Yr6/4/CHEM/HP2/Sep2020

CHEMISTRY
Higher level
Paper 2
Preliminary Examinations

Tuesday 1 September 2020

2 hours 15 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name, class and index number in the blanks below.
- Do not open this examination paper until instructed to do so.
- Answer all questions.
- Answers must be written within the answer boxes provided.
- A calculator is required for this paper.
- A clean copy of the **chemistry data booklet** is required for this paper.
- The maximum mark for this examination paper is **[90 marks]**.

Name: ______________________________

Class: ______________________________

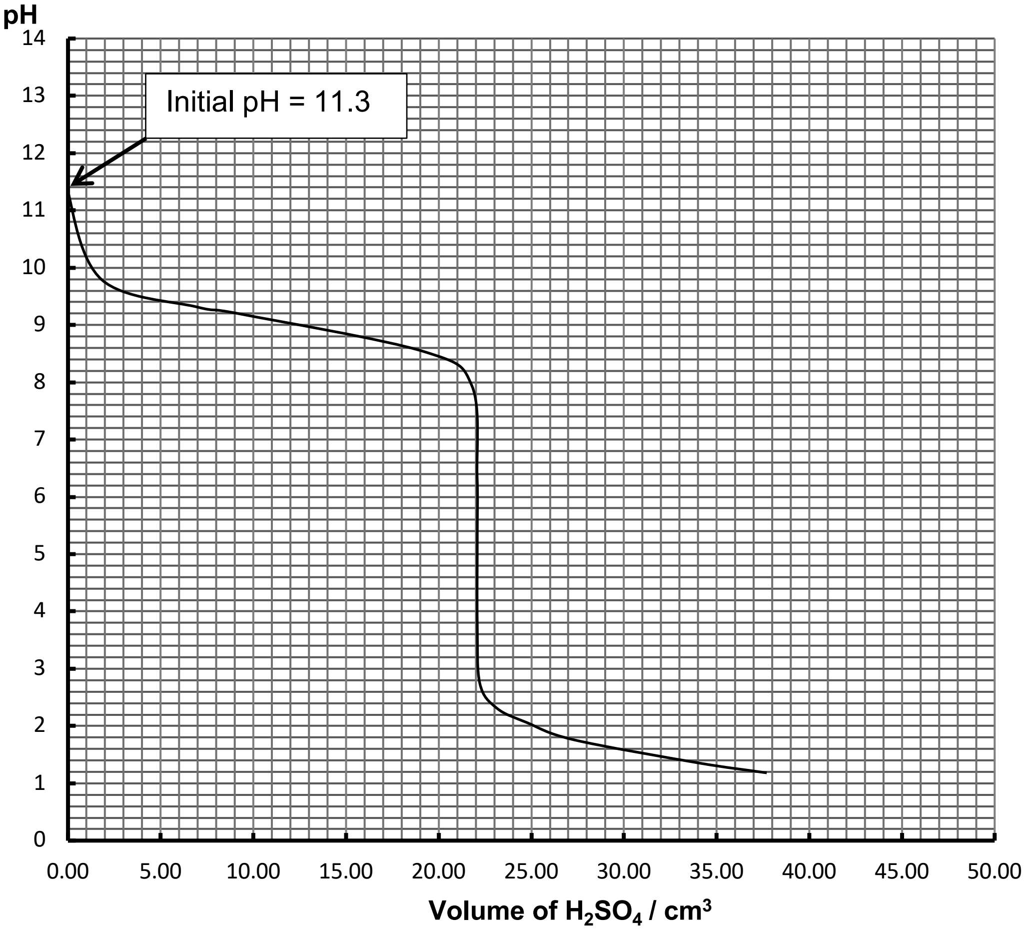
Index: ______________________________

90

22pages

1. Ammonia and ammonium salts have a wide range of uses.

(a) In an experiment, 20.0 cm^3 of aqueous ammonia is titrated with dilute sulfuric acid. The titration curve for this experiment is shown below.



The chemical equation for the reaction between ammonia and sulfuric acid is as follows.

$$2\ NH_3\ (g) + H_2SO_4\ (aq) \rightarrow 2\ NH_4^+\ (aq) + SO_4^{2-}\ (aq)$$

(i) Outline why ammonia is classified as a weak base. [1]

It dissociates/ ionises partially << in water>>.

(ii) Using the titration curve, estimate the pH at equivalence point of this titration. [1]

pH at equivalence point: Accept range from 4.8 to 5.8.

(iii) Using a relevant chemical equation, explain why pH is low at the equivalence point. [2]

$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$;
Ammonium is conjugate acid of weak base/ acts as weak acid.

(iv) Using information from section 22 of the data booklet, state a suitable indicator that can be used to detect the equivalence point of this titration. [1]

Methyl orange/ bromophenol blue/ bromocresol green/ methyl red/ bromothymol blue

(v) The concentration of the sulfuric acid used for this titration is 0.100 mol dm^{-3}. Using information from the graph only, calculate the initial concentration of the aqueous ammonia. [1]

$[NH_3] = \frac{0.100 \times 0.0220 \times 2}{0.0200} = 0.220$ mol dm^{-3}

(vi) The initial pH of the ammonia solution is 11.3.

Using your answer from part (a)(v) and the initial pH of the ammonia solution, calculate the base dissociation constant, K_b, for ammonia. [2]

pOH = 2.7, $[OH^-] = 2.00 \times 10^{-3}$ mol dm^{-3} ;

$K_b = (2.00 \times 10^{-3})^2 / 0.220 = 1.82 \times 10^{-5}$ mol dm^{-3}

Do not penalise if unit is missing or incorrect.
Allow ECF from (v).

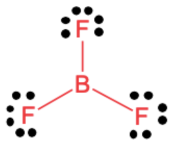
(b) Ammonia reacts with boron trifluoride, BF_3, to form NH_3BF_3. The chemical equation for this reaction is as shown.

$$NH_3 + BF_3 \rightarrow NH_3BF_3$$

(i) Using Lewis acid-base theory, explain the role of NH_3 in this reaction. [1]

Lewis base as it is electron pair donor.

(ii) Draw the Lewis structure for boron trifluoride, BF_3. [1]



Do not award mark if LP on F is missing.

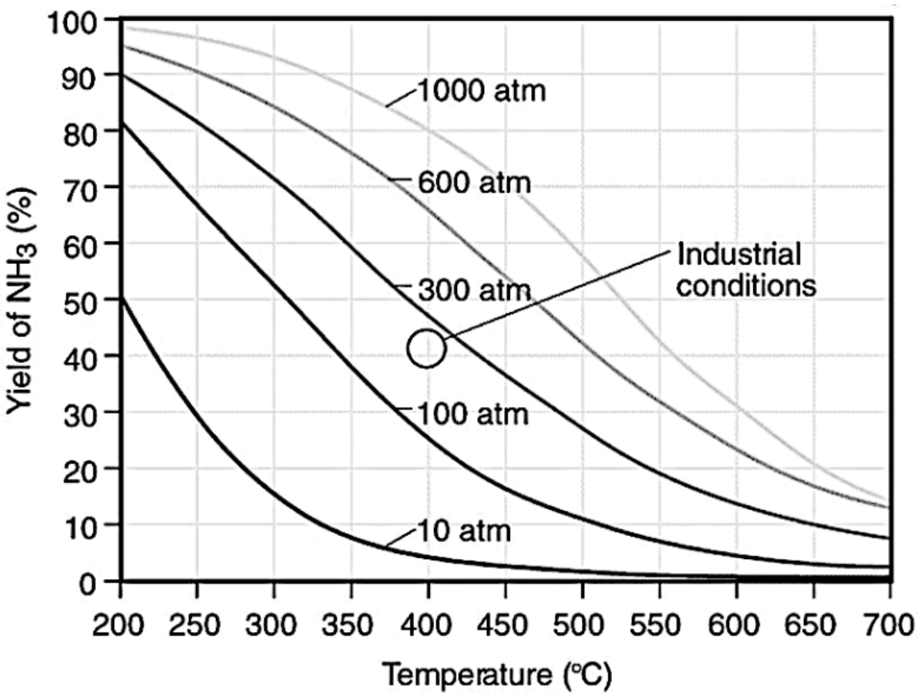
(iii) Use the VSEPR theory to predict the electron domain geometry of boron and the F-B-F bond angle in BF_3 and NH_3BF_3. [2]

	BF_3	NH_3BF_3
Electron domain geometry	Trigonal planar	Tetrahedral
F-B-F bond angle	120°	109°/ 109.5°

(c) Ammonia is produced industrially via the Haber process. This process involves a reversible reaction as shown.

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

The industrial yield of ammonia produced under different temperature (°C) and pressure (atm) is shown in the graph below.



Source: QS Study, Chemistry

(i) Using information from the graph, deduce if the forward reaction is an exothermic or endothermic reaction. [2]

Yield decrease with increase in temperature;

Forward reaction is not favoured/ POE shift left at high temperature, thus forward reaction is exothermic / OWTTE

(ii) Essentially the Haber process involves *"the mixing of nitrogen and hydrogen gases in a 1:3 ratio, and the gaseous mixture is then flushed through beds of finely divided iron filings(powder) at 400 °C and at 250 atm"*.

Explain why iron filings (powder) is used instead of iron blocks. [1]

To maximise/ increase surface area of iron

(iii) Write down the expression of the K_c for the Haber process. [1]

$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$

(iv) At 472 °C, the value of the K_c for the Haber process is 0.104.

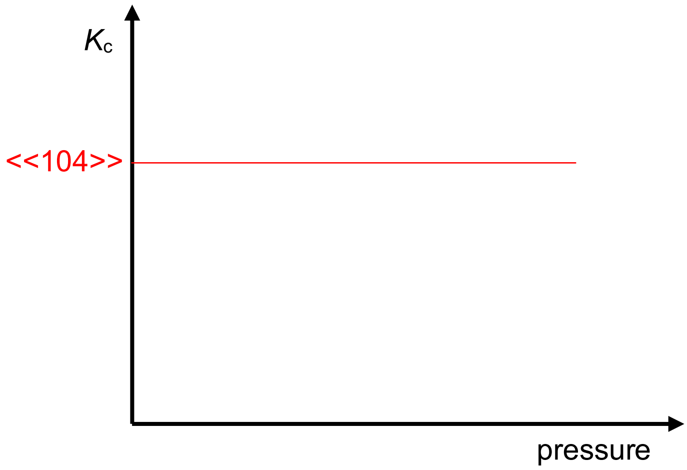
Deduce how the position of equilibrium will shift when 0.100 mol N_2, 0.300 mol H_2 and 0.200 mol NH_3 is mixed in a 1 dm^3 reacting chamber at 472 °C. [2]

Reaction quotient, $Q = \frac{(0.200)^2}{[0.300]^3[0.100]} = 14.8$;

Since Q > Kc(=0.104), POE will shift to the left/ backward reaction will be favoured.

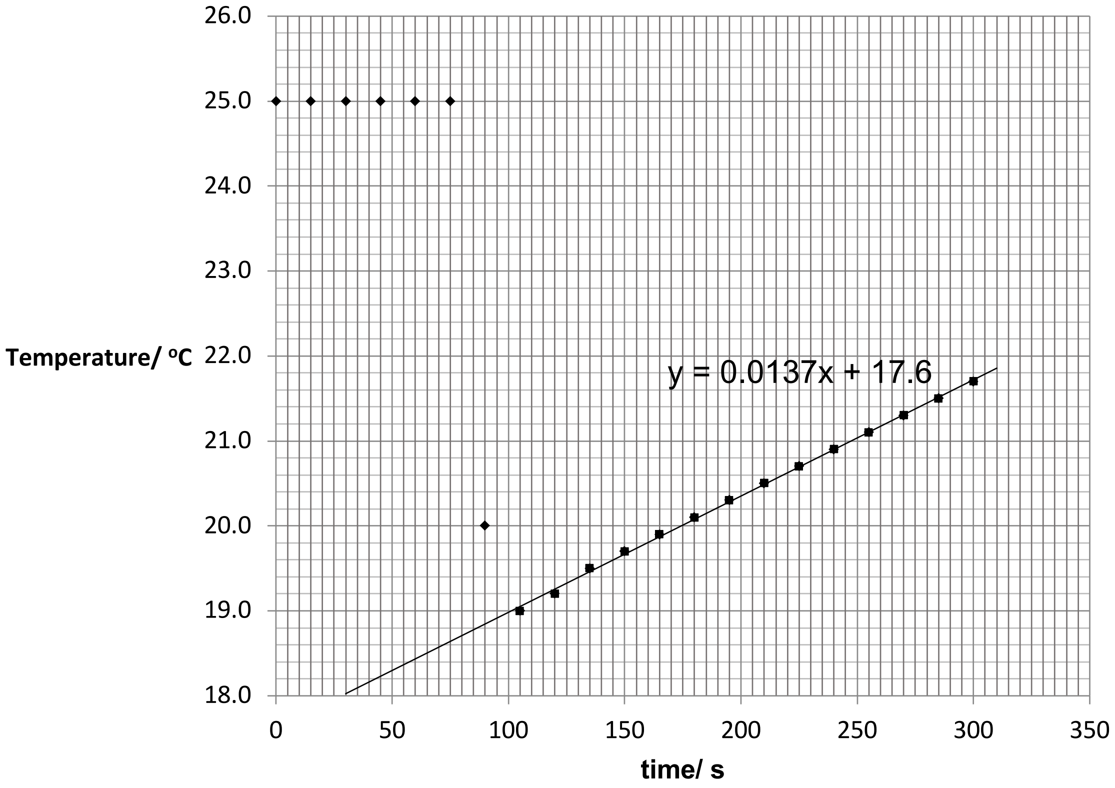
Do not award M2 if Q is not mentioned in the answer.

(v) On the axes below, sketch how K_c will change with pressure of reacting conditions, keeping the temperature constant at 472 °C. [1]



(d) When some compounds dissolve in water, the process can be exothermic or endothermic. This enthalpy change is commonly used in heat packs or cold packs.

In an experiment, 4.50 g of ammonium nitrate, NH_4NO_3, was added to a beaker containing 50.0 cm^3 of deionized water. The temperature of the solution during the experiment was recorded and presented in the graph below. (Ammonium nitrate was added at t = 75 s.)



(i) Using information from the graph only, estimate the lowest temperature reached in this investigation. [1]

18.6 °C / 0.0137(75) + 17.6) = 18.6 °C

Accept range 18.5 - 18.7 °C.

(ii) Using relevant information from section 2 of the data booklet, calculate the amount of heat (in kJ) involved in this process. [1]

Q = 50.0 x 4.18 x (25.0 – 18.6) = 1337 J = 1.34 kJ

Accept range 1.32 – 1.36 kJ

(iii) Calculate the amount of ammonium nitrate (in mol) used for this experiment. [1]

$\frac{4.50}{80.06} =$ 0.0562 mol

(iv) Using your answers to part (d)(ii) and (iii), calculate the standard enthalpy change of the solution, $\Delta H^{\ominus}_{\text{sol}}$, of ammonium nitrate (in kJ mol^{-1}). [1]

$\Delta H^{\ominus}_{\text{sol}} = \frac{1.34}{0.0562} = +23.8$ kJ mol^{-1}

Allow ECF from (ii)

(v) Predict the signs of standard Gibbs free energy change, $\Delta G^{\ominus}$, and standard entropy change, $\Delta S^{\ominus}$, for the process of dissolving of ammonium nitrate in deionized water. [2]

	Sign
Standard Gibbs free energy change, $\Delta G^{\ominus}$	"-"/ < 0
Standard entropy change, $\Delta S^{\ominus}$	"+" / > 0

(vi) Explain your answer for the signs of standard Gibbs free energy change, $\Delta G^{\ominus}$, and standard entropy change, $\Delta S^{\ominus}$. [2]

ΔG is negative as process is spontaneous;

As ΔH is positive, ΔS has to be positive such that value of $T\Delta S$ is larger than ΔH / there is increase in disorderliness as solid salt dissolved into aqueous state.

(vii) The standard enthalpy change of hydration, $\Delta H^{\ominus}_{\text{hyd}}$, of ammonium and nitrate ions are shown in the table below.

Ions	$\Delta H^{\ominus}_{\text{hyd}}$ **/ kJ mol^{-1}**
NH_4^+	– 307
NO_3^-	– 314

Source: Dasent, p. 152; D.W. Smith, J. Chem. Educ., 54, 540 (1977).

Using your answer to part (iv) and the information provided, construct an energy cycle to determine the lattice enthalpy, $\Delta H^{\ominus}_{\text{lattice}}$, of ammonium nitrate. [3]

$$\begin{tikzcd}
NH_4NO_3(s) \arrow[rr, "\Delta H^{\ominus}_{\text{sol}}"] \arrow[dr, "\Delta H^{\ominus}_{\text{lattice}}"'] & & NH_4^+(aq) + NO_3^-(aq) \\
& NH_4^+(g) + NO_3^-(g); \arrow[ur, "\Delta H^{\ominus}_{\text{hyd}}(NH_4^+) + \Delta H^{\ominus}_{\text{hyd}}(NO_3^-)"'] &
\end{tikzcd}$$

$$\Delta H^{\ominus}_{\text{lattice}} = \Delta H^{\ominus}_{\text{sol}} - (\Delta H^{\ominus}_{\text{hyd}}(NH_4^+) + \Delta H^{\ominus}_{\text{hyd}}(NO_3^-));$$

$$\Delta H^{\ominus}_{\text{lattice}} = +23.8 - (-307 + (-314)) = +644.8 \text{ kJ mol}^{-1}$$

Do not award M3 if "-" is shown instead.

Award max 2m if energy cycle is missing.

Allow ECF from (iv)

2. The ionic equation for the reaction between aqueous potassium peroxodisulfate, $K_2S_2O_8$, and aqueous potassium iodide, KI, is shown below.

$$S_2O_8^{2-}\text{ (aq)} + 2I^-\text{ (aq)} \rightarrow 2SO_4^{2-}\text{ (aq)} + I_2\text{ (aq)} \qquad E^\ominus = +1.47\text{ V}$$

(a) The reaction between peroxodisulfate and iodide ions is a spontaneous reaction. However the two reactants do not react readily when mixed together.

(i) Suggest a reason for the high activation energy of this reaction. [1]

Involves the collision of anions/ negatively charged ions.

(ii) Outline how the rate of this reaction may be measured. [2]

Measure colour/ conductivity of solution;

At regular time intervals (OWTTE).

(b) Identify the oxidizing agent in this reaction. [1]

$S_2O_8^{2-}$

Do Not accept sulfur/ S.

(c) Using information from section 24 of the data booklet, calculate the value of $E^\ominus(S_2O_8^{2-} / SO_4^{2-})$. [2]

$1.47 = E^\ominus(S_2O_8^{2-} / SO_4^{2-}) - (+0.54)$;

$E^\ominus(S_2O_8^{2-} / SO_4^{2-}) = 1.47 + 0.54 = +2.01\text{ V}$

Award 2m if final answer is correct.

Do Not penalise if "+" is missing in final answer.

Award 1m if final answer is negative.

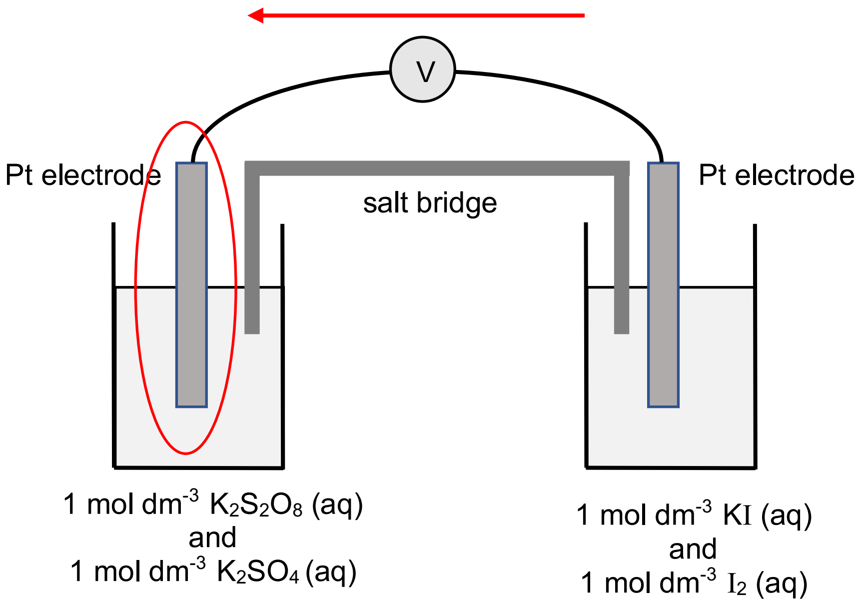
(d) Using information from section 1 of the data booklet, calculate the standard Gibb's Free energy, $\Delta G^{\ominus}$, for this reaction.
Express your final answer in **kJ mol^{-1}** to 3 significant figures. [2]

$\Delta G^{\ominus} = -nFE = -2 \times 96500 \times 1.47 = -283\ 710$ J mol^{-1} ;

$\Delta G^{\ominus} = -284$ kJ mol^{-1}

Allow ECF for M2 if wrong value of n(=1) is used.

A set-up of the voltaic cell based on this reaction is shown below.



(i) Label on the diagram the flow of electrons in the external wire. [1]

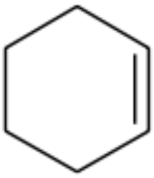
(ii) Circle the Pt electrode that functions as the cathode. [1]

(iii) Outline the function of the salt bridge. [1]

To maintain overall electrical neutrality of the cell/ allow movement of ions between the 2 half-cells.

3. Benzene is an important raw material in the chemical industries. The structural formulas of benzene and cyclohexene are shown below.

benzene



cyclohexene

(a) Compare and contrast the molecular structure and bonding in benzene and cyclohexene. [2]

Compare:

Both are unsaturated/ contains π-bond/ C=C double bonds / contains sp^2 carbon atoms / 6-member carbon ring

Contrast:

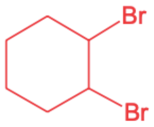
C-C bond lengths in benzene are identical but there are different C-C bond lengths in cyclohexene/ benzene has 6 π-electrons while cyclohexene has only 2/ all the C-atoms in benzene are co-planar while they are not in the same plane in cyclohexene/ all C in benzene is sp^2 while there are both sp^2 and sp^3 C atoms in cyclohexene.

b. Cyclohexene reacts with liquid bromine in the dark.

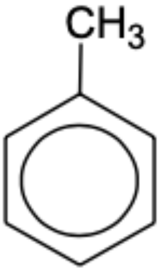
(i) Identify the reaction mechanism for this reaction. [1]

Electrophilic addition

(ii) Draw the structural formula of the product formed. [1]



(c) Methylbenzene, $C_6H_5CH_3$, commonly known as toluene, is a substituted benzene. Like benzene, it is also an important raw material in the chemical industries.
The structure of methylbenzene is shown below.



Under UV radiation, methylbenzene reacts with bromine via free radical substitution.

List the chemical equations of the reactions involved in the three stages of this reaction.
(You only need to list one chemical equation for the termination stage.) [4]

Initiation: $Br_2 \rightarrow 2\,Br\bullet$

Propagation: $C_6H_5CH_3 + Br\bullet \rightarrow C_6H_5CH_2\bullet + HBr$

$C_6H_5CH_2\bullet + Br_2 \rightarrow C_6H_5CH_2Br + Br\bullet$

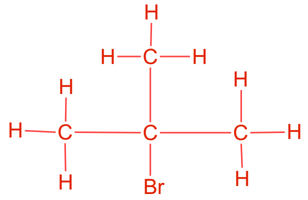
Termination: $C_6H_5CH_2\bullet + Br\bullet \rightarrow C_6H_5CH_2Br$

$C_6H_5CH_2\bullet + C_6H_5CH_2Br\bullet \rightarrow C_6H_5CH_2CH_2C_6H_5$

$2Br\bullet \rightarrow Br_2$

4. 2-bromo-2-methylpropane, 1-bromobutane and 2-bromobutane are isomers with the molecular formula, C_4H_9Br.

(a) Draw the full structural formula of 2-bromo-2-methylpropane. [1]



(b) Outline which of the three isomers would exhibit optical isomerism. [2]

2-bromobutane;

It contains one asymmetrical/ chiral carbon atom.

(c) The reaction kinetics between a halogenoalkane, C_4H_9Br, and sodium hydroxide, NaOH, was investigated. The table shows the data collected for this investigation.

Concentration of C_4H_9Br/ mol dm^{-3}	Concentration of NaOH/ mol dm^{-3}	Relative rate
0.100	0.500	1
0.100	0.100	1
0.200	0.500	2
0.0500	0.100	x

(i) Deduce the order of reaction with respect to C_4H_9Br and NaOH for this reaction. [2]

Reagent	Order of reaction
C_4H_9Br	1
NaOH	0

(ii) Deduce the value of the relative rate, x, in the table. [1]

x : 0.5

(iii) Write the rate expression for this reaction. [1]

Rate = k[C_4H_9Br]

(iv) Identify the type of reaction mechanism. [1]

S_N1

(v) The halogenoalkane, C_4H_9Br, for this reaction could either be 2-bromo-2-methylpropane or 1-bromobutane.

Using your answer to (c)(iii) and (iv) , deduce the name of the halogenoalkane involved in this reaction. [2]

2-bromo-2-methylpropane;

it is a tertiary halogenoalkane which undergoes S_N1 reaction.

Allow ECF from (iii) and (iv) , if S_N2 stated, accept 1-bromobutane as answer.

(vi) Using curly arrows to represent the movement of electron pairs, explain the reaction mechanism for the reaction between the halogenoalkane, identified in (v), and aqueous sodium hydroxide. [4]

curly arrow showing breaking of C-Br bond;

labelling step 1 as slow step;

correct structure of carbocation and resulting Br^- ion;

curly arrow showing from hydroxide to C in carbocation to form products.

Allow ECF from (v), if S_N2 stated.

Partial positive and negative charges shown on C-Br;

Arrow from OH^- to C;

Arrow showing bond breaking of C-Br bond;

Correct penta-bonded C in transition state
(Stereochemical of the 5 bonds not required.)

(vii) Predict how the rate of reaction would change if C_4H_9Br is replaced with C_4H_9Cl. [1]

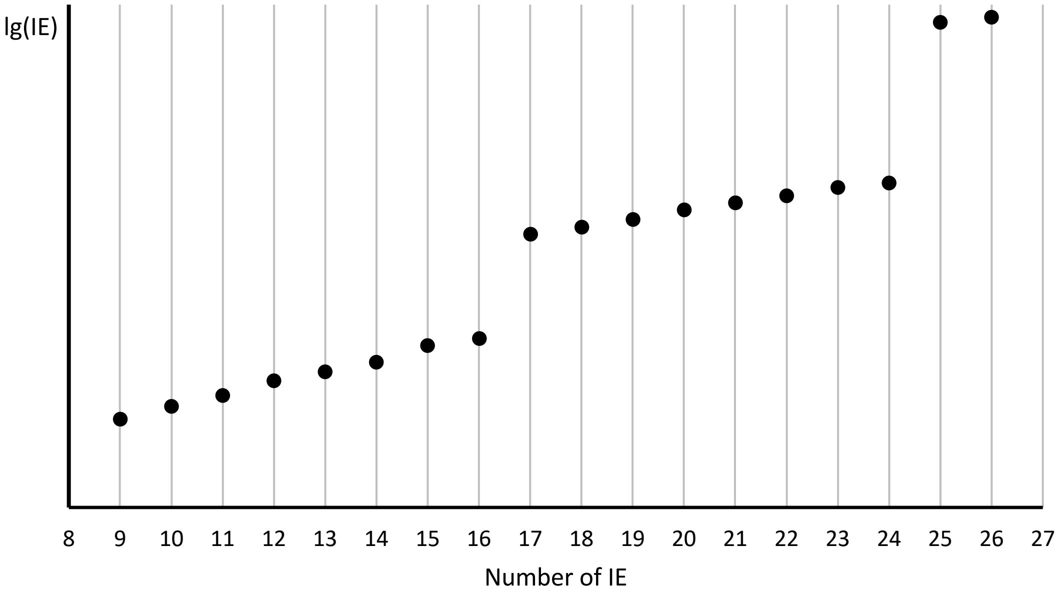
Slower <<as C-Cl bond is stronger than C-Br bond.>>

5. Iron is an important metal with a wide range of uses. The two stable oxidation states of iron are +2 and +3.

(a) Write down the full electron configuration of an iron atom. [1]

$1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 4s^2 3d^6$

(b) The log(ionization energy) for the 9th to 26th ionization energies of iron is shown in the graph below.



Account for the trend observed in the graph. [2]

IE increases as attraction force for remaining electrons increases as electrons are removed/ more difficult to remove electron as positive charge of the ion increase.;

Big jump between 16th and 17th, and, 24th and 25th , is due to removal of an inner shell electron.

(c) Iron(II) ions readily form complex ions with many ligands. $Fe(H_2O)_6^{2+}$ and $Fe(CN)_6^{4-}$ are two examples of iron(II) complex ions. Both aqueous solutions $Fe(H_2O)_6^{2+}$ and $Fe(CN)_6^{4-}$ are coloured.

(i) Explain why solutions of iron(II) complex ions are coloured. [3]

Incompletely filled 3d-orbitals split into 2/ different energy levels (in presence of water ligands);

d-d electronic transition absorb specific wavelength in visible light region;

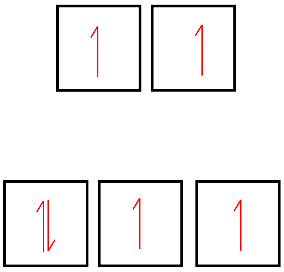
colour of solution is complementary of the absorbed wavelength

(ii) List **one** factor that will affect the colour of the solution of a complex ion. [1]

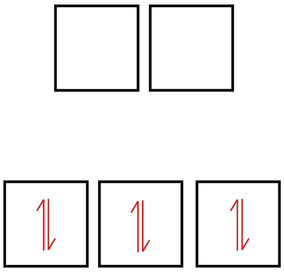
Oxidation of cation/ type of ligands/ type of cation/ coordination number

(iii) The aqueous solution of $Fe(H_2O)_6^{2+}$ is paramagnetic while aqueous solution of $Fe(CN)_6^{4-}$ is diamagnetic.

With reference to this information, complete the 3d-orbital diagram of iron(II) ions in $Fe(H_2O)_6^{2+}$ and $Fe(CN)_6^{4-}$. [2]

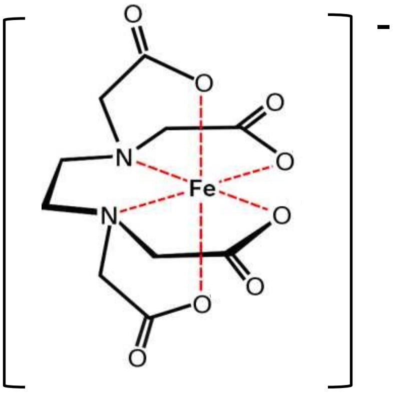


$Fe(H_2O)_6^{2+}$



$Fe(CN)_6^{4-}$

(d) Ethylenediaminetetraacetic acid is commonly known as EDTA. Its ion, EDTA^{4-} is a polydentate ligand that forms complex ion with the iron ion readily. The structure of the [Fe(EDTA)]$^{-}$ complex ion is shown below.



Source: Buryan, Petr. (2016). Making biogas desulphurisation more effective by using surfactants. Acta Montanistica Slovaca. 21. 37-42. 10.3390/ams21010037.

(i) Deduce what a polydentate ligand is. [1]

ligand that can donate more than 1 LP of electrons to / form more than 1 dative bond with cations

(ii) State the oxidation state of iron in the [Fe(EDTA)]$^{-}$ complex ion. [1]

Oxidation state: +3

Do not accept 3+ or III

6. Lithium forms two ionic compounds, lithium nitride, Li_3N and lithium azide, LiN_3, with nitrogen. The chemical formulas of the nitride and azide ions are N^{3-} and N_3^- respectively.

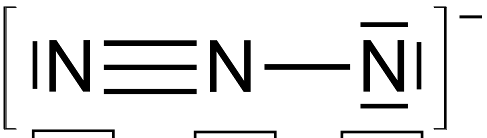
(a) State, giving a reason, whether Li_3N or LiN_3 has a higher melting point. [2]

Li_3N higher mp as N^{3-} is higher charge/ smaller radius than N_3^-;

Thus greater electrostatic forces of attraction between Li^+ ion and N^{3-} than Li^+ and N_3^-

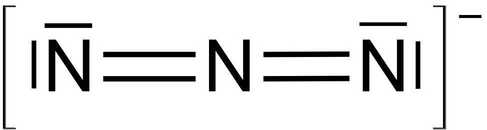
(b) The two resonance structures for the azide ion, N_3^-, are shown below. State the formal charge of each nitrogen atom in the two structures. [2]

Structure I



Formal charge	0	+1	-2

Structure II



Formal charge	-1	+1	-1

(c) Predict which is the more stable resonance structure for the azide ion. [1]

Structure II <<as the difference in FC (2)is smaller than that in structure I (3)/ FC values are closer to 0>>

Not necessary to state reason.

(d) Outline **one** spectroscopic technique that can be used to identify which is the resonance structure of the azide ion. [2]

X-ray crystallography;

Measure the N-N bond length as Structure I would have 2 different bond lengths but Structure II would only have 1.

7. Propanoic acid (CH_3CH_2COOH), methyl ethanoate (CH_3COOCH_3) and ethyl methanoate ($HCOOCH_2CH_3$) are isomers with the molecular formula, $C_3H_6O_2$.

(a) State, giving a reason, the isomer which has the highest boiling point. [2]

Propanoic acid due to presence of stronger hydrogen bonding;

Both esters would only have weaker DP-DP forces/ LDF

(b) State **one** fragment and its corresponding m/z value that will be present in the mass spectrum of propanoic acid but not in the two esters. [1]

Fragment : $[OH]^+$/ $[CH_3CH_2CO]^+$

m/z value: 17/ 57

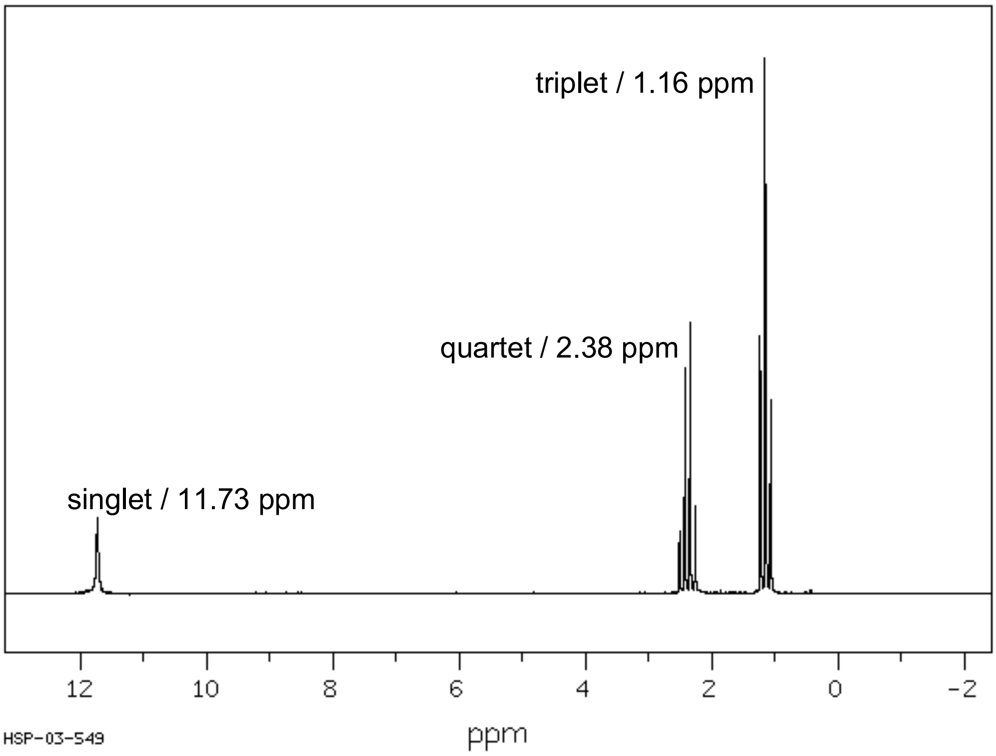
Do not award mark if charge is missing.

(c) State the chemical bond and the wavenumber of one peak that will appear in the IR spectra of all the three isomers. [1]

Chemical bond : C=O/ C-O/ C-H

Wavenumber : 1700-1750/ 1050-1410/ 2850-3090 cm^{-1}

(d) Both the ^1H NMR spectra of propanoic acid and ethyl methanoate would show three peaks. Explain which of the two compounds would give rise to the following ^1H NMR spectrum. [2]



Source: Chemical Book CAS 79-09-4

Propanoic acid as singlet at 11.73ppm indicates presence of O-H in acid;

Singlet in ethyl methanoate due to H-COO would appear at 2.0-2.5ppm.

(e) Two signals were observed in ^1H NMR spectra of methyl ethanoate. Deduce the multiplicity of peak and ratio of integration trace for each of the peaks observed. [2]

Chemical Shift/ ppm	2.06	3.07
Multiplicity of peak	Singlet/ 1	Singlet/ 1
Ratio of integration trace	**1**	**1**

-End of Paper-