Class	Adm No

Candidate Name: ____________________

H

millennia institute

2020 End-of-Year Examinations
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **18th Sep 2020**

2 hours

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission 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.

Section A: Answer **all** questions

Section B: Answer any **1** question

A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

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.

	Section A			**Section B**		Total
Question	**1**	**2**	**3**	**4**	**5**	
Marks	**25**	**20**	**15**	**20**	**20**	**80**

Section A

Answer **all** questions from this section.

1 Phenylamine, $C_6H_5NH_2$, otherwise known as aniline, is commonly used in the manufacture of industrial chemicals.

The family of amines tend to exhibit strong odours. The more volatile the amine, the stronger the odour. Trimethylamine, $(CH_3)_3N$, is the compound responsible for the fishy odour associated with rotting fish.

(a) **(i)** Suggest, with explanation, whether phenylamine or trimethylamine is likely to exhibit a stronger fishy odour. [2]

Trimethylamine has a smaller electron cloud size than phenylamine, and thus has weaker instantaneous dipole-induced dipole forces of attraction between its molecules. Less energy is required to overcome them, and hence ;

trimethylamine is likely to be more volatile / have a lower boiling point, exhibiting a stronger odour. ;

(ii) When phenylamine and trimethylamine are burnt, only phenylamine burns with a smoky flame.

Explain the above observation. [1]

Phenylamine has a larger number of carbon atoms per molecule than trimethylamine, hence it undergoes incomplete combustion to produce soot / C(s). ;

(iii) The reaction between phenylamine and ethanoyl chloride, CH_3COCl, takes place rapidly at room temperature, releasing a gas in the process.

Write a balanced chemical equation for the reaction between phenylamine and ethanoyl chloride, and identify the functional group formed in the product. [2]

$C_6H_5NH_2 + CH_3COCl \rightarrow CH_3CONHC_6H_5 + HCl$;

Amide ;

(iv) A laboratory assistant wants to synthesise the product in **(iii)**. However, ethanoyl chloride is unavailable, so he opts to use ethanoic acid in place of ethanoyl chloride.

Explain why the desired product is not obtained. [1]

Acid-base reaction takes place between the basic phenylamine and carboxylic acid instead ;

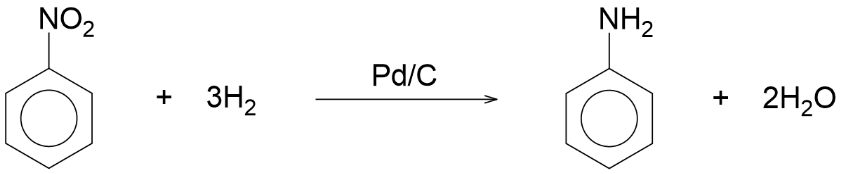
or

The carboxyl carbon in ethanoic acid is not sufficiently electron-deficient / electrophilic enough. ;

(v) State the reagents and conditions needed to produce ethanoyl chloride from ethanoic acid. [1]

PCl_5, r.t. / PCl_3, r.t. / $SOCl_2$, r.t. / $NaCl(s)$, conc H_2SO_4, heat under reflux;

(b) Phenylamine can be synthesised from nitrobenzene via many different reactions. One such reaction involves using palladium on carbon (Pd/C) catalyst, at 200–300 °C:



(i) Identify the *type of reaction* carried out above. [1]

Reduction. ;

(ii) Palladium on carbon (Pd/C) is a fine powder made by depositing palladium metal in the porous cavities of activated charcoal.

State the type of catalysis involved, and suggest why palladium metal needs to be in the form of a fine powder. [2]

Heterogeneous catalysis ;

As a fine powder, Pd/C will have a larger surface area, increasing frequency of effective collisions and hence a faster rate of reaction. ;

accept any reasonable answer

(iii) A chemist carries out this reaction and obtains a percentage yield of 96%.

Suggest why it is difficult to achieve 100% yield. [1]

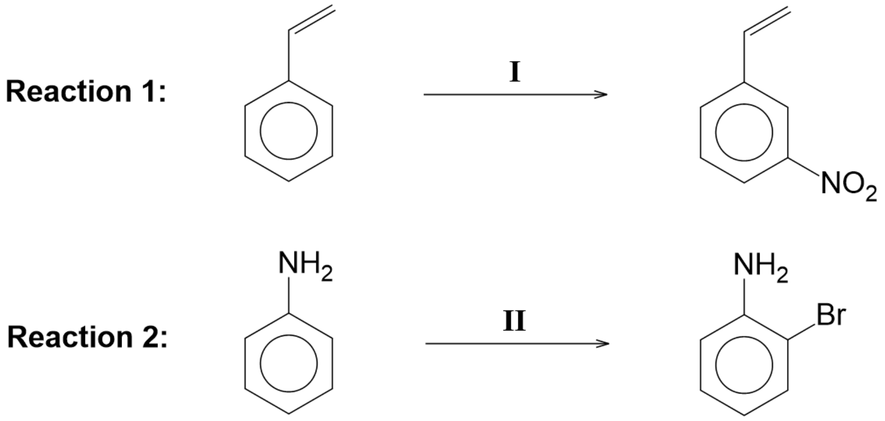
Unwanted side-reactions could have occurred in the synthesis / some reagents or product was lost during the transfer across apparatus / some product was lost during the purification process.

accept any reasonable answer

(c) The $–CH=CH_2$ group of phenylethene directs incoming substituents to the 3-position of the benzene ring, while the $–NH_2$ group of phenylamine directs incoming substituents to the 2-position of the benzene ring. This is known as the *orienting effect*.

A student claims that this *orienting effect* is due to "–CH=CH_2 and –NH_2 having orbital overlaps with the benzene ring".

Under the right set of reagents and conditions used, the following products are obtained from phenylethene and phenylamine respectively:



(i) State the corresponding reagents and conditions for steps **I** and **II**. [2]

I: conc HNO_3, conc H_2SO_4, heat

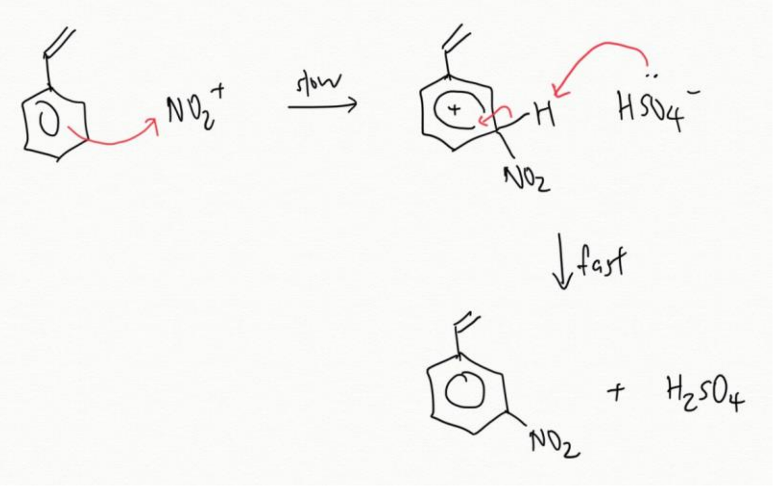
II: Br_2 in CCl_4, room temperature

(ii) Describe the mechanism of **Reaction 1**.

In your answer, show all relevant lone pairs and curly arrows involved in the mechanism. [4]

Electrophilic Substitution ;

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$;



;;

(iii) State the hybridisation for each of the two carbon atoms in the $–CH=CH_2$ substituent of phenylethene. [1]

Both are sp^2. ;

(iv) With the aid of an appropriate orbital diagram, illustrate in phenylethene, the orbital overlaps of $–CH=CH_2$ with the benzene ring. You need only show the relevant orbitals of the carbon atoms involved. [2]

p orbitals of benzene 6C ; overlapped with

p orbitals of 2C in $–CH=CH_2$; denoted by dotted lines and labelled

(v) Briefly explain why it would be incorrect to say that "$–CH=CH_2$ is an electron-withdrawing group". [1]

Phenylethene is a hydrocarbon, and all the C and H atoms have similar electronegativities / $–CH=CH_2$ does not have a lone-pair that can delocalise into the ring.

OWTTE

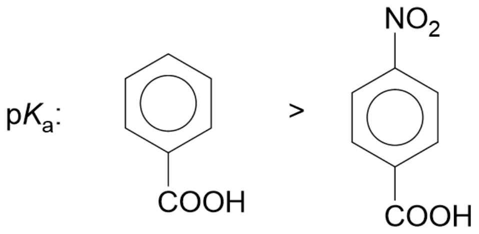
(vi) Suggest a chemical test to distinguish between phenylethene and phenylamine. [2]

R&C: $Br_2(aq)$, r.t.
Obsv: Orange $Br_2(aq)$ decolourises for both phenylethene and phenylamine, but a white precipitate forms for only phenylamine.

or

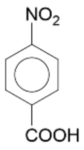
R&C: $KMnO_4$, dil H_2SO_4, heat
Obsv: Purple $KMnO_4$ decolourises for phenylethene with effervescence of a gas that forms a white precipitate in limewater / $Ca(OH)_2$. Purple $KMnO_4$ remains for phenylamine.

(d) Given that $–NO_2$ is an electron-withdrawing group, explain the following observation.



[2]

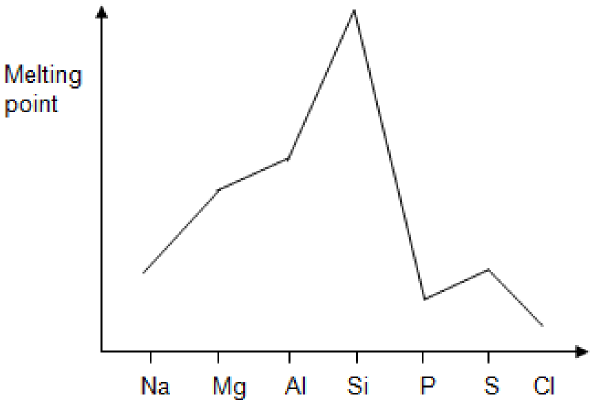
The electron-withdrawing $–NO_2$ group <u>reduces the intensity of the negative charge on the carboxylate group, stabilising its conjugate base more</u>. ;

Hence  is <u>a stronger acid</u> and has a lower pK_a. ;

[Total: 25]

2 **(a)** **(i)** The Period 3 elements vary in their physical properties, such as melting point and electrical conductivities.

Sketch the melting point trend of the elements in Period 3 (from Na to C*l*). [1]



(ii) The Period 3 metals Na and A*l* undergo vigorous reactions with chlorine gas upon heating to form their respective metal chlorides. When these chlorides are dissolved into water separately, solutions of different p*H* values are obtained.

Write balanced equations to explain the differences in p*H*, stating the p*H* value of the solutions formed for each metal chloride. [3]

Polarising power of $Na^+ < Al^{3+}$ as it is proportional to charge density. ;

- NaC*l* (s) dissolves in water to form Na^+(aq) and Cl^-(aq) with no hydrolysis.
  $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
  pH ≈ 7
- $AlCl_3$ dissolves in water with hydrolysis, polarising water molecules and weakening the O–H bond to give H^+ ions.
  $AlCl_3\ (s) + 6\ H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}\ (aq) + 3Cl^-\ (aq)$
  $[Al(H_2O)_6]^{3+}\ (aq) \longrightarrow [Al(H_2O)_5(OH)]^{2+}\ (aq) + H^+\ (aq)$
  pH ≈ 3

pH values correctly matched ;
balanced equations ;

(iii) A Period 3 element forms a giant covalent oxide and simple covalent chloride. This chloride reacts readily with water.

Identify this element and give a balanced chemical equation for the reaction of its chloride with water. [2]

Si. ;

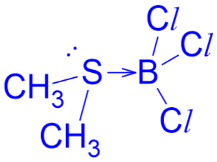
$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$;

(b) When boron trichloride, BCl_3, is reacted with dimethyl sulfide, $(CH_3)_2S$, the adduct $(CH_3)_2S{\cdot}BCl_3$ is produced. At room temperature, $(CH_3)_2S{\cdot}BCl_3$ exists in the solid state.

The adduct can act as a convenient source of BCl_3. When heated slightly, BCl_3 is released from the adduct, as given in the following dissociation equation:

$$(CH_3)_2S{\cdot}BCl_3(s) \rightleftharpoons (CH_3)_2S(l) + BCl_3(g)$$

(i) Draw the structure of the adduct, $(CH_3)_2S{\cdot}BCl_3$. [1]



correct structural formula w dative bond (do not mark for shape) ;

(ii) State the properties of BCl_3 and $(CH_3)_2S$ respectively that enable them to form the adduct. [2]

The B atom in BCl_3 is electron-deficient and has energetically accessible vacant orbitals ;

that can accept a lone pair of electrons donated from $(CH_3)_2S$. ;

(iii) Write the expression for the equilibrium constant for the dissociation, K_c, stating its units. [2]

$K_c = [BCl_3]$ mol dm^{-3}

(iv) BCl_3 is only released from the adduct upon heating.

Use Le Chatelier's Principle to explain this observation. [2]

ΔH of the forward reaction is endothermic as energy is required to break the dative bond. ;

By LCP, when temperature increases upon heating, position of equilibrium shifts to the right to remove the excess heat. This favours the forward reaction to release BCl_3. ;

(v) Hence or otherwise, predict the change in value of K_c after heating, if any. [1]

The value of K_c will increase. ;

(c) Methanol and boron trichloride react readily in the gas phase.

$$CH_3OH + BCl_3 \rightarrow CH_3OBCl_2 + HCl$$

Two mechanisms for this reaction have been proposed:

Mechanism 1	**Mechanism 2**
$CH_3OH + BCl_3 \xrightarrow{slow} CH_3OHBCl_3$ $CH_3OHBCl_3 \xrightarrow{fast} CH_3OBCl_2 + HCl$	$CH_3OH \xrightarrow{slow} CH_3O^- + H^+$ $CH_3O^- + BCl_3 \xrightarrow{fast} CH_3OBCl_2 + Cl^-$ $H^+ + Cl^- \xrightarrow{fast} HCl$

(i) Experimental data from the reaction are as follows:

Experiment	$[CH_3OH]$ /mol dm^{-3}	$[BCl_3]$ /mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.055	0.330	1.5×10^{-3}
2	0.110	0.330	3.0×10^{-3}
3	0.110	0.165	1.5×10^{-3}

Determine the rate equation of the reaction. [3]

Comparing Expts 1 and 2,
When $[CH_3OH]$ is doubled, initial rate is doubled.
Hence order of reaction wrt $[CH_3OH]$ is 1. ;

Comparing Expts 2 and 3,
When $[BCl_3]$ is doubled, initial rate is doubled.
Hence order of reaction wrt $[BCl_3]$ is 1. ;

Rate = $k[CH_3OH][BCl_3]$;

(ii) Hence, identify whether the reaction proceeds via **Mechanism 1** or **Mechanism 2**. [1]

Mechanism 1. ;

(iii) The concentration of BCl_3 used in Experiment 1 can be considered to be in large excess relative to the concentration of CH_3OH.

Using this information, determine an expression for the half-life of the reaction. You may leave your answer in terms of the rate constant, *k*. [2]

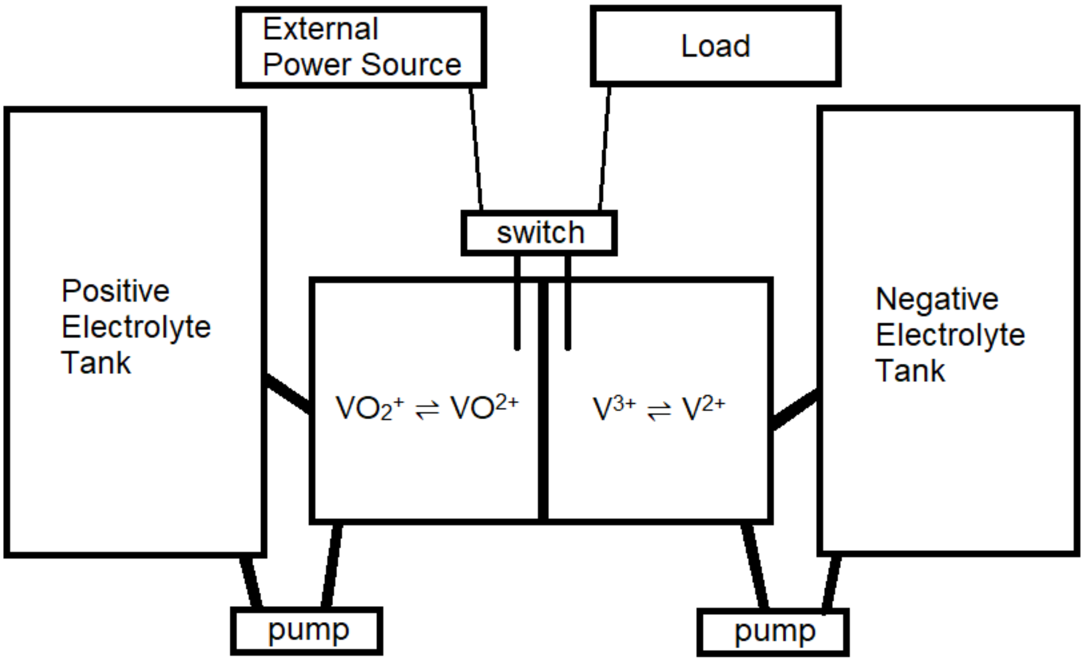
Rate = $k[CH_3OH][BCl_3] = k'[CH_3OH]$; where $k' = k[BCl_3]$ (pseudo-first order)

$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[BCl_3]} = \frac{\ln 2}{0.33k}$; (do not mark for units)

[Total: 20]

3 A flow battery is a rechargeable fuel cell that can be rapidly "recharged" by simply replacing the electrolyte liquid with fresh electrolyte. At the same time, the spent electrolyte is recovered for re-energisation. This additional electrolyte is stored externally, generally in tanks.

One such battery involving the use of vanadium ions in different oxidation states is the Vanadium Redox Flow Battery (VRFB).



The specific ions used in the VRFB are VO_2^+ and VO^{2+} for the positive electrolyte tank, and V^{3+} and V^{2+} for the negative electrolyte tank. The electrode reactions are as follows:

Positive electrolyte tank: $VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ $E^\ominus = +1.00\text{ V}$

Negative electrolyte tank: $V^{3+} + e^- \rightleftharpoons V^{2+}$ $E^\ominus = -0.26\text{ V}$

When the VRFB is in use,

Discharging reaction: $\mathbf{VO_2^+ + V^{2+} + 2H^+ \rightarrow VO^{2+} + V^{3+} + H_2O}$ $\Delta H^\ominus_{rxn}$

(a) **(i)** Determine the $E^\ominus_{cell}$ of the VRFB and explain whether the positive electrolyte tank is the anode or cathode **during discharge**. [2]

$E^\ominus_{cell} = +1.00 - (-0.26) = +1.26\text{ V}$;

During discharge, positive tank is cathode as it undergoes reduction, and negative tank is anode as it undergoes oxidation. ;

(ii) Calculate the standard Gibbs free energy change of the discharging reaction. [1]

$\Delta G^{\ominus}_{rxn} = -nFE^{\ominus}_{cell} = -(1)(96500)(+1.26) = -122$ kJ mol^{-1} (3sf)

(iii) Explain the significance of the sign of your value obtained in **(a)(ii)**. [1]

The negative sign indicates that the reaction is spontaneous and will happen without any continuous external supply of energy.

(iv) Based on your answer in **(a)(ii)**, and given that standard entropy change of the discharging reaction is –122 J mol K^{-1}, calculate $\boldsymbol{\Delta H^{\ominus}_{rxn}}$. [1]

$\boldsymbol{\Delta H^{\ominus}_{rxn}} = \Delta G^{\ominus}_{rxn} + T\Delta S^{\ominus}_{rxn} = -122 + (25+273)(-\frac{122}{1000}) = -158$ kJ mol^{-1} (3sf)

(v) Hence, calculate the value for the standard enthalpy change of formation of V^{3+}, $\Delta H^{\ominus}_{f}(V^{3+})$, given the following data:

Species	**$\Delta H^{\ominus}_{f}$ / kJ mol^{-1}**
VO_2^+	–650
VO^{2+}	–487
V^{2+}	–226
H^+	0
H_2O	–286

Discharging reaction: $\mathbf{VO_2^+ + V^{2+} + 2H^+ \rightarrow VO^{2+} + V^{3+} + H_2O \quad \Delta H^{\ominus}_{rxn}}$

[2]

$\boldsymbol{\Delta H^{\ominus}_{rxn}} = [\Delta H^{\ominus}_f(VO^{2+}) + \Delta H^{\ominus}_f(V^{3+}) + \Delta H^{\ominus}_f(H_2O)] - [\Delta H^{\ominus}_f(VO_2^+) + \Delta H^{\ominus}_f(V^{2+}) + \Delta H^{\ominus}_f(H^+)]$;

$-158 = [(-487) + \Delta H^{\ominus}_f(V^{3+}) + (-286)] - [(-650) + (-226) + (0)]$

$\Delta H^{\ominus}_f(V^{3+}) = -261$ kJ mol^{-1} ;

(b) The spent electrolyte is re-energised after complete discharge, via an external power source.

(i) Write the overall balanced equation for the **re-energisation** of the VFRB. [1]

Recharging process is reverse of discharging reaction.

Overall: $VO^{2+} + H_2O + V^{3+} \rightarrow VO_2^+ + 2H^+ + V^{2+}$;

(ii) During the re-energisation process, an external power source of current 20 A is used and 6 hours was required to fully recharge the VFRB.

Calculate the amount of electrons that was passed through the VFRB. [2]

Q = It = nF ;

$n = \frac{It}{F} = \frac{(20)(6\times60\times60)}{96500} = 4.48$ mol ;

(iii) Sulfuric acid was used in the positive electrolyte tank as the source of H^+.

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

By citing relevant data from the *Data Booklet*, explain why the sulfate ion does not interfere with the **re-energisation** process at the positive electrolyte tank. [3]

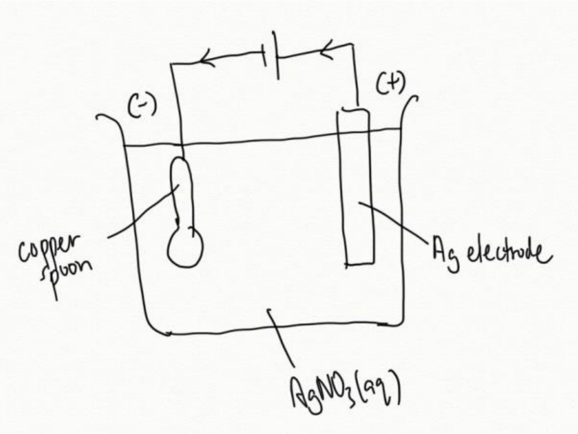
$VO_2^+ + 2H^+ + e^- \rightleftharpoons \boxed{VO^{2+}} + H_2O$ $E^\ominus = +1.00$ V

$S_2O_8^{2-} + 2e^- \rightleftharpoons \boxed{SO_4^{2-}}$ $E^\ominus = +2.01$ V ;

Although the anode is positively charged and will attract the negatively charged SO_4^{2-} / repel the positively charged VO^{2+}, ;

the SO_4^{2-} half-equation has a significantly more positive $E^\ominus$ value and is thus not selectively discharged. ;

(c) Draw a simplified diagram to illustrate how a copper spoon can be electroplated with silver metal. Label all key components of your diagram. [2]

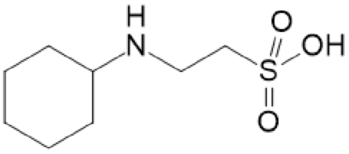


[Total: 15]

Section B

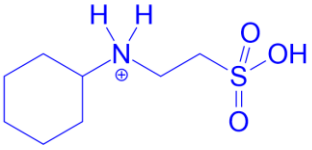
Answer **one** question from this section.

4 N-cyclohexyl-2-aminoethanesulfonic acid, also known as CHES, is a buffering agent commonly used in biochemistry and molecular biology. It has a pK_a value of 9.3, and is used for enzymatic processes above physiological pH.



CHES
($C_8H_{17}NO_3S$)

(a) **(i)** Draw the structure of the relevant conjugate acid/base ion of CHES, and state whether it is an acidic or alkaline buffer. [2]

Conjugate acid:  ;

Alkaline buffer as pK_a value > 7 (9.3) ;

(ii) A solution of CHES buffer is prepared in the laboratory.

Determine the ratio of CHES to its relevant conjugate acid/base ion required in order to obtain a buffer solution of pH 10.0. [2]

$$\text{pOH} = \text{p}K_b + \lg\frac{[BH^+]}{[B]}$$

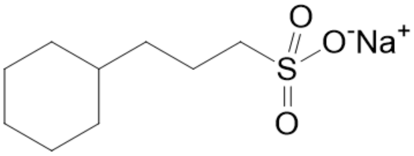
$$14 - 10.0 = (14 - 9.3) + \lg\frac{[BH^+]}{[B]} \;;$$

$$\lg\frac{[BH^+]}{[B]} = -0.7$$

$$\frac{[BH^+]}{[B]} = 0.1995$$

Ratio, $\frac{[B]}{[BH^+]} = \frac{1}{0.1995} = 5.01$ (3 sf) ; (accept answer left as fraction ratio)

(b) Without the amino group, the following analogue of CHES is very poorly soluble, even as a sodium salt, $C_9H_{17}O_3SNa$.



($C_9H_{17}O_3SNa$)

The compound is known to have a K_{sp} value of 6.20 x 10^{-23}.

(i) Solid $C_9H_{17}O_3SNa$ salt is added to water until no further solid dissolves.

Determine the concentration of Na^+ ions in this resultant solution. [2]

$$C_9H_{17}O_3SNa \rightleftharpoons C_9H_{17}O_3S^- + Na^+$$

$K_{sp} = [C_9H_{17}O_3S^-][Na^+]$;
Since $[C_9H_{17}O_3S^-] = [Na^+]$
$6.20 \times 10^{-23} = [Na^+]^2$
$[Na^+] = 7.87 \times 10^{-12}$ mol dm^{-3} (3sf) ;

(ii) The solid $C_9H_{17}O_3SNa$ salt was added to a solution of 0.10 mol dm^{-3} Na^+ instead.

Determine the solubility of $C_9H_{17}O_3SNa$ in the 0.10 mol dm^{-3} Na^+ solution. [1]

Let the solubility of $C_9H_{17}O_3SNa$ in 0.10 mol dm^{-3} Na^+ solution be y.

$6.20 \times 10^{-23} \approx (y)(0.10)$
$y = 6.20 \times 10^{-22}$ mol dm^{-3} ;

(c) Compared to other buffers, CHES is useful for biochemistry reactions as it does not form complexes easily with metal cations such as Na^+ and K^+.

(i) Compare and explain the difference in first ionisation energies of Na and K. [2]

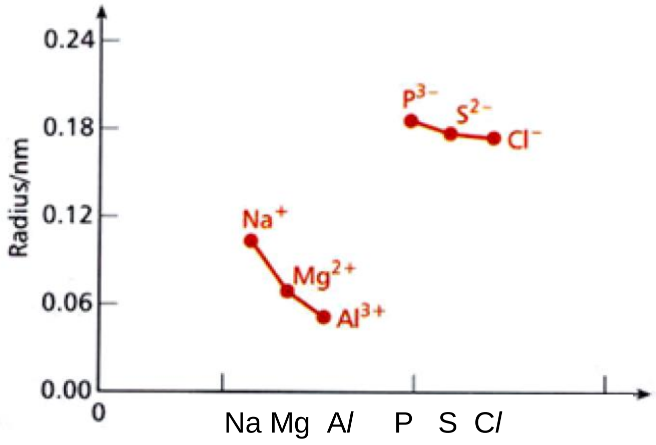
First ionisation energy of Na > K. ;

Down the group, although the increase in nuclear charge outweighs the increase in shielding effect and effective nuclear charge increases, the distance of the valence electron from nucleus is further for K compared to Na. ;

(ii) State the full electronic configuration of K^+. [1]

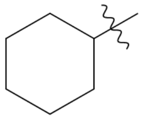
K^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(iii) Sketch a well-labelled graph of the **ionic radii** across the Period 3 elements Na, Mg, A*l*, P, S and C*l*. [2]



1m for decreasing trends
1m for cationic radii < anionic radii

(d) Compound **A** has the molecular formula $C_{10}H_{15}OCl$, and contains an unsubstituted cyclohexyl ring.



unsubstituted cyclohexyl ring

A does not rotate plane-polarised light. When Fehling's reagent is added to **A**, a brick-red precipitate forms.

B is produced when alkaline $KMnO_4$ is added to **A** in an ice bath. When compound **B** is heated with NaOH(aq) followed by acidification, **C**, $C_{10}H_{18}O_5$ is produced.

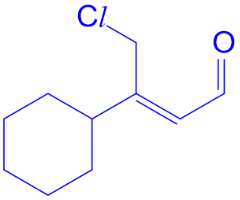
Upon addition of sodium carbonate to **C**, effervescence is observed.

Deduce structures for **A**, **B** and **C**, and explain the chemistry of the reactions described.. [8]

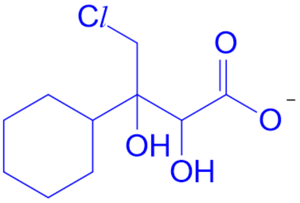
Observation	**Deduction**
Compound **A** has the molecular formula $C_{10}H_{15}OCl$, and contains an unsubstituted cyclohexyl ring	DBE = 10 – 15/2 – ½ +1 = 3 (ring + alkene + aldehyde)
A does not rotate plane-polarised light	**A** does not contain a chiral centre
When Fehling's reagent is added to **A**, a brick-red precipitate forms	**A** undergoes oxidation **A** contains aldehyde
B is produced when alkaline $KMnO_4$ is added to **A** in an ice bath	**A** undergoes mild oxidation to form **B** **A** contains alkene **B** is a diol

When compound **B** is heated with NaOH(aq) followed by acidification, **C**, $C_{10}H_{18}O_5$ is produced	**B** undergoes nucleophilic substitution to form **C** **B** contains alkyl chloride **C** is an alcohol / triol
Upon addition of sodium carbonate to **C**, effervescence is observed.	**C** undergoes acid-carbonate reaction to give off CO_2(g) **C** contains carboxylic acid

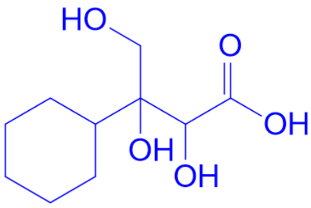
A:



B:



C:



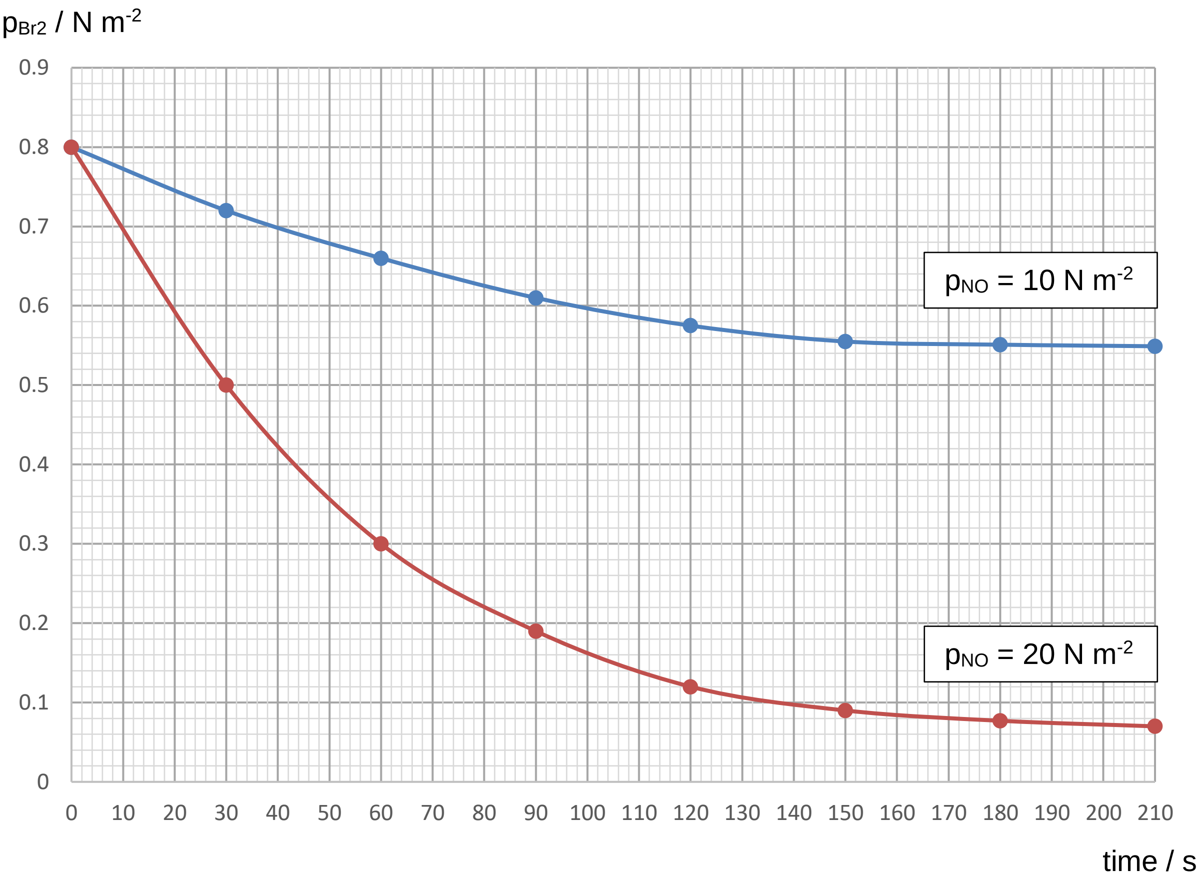
[Total: 20]

5 Nitrosyl bromide, NOBr, is a highly corrosive reddish gas. The reaction to synthesise NOBr is as follows:

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

(a) NO and Br_2 gases were mixed together in a sealed vessel under an ice bath.

The partial pressures of NO and Br_2 gases (units for pressure used: N m^{-2}) were monitored over time for 2 separate experiments to obtain **Graph 1**.



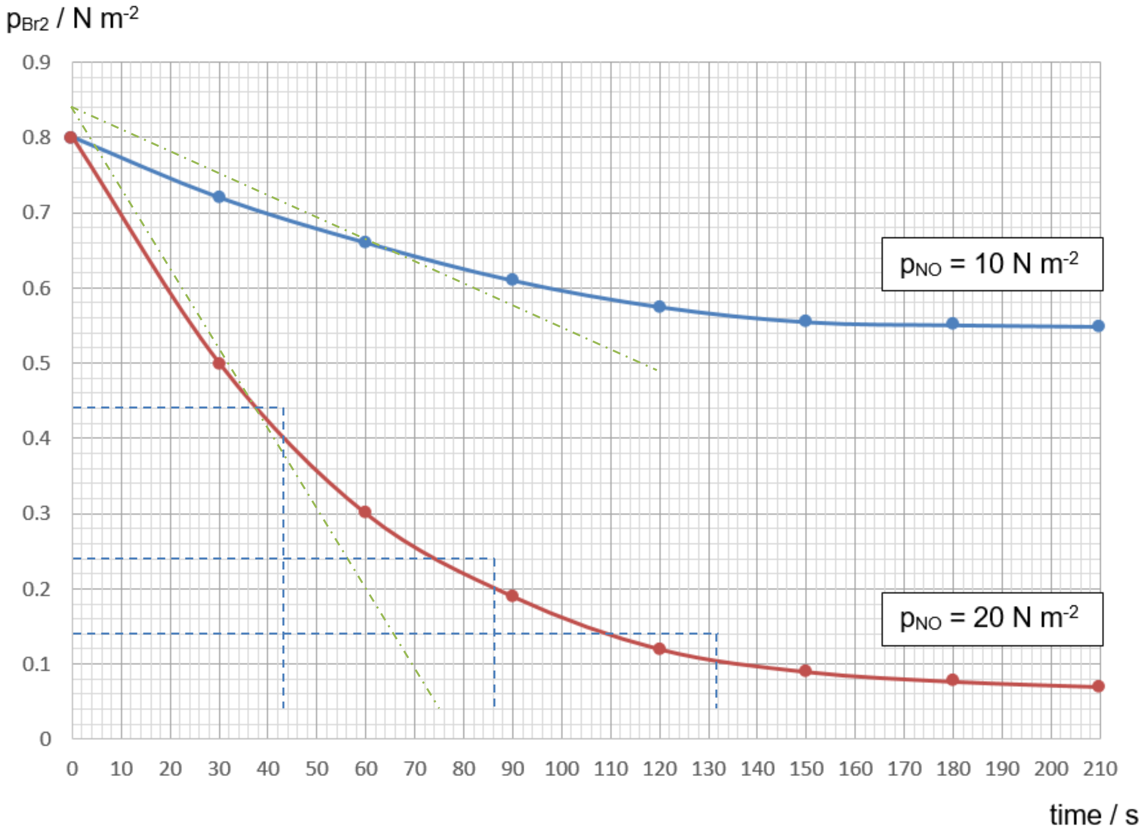
Graph 1

In both experiments, NO gas was used in large excess.

(i) Using **Graph 1**, prove that the rate equation for the reaction between NO and Br_2 is:

$$\boxed{\text{Rate} = k(p_{NO})^2(p_{Br2})}$$

Show all relevant working and calculations. [3]



From p_{NO} = 20 N m^{-2} curve (p_{NO} relatively constant),
$t_{1/2}(1) \approx t_{1/2}(2) \approx t_{1/2}(3) = 43$ s ;
∴ order of reation wrt p_{Br2} is 1.

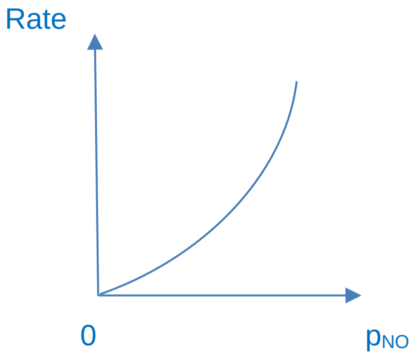
From tangents drawn,
Initial rate for (p_{NO} = 10 N m^{-2}) = $\frac{0.8-0.45}{120-0}$ = 0.002916
Initial rate for (p_{NO} = 20 N m^{-2}) = $\frac{0.8-0}{75-0}$ = 0.01066 ; *both*
When p_{NO} doubles, initial rate increases by 3.65 (≈4) times. ;
∴ order of reation wrt p_{NO} is 2.

(ii) Hence, and with the aid of units used in **Graph 1**, determine the units of the rate constant for this reaction. [1]

Units of *k* = $\frac{\text{N m}^{-2}\text{ s}^{-1}}{(\text{N m}^{-2})^2(\text{N m}^{-2})}$ = N^{-2} m^{4} s^{-1}

accept if students used s^{-1} for units of rate

(iii) Sketch a graph of rate against p_{NO} for the same reaction, given that Br_2 gas is used in excess instead. [1]

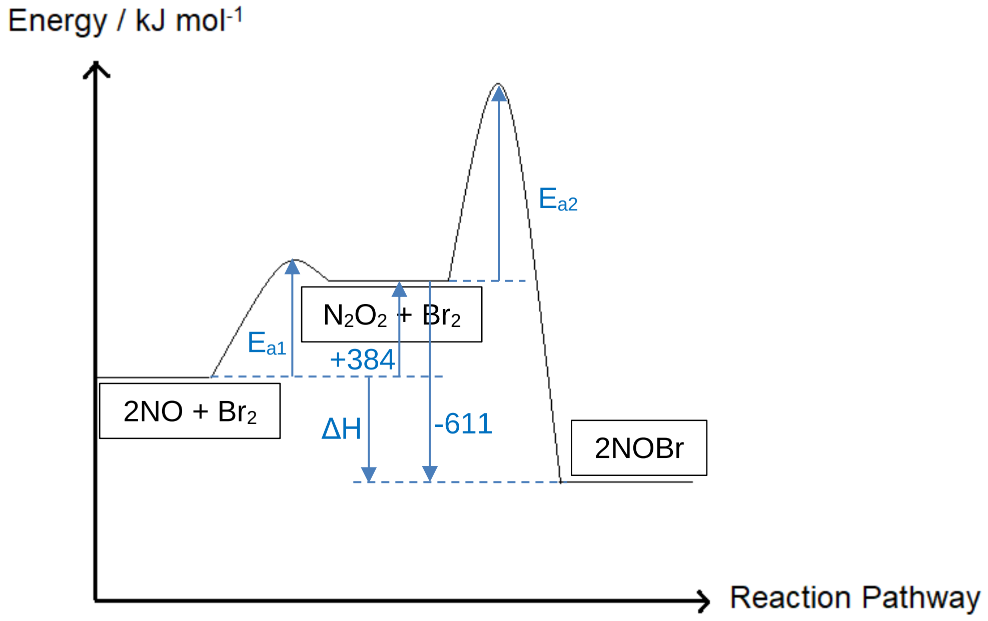


(b) The same synthesis reaction is known to take place via the following mechanism:

Step 1: $N{=}O(g) + N{=}O(g) \rightleftharpoons O{-}N{=}N{-}O(g)$ (fast) $\Delta H = +384\ kJ\ mol^{-1}$

Step 2: $O{-}N{=}N{-}O(g) + Br{-}Br(g) \rightarrow 2N{=}O{-}Br(g)$ (slow) $\Delta H = -611\ kJ\ mol^{-1}$

(i) Sketch a **fully labelled** Energy Profile Diagram for the overall synthesis reaction of NOBr. [2]



All axes labels, species (even if partial)
Correct relative energy levels
Obvious $E_a(1) < E_a(2)$, ΔH label

All 3pts for 2m, 2pts for 1m. No m for 0-1pt.

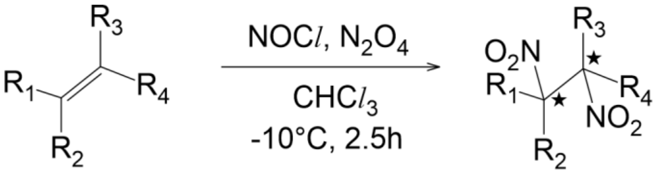
(ii) Predict the sign of entropy change for the overall reaction, explaining your answer. [2]

$\Delta S < 0$;

There is a decrease in no. of gaseous particles ($\Delta n = -1$), leading to fewer ways to arrange the particles and hence less disorder. ;

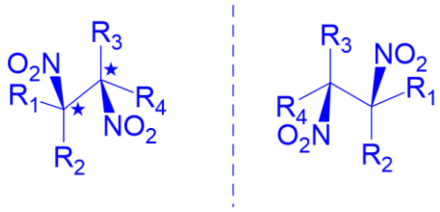
(c) Nitrosyl chloride, NOC*l*, is a reagent that is used together with N_2O_4 in order to achieve dinitration of some alkenes.

In particular, the reaction with Achillin results in the formation of a specific pair of enantiomers at the chiral carbons indicated (*).

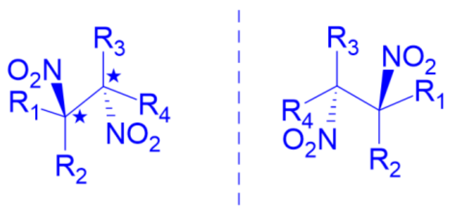


Achillin

(i) Illustrate with appropriate structures the enantiomerism in any one possible pair of enantiomers formed. [1]



or



(ii) *Enantiomeric excess* (e.e.) reflects the degree to which a sample contains one enantiomer in greater amounts than the other. For example, a racemic mixture has an e.e. of 0%, while a single completely pure enantiomer has an e.e. of 100%.

For the reaction of Achillin, the product obtained has an e.e. of 80%. Label on your structures drawn in **(c)(i)** the possible percentages of each enantiomer produced. [1]

90:10 *or* 10:90

(iii) Comment on the similarities and differences in chemical properties for a pair of enantiomers. [1]

Enantiomers have similar chemical properties in general, except for when reacting with other chiral compounds / biological functions / enzymes.

(iv) To measure the e.e. of the enantiomers formed, the product sample is passed through a long column packed with chemical beads to separate the pair of enantiomers.

State the crucial property these chemical beads must have. [1]

The chemical beads must contain chiral compounds. ; *OWTTE*

(v) The reaction is found to occur via a *free radical* mechanism.

Define the term *free radical*. [1]

A free radical refers to any species whereby one of the atoms has an odd number of electrons / 1 unpaired electron.

(vi) Data on the relevant bond energies of NOC*l* are as follows:

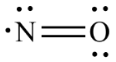
Bond	**Bond Energy / kJ mol^{-1}**
N–O	210
N=O	607
O–C*l*	200

Suggest with explanation the most plausible free radical produced from NOC*l* upon activation with UV light, and draw its dot-and-cross diagram. [2]

Structure: N=O–C*l*

BE(O–C*l*) << BE(N=O), so O–C*l* bond most likely to break. ;

Radical:



;

(d) The nitrate anion, NO_3^-, is an example of an inorganic nitrogen-containing species.

$Ba(NO_3)_2$ and $Ca(NO_3)_2$ are heated separately in crucibles under a strong Bunsen flame.

(i) Write an equation for the thermal decomposition of $Ba(NO_3)_2$. [1]

$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + ½O_2$ *or*
$2Ba(NO_3)_2 \rightarrow 2BaO + 4NO_2 + O_2$

(ii) Predict and explain which metal nitrate has a higher thermal decomposition temperature. [2]

Ca^{2+} is higher up in Group 2 compared to Ba^{2+} and has a higher charge density (q/r) as it has the same charge but larger ionic radius. Hence, Ca^{2+} has a larger polarising power and polarises the electron cloud of NO_3^- to a larger extent than Ba^{2+}, increasing the ease of thermal decomposition of $Ca(NO_3)_2$. ;

$Ba(NO_3)_2$ will have a higher thermal decomposition temperature. ;

(iii) Briefly suggest why $BaCO_3$ has a higher thermal decomposition temperature than $Ba(NO_3)_2$. [1]

CO_3^{2-} and NO_3^- have a similar anionic size (C and N in same period), but there are 2 anions in $Ba(NO_3)_2$ compared to 1 anion in $BaCO_3$. Thus, the electron cloud size of the anion in $Ba(NO_3)_2$ is larger, hence more polarisable, resulting in a lower decomposition temperature.

[Total: 20]

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