ACJC solutions for H2 Chemistry Prelim Paper 3 2022

Section A

1	**(a)**	Explain what is meant by the term *Lewis acid*. [1]	
		Lewis acid is a substance that accepts an electron pair from a base via a dative covalent bond (i.e. an electron-pair acceptor) Examiner's comments: • Do not be confused with the Bronsted-Lowry or Arrhenius' definition of acids.	
	(b)	The water molecule can react in various ways: as an acid, as a base, as a nucleophile, as an oxidising agent and as a reducing agent. Study the following reactions and decide in which way water is reacting in each case. Explain your answers fully. [5]	
		(i)	$2F_2 + 2H_2O \rightarrow 4HF + O_2$
			Reducing agent as itself is being oxidised. The oxidation number of O increases from −2 in H_2O to 0 in O_2. Or water reduces F_2 to HF as the oxidation number of F decreases from 0 in F_2 to −1 in HF. Examiner's comments: • Change in oxidation number and relevant substance must be clearly stated as question stated to explain your answers fully.
		(ii)	$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$
			Nucleophile. The carbon of the acyl chloride functional group is electron deficient and is susceptible to nucleophilic attack by water, which has a lone pair of electrons on its oxygen atom. Examiner's comments: • Your answer should clearly reflect the definition of a nucleophile. • Base is not acceptable as a base involve donation of electron pair but without the expulsion of any groups. In this case, Cl is expelled and replaced with OH hence the reaction is a nucleophilic substitution rather than acid base.
		(iii)	$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$
			Base. H_2O accepts a proton from $H_2PO_4^-$ to form H_3O^+ and HPO_4^{2-}. Examiner's comments: • Your answer should clearly reflect the definition of a base, i.e. mention of the accepting of proton.

(iv) $Li + H_2O \rightarrow LiOH + ½ H_2$

Oxidising agent. Water oxidises Li to Li^+ as the oxidation number of Li increases from 0 in Li to +1 in LiOH

Examiner's comments:

- Change in oxidation number and relevant substance must be clearly stated as question stated to explain your answers fully.

(v) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

Acid. H_2O donates a proton to NO_2^- to form OH^- and HNO_2.

Examiner's comments:

- Your answer should reflect the definition of an acid, i.e. proton donor.

(c) The p*K*a values of three acids are listed in the Table 1.1 below:

Table 1.1

acid	formula	pK_a
1	CH_3CH_2COOH	4.9
2	$CH_3CHClCOOH$	2.8
3	CH_2ClCH_2COOH	*z*

(i) Explain the difference in pK_a values between acid 1 and acid 2. [2]

The presence of the electron withdrawing chlorine group in acid 2 disperses the negative charge on the conjugate base, $CH_3CHClCOO^-$, hence making it a more stable conjugate base than $CH_3CH_2COO^-$.

Therefore, acid 2 has a lower pK_a as this increases the acid strength of $CH_3CHClCOOH$.

Examiner's comments:

- The difference between acids 1 and 2 lie in the presence of the electron withdrawing Cl group hence this must be clearly stated.
- Dispersal of negative charge in a conjugate base contributes to its stability so this should also be clearly stated.

(ii) Suggest a value for *z* and explain your answer. [1]

4.0 (accept any value between 2.8 and 4.9)

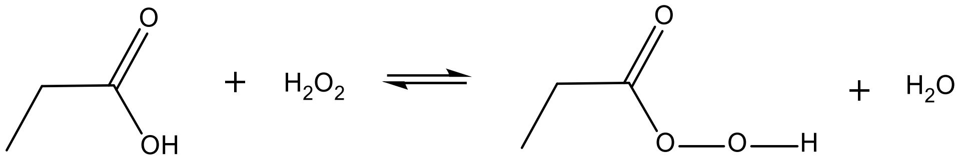
As the distance between the –COOH group and the Cl atom increases, the negative charge on the conjugate base is less dispersed. The conjugate base becomes less stable and hence acid strength decreases.

However, acid 3 should still be more acidic than acid 1 due to the presence of the electron withdrawing Cl group.

Examiner's comments:

- The main difference between acid 2 and 3 is the proximity of the Cl group.
- Dispersal of negative charge in a conjugate base contributes to its stability so this should also be clearly stated.

(iii) Peroxyacids are weak acids. One way to prepare peroxypropanoic acid is to treat the corresponding carboxylic acid with hydrogen peroxide.



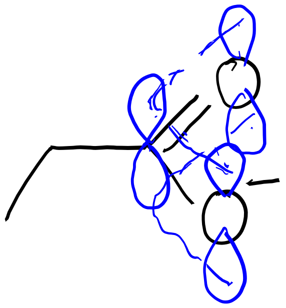
acid 1 peroxypropanoic acid

Suggest why the pK_a of peroxypropanoic acid is higher than that of acid 1. [1]

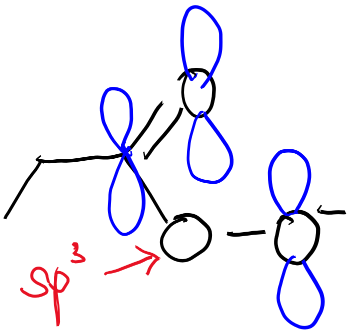
$CH_3CH_2CO_3H$ is less acidic than CH_3COOH as $CH_3CH_2CO_3^-$ is less stable than $CH_3CH_2CO_2^-$ because the negative charge on $CH_3CH_2CO_3^-$ cannot be delocalised over the C=O group due to the additional oxygen atom, hence the resonance stabilisation of the conjugate base is lost.

Examiner's comments:

- The main difference between acid 1 and peroxypropanoic acid is the fact that the negative charge on the conjugate base of peroxypropanoic acid, $CH_3CH_2CO_3^-$ cannot be delocalised as the p orbitals of O with the negative charge cannot overlap with the pi electron cloud of the C=O.
- As shown below, the oxygen atom preventing the continuous p orbital overlap $CH_3CH_2CO_3^-$ is sp^3 hybridised as it has 2 lone pairs and 2 bond pairs.



Conjugate base of acid 1



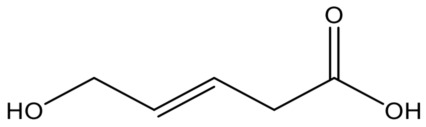
Conjugate base of peroxypropanoic acid

(d) **A**, **B** and **C** are isomers with the molecular formula $C_5H_6O_2$. All three compounds decolourise bromine water in the dark.

A produces effervescence in the presence of Na_2CO_3(aq) whereas **B** and **C** do not. **A** also reacts with hot acidified $KMnO_4$ to form **D**, $C_3H_2O_5$.

B forms a brick-red precipitate when heated with Fehling's solution.

C reacts with hot aqueous sodium hydroxide. Upon acidification, it forms $C_5H_8O_3$.

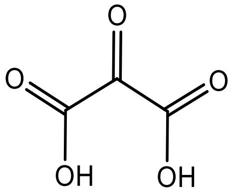


$C_5H_8O_3$

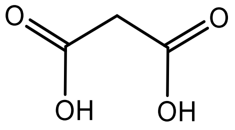
When **B** and **C** are separately reacted with hot acidified $KMnO_4$, they form the same mixture of **E** $C_3H_4O_4$ and **F** $C_2H_2O_4$. **F** undergoes further oxidation to give effervescence.

(i) Draw the structures of **D**, **E** and **F**. [3]

D is



E is



F is HOOC–COOH

Examiner's comments:

- Since **D**, **E** and **F** are formed from oxidation with acidified $KMnO_4$, they contain functional groups that do not undergo further oxidation. Thus **D**, **E** and **F** have carboxylic acid, ketone and / or tertiary alcohol functional groups, but not primary alcohol, secondary alcohol or aldehyde.

(ii) Deduce the structures of **A**, **B** and **C** with reasoning. [7]

A, **B** and **C** have 3 degrees of unsaturation.

A, **B** and **C** have alkene functional group that undergoes electrophilic addition with bromine water.

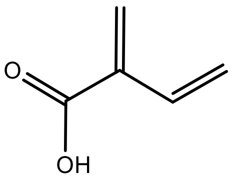
A, **B** and **C** undergoes vigorous oxidation / oxidative cleavage of the alkene functional group.

A has the carboxylic acid functional group that undergoes acid-carbonate / acid-base reaction with carbonate.

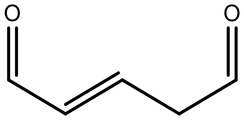
B has the aldehyde functional group that undergoes oxidation in the presence of Fehling's solution.

C undergoes alkaline hydrolysis, so it has an ester functional group.

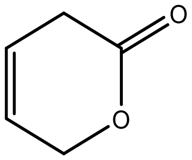
A



B



C



Examiner's comments:

- Good answers made deductions based on the types of reactions and functional groups present
- "Double bond" is not an acceptable description of the alkene functional group
- "Carboxylic group" or "acidic group" is not an acceptable description of the carboxylic acid functional group

- Students should be specific about the deduction from the positive Fehling's test – it shows that an aliphatic aldehyde is present, but not ketone or aromatic aldehyde

[Total: 20]

2 **(a)** The acid-base behaviour of aluminium oxide, Al_2O_3, shows similarities to that of magnesium oxide, MgO, on the one hand, and sulfur trioxide, SO_3, on the other.

Describe what these similarities are, and explain why aluminium oxide occupies this in-between position.

Write equations for all the reactions you choose to illustrate your answer. [5]

MgO is an ionic oxide. Hence it is basic and is able to react with acids.

$MgO + 2HCl \rightarrow MgCl_2 + H_2O$ or $MgO + 2H^+ \rightarrow Mg^{2+} + H_2O$

SO_3 is a covalent oxide, hence it is acidic and is able to react with bases.

$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$ or $SO_3 + 2OH^- \rightarrow SO_4^{2-} + H_2O$ or
$SO_3 + H_2O \rightarrow H_2SO_4$

Al_2O_3: amphoteric oxide hence it react with both acids and bases.

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ or $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$
$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$ or $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$

Al^{3+} has high charge density/polarizing power which is able to polarise the electron cloud of O^{2-}/anion , hence giving the oxide some covalent character.

Therefore, Al_2O_3 has a giant ionic lattice structure with covalent character, making it an amphoteric oxide that reacts with both acids and alkalis.

Examiner's comments:

- Al_2Cl_6 was not accepted as a product for reaction of Al_2O_3 with HCl as the dimer form only exist in gaseous form or when dissolved in an organic solvent.

(b) **(i)** Explain what is meant by the term *standard enthalpy change of atomisation of magnesium*. [1]

Standard enthalpy change of atomisation of magnesium is the energy absorbed/required/taken in when one mole of gaseous Mg atom/Mg(g) is formed from Mg at 298 K and 1 bar.

Examiner's comments:

- Clear reference to the context of Mg must be made. All keywords in the definition from lecture notes must be included.

(ii) An experiment was carried out by adding 0.05 g of magnesium ribbon to 50 cm^3 of excess hydrochloric acid solution. The increase in temperature was 4.5 °C.

The reaction is represented by the ionic equation as shown:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g) \qquad \Delta H_1^\ominus$$

Use data from the *Data Booklet* to calculate $\Delta H_1^\ominus$, the standard enthalpy change of this reaction. [2]

Heat released = $mc\Delta T$
= $50 \times 4.18 \times 4.5$
= 940.5 J

$\Delta H_1^\ominus = -[940.5 / (0.05 / 24.3)]$
$= -457$ kJ mol^{-1}

Examiner's comments:

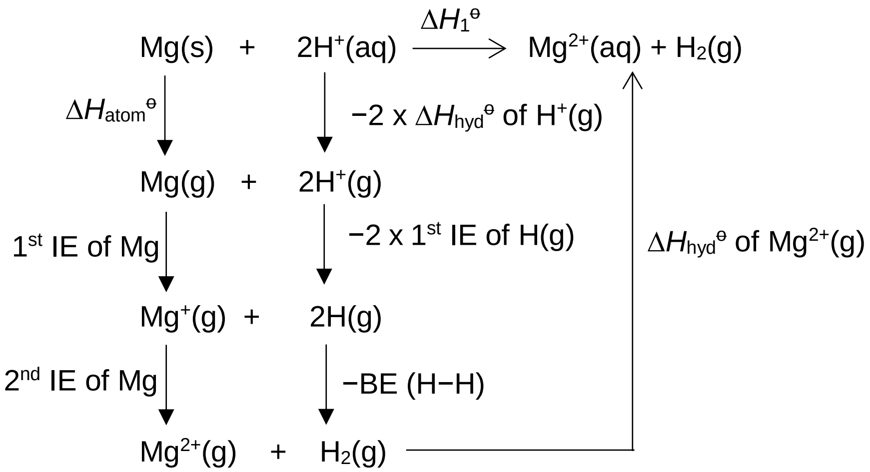
- Do NOT add 273K to the change in temperature 4.5.
- $\Delta T = (T_f + 273) - (T_i + 273)$ hence the 273K will cancel out.

(iii) Besides using an experimental method, another way to determine $\Delta H_1^\ominus$, the standard enthalpy change of the above reaction, is to construct an energy cycle.

Use the data in Table 2.1, together with data from the *Data Booklet*, to calculate another value of $\Delta H_1^\ominus$. [4]

Table 2.1

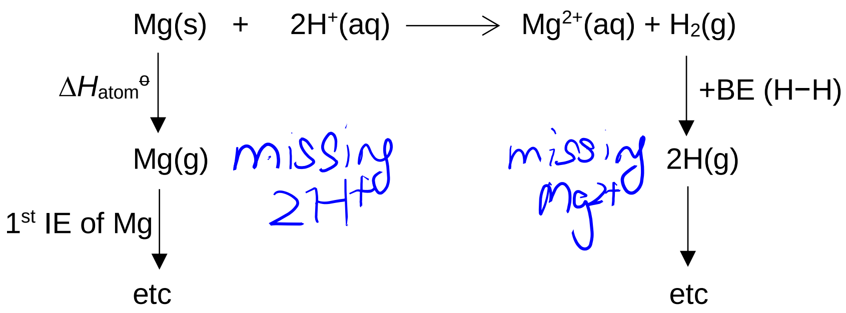
	$\Delta H^\ominus$ / kJ mol^{-1}
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of hydration of $Mg^{2+}(g)$	−1921
standard enthalpy change of hydration of $H^+(g)$	−1090



$\Delta H_1^\ominus = \Delta H_{atom}^\ominus$ + 1st IE of Mg + 2nd IE of Mg + (−2 x $\Delta H_{hyd}^\ominus$ of $H^+(g)$) + (−2 x 1st IE of H(g)) + (−BE (H−H)) + $\Delta H_{hyd}^\ominus$ of $Mg^{2+}(g)$
$= +148 + 736 + 1450 + (-2 \times -1090) + (-2 \times 1310) + (-436) + (-1921)$
$= -463$ kJ mol^{-1} [1]

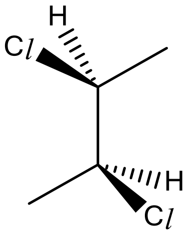
Examiner's comments:

- Do NOT combine different energetics terms, e.g. ΔHatm (Mg) with IE of Mg. You may however choose to combine 1st and 2nd IE of Mg since both are ionisation energies.
- Cycles that were not "closed" or "balanced" was not accepted.
- E.g. The following is not balanced. Do NOT start your cycle as follows.

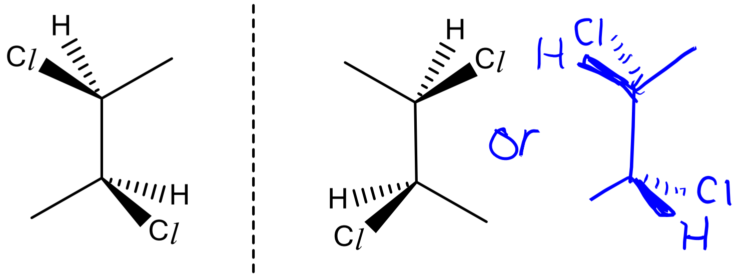


- The cycle needs to be balanced at every stage.

(c) 2,3-dichlorobutane exhibits stereoisomerism, one of which is enantiomerism. One enantiomer of 2,3-dichlorobutane is shown below.



(i) Draw the other enantiomer. [1]

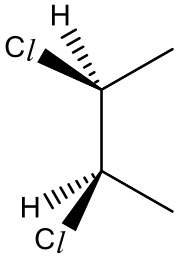


Examiner's comments:

- Hash and wedge bonds and tetrahedral geometry at every chiral carbon must be shown.

(ii) A molecule with *n* chiral centres can have a maximum of 2^n stereoisomers. 2,3-dichlorobutane has two chiral centres but it only has three stereoisomers.

Draw the third stereoisomer of 2,3-dichlorobutane and explain why it has only three stereoisomers. [2]



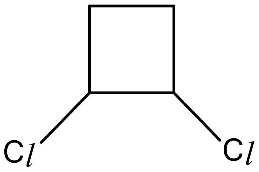
The diastereomer of 2,3-dichlorobutane is a meso compound which has an internal plane of symmetry.

Hence, 2,3-dichlorobutane has a pair of enantiomers and only one diastereomer.

Examiner's comments:

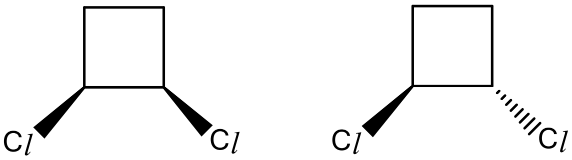
- Hash and wedge bonds and tetrahedral geometry at every chiral carbon must be shown.
- The keyword "internal plane of symmetry" must be given. By just stating "symmetry" is insufficient.

(iii) Suggest why 1,2-dichlorocyclobutane can exhibit cis−trans isomerism and draw the pair of cis−trans isomers. [2]



There is restricted rotation about the C–C bond that is bonded to the 2 Cl groups due to the presence of a ring structure. There are also two different groups bonded to each of the two adjacent carbon atoms with restricted rotation.

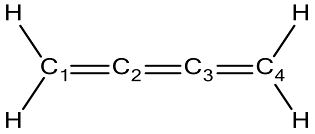
Thus, 1,2-dichlorocyclobutane can exhibit cis−trans isomerism.



Examiner's comments:

- Keywords: restricted rotation due to the ring.
- Two different groups on each C

(iv) A cumulene is a hydrocarbon with three or more consecutive double bonds. The simplest molecule in this class is butatriene, C_4H_4.

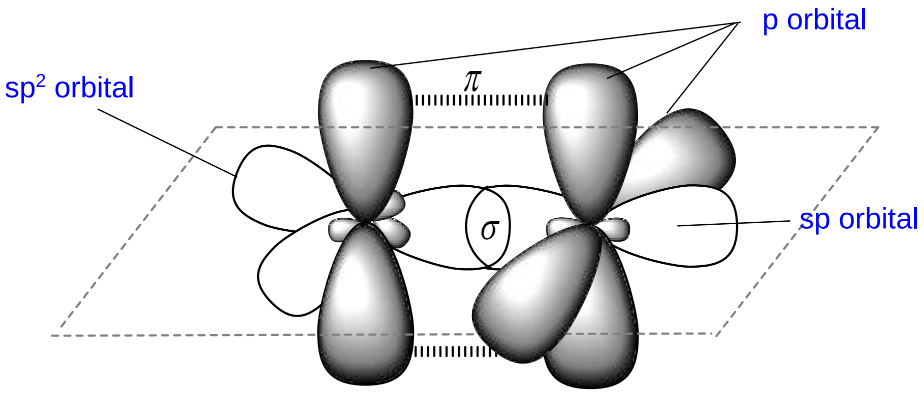


With the aid of a labelled diagram, describe the orbitals that form the C_1=C_2 bond in butatriene, and state the type of hybridisation involved. [3]

In butatriene, the double bond of C=C is made of one σ bond and one π bond.

C-C σ bond: Formed by head-on overlap of the sp^2 hybrid orbitals of C_1 atom and sp hybrid orbitals of C_2 atom.

C-C π bond: Formed by sideways overlap of the two unhybridised p orbitals, forming an electron cloud above and below the plane.



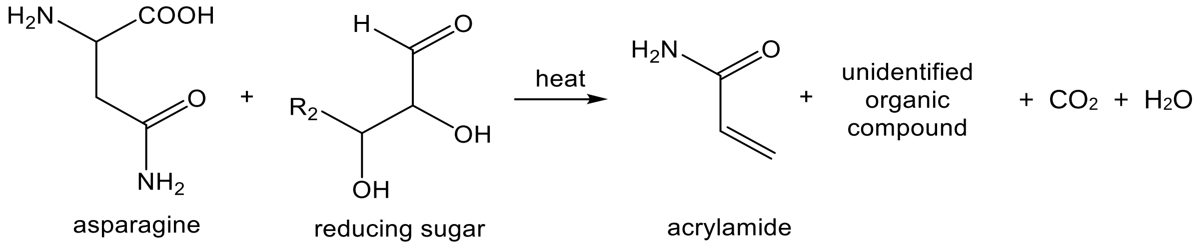
Examiner's comments:

- The diagram should be clearly labelled in terms of the orbital type and the type of overlap even if you have explained in your answer.
- C1 is sp^2 as it has 3 bond pairs and no lone pairs while C2 is sp as it has 2 bond pairs and no lone pairs.

[Total: 20]

3 **(a)** The Maillard reaction is an important process that occurs between sugars with amino acids during cooking. Its occurrence is responsible for the golden brown colouration and crispy texture that makes food appealing and tasty.

In 2002, it was discovered that Maillard reaction involving asparagine, an amino acid, forms acrylamide, a known carcinogen. Reaction **1** shows the chemical equation for the formation of acrylamide.



reaction **1**

To determine the kinetics of reaction **1**, three experiments were carried out and the results are shown in Table 3.1.

Table 3.1

experiment	concentration / mol dm^{-3}		initial rate / 10^{-3} mol dm^{-3} s^{-1}
	asparagine	reducing sugar	
1	0.100	0.500	2.46
2	0.100	0.625	3.08
3	0.200	0.750	3.69

(i) Deduce the order of reaction with respect to asparagine and the reducing sugar. Hence write the rate equation. [3]

Comparing Experiment 1 and 2,

When [reducing sugar] was increased 1.25x while keeping [asparagine] constant, rate of reaction was increased 1.25x.

Order of reaction with respect to the reducing sugar is 1.

Comparing Experiment 1 and 3,
Let the rate equation be rate = k[reducing sugar] $[\text{asparagine}]^m$

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k\,(0.750)(0.200)^m}{k\,(0.500)(0.100)^m}$$

$$\frac{0.00369}{0.00246} = \frac{k\,(0.750)(0.200)^m}{k\,(0.500)(0.100)^m}$$

$m = 0$
Order of reaction with respect to asparagine is 0.

OR
Comparing Experiment 1 and 3,
When [reducing sugar] x1.5 while keeping the rest constant, rate of reaction x1.5.

Since observed rate of reaction was increased 1.5 times when [asparagine] was doubled, it implies that doubling [asparagine] has no effect on the rate.
Order of reaction with respect to asparagine is 0.

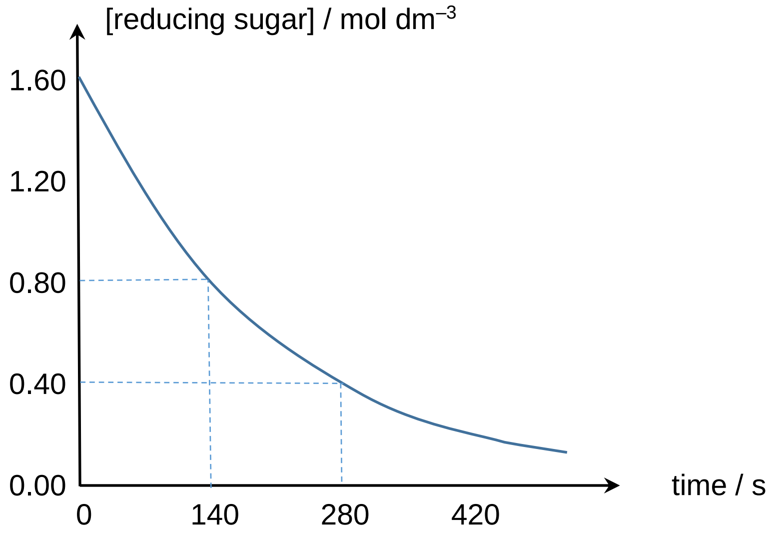
Rate = k [reducing sugar]

Examiner's comments:

- Many students are able to determine the order of reaction wrt asparagine using the substitution method
- Some students did not write the rate equation despite finding the order of reaction for both reactants

(ii) The reducing sugar is at an initial concentration of 1.60 mol dm^{-3} and its half-life is 140 s.

Sketch a graph of concentration of the reducing sugar against time for reaction **1**. [2]



<u>Examiner's comments:</u>

- The axis should be labelled, including the units
- Since this is an overall first order reaction, students should show two constant half lives
- The values given in the question should be used in the graph

(iii) Determine the rate constant, *k*, for reaction **1**. [1]

$t_{½} = \ln 2 \div k$

$k = \ln 2 \div t_{½} = \ln 2 \div 140 = 0.00495\ s^{-1}$

OR

Using experiment 1,

Rate = k [reducing sugar]

$0.00246 = k\ 0.500$

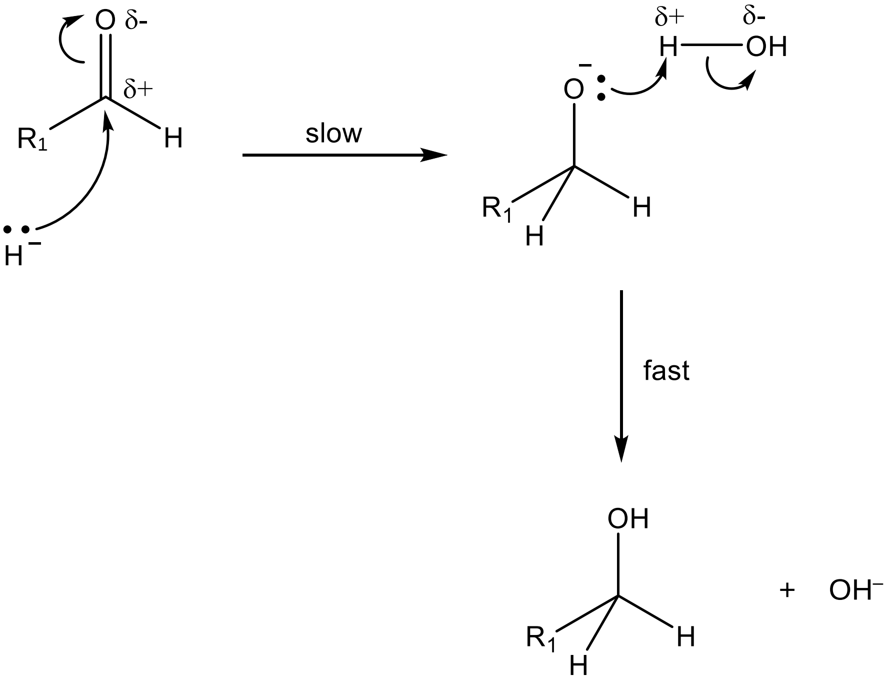
$k = 0.00492\ s^{-1}$

<u>Examiner's comments:</u>

- Many students are able to calculate the rate constant by substituting experimental values from table 3.1 or using the formula, $t_{½} = \ln 2 \div k$
- Students should note that the header of table 3.1 shows that rate of reaction is multiplied by 10^{-3} of the given value
- Units of k = units of rate ÷ units of concentration = $mol\ dm^{-3}\ s^{-1} \div mol\ dm^{-3} = s^{-1}$

(b) The reaction between the reducing sugar and aqueous sodium borohydride is a nucleophilic addition reaction.

Draw the mechanism for this reaction, assuming that sodium borohydride produces the hydride ion, **:**H^-, as the reacting species. In your answer, you may represent the reducing sugar as RCHO. [3]

		
	(c)	The following mechanism in figure 3.1 has been proposed for the Maillard reaction involving asparagine.

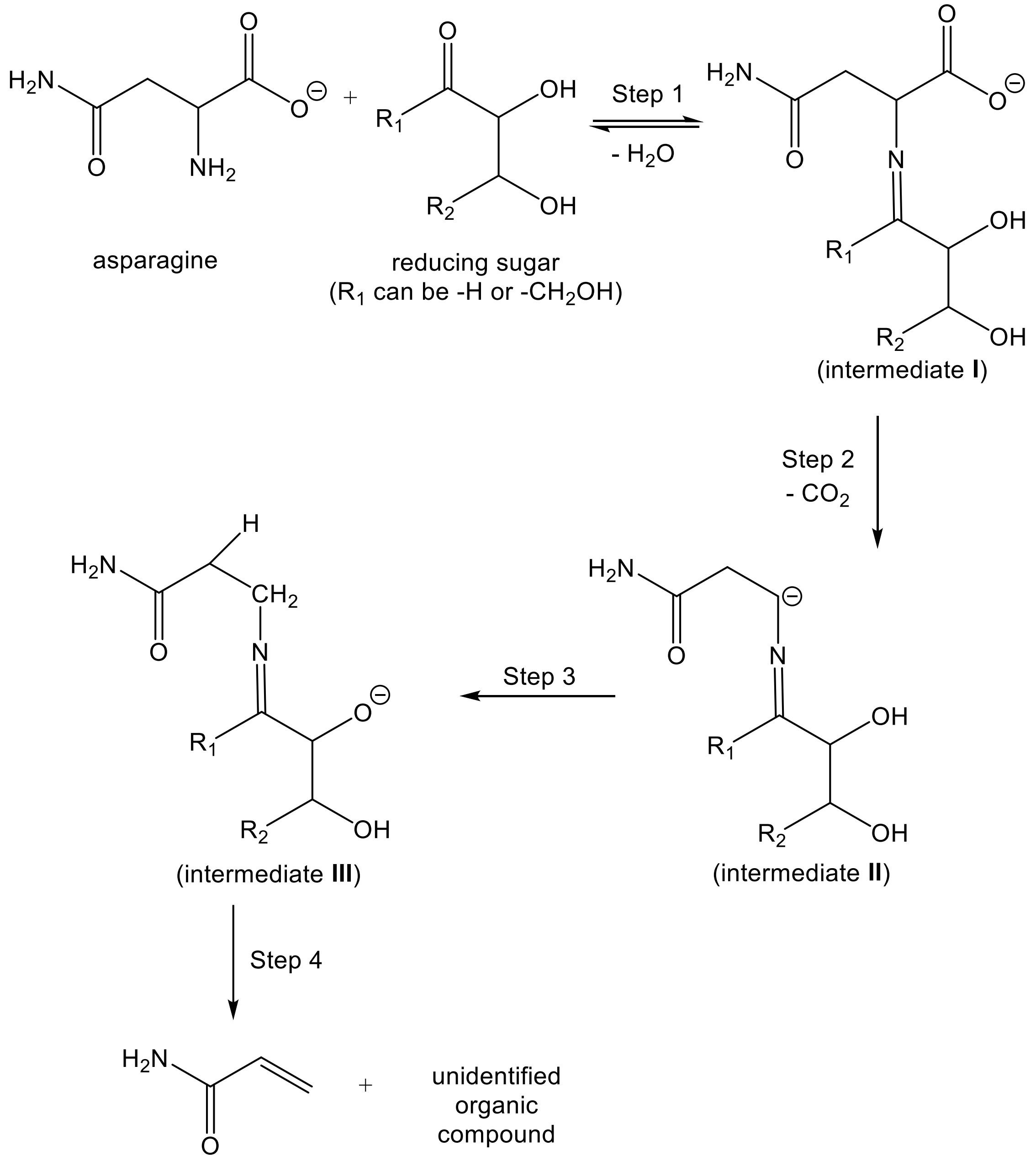


Fig. 3.1

(i) State the role of asparagine in step 1. [1]

Nucleophile

Examiner's comments:

- Asparagine is an electron rich species that reacted at the electron deficient carbonyl C atom. Hence it is a nucleophile.

(ii) Suggest and explain the effect on the rate of step 1 when R_1 is changed from –H to –CH_2OH. [1]

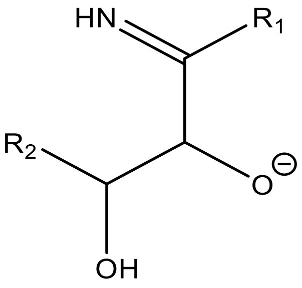
The electron-donating alkyl (or –CH_2OH) group causes the carbonyl carbon to be less electron deficient. Hence there is a slower rate of nucleophilic addition.
OR
The –CH_2OH group poses greater steric hindrance to the nucleophile, so there is a slower rate of nucleophilic addition.
OR

The electron-withdrawing $–CH_2OH$ group causes the carbonyl carbon to be more electron deficient. Hence there is a faster rate of nucleophilic addition.

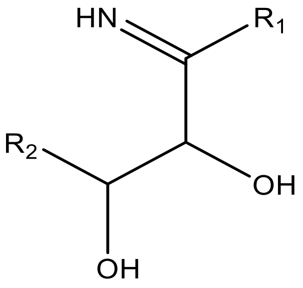
Examiner's comments:

- The steric effect or inductive effect of $–CH_2OH$ is similar to the relative rate ketones and aldehydes in the nucleophilic addition reaction (refer to Carbonyl Compounds lecture notes, pg 13-14)

(iii) Draw the structure of the unidentified product of the above mechanism. [1]



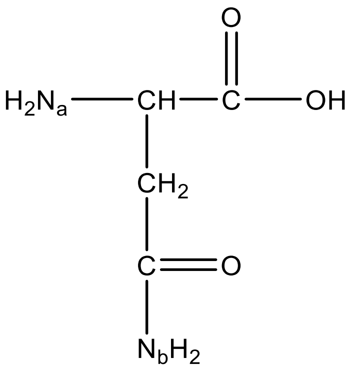
or



Examiner's comments:

- Many students made a mistake in the valency of the N atom. The correct structure shows N atom with 3 covalent bonds.

(d) Compare and explain the base strength of the atoms N_a and N_b in asparagine.



$H_2N_a–CH(CH_2C(=O)N_bH_2)–C(=O)OH$

asparagine

[2]

N_b is less basic than N_a.

The amide functional group at N_b is neutral / not basic. This is because the lone pair of electron on N_b delocalises to the electron withdrawing C=O group, making it unavailable to accept protons/H^+ / coordinate to protons / protonation.

OR

The amine functional group at N_a is a stronger base. It is bonded to an electron-donating alkyl group that increases electron density at the N_a atom. This makes the lone pair of electrons on N_a more available to accept protons.

Examiner's comments:

- Students should note that **amides are neutral** (or not basic). It does **not** donate the lone pair of electrons from the N atom
- Some students should be more accurate in describing the basic property. The N atom donates its lone pair of electrons **to a proton.**

(e) In the 2020 Olympic Games, winners received medals made from recycled gold, silver and bronze. These metals were from recycled from electronic waste collected throughout Japan. In the recycling process, metal parts are physically removed from the plastics, and the metals are sorted by elements and levels of purity.

Low purity silver is refined using electrolysis to remove metal impurities such as gold and copper.

(i) The electrode potential for Au^+/Au is given below.

$$Au^+ + e^- \rightleftharpoons Au \qquad E^\ominus = +1.83\ V$$

Define the term *standard electrode potential of* Au^+/Au. [1]

Standard Electrode (Redox) Potential, $E^\ominus$ is defined as the potential difference between a standard hydrogen electrode OR H^+/H_2 half cell and the Au^+/Au half cell under standard conditions at 1 mol dm^{-3}, 25 °C / 298K and 1 bar.

Examiner's comments:

- Students are reminded to write down the standard conditions in the definition

(ii) Describe the electrode reactions that take place during this electrolysis and explain in detail how each of the two impurity metals is removed from the silver. [3]

At the anode:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e$ and $Ag(s) \rightarrow Ag^+(aq) + e$

Since the $E^\ominus_{Cu2+/Cu}$ is more negative than $E^\ominus_{Ag+/Ag}$, Cu is oxidised to Cu^{2+} ions at the anode, followed by Ag.

Since the $E^\ominus_{Au+/Au}$ is more positive than $E^\ominus_{Ag+/Ag}$, Au will not be oxidised to Au^+ ions at the anode but will drop just off at the anode as anodic sludge.

At the cathode: $Ag^+(aq) + 2e \rightarrow Ag(s)$

Since $E^\ominus_{Ag+/Ag}$ is more positive than $E^\ominus_{Cu2+/Cu}$, Cu^{2+} will remain in the solution as Ag^+ is preferentially reduced over Cu^{2+}.
Thus, both Cu and Au are removed from the silver.

Examiner's comments:

- Some students explained how Au is purified instead of Ag
- Good answers compared $E^\ominus$ values to explained why Cu is oxidised at the anode, but Cu^{2+} remains in the solution at the cathode.
- They also explained the oxidation of Ag at the anode and reduction of Ag^+ at the cathode
- Au does not oxidise at the anode, so there are no Au^+ ions to be reduced at the cathode

		(iii)	The electrolytic refining of silver was carried out for 90 minutes using a current of 10.2 A. Using data from the *Data Booklet*, calculate the expected mass of silver deposited in this process. [2]
			Q = (90 × 60) × 10.2 = 55080 C n(e) = 55080 ÷ 96500 = 0.5707 mol n(Ag) deposited = 0.5707 mol Mass of silver deposited = 0.5707 × 107.9 = 61.6 g
			[Total: 20]

Section B

Answer **one** question from this section.

4	**(a)**	**(i)**	A glass rod was heated in a Bunsen burner flame and placed into a sample of hydrogen chloride gas. The experiment was repeated using a sample of hydrogen iodide gas. Use data from the *Data Booklet* to explain why a colour change was observed for hydrogen iodide but not hydrogen chloride. [2]
			The bond energy of H-I is 299 kJ mol^{-1} while bond energy of H-C*l* is 431 kJ mol^{-1}. Less energy is required to break the weaker H-I bond than H-C*l*, hence purple fumes of I_2 will be obtained for HI but no colour change for HCl [1] OR The heat energy in a Bunsen burner flame is sufficient to break H-I bond but not H-C*l* bond. $2HI\ (g) \rightarrow H_2\ (g) + I_2\ (g)$ A purple vapour I_2 will be seen in the sample of hydrogen iodide gas. Examiner's comments: • Please ensure you quote the bond energy value with units. • The reaction is a decomposition reaction so you should be discussing about the relative strength of the HCl and HI bonds broken. As the answer is only 2m, you do NOT have to calculate the enthalpy change of each reaction and then compare them. • Electrode potential values are NOT accepted as the key reason here is NOT the ease of oxidation of chloride vs iodide but rather, the strength of the bond. This is because NO oxidising agent was added to HCl or HI, so you should not be discussing on the ease of oxidation.

		(ii)	Hydrogen chloride can be oxidised to chlorine and water in the presence of CuC*l*. Likewise, hydrogen cyanide can be oxidised to cyanogen and water in the presence of Cu according to the following equation. $2HCN + \frac{1}{2} O_2 \rightarrow (CN)_2 + H_2O$ Describe the change in oxidation state of carbon which occurs during this reaction. [1]
			C in HCN is oxidised from +2 to +3 in $(CN)_2$ Examiner's comments: - Correct elements, oxidation numbers and reference compounds must be given as the question asked you to "describe" not state the change in oxidation number.
		(iii)	Cyanogen can be converted to ethanedioic acid by heating with aqueous acid. State the type of reaction for this conversion. [1]
			Acid hydrolysis Examiner's comments: $-C \equiv N$ to $-COOH$ is NOT an oxidation reaction as in both cases, the oxidation number of C is +3.
	To determine the solubility product, K_{sp}, of calcium ethanedioate, CaC_2O_4, at 20 °C, an excess of solid calcium ethanedioate was shaken with 6.25×10^{-5} mol dm^{-3} of sodium ethanedioate. The resulting mixture was allowed to equilibrate at 20 °C in a water bath and then the mixture was filtered to obtain the filtrate, Solution **A**, which contains a saturated solution of calcium ethanedioate. 25.0 cm^3 of Solution **A** was titrated with 5.0×10^{-5} mol dm^{-3} of acidified potassium manganate(VII). 16.60 cm^3 of potassium manganate(VII) was required for complete reaction. The reaction of ethanedioate ions and acidified manganate(VII) ions is shown below. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$		
	(b)	**(i)**	The reaction between ethanedioate ions and acidified potassium manganate(VII) has a high activation energy, hence solution **A** was heated to 60 °C before titration. Explain why the reaction has a high activation energy. [1]
			There is repulsion between two anions MnO_4^- and $C_2O_4^{2-}$ thus energy is required to overcome the repulsion.
		(ii)	Calculate the amount of ethanedioate ions in 25.0 cm^3 of Solution **A**. [2]
			Amount of MnO_4^- = $5.0 \times 10^{-5} \times \frac{16.60}{1000}$ = 8.30×10^{-7} mol Amount of ethanedioate ions in 25.0 cm^3 of Solution A = $\frac{5}{2} \times 8.30 \times 10^{-7}$ = 2.08×10^{-6} mol

(iii) Calculate the concentration of ethanedioate ions in Solution **A.** [1]

[ethanedioate ions] in 25.0 cm^3 of Solution **A** = $\frac{1000}{25}$ x 2.075 x 10^{-6}
= 8.30 x 10^{-5} mol dm^{-3}

(iv) Calculate the concentration of calcium ions in solution **A**. [1]

[ethanedioate ions] from CaC_2O_4 = 8.30 x 10^{-5} – 6.25 x 10^{-5}
= 2.05 x 10^{-5} mol dm^{-3}

[Ca^{2+}] = 2.05 x 10^{-5} mol dm^{-3} since [Ca^{2+}] = [$C_2O_4^{2-}$] from CaC_2O_4

Examiner's comments:

- Common mistake was to state that [Ca^{2+}] = [$C_2O_4^{2-}$] in solution A.
- Note that [$C_2O_4^{2-}$] in solution A came from BOTH $Na_2C_2O_4$ and the dissolved CaC_2O_4, hence you need to subtract the $C_2O_4^{2-}$ contributed by $Na_2C_2O_4$ which is given as 6.25 x 10^{-5} $moldm^{-3}$.

(v) Write an expression for the solubility product, K_{sp}, of calcium ethanedioate and calculate its value at 20 °C, stating the units clearly in your answer. [3]

K_{sp} = [Ca^{2+}][$C_2O_4^{2-}$]
= (2.05 x 10^{-5})(8.30 x 10^{-5})
= $\underline{1.70 \text{ x } 10^{-9}}$ mol^2 dm^{-6}

Examiner's comments:

- Note that K_{sp} is the ionic product at saturation point, i.e. the product of [Ca^{2+}] and [$C_2O_4^{2-}$] in the saturated solution. The satutrated solution was formed when CaC_2O_4 dissolved in the original $Na_2C_2O_4$, hence you should take [Ca^{2+}] in part iv multiplied by [$C_2O_4^{2-}$] total that came from $Na_2C_2O_4$ and CaC_2O_4 in part iii.

(c) When a precipitate of calcium ethanedioate is formed, $\Delta G^{\ominus}_{ppt}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = RT\ln K_{sp}$$

(i) Given that the K_{sp} value of calcium ethanedioate at 25 °C is 2.70 x 10^{-9} mol^2dm^{-6}, calculate the $\Delta G^{\ominus}_{ppt}$ of calcium ethanedioate. [1]

ΔG^{θ}_{ppt} = RTln K_{sp}
= 8.31 x 298 x ln(2.70 x 10^{-9})
= –48859 J mol^{-1}
= –48.9 kJ mol^{-1}

(ii) The standard entropy change of the precipitation of calcium ethanedioate, $\Delta S^{\ominus}_{ppt}$ is +93.2 J mol^{-1} K^{-1}.

Calculate the standard enthalpy change of precipitation of calcium ethanedioate, $\Delta H^{\ominus}_{ppt}$. [1]

$-48859 = \Delta H^{\theta}_{ppt} - 298(+93.2)$

$\Delta H^{\theta}_{ppt} = -21.1$ kJ mol^{-1}

Examiner's comments:

Please ensure you convert your units for ΔG to J mol^{-1} or ΔS to kJ mol^{-1} ^{j}K^{-1} before you calculate ΔH^{θ}_{ppt}

(d) The precipitation of calcium ethanedioate is one of the reasons for the formation of kidney stones.

Given that the stomach has a pH of about 2.0 while the kidney has a pH of about 6.5, explain why stones are not formed in the stomach but stones can be formed in the kidney. [2]

At pH 2.0 in the stomach, $[H^+]$ is higher than at pH 6.5 in the kidney.
The high $[H^+]$ in the stomach reacts with $C_2O_4^{2-}$ to form $H_2C_2O_4$ (or $HC_2O_4^-$), hence $[C_2O_4^{2-}]$ is much lower in the stomach than kidney.

Thus the ionic product of calcium ethanedioate remains below K_{sp} in the stomach but can rise above K_{sp} in the kidney.

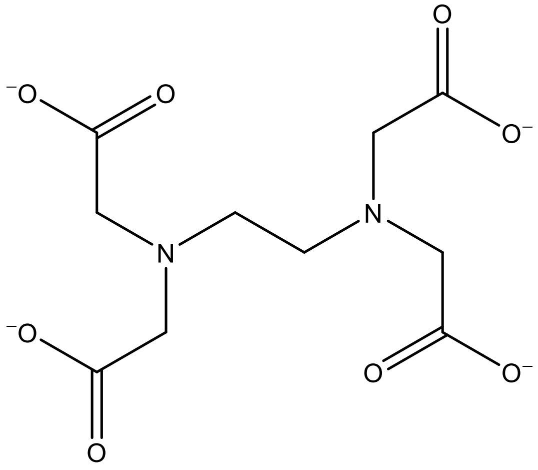
Important points:

- Formation of $H_2C_2O_4$ and $[C_2O_4^{2-}]$ decreases
- ionic product below K_{sp} or POE shift with equation given
- Comparison of $[H^+]$ in stomach and kidney

Examiner's comments:

- Vague answers such as H^+ reacted with $C_2O_4^{2-}$ without stating what is formed was not accepted.
- If you discuss about POE shift, please write the relevant equation.

(e) Ethylenediaminetetraacetate, also known as EDTA has the structure shown below.



Suggest a reason why EDTA can be used as a treatment for kidney stones. [2]

EDTA can form a complex / chelates/ binds via a dative bond with Ca^{2+}, thus $[Ca^{2+}]$ decreases.

Ionic product in the kidney can fall below K_{sp} thus the calcium ethanedioate precipitate will not form. (or is soluble)

OR

$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$ OR make reference to earlier part's equation.

POE shifts right as $[Ca^{2+}]$ decreases, thus calcium ethanedioate dissolves.

Examiner's comments:

- Vague answers such as EDTA reacts with Ca^{2+}, forms a soluble compound with CaC_2O_4 or binds to Ca^{2+} was not accepted. You need to identify a complex is formed (or wtte such as chelate or form dative bonds with Ca^{2+})

(f) Calcium ethanedioate decomposes at a temperature of 400 °C according to the equation shown below.

$$CaC_2O_4(s) \rightarrow CaO(s) + CO_2(g) + CO(g)$$

Explain why magnesium ethanedioate decomposes at a lower temperature than calcium ethanedioate. [2]

Mg^{2+} has a higher charge density/polarising power than Ca^{2+}.
The electron cloud of $C_2O_4^{2-}$ in MgC_2O_4 is distorted to a greater extent hence the bonds in anion are weakened more than in CaC_2O_4.
Less energy is required to break the bonds in MgC_2O_4.

Examiner's comments:

- All key points underlined should be included. Note that it is the cation that has high charge density/polarising power.
- Answers that stated Mg or MgC_2O_4 has higher charge density/polaring power was NOT accepted.
- Common mistake: Discussion about lattice energy. Note that lattice energy is used to explain strength of ionic bonds between M^{2+} and $C_2O_4^{2-}$, hence is related to melting point and NOT thermal decomposition temperature.

[Total: 20]

5 **(a)** The equilibrium constant, K_p, of the following reaction is 1.64 at a certain temperature.

equation 1

$$I_2(s) + Br_2(g) \rightleftharpoons 2IBr(g) \qquad \Delta H < 0$$

In a study, some bromine gas was introduced into a vessel with excess solid iodine at the same temperature and the reaction was allowed to take place until equilibrium was reached. The partial pressure of IBr(g) at equilibrium was found to be 0.80 atm. Assume that all the bromine is in the gaseous state and that the vapour pressure of iodine is negligible.

(i) State the K_p expression for equation 1.

Hence, calculate the partial pressure of Br_2 at equilibrium. [2]

$K_p = \frac{(P_{IBr})^2}{(P_{Br2})}$

$1.64 = \frac{0.8^2}{(P_{Br2})}$

$P_{Br2} = \frac{0.8^2}{1.64} = 0.39024 = 0.390$ atm

Examiner's comments:

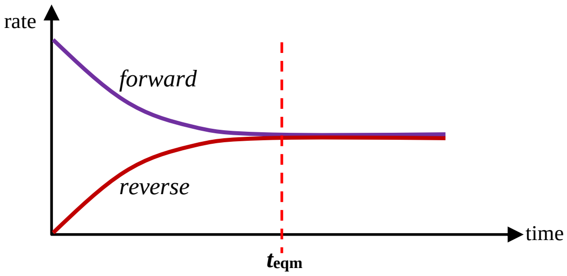
- Iodine is a solid so the K_p should not include its partial pressure

(ii) Hence calculate the initial pressure of Br_2 in the container. [1]

	$I_2(s)$	+ $Br_2(g)$	$\rightleftharpoons$	$2IBr(g)$
Initial / atm	-	x + 0.4		0
Change / atm	-	−0.4		+0.80
Equilibrium / atm	-	x		0.80

Initial pressure = 0.390 + 0.4 = 0.790 atm

(iii) Sketch a graph of rate against time, showing how the rates of the forward and reverse reactions change with time, from the point of mixing to the point after equilibrium is established. Label your graphs clearly. [2]



Examiner's comment:

Answers should show

- labelling of axes and graphs
- decreasing rate of 'forward' reaction
- increasing rate of 'backward' reaction
- same and constant rates of forward and backward reaction at equilibrium
- label the time that equilibrium is reached

(iv) State and explain the effect on the rate of production and yield of IBr when temperature is decreased. [3]

As temperature is decreased, the system would favour the forward, exothermic reaction to release heat. POE shifts to the right.

Frequency of effective collision decreases as fewer particles have kinetic energy greater than activation energy.

The yield of IBr increases and rate of production of IBr decreases. [1]

Examiner's comments:

- The POE shifts to **release heat** (not increase temperature)
- Students need to justify the decrease rate of reaction by relating to the number of particles that have energy greater then E_a and the frequency of effective collisions

(v) State and explain the effect on the equilibrium partial pressure of Br_2 when the pressure of the system is halved at constant temperature. [2]

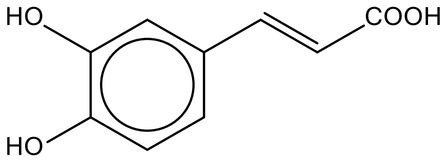
When the pressure of the system is halved, the system will respond by increasing the number of gaseous particles present, to increase pressure.

This favours the forward reaction for the position of equilibrium to shift to the right and the partial pressure of Br_2 will decrease.

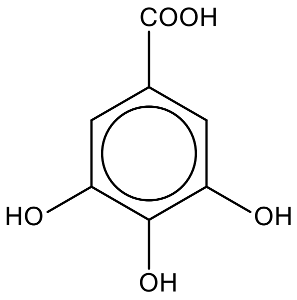
Examiner's comments:

- For this question, the total pressure decreased (e.g. due to increase in volume), so the POE shifts to the side of the equilibrium that has fewer moles *of gas*.

b Caffeic acid and gallic acid are organic compounds that can be found in coffee and tea leaves respectively.



caffeic acid



gallic acid

(i) Describe a chemical test to distinguish the above two compounds and state the expected observations. [2]

Add $KMnO_4$, H_2SO_4(aq) to both compounds and heat

For caffeic acid, purple $KMnO_4$ will decolorise. Colourless, odourless gas (CO_2) produced will form white ppt with limewater. For gallic acid, purple $KMnO_4$ will remain.

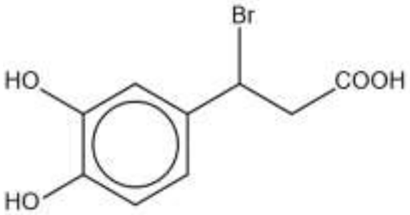
Or add $KMnO_4$ in NaOH
For caffeic acid, purple $KMnO_4$ will decolorise and brown ppt form while for gallic acid, purple $KMnO_4$ will remain.

Or $KMnO_4$, H_2SO_4(aq)
For caffeic acid, purple $KMnO_4$ will decolorise while for gallic acid, purple $KMnO_4$ will remain.

Examiner's comments:

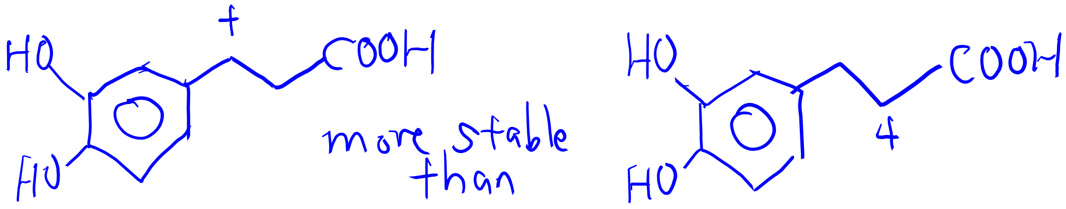
- Observations for BOTH compounds should be clearly stated. Do not write no visible reaction.
- The acid dilute H_2SO_4 or H_2SO_4(aq) should be stated for $KMnO_4$. Cannot just state acidified $KMnO_4$.
- It is important to state "dilute" or (aq) for H_2SO_4 as without this, it would mean the H_2SO_4 is in pure form which is incorrect.
- Common mistake was to use Br_2. Note that both compounds have phenol groups that will react with Br_2 to decolourise it and form white ppt.

(ii) Draw the structure of the major product that is formed when caffeic acid reacts with HBr. [1]



Examiner's comments:

- Please draw the major product above.
- By comparing the carbocations shown below, the carbocation with the positive charge on the C next to the benzene is more stable.
- This is because the p orbitals of the C with the positive charge can overlap with the pi electron cloud of the benzene ring, thus the pi electrons in the ring delocalises to the positively charged carbon to disperse the charge.



(c) Buffer solutions are very important in many biological reactions as enzymes need a specific pH range to function properly. One of the most important buffer systems is the carbonic acid, H_2CO_3, and bicarbonate, HCO_3^-, buffer system in blood.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The above equilibrium has a K_a value of 7.90×10^{-7} mol dm^{-3} and is responsible for buffering the pH of the blood at 7.4.

(i) A blood buffer can be simulated by mixing 0.500 mol dm^{-3} H_2CO_3 and 2.00 mol dm^{-3} of $NaHCO_3$.

Show that the volumes of H_2CO_3 and $NaHCO_3$ required to make 200 cm^3 of this buffer solution with pH 7.4 are 34 cm^3 and 166 cm^3 respectively [3]

$pK_a = -\lg(7.90 \times 10^{-7}) = 6.102$

$$pH = pK_a + \lg \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$7.4 = -\lg(7.90 \times 10^{-7}) + \lg \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\lg \frac{[HCO_3^-]}{[H_2CO_3]} = 1.298$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 19.86$$

Since volume of H_2CO_3 + HCO_3^- = 0.200 dm^3, let the volume of HCO_3^- be A dm^3 and the volume of H_2CO_3 be (0.200 – A) dm^3.

$$\frac{\dfrac{A \times 2}{0.200}}{\dfrac{(0.200 - A) \times 0.5}{0.200}} = 19.86$$

A = 0.166 dm^3
= 166 cm^3

Volume of HCO_3^- = 166 cm^3
Volume of H_2CO_3 = 200 – 166 = 34 cm^3 for showing both volumes
Examiner's comments:

- Please ensure that you include the volume 200 cm^3 in your calculation for

$$\frac{\dfrac{A \times 2}{0.200}}{\dfrac{(0.200 - A) \times 0.5}{0.200}} = 19.86$$

This is because it is $\dfrac{[HCO_3^-]}{[H_2CO_3]}$ = 19.86 and not no. Of moles of HCO_3^- and no.of moles of H_2CO_3

Your working should show clearly that you understand that volume should be included in the calculation even though it cancels out.

You should prove the volumes are 166cm^3 and 34cm^3, NOT use 166 cm^3 and 34 cm^3 to prove pH is 7.4.

		(ii)	With the aid of an equation, explain how the buffer solution prepared in **c(i)** helps to maintain the pH at around 7.4 when a small amount of sodium hydroxide is added. [2]
			$H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$ H_2CO_3 will react with hydroxide added to minimise the decrease in $[H^+]$/no significant increase in $[OH^-]$. Hence, the increase in pH of the solution is not significant. Examiner's comments: • Reversible arrow is NOT accepted as all OH^- is taken up by H_2CO_3. • Do not write the equation where HCO_3^- reacts with H^+ as it is irrelevant. • Your answer should also explain how the buffer helps maintain pH, i.e. by minimising the change in OH^- or H^+.
		(iii)	Hence calculate the resultant pH of the above buffer solution when 0.003 mol of solid sodium hydroxide is added. [2]
			Amount of H_2CO_3 consumed = [(34/1000) x 0.5] − 0.003 = 0.0140 mol Amount of HCO_3^- produced = [(166/1000) x 2] + 0.003 = 0.335 mol $\mathrm{pH} = \mathrm{p}K_a + \lg\frac{[HCO_3^-]}{[H_2CO_3]} = 6.102 + \lg\frac{\frac{0.335}{0.200}}{\frac{0.0140}{0.200}} = 7.48$ Examiner's comments: Please ensure that you include the volume 200 cm^3 in your calculation as concentration is calculated not amount.
			[Total: 20]