarised light.

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The <u>carbocation</u> intermediate formed in the rate-determining step has a <u>trigonal</u>

planar shape around the carbon centre. The OH<sup>-</sup> nucleophile can attack from

above and below the plane with equal probability to form an equal amount of

enantiomers, thus forming a <u>racemic mixture</u>. [2]

#### Comments: Generally well done!

(v) With reference to the mechanism in (a)(iii), write the rate equation for the reaction between (C<sub>6</sub>H<sub>5</sub>)CHBrCH<sub>3</sub> and NaOH(aq). Hence, calculate the rate constant.

rate = 
$$k[(C_6H_5)CHBrCH_3]$$
  
 $t_{\frac{1}{2}} = \frac{\ln 2}{k}$   
 $k = \frac{\ln 2}{t_{\frac{1}{2}}}$   
 $= \frac{\ln 2}{277 \text{ s}}$   
 $= 2.50 \times 10^{-3} \text{ s}^{-1}$  (to 3 s.f.)

[2]

#### Comments:

Generally badly done. Some candidates did not write the rate equation with reference to (a)(iii). For those who wrote the correct rate equation, some were not able to calculate rate constant even though this is a simple and direct calculation. Many candidates also missed out the units for rate constant which is not acceptable as values without units cannot be accurately defined.

(vi) Suggest and explain how the rate of reaction would change if

• the temperature of the reaction was increased

The reaction will proceed at a faster rate as a greater fraction (or number) of

particles will have energy greater or equal to the activation energy of the

reaction. Furthermore, the particles move faster, which results in an increase

in frequency of collisions, and hence resulting in an increase in the frequency

of effective collisions. [2]

Very few candidates managed to score full credit for this question. A common mistake includes missing out the phrase 'increase in frequency of collisions', as most candidates only wrote 'increase in frequency of effective collision'. When temperature increases, the reactant particles collide more frequently and with more energy, which explains why both 'frequency of collision' and 'frequency of effective collisions' increase.

•  $(C_6H_5)CHBrCH_3$  was changed to  $(C_6H_5)CHCICH_3$  of the same concentration.

Since Br is larger than Cl, the orbital overlap between the halogen and carbon

atoms is less effective, causing the bond energy of C-Br to be lower than

that of C-C1 and requiring less energy to cleave. Thus, the activation energy

increases for the reaction involving ( $C_6H_5$ )CHC $lCH_3$ , resulting in a lower rate

constant and hence lowered rate of reaction. [2]

#### Comments:

Generally badly done. Many candidates have this common misconception: Cl is more electronegative than Br, which makes C-Cl bond more polar, and thus C-Cl bond is weaker than C-Br bond and easier to cleave. A more polar C-Cl bond does not mean it is a weaker bond.

(vii) Water is a more polar solvent than ethanol. With reference to the mechanism in
 (a)(iii), explain why the rate of S<sub>N</sub>1 substitution is lowered when NaOH(aq) is replaced by ethanolic NaOH.

As ethanol is less polar than water, it is less able to stabilise the carbocation

intermediate formed in the rate-determining step, increasing the activation

energy of the slow step, which results in a slower rate of formation. [1]

#### Comments:

Only a handful of candidates managed to get credit for this question. The common misconceptions in this question are:

- 1) NaOH is less soluble in ethanol, thus in ethanol, [OH] decreases, and react of reaction decreases. However, NaOH is not in the slow step of  $S_N1$  mechanism.
- 2) Elimination of HBr occurs when ethanolic NaOH is used. Even if elimination reaction occurs, it should not affect the rate of nucleophilic substitution.

For Examiner's Use (b) The Haber process uses atmospheric nitrogen and hydrogen to produce ammonia gas. When a mixture comprising 1.0 mol of nitrogen and 3.0 mol of hydrogen initially was left to equilibrate in a closed vessel maintained at 500 °C and 250 atm, 0.70 mol of ammonia was attained when the system reached equilibrium.

 $N_2 + 3H_2 \rightleftharpoons 2NH_3$ 

(i) Calculate the  $K_p$  for the following equilibrium.

	N <sub>2</sub>	+	<b>3H</b> <sub>2</sub>	$\rightleftharpoons$	<b>2NH</b> <sub>3</sub>
initial amt / mol	1.0		3.0		0
change in amt / mol	-0.35		-0.35×3		+0.70
equilibrium amt / mol	0.65		1.95		0.70

total amount of gas at equilibrium: 0.65 + 1.95 + 0.70 = 3.30 mol

$$K_{p} = \frac{\left(p_{NH_{3}}\right)^{2}}{p_{N_{2}} \times \left(p_{H_{2}}\right)^{3}} = \frac{\left(\frac{0.70}{3.30} \times 250\right)^{2}}{\left(\frac{0.65}{3.30} \times 250\right) \times \left(\frac{1.95}{3.30} \times 250\right)^{3}}$$
$$= 1.771 \times 10^{-5} \text{ atm}^{-2}$$
$$= \frac{1.77 \times 10^{-5} \text{ atm}^{-2}}{1.77 \times 10^{-5} \text{ atm}^{-2}}$$

**Comments:** 

Generally badly done. Majority of the cohort did not know how to calculate partial pressure of the respective gases, and hence  $K_p$ . Some candidates tried to calculate concentrations of the reactants and products to substitute into the  $K_p$  expression, which is worrying!

Candidates should try to leave the units of  $K_p$  in atm (as given in the question) instead of Pa, to avoid the hassle of units conversion and the possibility of making conversion error.

(ii) Hence or otherwise, calculate the  $K_{p}$  for the following equilibrium.

$$4NH_3 \rightleftharpoons 2N_2 + 6H_2$$

$$\mathcal{K}_{p} = \frac{\left(\mathcal{P}_{N_{2}}\right)^{2} \times \left(\mathcal{P}_{H_{2}}\right)^{6}}{\left(\mathcal{P}_{NH_{3}}\right)^{4}} = \left(\frac{1}{1.771 \times 10^{-5} \text{ atm}^{-2}}\right)^{2}$$
  
= **3.19 × 10<sup>9</sup> atm<sup>4</sup>**

[1]

**Comments:** 

Generally badly done. Many candidates do not know how to relate the  $K_p$  in question (i) to the new  $K_p$  in (ii), and just inverted the  $K_p$  in (i) without squaring the whole expression. Candidates also failed to realise that the units of  $K_p$  in (ii) will change.

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[3]

(iii) Helium gas was injected into the equilibrium mixture under constant volume. Explain how the amount of ammonia would change.

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The amount of ammonia would not change, as there is no change to the the

partial pressures of the reactant gases and products. [2]

#### Comments:

Generally badly done. Many students could state that the amount of ammonia would not change, but could not give the reason. Common mistakes include:

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- Total pressure increases and hence POE shifts to the right to decrease pressure, and amount of ammonia increases. This is not true as the mole fraction of gases decreases, which offsets the increases in total pressure, hence partial pressure of gases remains the same.
- 2) Temperature is the same, hence K<sub>p</sub> does not change and amount of ammonia does not change. However, this is not true as even though K<sub>p</sub> does not change, it is still possible for the partial pressure of gases to change, which will affect the final amount of gases.

[Total: 20]

**3** For redox reactions in acidic medium under standard conditions, their  $E^{\ominus}$  values from the *Data Booklet* are valid only at pH 0. However, the pH in typical biological systems is usually around 7. Hence, a new type of reduction potential specific to pH 7 has been defined, which is known as formal reduction potential,  $E_{\text{formal}}^{\ominus}$ .

The  $E^{\ominus}$  and  $E_{\text{formal}}^{\ominus}$  values for some important reactions are given in Table 3.1. Reactions which  $E^{\ominus}$  values have not been experimentally determined are not indicated.

	half-equation	<i>E</i> <sup>↔</sup> /V	$m{E}_{ ext{formal}}^{m{\Theta}}/m{V}$
1	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23	+0.82
2	oxaloacetate + $2H^+$ + $2e^- \rightleftharpoons$ malate	+0.33	-0.17
3	$NAD^+ + 2H^+ + 2e^- \rightleftharpoons NADH + H^+$	-0.11	-0.32
4	$FAD + 2H^+ + 2e^- \rightleftharpoons FADH_2$	_	-0.22

Table 3.1	
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(a) Based on the data in Table 3.1, explain why the  $E_{\text{formal}}^{\ominus}$  is less positive than  $E^{\ominus}$  for the reduction of O<sub>2</sub> gas.

 $E_{\text{tormal}}^{\ominus}$  is measured at pH higher than 0. Hence, [H<sup>+</sup>] is lower than 1 mol dm<sup>-3</sup>,

position of equilibrium shifts to the left, resulting in a less positive value. [1]

#### **Comments:**

This was generally well done. The main wrong answer given was that pH 7 has a higher concentration of H<sup>+</sup> than pH 0 since the pH is higher.

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Fig. 3.1 shows the schematic diagram of the citric acid cycle that involves some application of reactions given in Table 3.1. All reactants and products involved in the citric acid cycle are in the aqueous state.

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Fig. 3.1

(b) FAD and NAD<sup>+</sup> are two oxidising agents used in the citric acid cycle. With reference to the E<sup>⊕</sup><sub>formal</sub> values in Table 3.1, explain whether FAD or NAD<sup>+</sup> is a better oxidising agent.

The  $E_{\text{formal}}^{\ominus}$  for the reduction of FAD is **less negative (or more positive)** than the

reduction of NAD<sup>+</sup>, hence FAD is a better oxidising agent.

#### **Comments:**

This was generally well done. Students who lost credit here stated that FAD has a larger  $E_{\text{formal}}^{\ominus}$  than NAD<sup>+</sup> without specifying that it is more or less negative.

(c) Calculate  $\Delta G_{\text{formal}}^{\ominus}$  for step II.

$$E_{\text{cell, formal}}^{\ominus} = E_{\text{red, formal}}^{\ominus} - E_{\text{oxd, formal}}^{\ominus} = -0.32 - (-0.17) = -0.15 \text{ V}$$

$$\Delta G_{\text{formal}}^{\ominus} = -2 \times 96500 \times (-0.15)$$
$$= +29.0 \text{ kJ mol}^{-1}$$

[2]

#### **Comments:**

This was surprisingly poorly done. Many did not realise that step II is a complete redox reaction! Many calculated the  $\Delta G_{formal}^{\ominus}$  for either the conversion of malate to oxaloacetate or the conversion of NAD<sup>+</sup> to NADH + H<sup>+</sup>. Many also forgot about the '-' sign in front of the -nFE. Many also did not know the units of  $\Delta G_{formal}^{\ominus}$  and gave it as CV. It should be J mol<sup>-1</sup> or kJ mol<sup>-1</sup>. Many also did not use the  $E_{cell, formal}^{\ominus}$  to guide them in checking the sign of the calculated  $\Delta G_{formal}^{\ominus}$ . If the  $E_{cell, formal}^{\ominus}$  is negative, then the  $\Delta G_{formal}^{\ominus}$  must be positive!

(d) In the citric acid cycle, it is noted that the consumption of oxaloacetate in step I occurs Examiner's at a much faster rate than the production of oxaloacetate in step II.

(i) State the effect on the concentration of oxaloacetate due to the difference in reaction rates of the 2 steps.

For

Use

The concentration of oxaloacetate remains low OR close to zero. [1]

#### **Comments:**

This was generally well done. Answers stating that the oxaloacetate concentration would decrease were accepted.

(ii) Based on your answers in (c) and (d)(i), suggest how this can cause step II to become more spontaneous.

As the concentration of oxaloacetate remains low making

E<sub>formal</sub> (oxaloacetate malate) more negative, the E<sub>cell, formal</sub> of step II

becomes more positive, thus making the reaction more spontaneous. [1]

#### **Comments:**

This part was extremely poorly answered. Almost all answers did not differentiate between  $E_{formal}$  (oxaloacetate malate) and  $E_{formal}^{\ominus}$  (oxaloacetate malate), as well as between  $E_{cell, formal}$  and  $E_{cell, formal}^{\ominus}$ . A majority of students wrote that will  $E_{\text{formal}}^{\ominus}$  (oxaloacetate malate) become more negative, thus making  $E_{\text{cell, formal}}^{\ominus}$  more positive. Please remember that any kind of  $E^{\odot}$  will NEVER change! Once the concentration or pressure varies from standard conditions, the standard sign must be omitted!

Many answers that were penalised vaguely mentioned that the  $E_{formal}$  will change, without specifying which reaction it is referring to. Is it E<sub>formal</sub> (oxaloacetate malate) or

E<sub>cell, formal</sub>?

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- (i) With reference to the *Data Booklet*, construct an equation for the overall reaction in the galvanic cell.
  - $Mn^{3+} + Fe^{2+} \rightarrow Fe^{3+} + Mn^{2+}$  [1]

# Comments:

This was decently done. Some students were confused as to which was the galvanic cell and erroneously included components of the electrolytic cell in this answer.

 (ii) Indicate the polarity of the electrodes in both the galvanic and electrolytic cells and the direction of electron flow between the galvanic and electrolytic cells in Fig. 3.2
 [3]

#### **Comments:**

This was very poorly done. Firstly, some students erroneously drew the electrons flowing across the salt bridge. A simple way to remember this is that "electrons cannot swim" (please note that this is not an official way of answering questions. It is merely a way to help you remember this concept.).

Secondly, some students do not seem to understand the term 'polarity'. This refers to whether the electrode is positive or negative, not whether the electrode is a cathode or an anode.

Thirdly, many students seem to be fixated on the idea that electrons always flow from the negative electrode to the positive electrode. You must remember the direction of electron flow and the respective polarities of EACH TYPE of electrochemical cell. This is why students are NOT ENCOURAGED to memorise polarities of each type of cell as it is likely that you will recall the wrong ones, especially when the question combines both the galvanic cell and the electrolytic cell into one single circuit. You should memorise AN OX and RED CAT and derive the polarities from there. (iii) Explain why the electrolytes used in the galvanic cell need to be separated into two half-cells in Fig. 3.2.

If the contents of the two half-cells in the galvanic cell were mixed, then a

spontaneous reaction would occur without any electrons flowing into the

electrolytic cell. [1]

#### Comments: This part was answered decently. Incomplete answers normally gave the answer as 'to prevent the reactants from mixing' without explaining why they cannot be mixed.

- (f) Celestine is a blue mineral that contains SrSO<sub>4</sub>. When SrSO<sub>4</sub> is heated strongly, it decomposes to form a metal oxide and releases two different colourless gases. One gas rekindles a glowing splint, while the other is SO<sub>2</sub>.
  - (i) Construct the balanced equation, including state symbols, for the thermal decomposition of SrSO<sub>4</sub>.

# $RSO_4(s) \rightarrow RO(s) + SO_2(g) + \frac{1}{2}O_2(g)$ [1]

#### **Comments:**

Many did not read the question and left out the state symbols. Some did not balance the equation properly and left out the  $\frac{1}{2}$  in front of the O<sub>2</sub>.

(ii) Explain why SrSO<sub>4</sub> decomposes at a higher temperature than MgSO<sub>4</sub>.

 $Sr^{2+}$  and  $Mg^{2+}$  both have same charge. Since  $Sr^{2+}$  has bigger ionic size, its **charge** 

density is lower. Thus, with the lower polarising power, Sr<sup>2+</sup> weakens the

intramolecular covalent bonds of the anion to a lower extent, leading to

stronger bonds to be overcome. Hence, SrSO<sub>4</sub> decomposes at a higher

temperature. [2]

#### Comments:

Many students still did not attend to details in their answers. Many stated that Sr has a larger ionic radius than Mg, resulting in a lower charge density. Sr and Mg are atoms and have no ionic radii and charge densities! Some students were also unaware that it is the polarising power of  $Sr^{2+}$  affecting the intramolecular covalent bonds of  $SO_4^{2-}$  that results in a higher decomposition temperature, not the ionic bonds in SrSO<sub>4</sub>.

(iii) 5.00 g of SrSO<sub>4</sub> and MgSO<sub>4</sub> were separately heated strongly using the same heat Examiner's source for an extended period of time. Fig. 3.3 shows how the volume of gas varies with time of heating for MgSO<sub>4</sub>. Sketch on Fig. 3.3 the graph of total volume of gas evolved against time of heating for SrSO<sub>4</sub>.



= 3.44 × 10<sup>-7</sup> mol<sup>2</sup> dm<sup>-6</sup>

[2]

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#### **Comments:**

This was reasonably well done. Wrong answers generally showed attempts at finding the amount of SO<sub>4</sub><sup>2-</sup>, without realising that the K<sub>sp</sub> is to be calculated from concentration instead. Some answers reflected correct numerical values of the final answer but did not give the correct units.

[Total: 18]

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- 18
- 4 Phenylamine, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, is the simplest aromatic amine. Its main use is in the manufacture of phenyl isocyanate, C<sub>6</sub>H<sub>5</sub>NCO, a precursor to polyurethane, dyes, and other industrial chemicals. *Ex* 
  - (a) The carbon atom of the isocyanate group has a similar shape as that in CO₂. Draw the displayed formula of phenyl isocyanate, C<sub>6</sub>H<sub>5</sub>NCO.

Kekule structure is not awarded marks – benzene must be drawn correctly to show the resonance of electrons. A small handful of students also connected the isocyanate at carbon atom (instead of N atom), and gave the wrong structure.

The drawing of displayed formula also needs to consider the shape of the molecule (as per the first line of the question). Hence, structures drawn also need to observe linear shape at C.

(b) The shape of the nitrogen atom of phenyl isocyanate is bent. Hence, state the hybridisation state of the nitrogen atom of phenyl isocyanate. Suggest a bond angle for this nitrogen atom.

There are 3 regions of electron densities around the N atom.

Hence, the hybridisation state is **sp**<sup>2</sup>.

Bond angle is <u>118°</u> [2]

# Comments:

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Some students did not recognise the correct hybridisation state for the N atom, hence no credit can be awarded for subsequently guessing a correct answer as that did not show any understanding. There was also weak understanding of the hybridisation, with some students even proposing sp<sup>4</sup> hybridisation.

- (c) At 380 °C, 1.00 g of gaseous phenylamine has a measured pressure of 950 kPa and volume of  $5.90 \times 10^{-5}$  m<sup>3</sup>.
  - (i) Assume ideal behaviour, show the molar mass of phenylamine is  $96.8 \text{ g mol}^{-1}$ .

assume ideal behaviour,

$$pV = nRT = \frac{m}{M}RT$$
$$M = \frac{mRT}{pV} = \frac{1.00 \times 8.31 \times (380 + 273)}{(950 \times 10^3) \times (5.90 \times 10^{-5})}$$
$$= 96.8 \text{ g mol}^{-1}$$

[1]

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[1]

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# Comments:

Generally well done. Answers which did not show the substitution of the values cannot be awarded any credit, as they did not lend any evidence to demonstrate students' understanding.

(ii) The actual relative molecular mass of phenylamine is 93.0. As all the data are measured accurately, explain why the experimental calculated molar mass in (c)(i) is higher than the actual value.

Gaseous phenylamine is actually non-ideal because there is hydrogen bonding

between the phenylamine molecules causing the *pV* to be smaller than the ideal

pV values, leading to a larger calculated molar mass. [1]

### Comments:

Some students forgot that the value for volume is already a measured value, and tried to explain "discrepancies between measured volume and actual volume", and that made no sense. Since all the values used are measured (actual) values, then the fault in fact lies with the ideal gas equation (need a better equation that better reflects behaviour of real gas!).

Ideal gas equation does not give a good value because p in ideal gas equation does not consider intermolecular forces of attraction (i.e. actual p smaller than ideal p) and volume of molecules (i.e. actual V smaller than ideal V). So this means that to get a closer value to the actual relative molecular mass (which is smaller), a larger pV value ought to be used.

It is also necessary to explain why the experimental calculated molar mass is <u>higher</u> instead of simply being different.

(d) When an equimolar mixture of phenylamine and ethene oxide is heated, a mixture of products was formed via the nucleophilic substitution mechanism.

Compound X that is first formed reacts further with unreacted ethene oxide, giving compound Y as the major product.



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Compound X is a stronger nucleophile than phenylamine because the electron-

donating alkyl group increases the electron density on the N atom, making

the lone pair more likely to react with unreacted ethene oxide. Thus Y is the

major product rather than X. [2]

Comments:

Some students have poor recognition of which the nucleophile or electrophile is - look at Compound X and Y, and you will realise that N is joined to C (instead of O is being joined to N). There were a handful of students who argued that the O on ethene oxide attacked the phenylamine, which was confusing.

Some students confounded the activating/ deactivating effect of a substituent on benzene ring with that for an alkyl chain. In the benzene ring, the mesomeric effects are also taken into account for activating/ deactivating effect, hence -OH is activating due to -I/+M. For an alkyl chain, the -OH is electron-withdrawing as O is electronegative.

Inductive effect decreases with distance. Hence, the electron density on the N atom increases even if O is highly electron-withdrawing.

(ii) Besides compound **Y**, the reaction between compound **X** and unreacted ethene oxide also gave a byproduct, compound **Z**, via nucleophilic substitution.

Compounds Y and Z are constitutional isomers. Suggest the structure of compound Z and explain why compound Z is not formed in significant quantities as compared to compound Y.



Explanation: <u>O atom is more electronegative</u> than N atom on compound X. Hence, the <u>O atom in compound X is less likely to donate its lone pair of</u> <u>electrons</u> compared to the N atom. Thus compound Z is not formed in significant guantities. [2]



Some answers proposed a product based on the electrophilic substitution on the benzene ring, which was clearly wrong. The question had in fact suggested that the product formed should be based on nucleophilic substitution.

The only other atom capable of effecting nucleophilic substitution is the O atom, albeit this is a poor nucleophile due to O being more electronegative. Some answers suggested that it was the C atom that contained the lone pair, which made absolutely no sense as there are no lone electrons on C.

Some answers even suggested that the ethene oxide attacked the C atom (on the alkyl chain) of Compound X, which was strange as there are no good leaving groups.

(e) The reactivity of three nitrogen-containing compounds with aqueous bromine is shown in Table 4.1

	CH <sub>2</sub> NH <sub>2</sub>	NHCOCH <sub>3</sub>	NH <sub>2</sub>	
	bonzulamina			
	benzylamine	acetaniiide	prienylamine	
reactivity with Br <sub>2</sub> (aq) at room temperature	no reaction	mono-substitution of benzene ring	tri-substitution of benzene ring	

#### Table 4.1

(i) Explain the difference in the reactivity of the three compounds with  $Br_2(aq)$ .

Phenylamine is the most reactive as the lone pair of electrons on N can

delocalise into the benzene ring due to overlap between p orbital of N and  $\pi$  electron cloud of benzene. This increases the electron density of the benzene

ring greatly, making it most susceptible to electrophilic attack.

Acetanilide is less reactive than phenylamine because delocalisation of the

lone pair of electrons on N into the C=O reduces the extent of delocalisation

of the lone pair into the benzene ring. Hence, the benzene ring is less electron-

rich than phenylamine.

Benzylamine is the least reactive as the lone pair of electrons on N cannot

delocalise into the benzene ring, causing the benzene ring to be the least

<u>electron-rich</u>. [3]

- It is incorrect to say that only the -CH<sub>2</sub>NH<sub>2</sub> group is electron-withdrawing because of the -NH<sub>2</sub> group. In fact, the -NH<sub>2</sub> group bonded to the benzene ring in phenylamine and the -NHCOCH<sub>3</sub> are all electron-withdrawing. So, what gives rise to the difference in reactivity?
  - It is the electron-richness of the benzene ring. Hence, the given explanation.
- Many say that the -CO- group in -NHCOCH<sub>3</sub> withdraw electron density from the N atom, hence, decreasing the delocalisation of lone pair on N into the benzene ring. IT IS IMPORTANT to REMEMBER that for amide, ya -NHCOCH<sub>3</sub> is an amide, the lone pair CAN delocalise into the C=O group! Hence, making amide a neutral compound at A-level.
  - (ii) Write a balanced equation for the reaction between phenylamine and Br<sub>2</sub>(aq) at room temperature.



#### **Comments:**

- Take note, FOR A-level, benzene ring undergoes electrophilic substitution! Hence, if Br-Br is to make an electrophilic attack on phenylamine, you can imageine the attack as being made by a "Br<sup>+</sup>", which means the "leftover" Br<sup>-</sup> (a nucleophile) CANNOT attack the electron-rich benzene again. Hence, the correct balanced equation MUST have three HBr lah.
- Take note because it is Br<sub>2</sub>(aq), therefore, we cannot have HBr(g) ah!
- (f) Lysine is an  $\alpha$ -amino acid that is used in the biosynthesis of proteins.



It is an essential amino acid because human body cannot make it, so it must be obtained from food.

The p $K_b$  values of lysine are 11.8, 5.1 and 3.5, with the  $\alpha$ -amino group being the weaker base between the two amino groups.

(i) The fully deprotonated form of lysine is shown in Fig. 4.1. Fill in the pK<sub>b</sub> values in Examiner's the respective boxes.





[1]

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### **Comments:**

The more available the lone pair of electrons, the larger the K<sub>b</sub>, the SMALLER the pK<sub>b</sub>. Many will think that  $-CO_2^-$  will be a stronger base because it has a negative charge. This is incorrect, why? RCO<sub>2</sub>H is a stronger acid than NH<sub>4</sub><sup>+</sup>, hence, RCO<sub>2</sub><sup>-</sup> must be a weaker base (more stable) than NH<sub>3</sub>. Giving RCO<sub>2</sub><sup>-</sup> the largest pK<sub>b</sub> value.

You will ask, how do we know?  $(NH_4)_2CO_3$  exist, for those that bake will know BUT RCO<sub>2</sub>H and Na<sub>2</sub>CO<sub>3</sub> cannot coexist as the acid will decompose the carbonate.

(ii) Suggest a reason why the  $\alpha$ -amino group of lysine is less basic than the amino group on the side chain.

Due to the electron-withdrawing -COOH group, the lone pair of electrons on

#### **Comments:**

- Take note that the alkyl group is common to BOTH -NH<sub>2</sub> group. Hence, you CANNOT use the "electron-donating of alkyl group" to explain why the  $\alpha$ -amino group of lysine is less basic than the amino group on the side chain! But if you look at the  $\alpha$ -amino group, did you notice that it is closer to the electron-withdrawing -CO<sub>2</sub><sup>-</sup> group?
- It is NOT POSSIBLE for the lone pair on the N atom of -NH<sub>2</sub> to delocalise into the -CO<sub>2</sub><sup>-</sup> group because there is an sp<sup>3</sup> carbon (the  $\alpha$ -carbon) in between. Very similar to the benzylamine question in part (e)(i).
  - (iii) Draw the zwitterionic form of lysine and state the pH range at which the zwitterion will exist as the major species.



8.9 - 10.5 pH range: ..... ......[1]

- Take note that a zwitterion is a NEUTRAL particle, containing equal number of positive and negative charges!
- How to determine how the zwitterion looks like? Imagine the fully protonated lysine, there is a -CO<sub>2</sub>H and two -NH<sub>3</sub><sup>+</sup>. If you added OH<sup>-</sup>, which will be neutralised first? It would be the -CO<sub>2</sub>H first (as it is the most acidic), follow by the –NH<sub>3</sub><sup>+</sup> bonded to the α-carbon (because this –NH<sub>3</sub><sup>+</sup> group is bonded nearest to the electron-withdrawing -CO<sub>2</sub>H, hence the electron deficiency on the N atom is greater than the –NH<sub>3</sub><sup>+</sup> group on the side-chain OR from part (e)(ii), the lone pair of the -NH<sub>2</sub> bonded to the α-carbon is the least basic, hence it "wouldn't like" to "hold on to a H<sup>+</sup>).

The above explains why the zwitterion looks as such!

Next, why the pH range is as such? At the 1<sup>st</sup> endpoint, we have one -CO<sub>2</sub><sup>-</sup> and two –NH<sub>3</sub><sup>+</sup> groups, which means, we will be at a pH value that is after the pK<sub>a</sub> of -CO<sub>2</sub>H, which is 14–11.8 = 2.2.

After the 2<sup>nd</sup> endpoint, we will have the -NH<sub>3</sub><sup>+</sup> on the  $\alpha$ -carbon being neutralised. Which means the pH value will be after the pK<sub>a</sub> of -NH<sub>3</sub><sup>+</sup> on the  $\alpha$ -carbon, which is 14–5.1 = 8.9.

Hence, the pH range for the zwitterion will be between the pK<sub>a</sub> of the -NH<sub>3</sub><sup>+</sup> on the  $\alpha$ -carbon and the pK<sub>a</sub> of the -NH<sub>3</sub><sup>+</sup> on the side-chain (14–3.5 = 10.5).

(iv) The zwitterion of lysine can act as a buffer agent in the blood. Write an equation showing how the zwitterion regulate the pH when a small amount of acid is added.



**Comments:** 

- As from part (e)(ii), the -NH<sub>2</sub> on the α-carbon is more basic than the -CO<sub>2</sub><sup>-</sup>, hence, it will be the one that accept the H<sup>+</sup>.

[Total: 17]