Victoria Junior College 2021 H2 Chemistry Prelim Exam 9729/3 Suggested Answers

1

Section A

Answer **all** the questions in this section.

1 (a) Elements in the same group tend to form products with similar physical properties.

However, the oxides of carbon and silicon have very different physical structures. While CO_2 exists as a gas at room temperature, SiO_2 is a solid.

(i) Explain, in terms of structure and bonding, the difference in the physical states of CO_2 and SiO_2 .

SiO₂ has a <u>giant molecular structure</u> where each <u>Si atom is covalently</u> <u>bonded to 4 other O atoms</u>. CO₂ has <u>simple molecular structure</u> with <u>weak</u> <u>instantaneous dipole-induced dipole interactions</u> (id-id) between the CO₂ molecules. Much <u>more energy is required to break the strong covalent</u> <u>bonds</u> in SiO₂ as compared to the weak id-id for CO₂. Hence, SiO₂ is a solid while CO₂ is a gas at room temperature.

[2]

(ii) Describe the bonding in **a single** CO₂ molecule. Include a fully labelled diagram showing how the different types of bonds are formed in terms of orbital overlap.

C–O σ bond is formed via <u>head-on overlap</u> between <u>sp hybridized orbital of</u> <u>C and sp² hybridised orbital of O</u> (accept p orbital of O).

C–O π bond is formed via <u>side-ways overlap</u> between <u>unhybridized p orbital</u> of C and unhybridised p orbital of O.



(iii) By considering the extent of overlap of the orbitals, suggest a reason why SiO_2 does not form bonds similar to that of CO_2 .

Si atom has a <u>larger atomic radius</u> than C. This leads to <u>less effective</u> <u>overlap of the p orbitals between Si and O</u>. Thus, <u>a π bond formed between</u> <u>S and O would be much weaker</u> and less likely to be formed.

[1]

- (b) The extraction of iron from its ores typically involves the use of a Blast Furnace. One of the most common impurities in iron ore is silicon dioxide. To remove silicon dioxide, limestone is added. The calcium carbonate in limestone decomposes due to the high temperatures in the Blast Furnace to form calcium oxide. The calcium oxide then reacts with silicon dioxide to form calcium silicate, Ca₂SiO₄, which runs to the bottom of the Blast Furnace to be removed easily.
 - (i) State the type of reaction between silicon dioxide and calcium oxide.

acid-base [OR neutralization]

[1]

(ii) Define the term *lattice energy*.

Lattice energy is <u>energy released when one mole of solid ionic solid is</u> formed from its isolated gaseous ions.

[1]

(iii) Using the information given in **Table 1.1** and relevant data from the *Data Booklet*, draw an energy level diagram and calculate a value for the lattice energy of calcium silicate, Ca₂SiO₄(s).

enthalpy change	value/kJ mol ⁻¹
standard enthalpy change of atomisation of Ca(s)	+178
standard enthalpy change of atomisation of Si(s)	+456
$O(g)$ + 2e ⁻ \rightarrow $O^{2-}(g)$	+650
$Si^{4+}(g) + 4O^{2-}(g) \rightarrow SiO_4^{4-}(g)$	-9304
standard enthalpy change of formation of Ca ₂ SiO ₄ (s)	-994

Table 1.1



[4]

(iv) The reaction between calcium oxide and silicon dioxide also forms another form of calcium silicate, CaSiO₃.

Deduce whether the magnitude of the lattice energy of $CaSiO_3$ is expected to be larger or smaller than that of Ca_2SiO_4 . Explain your answer.

L.E. $\propto \frac{\mathbf{q}_{+} \cdot \mathbf{q}_{-}}{\mathbf{r}_{+} + \mathbf{r}_{-}}$

The <u>cationic charge and cationic radius are the same</u> for both compounds. $SiO_3^{2^-}$ has a <u>smaller anionic charge and smaller ionic radius</u> than $SiO_4^{4^-}$. <u>Charge factor dominates</u> and hence, CaSiO₃ will have a <u>lattice energy with</u> <u>smaller magnitude</u>.

[2]

(c) Compound A, C₉H₉NO₂, is insoluble in both aqueous acids and alkalis and does not react with sodium metal. When heated with aqueous hydrochloric acid, followed by careful addition of aqueous sodium hydroxide, compound B, C₈H₁₁NO is formed. Gentle warming of A with acidified KMnO₄ gives the salt of compound C, C₈H₉NO. Further strong heating of the mixture forms the salt of compound D, C₇H₇NO₂.

Each mole of compounds **B**, **C** and **D** decolourises two moles of aqueous bromine. Compound **C** gives a pale yellow precipitate on warming with alkaline aqueous iodine.

Suggest structures for **A**, **B**, **C** and **D** and explain the reactions described.

	Hints	Deductions	
1	Compound A has C:H = 1:1	A contains a <u>benzene</u> ring.	
2	Compound A, C ₉ H ₉ NO ₂ , is insoluble in both aqueous acids and alkalis	A is a neutral compound. A does not contain –NH ₂ or –COOH. A contains <u>amide / ester</u> .	
	and does not react with sodium metal.	A <u>does not contain alcohol, phenol</u> or carboxylic acid.	
3	When heated with aqueous hydrochloric acid, followed by careful addition of NaOH, compound B, C ₈ H ₁₁ NO is formed.	A undergoes <u>acid hydrolysis of</u> <u>amide</u> (and ester) followed by neutralisation. B contains an <u>amine</u> (and alcohol). Loss of carbon suggests the carboxyl carbon was removed upon hydrolysis.	
4	Gentle warming of A with acidified $KMnO_4$ gives C, C ₈ H ₉ NO.	A undergoes hydrolysis to give B which undergoes <u>oxidation of</u> <u>2^o alcohol</u> to give ketone C	
5	Further strong heating of the mixture forms D, C ₇ H ₇ NO ₂ .	Loss of carbon suggests C undergoes side–chain oxidation to give <u>benzoic acid</u> in D.	
6	Each mole of compounds B, C and D decolourises two moles of aqueous bromine.	B, C and D undergoes <u>electrophilic</u> <u>substitution</u> . They contain <u>phenylamine</u> . The compounds are either <u>1,2 or 1,4</u> <u>substituted</u> .	
7	Compound C gives a pale yellow precipitate on warming with alkaline aqueous iodine.	C undergoes <u>oxidative cleavage</u> to give <u>CHI₃ yellow ppt</u> . C contains <u>–COCH₃ structural unit</u> .	



[8]

[Total: 21]

2 (a) (i) The reaction between an aqueous solution of permanganate(VII) ions, MnO_4^- , and ethanedioate ions, $C_2O_4^{2-}$, can be represented by the following equation:

 $5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(I)$

The presence of Mn^{2^+} , which are produced in the reaction between MnO_4^- and $C_2O_4^{2^-}$, is thought to catalyse this reaction.

An experiment was performed to measure the volume of CO₂ gas produced at regular time intervals until the reaction goes to completion.

The graph of volume of CO₂ gas produced against time has three distinct regions.

Sketch on **Figure 2.1**, the graph of volume of CO₂ gas produced against time you would expect to obtain.



time

Figure 2.1



[1]

(ii) Explain why there are three distinct regions of the graph you have drawn in (a)(i).

Initially, the <u>rate of reaction will be slow</u> due to the <u>electrostatic repulsion</u> <u>between the negatively charged</u> MnO_4^- and $C_2O_4^{2-}$, which results in <u>high</u> <u>activation energy</u> to overcome. Thus, the <u>gradient will be gentle</u>.

As the reaction progresses, the <u>autocatalyst Mn^{2+} is formed</u>. Mn^{2+} provides an <u>alternative pathway of lowered activation energy</u> for the reaction to take place. Thus, <u>rate of reaction increases</u> and <u>gradient will be steeper</u>.

Towards the end of the reaction, $[MnO_4^-]$ and $[C_2O_4^{2-}]$ would have decreased to a very low value. Less reactant particles will lead to less frequency of effective collisions. Thus, rate of reaction decreases and gradient will be gentle again.

[3]

(iii) Using your answer in (a)(ii), sketch on Figure 2.2, the graph of rate against time you would expect to obtain for the same reaction in (a)(i).

6



- [1]
- (iv) The reaction mechanism for the second region of the graph you have drawn in (a)(i) can be described as follows.

step 1: MnO_4^- reacts with Mn^{2+} , producing Mn^{3+} as one of the products.

step **2**: $C_2O_4^{2-}$ is then oxidised to form CO_2 gas as one of the products.

Using the information given above, write down the balanced equations for both steps of the mechanism. You may find the half-equation given below useful.

 $2\text{CO}_2 + 2\text{e}^- \rightleftharpoons \text{C}_2\text{O}_4^{2-} \qquad E^{\oplus} = -0.49 \text{ V}$

Step 1: [R]: $MnO_4^- + 8H^+ + 4e^- \rightarrow Mn^{3+} + 4H_2O$ [O]: $Mn^{2+} \rightarrow Mn^{3+} + e^-$ Overall: $MnO_4^- + 8H^+ + 4Mn^{2+} \rightarrow 5Mn^{3+} + 4H_2O$

Step 2: [R]: $Mn^{3+} + e^- \rightarrow Mn^{2+}$ [O]: $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ Overall: $2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2$

[2]

(v) Use of the Data Booklet is relevant to this question.

Calculate E^{\bullet}_{cell} for **each** step you have written in **(a)(iv)**. Explain how your calculated values support or contradict the proposed mechanism in **(a)(iv)**.

Step 1: $E^{\circ}_{cell} = +1.52 - (+1.54) = -0.02 V$ Since $E^{\circ}_{cell} < 0$, this step is <u>not expected to be spontaneous</u>, which contradicts the proposed mechanism. However, reaction is likely to still be possible if performed under non-standard conditions.

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Step 2:

E^{\circ}_{cell} = +1.54 - (-0.49) = +2.03 \text{ V}

Since \underline{E^{\circ}_{cell} > 0}, this step is <u>expected to be spontaneous</u>, which supports the proposed mechanism.
```

[2]

(vi) State the step in (a)(iv) you would expect to be the rate determining step. Explain your answer.

The rate determining step is likely to be <u>step 1</u> as the <u>(auto)catalyst Mn^{2+} is</u> <u>consumed</u> in step 1.

[1]

(vii) The same experiment was repeated but with Mn²⁺ added at the **beginning** of the reaction.

The initial concentrations of the different chemical species in the second experiment are given in **Table 2.1**.

species	initial concentration in reaction mixture / mol dm ⁻³	
MnO₄ [−]	0.00594	
$C_2O_4^{2-}$	0.0200	
H⁺	0.990	
Mn ²⁺	9.90 x 10 ⁻⁴	

Table 2	.1
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Using your answers to (a)(iv) and (a)(vi), determine the initial rate for the second experiment.

Note:

The rate equation can be written as rate = $k [MnO_4^{-}]^m [C_2O_4^{2-}]^n [H^+]^p [Mn^{2+}]^q$ where $k = 4.11 \times 10^{11} \text{ mol}^{-12} \text{ dm}^{36} \text{ min}^{-1}$.

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Since step 1 is the rate determining step, the rate equation is rate = k [MnO_4^-] [H^+]^8 [Mn^{2+}]^4
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initial rate = $4.11 \times 10^{11} [0.00594] . [0.990]^8 . [9.90 \times 10^{-4}]^4$ = $2.17 \times 10^{-3} \text{ mol } \text{dm}^{-3} \text{ min}^{-1}$

[1]

(b) KMnO₄ can also be used to determine the kinetics for the decomposition of H₂O₂ by withdrawing fixed aliquots at regular time intervals and perform titrimetric analysis. The graph of [H₂O₂] against time for this decomposition reaction is shown in Figure 2.3.



Figure 2.3

By drawing relevant construction lines on **Figure 2.3**, determine the order of reaction with respect to H_2O_2 . Explain your answer.



Time taken for $[H_2O_2]$ to fall from 2 mol dm⁻³ to 1 mol dm⁻³ \approx 200 s. Time taken for $[H_2O_2]$ to fall form 1.6 mol dm⁻³ to 0.8 mol dm⁻³ is \approx 200 s. (show two half lives on above graph) Since half-life of the reaction is <u>(approximately) constant at 200 s</u>, the order of reaction with respect to H_2O_2 is <u>one</u>. [2]

(c) (i) Ethanedioic acid, H₂C₂O₄, also known as oxalic acid, can be found in leafy greens, vegetables, fruits, cocoa, nuts and seeds.

Figure 2.4 shows a reaction scheme involving $H_2C_2O_4$ and $ClCH_2CH_2Cl$ as starting materials.



Figure 2.4

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Suggest the reagents and conditions for steps ${\bf 1}$ to ${\bf 3}$ and draw the structures of the ${\bf A}$ and ${\bf B}.$

step 1: excess PC*I*₅, r.t.p. OR excess SOC*I*₂, heat OR excess PC*I*₃, heat step 2: excess KCN(alcoholic), heat step 3: excess LiA/H₄ in dry ether, r.t.p. OR H₂, Ni, heat OR H₂, Pt, r.t.p.

A: $NCCH_2CH_2CN$, B: $H_2N(CH_2)_4NH_2$

[2]

(ii) Explain the difference in the rate of hydrolysis of $(COC_1)_2$ and $C_1/CH_2CH_2C_1$.

 $(COCI)_2$ undergoes hydrolysis more readily than C/CH₂CH₂CI. The presence of <u>two highly electronegative O and CI atoms</u> makes the <u>carboxyl C more electron deficient</u> and thus <u>more susceptible to</u> <u>nucleophilic attack</u>.

In C/CH₂CH₂C*I*, the alpha carbon bonded, which is <u>only bonded to one highly</u> <u>electronegative C*I* atom</u> is <u>less electron deficient</u> and thus <u>less susceptible</u> <u>to nucleophilic attack</u>.

[2]

[Total: 17]

element	К	Ca	Fe	Ga	As	Se
1 st I.E.	418	590	762	577	944	941
2 nd I.E.	3070	1150	1560	1980	1790	2050
3 rd I.E.	4600	4940	2960	2960	2740	3060
4 th I.E.	5860	6480	5400	6190	4840	4140
5 th I.E.	7980	8140	7240	8300	6060	6590

T-1-1-04

3 (a) **Table 3.1** shows the first five ionisation energies (I.E.) of some Period 4 elements:

(i) With reference to the electronic configurations of As and Se, explain why the 1st I.E. of Se is lower than that of As.

As: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p³ Se: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁴

The valence electron to be removed from Se is a paired 4p electron whereas the valence electron to be removed from As is an unpaired 4p electron. <u>Less</u> <u>energy is required</u> to remove the paired electron due to additional <u>inter-electronic repulsion</u> caused by the paired electrons.

[2]

(ii) With reference to the electronic configurations of Ca²⁺ and Ga²⁺, explain why the 3rd I.E. of Ca is higher than that of Ga.

Ca²⁺: 1s² 2s² 2p⁶ 3s² 3p⁶ Ga²⁺: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹

<u>Ca²⁺ has one less electron shell</u> compared to Ga²⁺. Thus, <u>more energy is</u> required to overcome the <u>valence electron of Ca²⁺ which is closer and thus</u> more strongly attracted to the nucleus.

[2]

(iii) Table 3.2 shows the increment for the first five I.E. of Fe.

Table 3.2						
element	1 st I.E.	2 nd I.E.	3 rd I.E.	4 th I.E.	5 th I.E.	
Fe	762	1560	2960	5400	7240	
	7	98 14	100 24	40 18	40	

With reference to the electronic configuration of Fe^{3+} , suggest a reason for the anomaly in increment from 3^{rd} to 4^{th} I.E. of Fe.

Fe³⁺: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵

The fourth electron to be removed is from a <u>stable $3d^5$ configuration/half-filled 3d orbitals</u>. Thus, more energy is required to remove the fourth electron.

[1]

(b) Potassium trisoxalatoferrate(III), K₃[Fe(C₂O₄)₃], is a green crystalline salt made up of potassium cations, K⁺, and ferrioxalate anions, [Fe(C₂O₄)₃]³⁻.

The ferrioxalate anion is photo-sensitive. In the presence of light, $[Fe(C_2O_4)_3]^{3-1}$ undergoes a redox reaction as shown in equation (1):

Equation (1):
$$[Fe(C_2O_4)_3]^{3-}(aq) \rightarrow Fe^{2+}(aq) + \frac{5}{2}C_2O_4^{2-}(aq) + CO_2(g)$$

(i) State and explain whether equation (1) is a disproportionation reaction.

Fe is being reduced from +3 to +2 while C is being oxidized from +3 to +4. Since <u>different elements are being reduced and oxidized</u>, / there is no one element that is simultaneously oxidised and reduced, equation (1) is <u>not a</u> <u>disproportionation reaction</u>.

[1]

(ii) Using the information given in **Table 3.3**, construct an energy cycle and calculate the standard Gibbs' free energy change of the reaction in equation (1).

Table 3.3				
half-equation	ΔG^{e} , kJ mol ⁻¹			
$[Fe(C_2O_4)_3]^{3-}(aq) + e^- \rightleftharpoons [Fe(C_2O_4)_3]^{4-}(aq)$	-4.8			
$[Fe(C_2O_4)_3]^{4-}(aq) + 2e^- \rightleftharpoons Fe(s) + 3C_2O_4^{2-}(aq)$	+113.9			
$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$	+85.0			
$2CO_2(g) + 2e^- \Rightarrow C_2O_4^{2-}(aq)$	+123.5			



- (iii) Hence, calculate the E^{e}_{cell} value of equation (1).

[1]

[3]

(iv) With reference to your answers in (b)(ii) and (b)(iii), suggest a reason why light is needed for the reaction in equation (1) to occur.

The reaction could be associated with <u>high activation energy</u> due to the need to break strong covalent bonds within $C_2O_4^{2-}$.

[1]

(c) To produce the medals for the Olympics Games, the Tokyo 2020 organising committee launched a campaign to collect unwanted electronic devices to harvest the necessary metals. The two-year campaign led to the collection of over 145,000 items, contributing 32 kg of gold, 3500 kg of silver and 2200 kg of bronze to the production of 5000 medals.

The medals for the Tokyo Olympic Games are made fully from the recovered metals. However, many replicas are produced by electroplating a layer of the necessary metal onto a relatively inexpensive base object.

(i) **Figure 3.1** shows an inaccurate diagram for electroplating silver onto a base object made of iron.



Figure 3.1

Identify and explain the error in Figure 3.1.

The <u>electrolyte should not be a solution of CuSO₄(aq)</u>. At the start of the electrolysis process, <u>Ag⁺ is not present</u>. Thus, <u>Cu²⁺ will undergo reduction</u> to form Cu on the iron object. In addition, due to the presence of SO₄²⁻, <u>Ag⁺</u> formed will also be precipitated as Ag₂SO₄...

[2]

(ii) The error in Figure 3.1 was corrected and a current of $4.0 \times 10^{-3} \text{ A cm}^{-2}$ was passed through the set-up.

Given that the iron object has a surface area of 135 cm^2 , calculate the time, to the nearest minute, needed for 0.5 g of silver to be plated.

[2]

(d) The ferric chloride test is used to test for the presence of phenols in a given sample, with a number of phenolic compounds showing a characteristic complex colouration in the presence of neutral $FeCl_3$.

Some examples are given below:

compound	structure	complex colouration	
phenol	ОН	violet	
sulfosalicylic acid	HO ₃ S CO ₂ H	red	
2-naphthol	ОН	green	

The ferric chloride test can be represented using equation (2):

Equation (2): $3ArOH(aq) + FeCl_3(aq) \Rightarrow Fe(OAr)_3(aq) + 3HCl(aq)$ complex colouration

where Ar represents an aromatic substituent

(i) With the aid of an equation, explain why a solution of $FeCl_3$ is acidic.

 $[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^{+}(aq)$

Due to the <u>high charge density of Fe^{3+} </u>, it will <u>hydrolyse H₂O to produce H⁺</u>, giving rise to an acidic solution.

[2]

(ii) The ferric chloride test solution is prepared by adding a controlled amount of $NH_3(aq)$ to a solution of FeC l_3 .

Explain why the complex colouration may not be observed if a solution of $FeCl_3$ is not neutralised.

By Le Chatelier's Principle, if the solution is not neutralised, <u>equilibrium</u> <u>position of equation (2) will shift left to counteract the higher [H⁺]</u>, resulting in <u>less complex being formed</u>. Thus the colour may not be observed.

[1]

(iii) State the expected observation if an excess of $NH_3(aq)$ is added to a solution of FeC l_3 . Write an equation, including state symbols, to support the observation.

 $Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_{3}(s)$

A <u>red-brown ppt. of Fe(OH)₃</u> would be observed, which is <u>insoluble in excess</u> $NH_3(aq)$.

[2]

(iv) Using your answer in (d)(iii), outline the experimental steps you would take to confirm the identity of the anion in $FeCl_3$.

No details regarding use of specific glassware are required.

- 1. To 1 cm depth of FeCl₃ solution, add an excess of NH₃(aq).
- 2. Filter and collect the filtrate.
- 3. Add excess HNO₃(aq) to the filtrate.
- 4. Add AgNO₃(aq) to the filtrate. A white ppt. of AgC/ will be formed.
- 5. Add excess NH₃(aq). The white ppt. will completely dissolve.

[2]

[Total: 22]

4 (a) Benzocaine is a local anesthetic used in many over-the-counter products. It acts by preventing transmission of impulses along nerve fibers and at nerve endings. It may be synthesised from methylbenzene by the reaction route shown below.



(i) Suggest a 3-step synthetic route to form compound **A** from methylbenzene. You should state the reagents and conditions for each step and draw the structures of the intermediates formed.



(ii) Suggest the reagents and conditions for steps 1 and 2.

Step 1: Conc. KMnO₄, heat Step 2: H₂SO₄(aq), heat, then controlled addition of NaOH(aq) OR NaOH(aq), heat, then controlled addition of H₂SO₄(aq)

[2]

[5]

(iii) In step 3, concentrated H_2SO_4 is used. By considering the products of step 3, suggest how concentrated H_2SO_4 helps to improve the yield of benzocaine.

 H^{+} $RCO_{2}H + R'OH \rightleftharpoons RCO_{2}R' + H_{2}O$

Step 3 is an <u>equilibrium reaction</u>. In addition to being a catalyst, concentrated H_2SO_4 is also a <u>dehydrating agent</u>, <u>removing H_2O during the reaction</u>. By Le Chatelier's Principle, <u>equilibrium position shifts right to counteract the loss of H_2O , resulting in a higher yield of benzocaine formed.</u>

[1]

(iv) Compound **B** reacts separately with the two reagents shown in the table below.

Copy out and complete the table by drawing the **skeletal formula** of the organic products formed and stating the types of reaction involved in each case.

reaction	reagent	organic product formed	type of reaction
Ι	LiA/H₄ in dry ether	(C ₉ H ₁₃ NO)	
Π	Br₂(aq)	(C₀H₅NO₃Br)	





Reaction II: electrophilic substitution



[3]

(v) Write a balanced equation for Reaction I.



[1]

(b) Lidocaine is also a local anesthetic.

18



(i) Suggest the reagents and conditions for a reaction that could be used to distinguish between benzocaine and lidocaine.

Test: I₂(aq), NaOH(aq), warm **Observations:** Benzocaine : pale yellow ppt. of CHI₃ formed Lidocaine: no pale yellow ppt. formed

[2]

(ii) To inhibit the sensation of pain, lidocaine act on peripheral nerves by binding to the inner pore of voltage-gated Na channels on the neurons. The drug is believed to interact with phenylalanine on the surface of the binding site.



Phenylalanine

Suggest two intermolecular interactions that can occur between lidocaine and phenylalanine.

hydrogen bonds OR permanent dipole-induced dipole interactions OR instantaneous dipole-induced dipole interactions OR ion-dipole interactions OR electrostatic interactions between oppositely charged ions

Examiner's Comments:

Generally well done. For students answered wrongly, most misinterpreted intermolecular interactions as reactions.

[2]

- Silver carbonate, Ag₂CO₃, is used as a catalyst in many organic synthesis. It is a (c) sparingly soluble salt. A saturated solution of Ag₂CO₃ was found to contain $2.50 \times 10^{-4} \text{ mol dm}^{-3} \text{ of Ag}^+ \text{ ions.}$
 - Calculate the K_{sp} of Ag₂CO₃ and state its units. (i)

 $K_{sp} = [Ag^{+}]^{2}[CO_{3}^{2-}]$ = $(2.50 \times 10^{-4})^2 (2.50 \times 10^{-4} \div 2)$ = 7.81 x 10⁻¹² mol³ dm⁻⁹

[2]

(ii) Hence, calculate the solubility of Ag₂CO₃ when 2.00 g of Na₂CO₃ solid was added to 100 cm³ of the solution above.

$$K_{sp} = [Ag^+]^2 [CO_3^{2-}]$$

7.81 x 10⁻¹² = $[Ag^+]^2$ x [2.00 / 106.0 ÷ (100/1000)]
[Ag⁺] = 6.43 x 10⁻⁶ mol dm⁻³

Solubility of Ag₂CO₃ = $\frac{1}{2} \times 6.43 \times 10^{-6} = 3.22 \times 10^{-6} \text{ mol dm}^{-3}$

[2]

[Total: 20]

5 (a) The Strecker synthesis is a route to prepare amino acids. The protonated form of alanine, 2-aminopropanoic acid, can be prepared in the laboratory from ethanol in five steps as shown in the reaction scheme below.



- (i) In step I, the student is provided with a set of instructions to prepare the ethanal.
 - 1. Add concentrated sulfuric acid to x g of ethanol in a round-bottomed flask, a few drops at a time.
 - 2. Dissolve y g of potassium dichromate(VI) in a few cm³ of distilled water.
 - 3. Add this aqueous potassium dichromate(VI) slowly to the mixture in the round-bottomed flask.
 - 4. Heat the mixture with immediate distillation.
 - 5. Collect the ethanal from the reaction mixture.

Complete **Figure 5.1** to show the distillation set-up used to separate ethanal from the reaction mixture. Label your diagram fully including the location of ethanol and ethanal after distillation has taken place. It is not necessary to include clamps.



21

- thermometer bulb level with side arm
- condenser with water in (at bottom) and out (at top)
- sealed around the round bottomed flask and thermometer, and not sealed around collection flask

[3]

(ii) Suggest the structure of compounds A.



[1]

(iii) The product of step III is an imine, which has a C=N bond.

Given that imines are the nitrogen analogues of carbonyl compounds, name the type of reaction in step IV.

Hence suggest the structure of compound **B**.



[2]

(iv) Ethanal reacts with 2,4-dinitrophenylhydrazine to form an orange solid **C** which also has a C=N bond.

Draw the structure of solid **C**. Use the VSEPR Theory to predict the shape around the =N in solid **C**. Suggest a value for its bond angle.



Since there are 2 bond pairs and 1 lone pair, shape: bent bond angle: 117.5° or 118°

(v) Suggest reagents and conditions for step V.

[1]

[2]

(vi) The student proposed an alternative synthetic route by reacting ethanal directly with HCN and traces of aqueous NaOH. The route will also produce compound **B** as the precursor to protonated alanine.

Suggest how this synthetic route can proceed. You should state the reagents and conditions for each step and draw the structures of the intermediates formed. Omit the last step that converts compound **B** to protonated alanine.



[4]

(b) Protonated alanine, H₂A, dissociates in two stages as shown below.



The percentage composition of H_2A , HA^- and A^{2-} changes with pH as shown in **Figure 5.2**.



(i) State the values of pK_{a1} and pK_{a2} of alanine.

At 1st maximum buffering capacity where percentage composition of H₂A = HA⁻ = 50%, pH = pK_{a1} = 2.30

At 2^{nd} maximum buffering capacity Where percentage composition of HA⁻ = A²⁻ = 50%, pH = pK_{a2} = 9.70

[1]

(ii) A buffer of pH 10.0 is prepared by adding solid NaOH to 0.100 mol dm⁻³ of protonated alanine, H₂A.

Using the graph above, determine the amount of HA^- and A^{2-} present in the buffer and hence, calculate the mass of solid NaOH added.

At pH 10.0, the mixture contains 34% HA^- and 66% A^{2-} .

Amount of $HA^- = 0.100 \times 34\% = 0.0340$ mol Amount of $A^{2-} = 0.100 \times 66\% = 0.0660$ mol 24

 $\begin{array}{l} H_2A + OH^- \rightarrow HA^- + H_2O & \mbox{--- eqn 1} \\ HA^- + OH^- \rightarrow A^{2-} + H_2O & \mbox{--- eqn 2} \\ \mbox{Amount of NaOH required for eqn 1 = 0.100 mol} \\ \mbox{Amount of NaOH required for eqn 2 = 0.0660 mol} \\ \mbox{Total amount of NaOH required = 0.166 mol} \\ \mbox{Mass of NaOH required = 0.166 \times 40.0 = 6.64 g} \end{array}$

(c) The solubility of alanine under different pH was investigated and the results are shown in **Figure 5.3**.



Figure 5.3

The isoelectric point of alanine is 6.0. The isoelectric point is the pH at which an amino acid has no net electrical charge.

With reference to the electrostatic forces involved, explain

(i) the low solubility of alanine at its isoelectric point of 6.0.

At isoelectric point, alanine exist as zwitterions, HA⁻. The opposite charges favours attraction between zwitterions. Thus, less ion-dipole interactions can be formed between the zwitterions and water molecules. The energy released from the <u>ion-dipole interactions</u> formed between the zwitterion and water molecules <u>release insufficient energy to overcome</u> the <u>strong</u> <u>electrostatic forces of attractions between the zwitterions</u> and the <u>hydrogen</u> <u>bonds</u> between water molecules. Hence, the solubility of alanine is low at pH 6.0.

[2]

[2]

(ii) the high solubility of alanine at low and high pH.

You may refer to alanine as H_2A , HA^- or A^{2-} where appropriate.

At low and high pH, alanine exist as cation and anion respectively. At low pH, the <u>cations repel each other</u> and at high pH, the <u>anions repel each other</u>. Thus, more ion-dipole interactions can be formed between the ions and water molecules. The energy released from the <u>ion-dipole interactions</u> formed between the ions and water molecules <u>release sufficient energy to</u> <u>overcome</u> the the <u>hydrogen bonding</u> between water molecules. Hence, the solubility of alanine is high at low and high pH.

[2] [Total: 20]