For each question, there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 A sample of iron contains three isotopes: iron-54, iron-56 and iron-58. Its relative atomic mass is 55.849. One of the isotopes has a percentage abundance of 91.8%.

isotope	accurate isotopic mass	percentage abundance
iron-54	53.94	x
iron-56	55.94	y
iron-58	57.93	z

Which row gives the correct values of x, y and z?

	x	y	z
A	91.8	6.37	1.83
B	1.83	91.8	6.37
C	6.37	91.8	1.83
D	1.83	6.37	91.8

2 S_2Cl_x disproportionates completely in water to give S and SO_2 in the ratio of 3:1.

What is the value of x?

A 2

B 4

C 6

D 8

3 Which ion would undergo the greatest deflection in an electric field?

A $^{15}N_2^{+}$

B $^{12}C^{16}O_2^{3+}$

C $^{12}C^{16}O^{2+}$

D $^{16}O^{18}O^{2+}$

4 The radioactive isotope $^{241}_{95}\text{Am}$ is a synthetic isotope used in ionisation smoke detectors.

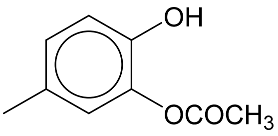
$^{241}_{95}\text{Am}$ decays to give an element **E** and emits a high energy α-particle (which is a helium nucleus, $^{4}_{2}\text{He}$). No other particle is produced.

$$^{241}_{95}\text{Am} \rightarrow \ ^{4}_{2}\text{He} + \textbf{E}$$

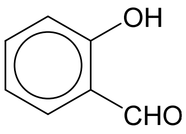
Which row in the table correctly describes the nuclear make-up of element **E**?

	number of protons	number of neutrons
A	91	144
B	91	237
C	93	144
D	93	237

5 Which statement about both molecules shown below is correct?



F



G

A Both can turn hot acidified potassium dichromate(VI) from orange to green.

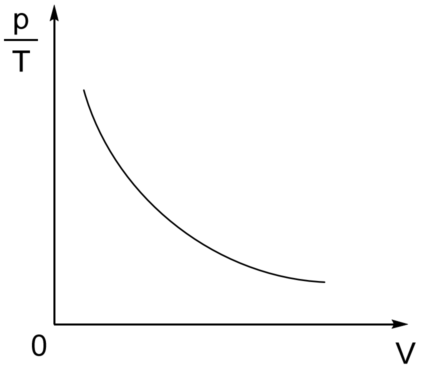
B **G** can form intramolecular hydrogen bonding while **F** cannot.

C Both molecules have the same number of π electrons.

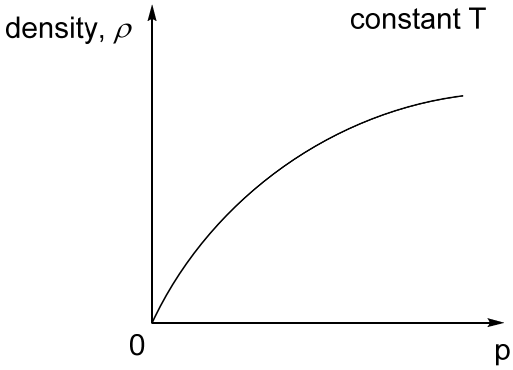
D Both molecules are planar.

6 Which graph represents the correct behaviour for a fixed mass of an ideal gas? (Assume that all temperatures are measured in Kelvin.)

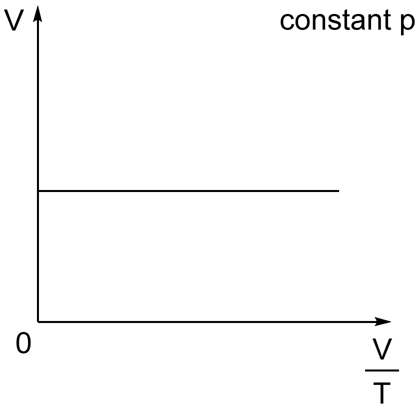
A



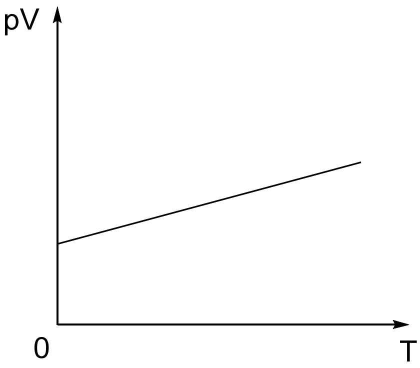
C



B



D

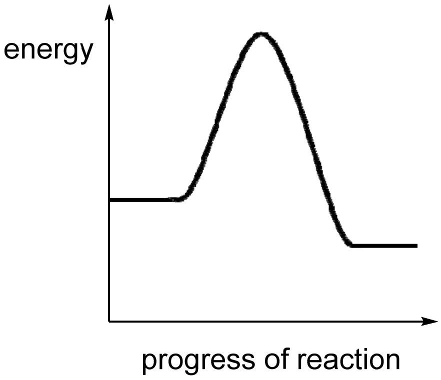


7 *Use of the Data Booklet is relevant to this question.*

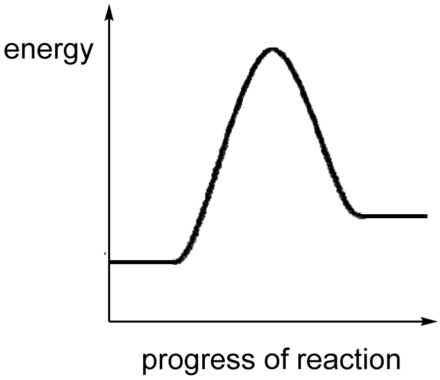
Methane undergoes free radical substitution with bromine in the presence of UV light.

Which energy profile diagram represents the propagation steps that lead to the formation of bromomethane?

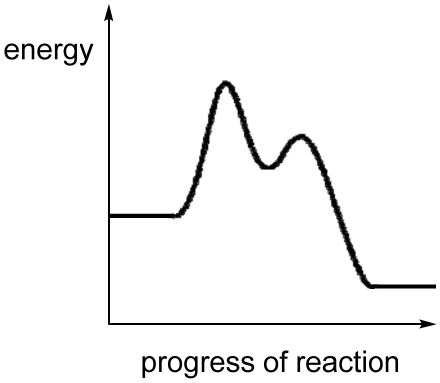
A



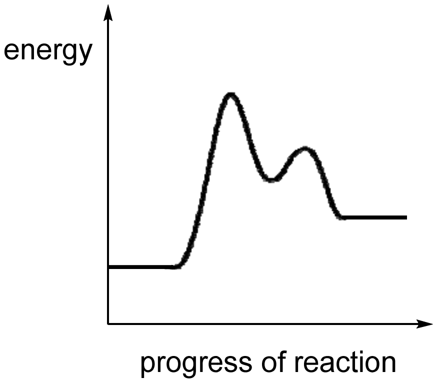
C



B



D



8 Which is **not** a trend from left to right across the elements of the third period of the Periodic Table?

A The maximum oxidation number increases.
B The melting point of the oxides decreases.
C The pH of the aqueous solutions of the chlorides decreases.
D The nature of bonding of the chlorides change from ionic to covalent.

9 Elements **J**, **K** and **L** are elements in Period 3 of the Periodic Table. The melting point of element **J** is higher than that of element **K**. Only the oxide of element **L** is insoluble in water.

Which row in the table gives the correct identities of elements **J**, **K** and **L**?

	J	**K**	**L**
A	C*l*	P	Mg
B	Na	Mg	Si
C	P	S	A*l*
D	S	P	Si

10 The reaction between NO_2 and SO_2 is a key stage in the formation of acid rain.

$$NO_2(g) + SO_2(g) \longrightarrow NO(g) + SO_3(g)$$

A series of experiments was conducted with various concentrations of NO_2 and SO_2 in the absence of air.

experiment	$[NO_2]$ / mol dm^{-3}	$[SO_2]$ / mol dm^{-3}	relative rate
1	0.010	0.20	1
2	0.020	0.20	2
3	0.040	0.40	8

The half-life of NO_2 in experiment 1 was 48 seconds.

Which row gives the correct half-life of NO_2 in experiments 2 and 3?

	half-life in experiment 2	half-life in experiment 3
A	24 s	6 s
B	24 s	24 s
C	48 s	24 s
D	48 s	48 s

11 A pink coloured compound, **M**, reacts with OH^- to give a colourless compound, **N**.

$$\underset{\text{pink}}{\mathbf{M}} + OH^- \longrightarrow \underset{\text{colourless}}{\mathbf{N}}$$

A series of experiments was carried out using different volumes of the 2 reagents, **M**(aq) and NaOH(aq).

The following results were obtained.

experiment	volume of 0.001 mol dm^{-3} **M** / cm^3	volume of 0.1 mol dm^{-3} NaOH / cm^3	volume of water / cm^3	time taken for pink colour to fade / s
1	1	10	4	100
2	2	10	3	100
3	1	5	9	200
4	2	20	8	?

Which conclusions follow from these results?

1 The reaction is first order with respect to **M**.
2 The reaction is first order with respect to OH^-.
3 The time taken for the pink colour to fade in experiment 4 was 50 s.

A 1 and 2
B 2 and 3
C 1 and 3
D 1, 2 and 3

12 Consider the following reversible reaction.

$$\mathbf{Q}(g) + \mathbf{R}(g) \rightleftharpoons \mathbf{S}(g) \qquad \Delta H < 0$$

After equilibrium was reached, the system was disturbed and the changes to the system were monitored. The changes were as follows.

[**S**]	K_p	rate of forward reaction	rate of backward reaction
increased	unchanged	increased	increased

What was the disturbance applied?

A addition of a catalyst

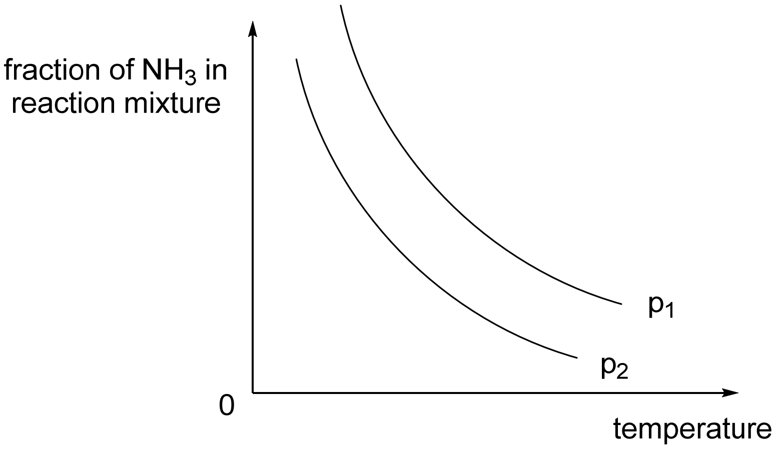
B increase in temperature

C compression of reaction mixture

D addition of an inert gas at constant volume

13 The graph below shows how the fraction of $NH_3(g)$ in the equilibrium mixture of the Haber process varies with temperature at pressures of p_1 and p_2.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H_r = \boldsymbol{x} \text{ kJ mol}^{-1}$$



Which row in the table is correct?

A	$x < 0$	$p_1 > p_2$
B	$x < 0$	$p_1 < p_2$
C	$x > 0$	$p_1 > p_2$
D	$x > 0$	$p_1 < p_2$

14 *Use of the Data Booklet is relevant to this question.*

Which expression gives the pH of a 0.2 mol dm^{-3} NH_3(aq) solution at 25 °C?
(K_a of NH_4^+ = 5.6 × 10^{-10} mol dm^{-3})

A $-\lg\sqrt{0.2 \times 5.6 \times 10^{-10}}$

B $14 + \lg\sqrt{0.2 \times 5.6 \times 10^{-10}}$

C $-\lg\sqrt{0.2 \times \dfrac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}}}$

D $14 + \lg\sqrt{0.2 \times \dfrac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}}}$

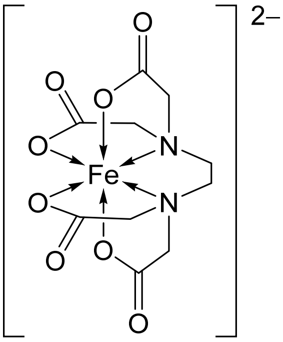
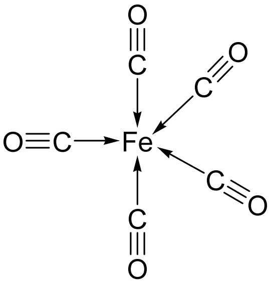
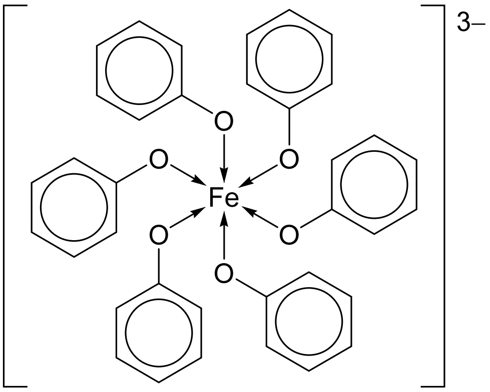
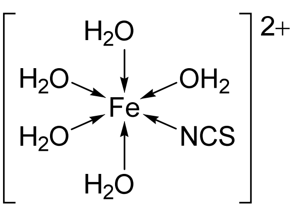
15 Which pairs of substances, when mixed in equal volumes, produce a buffer solution?

1 0.05 mol dm^{-3} HCl(aq) and 0.08 mol dm^{-3} Na_3PO_4(aq)
2 0.05 mol dm^{-3} CH_3CO_2H(aq) and 0.08 mol dm^{-3} NaOH(aq)
3 0.08 mol dm^{-3} $HO_2C–CO_2H$(aq) and 0.05 mol dm^{-3} NaOH(aq)

A 1 only
B 1 and 3
C 2 and 3
D 1, 2 and 3

16 Iron can form complexes with variable oxidation states.

Which row gives the **incorrect** oxidation number of Fe in the iron complex?

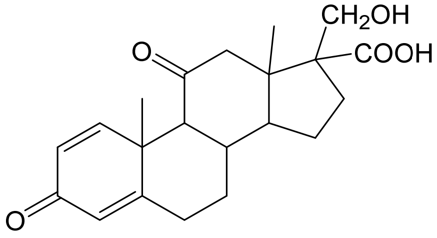
	iron complex	oxidation number of Fe
A		+4
B		0
C		+3
D		+3

17 Adding concentrated HC*l* to $CuSO_4$(aq) causes the colour of the solution to change from blue to green.

Which row best explains this observation?

	number of d-electrons in copper	energy gap between the d-orbitals
A	changes	changes
B	changes	remains the same
C	remains the same	changes
D	remains the same	remains the same

18 Compound **T** is a derivative of a drug used to treat inflammatory and autoimmune diseases.



T

Compound **T** is heated with hydrogen in the presence of a nickel catalyst.

What is the number of stereoisomers for the product formed?

A 2^5

B 2^6

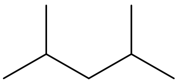
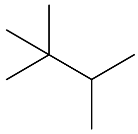
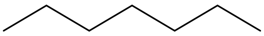
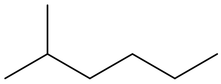
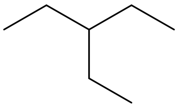
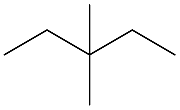
C 2^8

D 2^9

19 **U** and **V** are structural isomers with molecular formula C_7H_{16}.

Both **U** and **V** produce the same number of possible structural isomers upon reaction with chlorine to form monochlorinated compounds with the formula $C_7H_{15}Cl$.

Which pairs are possible structures of **U** and **V**?

	U	**V**
1		
2		
3		

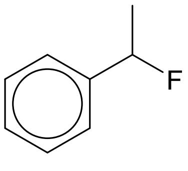
A 1 only

B 1 and 3

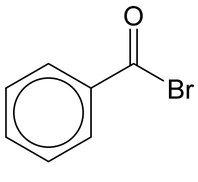
C 2 and 3

D 1, 2 and 3

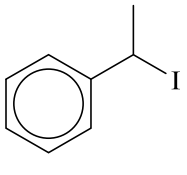
20 Equal amounts of compounds **X**, **Y** and **Z** are added separately to three test-tubes containing equal concentrations of ethanolic silver nitrate solution. The test-tubes are then placed in a heated water bath. No precipitate forms in one of the tubes. In the other two tubes, precipitates form at different rates.



X



Y

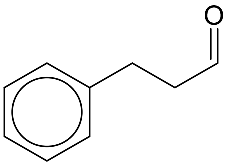


Z

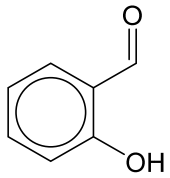
Which row in the table is correct?

	compound which does not form precipitate	colour of precipitate which forms the fastest
A	**Y**	yellow
B	**Z**	pale cream
C	**X**	yellow
D	**X**	pale cream

21 3-phenylpropanal and 2-hydroxybenzaldehyde are used in essential oils.



3-phenylpropanal



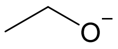
2-hydroxybenzaldehyde

Which reagents could be used to distinguish between the two compounds?

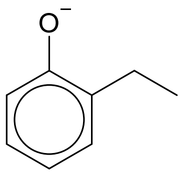
1 Fehling's reagent
2 $[Ag(NH_3)_2]^+$
3 $SOCl_2$

A 1 only
B 1 and 2
C 2 and 3
D 3 only

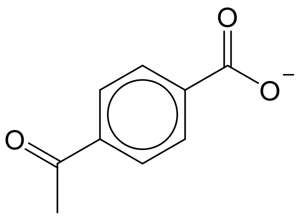
22 Consider the following four compounds.



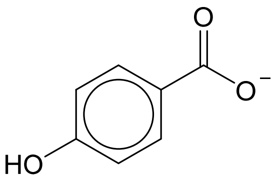
E



F



G

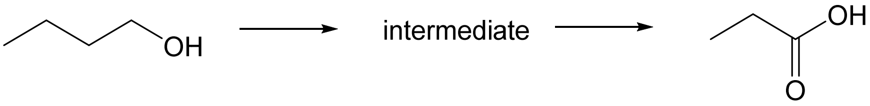


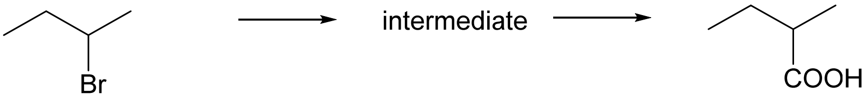
H

What is the relative order, in decreasing basicity, of these compounds?

A **E** > **F** > **H** > **G**
B **G** > **H** > **F** > **E**
C **E** > **F** > **G** > **H**
D **H** > **G** > **F** > **E**

23 Which pair of reactions could have the same reaction intermediate?

1 

2 

3 

4 

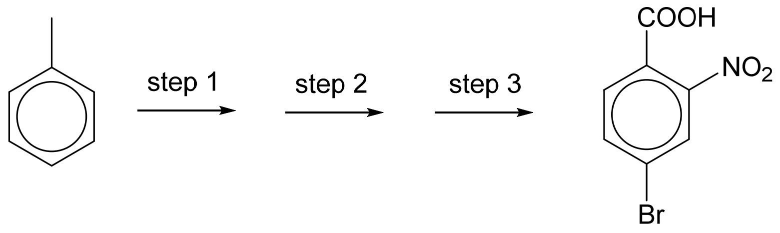
A 1 and 2

B 1 and 4

C 2 and 3

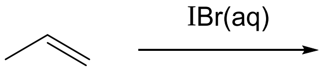
D 3 and 4

24 Which row gives the synthetic route that will lead to the highest yield of the product?

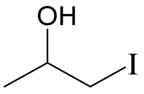


	step 1	step 2	step 3
A	FeBr$_3$, Br$_2$	KMnO$_4$, H$_2$SO$_4$, heat	conc. H$_2$SO$_4$, conc. HNO$_3$, heat
B	KMnO$_4$, H$_2$SO$_4$, heat	FeBr$_3$, Br$_2$	conc. H$_2$SO$_4$, conc. HNO$_3$, heat
C	conc. H$_2$SO$_4$, conc. HNO$_3$, heat	KMnO$_4$, H$_2$SO$_4$, heat	FeBr$_3$, Br$_2$
D	conc. H$_2$SO$_4$, conc. HNO$_3$, heat	FeBr$_3$, Br$_2$	KMnO$_4$, H$_2$SO$_4$, heat

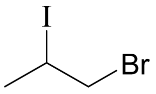
25 Which product will **not** be formed in the following reaction?



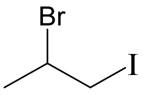
A



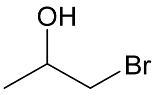
C



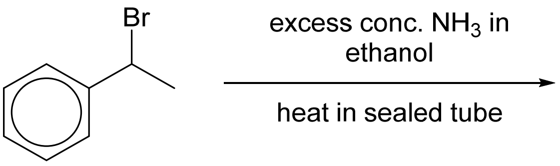
B



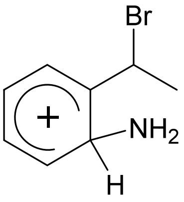
D



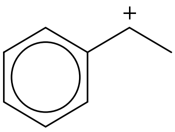
26 Which species could be an intermediate of the following reaction?



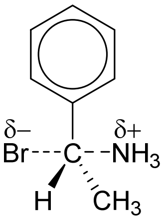
A



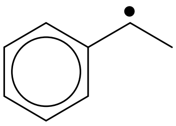
C



B



D



27 A non-cyclic organic compound has the molecular formula $C_4H_5O_2N$. The compound is neutral and does not decolourise Br_2 in CCl_4.

Which pair of functional groups could be present in this molecule?

1 one amide group and one ketone group
2 one ester group and one amine group
3 one ester group and one nitrile group

A 1 only
B 3 only
C 1 and 2
D 2 and 3

28 The solubility products of $ZnCO_3$ and Ag_2CO_3 in water are shown in the table below.

carbonate	solubility product at 25 °C
$ZnCO_3$	1.46×10^{-10} mol^2 dm^{-6}
Ag_2CO_3	8.46×10^{-12} mol^3 dm^{-9}

A solution contains 0.02 mol dm^{-3} $Zn(NO_3)_2$ and 0.02 mol dm^{-3} $AgNO_3$ at 25 °C.
Zn^{2+} and Ag^+ can be separated by adding solid Na_2CO_3 slowly.

Which statement is correct?

A Ag_2CO_3 will be precipitated before $ZnCO_3$.

B The solubility of Ag_2CO_3 in water is 2.04×10^{-4} mol dm^{-3}.

C At any point in time, only one compound, Ag_2CO_3 or $ZnCO_3$, can be precipitated.

D When the more soluble compound first starts to precipitate, the concentration of carbonate ions in the solution is 2.12×10^{-8} mol dm^{-3}.

29 *Use of the Data Booklet is relevant to this question.*

The anodising of aluminium allows highly reactive aluminium to be safely used as a construction material.

A piece of aluminium object was placed in dilute sulfuric acid and anodised with a direct current of 1.4 A. After *t* seconds, the mass of the oxide layer formed is 23.7 g.

Which expression gives the time taken, *t*, for this anodisation?

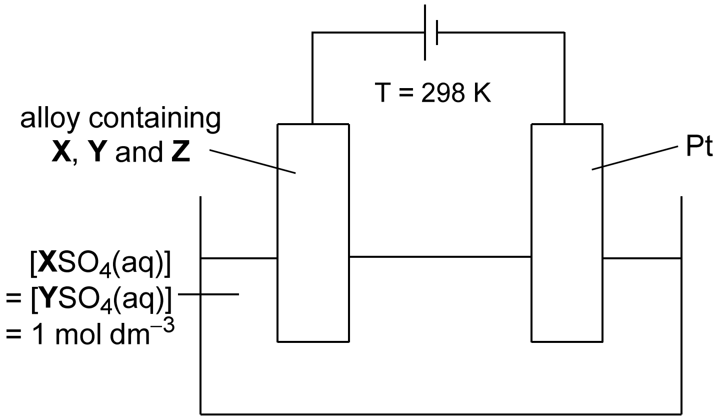
A $\dfrac{23.7 \times 96500}{102 \times 1.4}$

B $\dfrac{3 \times 23.7 \times 96500}{2 \times 102 \times 1.4}$

C $\dfrac{3 \times 102 \times 1.4}{2 \times 23.7 \times 4 \times 96500}$

D $\dfrac{3 \times 23.7 \times 4 \times 96500}{2 \times 102 \times 1.4}$

30 In an electrolysis set-up in a beaker, an alloy containing **X**, **Y** and **Z** was used as an electrode as shown.



After some time, the amounts of **X** and **Y** in the alloy decreased while unreacted **Z** was found at the bottom of the beaker. **X** was also deposited on the platinum electrode.

Based on the information above, which options are correct?

1 $E^\ominus(\mathbf{X}^{2+}/\mathbf{X}) > E^\ominus(H_2O/H_2)$

2 $E^\ominus(\mathbf{Z}^{2+}/\mathbf{Z}) < E^\ominus(\mathbf{X}^{2+}/\mathbf{X}) < E^\ominus(\mathbf{Y}^{2+}/\mathbf{Y})$

3 When the polarity of the battery is reversed, H_2 is produced at the Pt electrode.

A 1 only

B 1 and 3

C 2 and 3

D 1, 2 and 3

2018 Y6 H2 Chemistry Preliminary Examinations Paper 1 (Suggested Solutions)

Question	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Answer	C	A	C	C	C	A	B	B	D	C	A	C	A	D	B
Question	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
Answer	A	C	D	B	D	A	A	B	D	D	C	B	D	D	A

Answer **all** the questions in the spaces provided.

1 Gemstones such as amethysts, pearls and malachites contain compounds of main group and transition elements.

Fig. 1.1 shows the logarithm of the ionisation energies, log (IE), for the outermost ten electrons in an atom of an element **X**, which has atomic number smaller than 20.

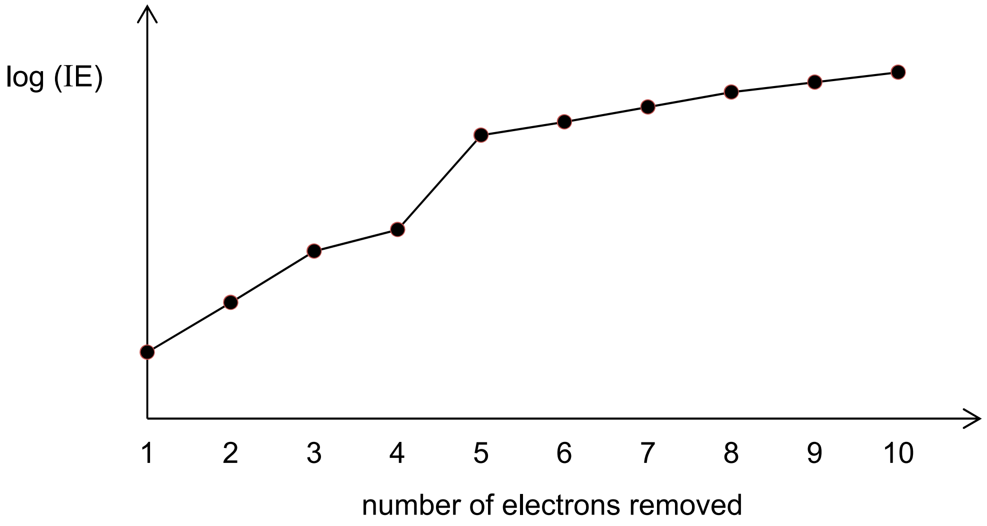


Fig. 1.1

(a) Deduce which Group in the Periodic Table **X** belongs to and state the identity of **X**. Explain your answer.

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…………………………………………………………………………………………………[3]

(b) The colour of amethyst is caused by the presence of compounds containing manganese and iron.

Explain why the first ionisation energies of manganese and iron are similar.

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…………………………………………………………………………………………………[3]

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

Malachites contain copper(II) carbonate while pearls contain calcium carbonate. Predict whether calcium carbonate or copper(II) carbonate has a higher decomposition temperature. Explain your answer.

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[Total: 8]

2 **(a)** Polycyclic aromatic hydrocarbons (PAHs) are potential carcinogens.

Anthracene is an example of a PAH and its Kekulé structure is shown in Fig. 2.1.

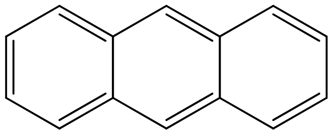

Fig. 2.1

(i) A compound is aromatic if it satisfies the following criteria:

- it is a cyclic planar molecule,
- it has a delocalised π electron system, and
- it has $(4n + 2)$ π electrons, where n is an integer.

By considering the hybridisation of the carbon atoms in anthracene and the criteria for aromaticity, explain why anthracene is aromatic.

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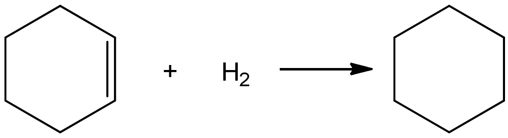
…………………………………………………………………………………………………[3]

(ii) The enthalpy change of hydrogenation of cyclohexene to cyclohexane is -118 kJ mol^{-1}.



Using the Kekulé structure given in Fig. 2.1, calculate the enthalpy change of complete hydrogenation of anthracene, ΔH_1.

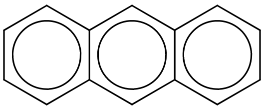
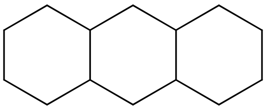
[1]

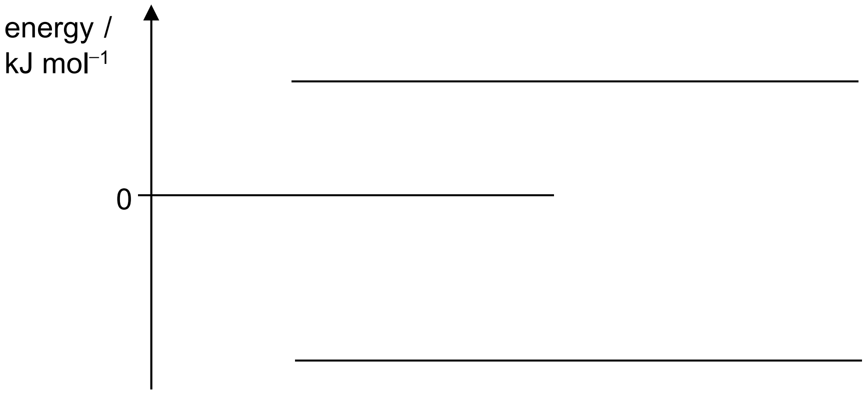
(iii) Fig. 2.2 is the actual representation of anthracene.

Fig. 2.2

Complete the energy level diagram below using the data in Table 2.1.
Hence, calculate the actual value for the enthalpy change of complete hydrogenation of anthracene, ΔH_2.

Table 2.1

compound	formula	enthalpy change of formation / kJ mol^{-1}
 anthracene	$C_{14}H_{10}(s)$	+129
 tetradodecahydroanthracene	$C_{14}H_{24}(s)$	–356



ΔH_2 = ………………………………..

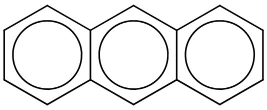
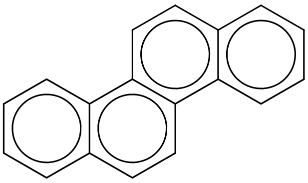
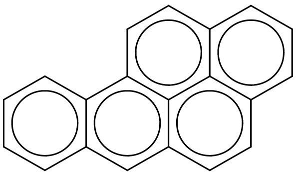
[3]

(iv) Using your answers to **(a)(ii)** and **(a)(iii)**, calculate the resonance energy of anthracene.

[1]

(b) Table 2.2 shows some information on anthracene and other PAHs found in smoked fish.

Table 2.2

PAH	structure	mean concentration (C_m) / ppm	Toxicity Equivalency Factor (TEF)
anthracene $C_{14}H_{10}$		0.029	0.01
chrysene $C_{18}H_{12}$		0.135	0.01
benzo[a]pyrene $C_{20}H_{12}$		0.204	1.00

(i) The carcinogenic toxic equivalent (TEQ) of PAHs in smoked fish can be calculated using equation 2.1.

$$\text{TEQ} = \text{Sum of } [C_m \text{ (in ppm)} \times \text{TEF}] \text{ ------ equation 2.1}$$

Using equation 2.1 and the data from Table 2.2, calculate the TEQ of smoked fish.

[1]

(ii) For an average person, the excess cancer risk (ECR) resulting from exposure to PAHs through smoked fish consumption can be determined using equation 2.2.

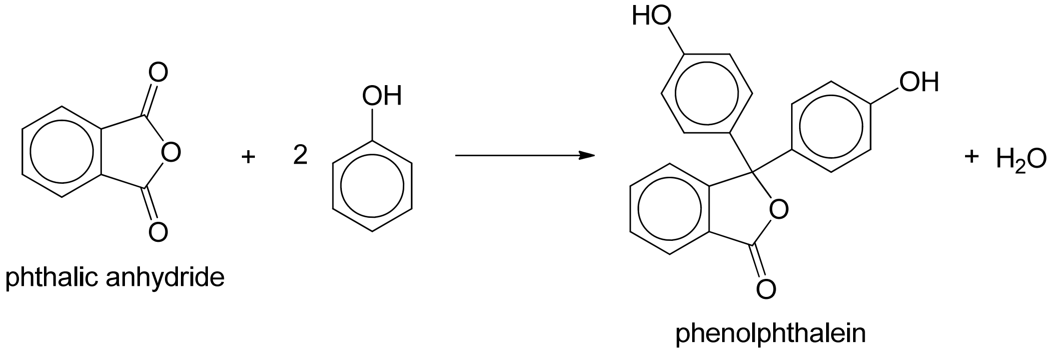
$$\text{ECR} = \frac{\text{TEQ}}{\text{body weight in kg}} \times 1.37 \times 10^{-3} \text{ ------ equation 2.2}$$

Given that the acceptable ECR value set by United States Environmental Protection Agency is 1.0×10^{-6}, use equation 2.2 to determine the ECR value due to the consumption of smoked fish by a 70 kg person. Hence, state whether the person is at risk of cancer.

[1]

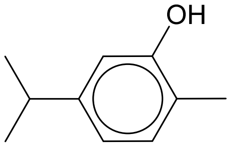
(c) Phenolphthalein is formed when phenol undergoes electrophilic substitution with phthalic anhydride.

The overall equation for the reaction is shown below.



(i) As phenolphthalein is a carcinogen, it has been replaced by thymolphthalein, which can be formed by a similar reaction between thymol and phthalic anhydride.

By using the structure of thymol as shown below, draw the structure of thymolphthalein.



thymol

[1]

(ii) Explain whether thymol or phenol undergoes electrophilic substitution more readily.

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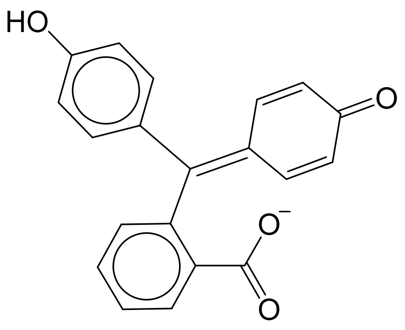
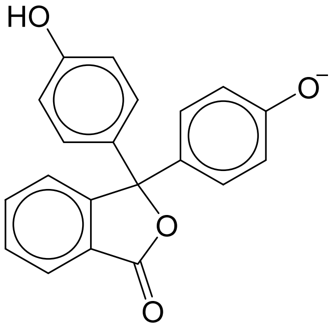
For examiner's use

(d) Phenolphthalein indicator is colourless. Under basic conditions, phenolphthalein undergoes dissociation to form its conjugate base, which is pink in colour.

The conjugate base of phenolphthalein is found to be **A** and **not B**.



A



B

Explain why the structure of **A** is more stable than that of **B**.

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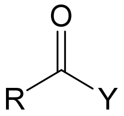
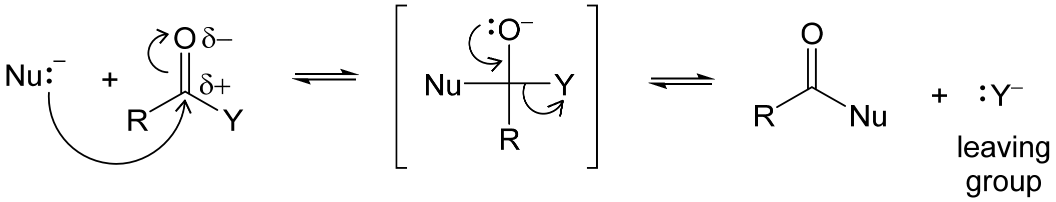
……………………………………………………………………………………………………….[1]

[Total: 13]

3 **(a)** Acid derivatives, RCOY, are compounds formed when the –OH group of carboxylic acid is replaced by a different group (Y). They have the general structure as shown below.



Acid derivatives undergo nucleophilic acyl substitution, with the general mechanism shown below:



The mechanism involves the heterolytic fission of the C−Y bond, resulting in Y leaving with a pair of electrons as Y^-. Y^- is called the leaving group.

When RCOY undergoes nucleophilic acyl substitution, one factor that affects its reactivity is the basicity of Y^-. In general, the stronger Y^- is as a Lewis base, the poorer it is as a leaving group. This results in RCOY being less reactive towards nucleophilic acyl substitution.

(i) Suggest why strong Lewis bases are poor leaving groups.

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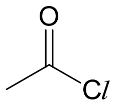
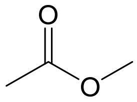
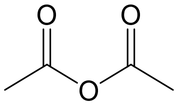
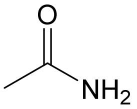
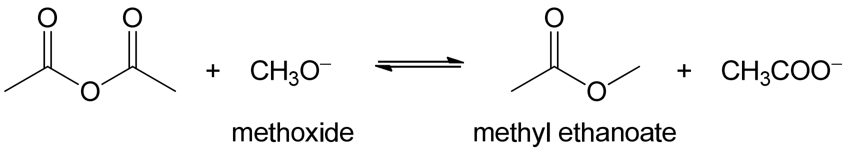
Table 3.1 shows the four most common types of acid derivatives and the pK_b of Y^-.

Table 3.1

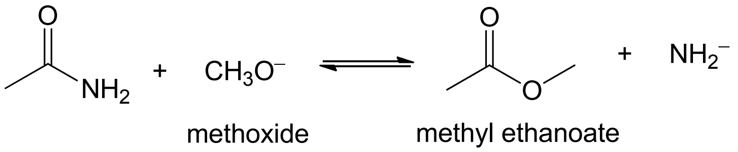
functional group	example of acid derivative	leaving group, Y^-	pK_b of Y^-
acyl chloride	 ethanoyl chloride	Cl^-	21
ester	 methyl ethanoate	CH_3O^-	−2
acid anhydride	 ethanoic anhydride	CH_3COO^-	9
amide	 ethanamide	NH_2^-	−24

(ii) A student proposed two reactions to synthesise methyl ethanoate using methoxide ions.

Reaction **1**



Reaction **2**



With reference to the pK_b values given in Table 3.1, explain why reaction **1** is a better method to synthesise methyl ethanoate than reaction **2**.

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(b) Methyl ethanoate can also be synthesised from methanol and ethanoic acid. The reaction is reversible and does not go to completion.

Reaction **3** $CH_3OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l)$

Table 3.2 shows the densities and molar masses of methanol and ethanoic acid.

Table 3.2

compound	density / g cm^{-3}	molar mass / g mol^{-1}
methanol	0.792	32.0
ethanoic acid	1.05	60.0

To determine the equilibrium constant, K_c, for this reaction, a student mixed 20.0 cm^3 of ethanoic acid with 20.0 cm^3 of methanol, and left the mixture to stand for one week to reach equilibrium.

5.0 cm^3 of the equilibrium mixture was pipetted out and added to 100 cm^3 of ice-cold water in a conical flask. The resultant mixture required 16.80 cm^3 of 0.500 mol dm^{-3} aqueous NaOH for complete reaction.

(i) Calculate the initial amount of methanol used in the reaction.

[1]

(ii) Calculate the amount of ethanoic acid present in the equilibrium mixture. Assume that the total volume of the equilibrium mixture is 40.0 cm^3.

[2]

(iii) Write an expression for the K_c of reaction **3**.

[1]

(iv) Given that the initial amount of ethanoic acid used is 0.350 mol, calculate a value for K_c.

[2]

(v) Explain why 5.0 cm^3 of the equilibrium mixture was added to 100 cm^3 of ice-cold water before it was titrated against aqueous NaOH.

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(c) Methyl ethanoate and ethyl methanoate are isomers. Suggest a simple chemical test which can distinguish between them. Write equations for the reactions that occur for the ester that gives the positive test.

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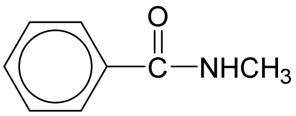
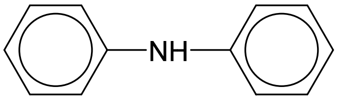
For examiner's use

(d) Compounds **P** and **Q** are solids at room temperature and are insoluble in water. They have the structures shown below.



compound **P**



compound **Q**

A student added some **Q** to **P** by mistake. Outline how **P** can be separated from **Q**. Briefly explain your answer.

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[Total: 16]

4 Magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$, commonly called Epsom salt, has been traditionally used as a component of bath salts.

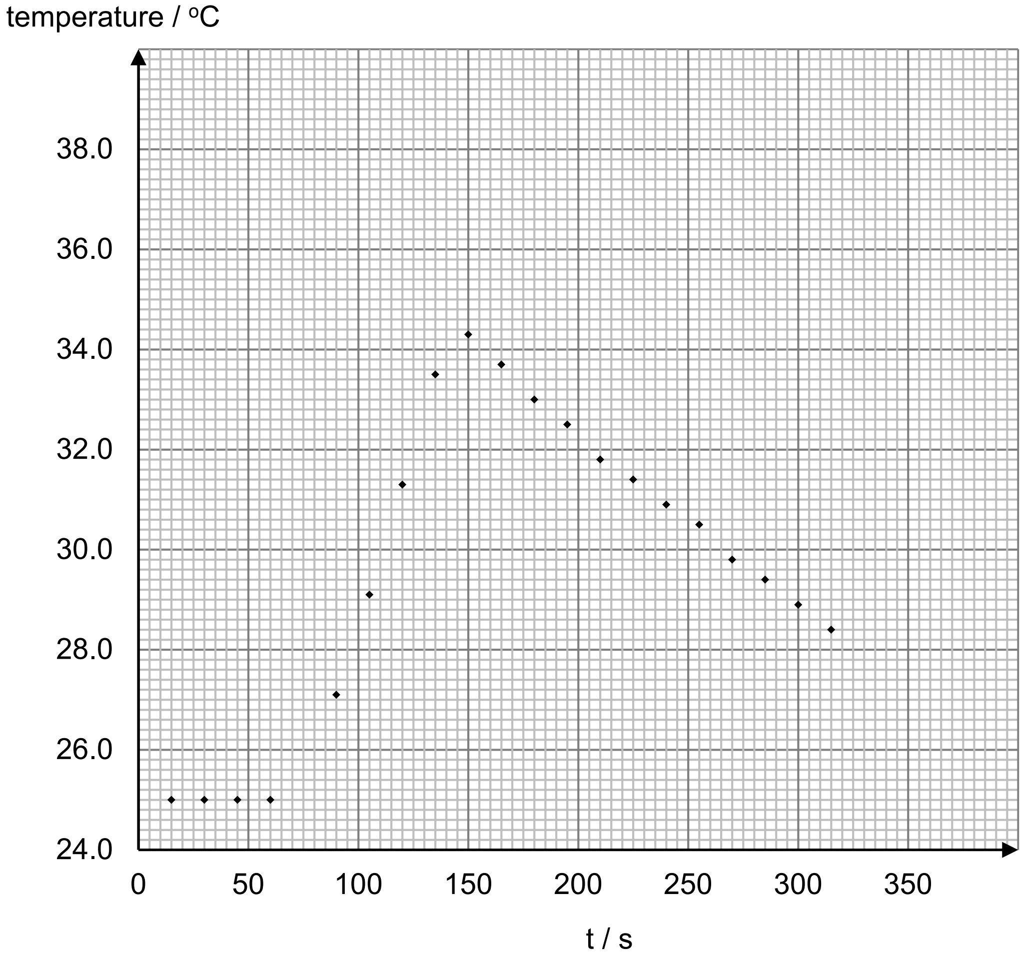
(a) The standard enthalpy change of the following reaction, $\Delta H_r^\ominus$, cannot be determined directly.

$$MgSO_4(s) + 7H_2O(l) \longrightarrow MgSO_4 \cdot 7H_2O(s) \qquad \Delta H_r^\ominus$$

An experiment was performed to determine the standard enthalpy change of solution, $\Delta H_{sol}^\ominus$, of anhydrous $MgSO_4$ and Hess' Law was then used to calculate $\Delta H_r^\ominus$.

The experimental procedure involved using a data logger to measure the temperature of the mixture when 7.500 g of anhydrous $MgSO_4$ was added to 100 cm^3 of water in a Styrofoam cup at t = 75 s.

A graph of temperature against time was plotted.



(i) Explain what is meant by the term *standard enthalpy change of solution*, $\Delta H_{sol}^\ominus$.

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....

....[2]

(ii) Determine the maximum temperature change of the reaction, ΔT, from the graph. Show all construction lines and working clearly.

[2]

(iii) Using your answer to **(a)(ii)**, calculate the experimental $\Delta H_{sol}^{\ominus}$ of anhydrous $MgSO_4$. You may assume that the density of the solution is 1 g cm^{-3} and its specific heat capacity is 4.18 J g^{-1} K^{-1}.

[2]

(iv) The actual value of $\Delta H_{sol}^{\ominus}$ of anhydrous $MgSO_4$ is –88.0 kJ mol^{-1}. Other than the assumptions made above, give a reason for the discrepancy between this value and your answer in **(a)(iii)**.

Hence, suggest a possible improvement to the experimental procedure.

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……………………………………………………………………………………………[2]

(v) The $\Delta H_{sol}^{\ominus}$ of hydrated magnesium sulfate, $MgSO_4{\cdot}7H_2O$, is +16.0 kJ mol^{-1}. Using the $\Delta H_{sol}^{\ominus}$ of anhydrous $MgSO_4$ given in **(a)(iv)**, calculate $\Delta H_r^{\ominus}$.

[1]

For examiner's use

(b) Using the data in Table 5.1 and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the standard enthalpy change of formation, $\Delta H_f^\ominus$, of $SO_4^{2-}(g)$.

Table 5.1

standard enthalpy change of formation of anhydrous $MgSO_4$, $\Delta H_f^\ominus(MgSO_4(s))$	-1278 kJ mol^{-1}
lattice energy of anhydrous $MgSO_4$	-2705 kJ mol^{-1}
standard enthalpy change of atomisation of Mg(s), $\Delta H_{at}^\ominus(Mg(s))$	$+148$ kJ mol^{-1}

[4]

[Total: 13]

5 **(a)** *Use of the Data Booklet is relevant to this question.*

The $Ag^+(aq)/Ag(s)$ half-cell was connected to the $Cu^{2+}(aq)/Cu(s)$ half-cell, and the standard e.m.f. was measured.

(i) Draw a fully labelled diagram to show the set-up for measuring the standard e.m.f. of the above cell.

In your diagram, show clearly the direction of the electron flow in the external circuit.

[3]

(ii) Calculate the $E^\ominus_{cell}$ for this set-up.

[1]

(iii) With the aid of equations, state what is observed in the $Cu^{2+}(aq)/Cu(s)$ half-cell when $NH_3(aq)$ is added slowly to it, until in excess.

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……………………………………………………………………………………….[3]

(iv) Predict and explain how the E_{cell} changes after the addition of $NH_3(aq)$.

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(b) The zinc-silver oxide alkaline battery is available in small sizes as button cells and the overall cell reaction is shown below.

$$Zn(s) + Ag_2O(s) \longrightarrow ZnO(s) + 2Ag(s) \qquad E^{\ominus}_{cell} = +1.60\ V$$

Calculate the $\Delta G^{\ominus}$ for the above reaction.

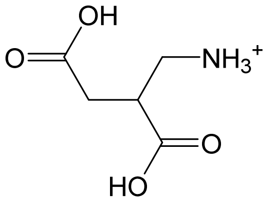
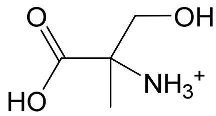
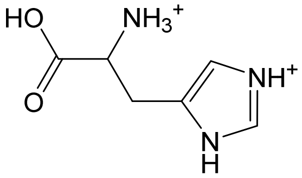
[1]

[Total: 10]

6 In 1969, a large meteorite fell in the village of Murchison, Australia. Over the years, more than 30 different amino acids have been identified in the meteorite by multiple studies. Some of these amino acids are commonly found in proteins, while others are unusual because they are not found in proteins.

The structures of three of the amino acids found in the Murchison meteorite are given in Table 4.1.

Table 4.1

amino acid three letter code	structure of fully protonated amino acid
ams	
msr	
his	

(a) Which two of the three amino acids in Table 4.1 are **not** found in proteins? With reference to their structures, explain your answer.

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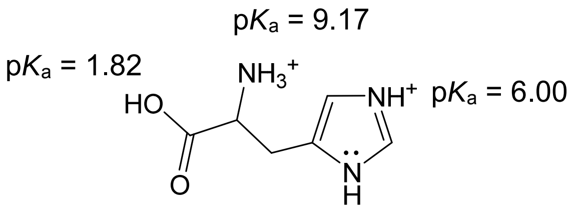
……………………………………………………………………………………………………[2]

(b) It was suggested that alien organisms could synthesise a dipeptide of the structure *his–msr*. Draw the structure of this dipeptide in the space below.

[1]

The pK_a values of the acidic groups at 25 °C in the fully protonated *his* are labelled below.

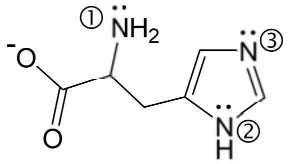


fully protonated *his*

(c) **(i)** Calculate the pK_b values of N① and N③ in the fully **deprotonated** *his* and write them in the boxes below.

[1]

pK_b of N① =



pK_b of N③ =

fully deprotonated *his*

Both N② and N③ in the ring are sp^2 hybridised.

- The lone pair on N② is located in the unhybridised p orbital.
- The lone pair on N③ is located in the sp^2 hybrid orbital.

(ii) State the hybridisation of N①.

……………………………………………………………………………………………[1]

(iii) With reference to your answers in **(c)(i)** and **(c)(ii)**, account for the relative pK_b values of N① and N③.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………………[2]

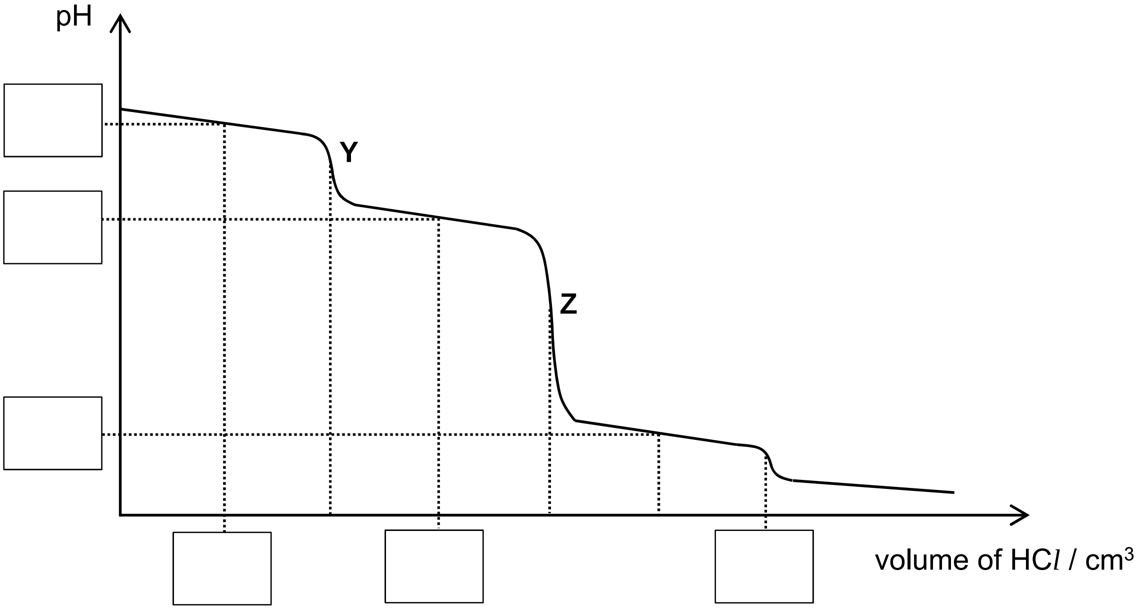
(iv) Explain why N② is **not** basic.

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

……………………………………………………………………………………………….[1]

10 cm^3 of 0.1 mol dm^{-3} of the fully **deprotonated** *his* was titrated against 0.1 mol dm^{-3} HCl(aq) from a burette. The titration curve is shown below.



(d) Fill in the boxes above with the correct pH values and HC*l* volumes. [2]

(e) Calculate the pH after 6.0 cm^3 of HC*l*(aq) was added from the burette.

[2]

For examiner's use

(f) **(i)** Draw the structures of the major species present at points **Y** and **Z** of the titration.

major species at point **Y**

major species at point **Z**

[2]

(ii) The isoelectric point of an amino acid can be defined as the pH at which the amino acid exists predominantly as zwitterions (with no net charge).

By considering your answer in **(f)(i)**, mark the isoelectric point of *his* with an "X" on the titration curve. [1]

[Total: 15]

2018 Y6 H2 Chemistry Preliminary Exams Paper 2 (Suggested Solutions)

1(a) **X** is likely to be in Group 14 as there is a large jump from the 4th to 5th ionisation energies. This shows that the 5th electron is removed from an inner electron shell and requires more energy for removal as it is more strongly attracted to the nucleus. Hence, there are 4 valence electrons in **X**.

Since **X** has at least 10 electrons but fewer than 20 electrons, X is Si.

1(b) Mn and Fe are first-row transition metals. Although Fe has a higher nuclear charge (greater proton number) than Mn, Fe has more 3d electrons which provide more shielding between the nucleus and the outer 4s shell of electrons. This increase in shielding effect offsets the increase in nuclear charge and hence, the increase in effective nuclear charge from Mn to Fe is minimal, resulting in the first ionisation energies of Mn and Fe to be similar.

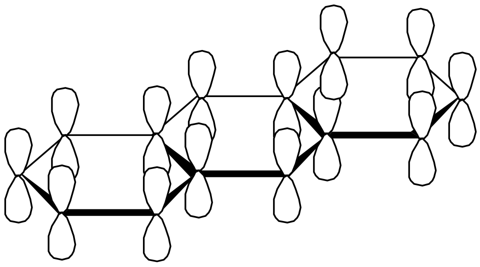
1(c) Ca^{2+} has a larger cationic radius than Cu^{2+}, thus Ca^{2+} has a lower charge density and weaker polarising power.

Consequently, there is lower extent of distortion of the electron cloud of the carbonate anion and hence covalent bonds within the carbonate anion are weakened to a lesser extent. Hence, $CaCO_3$ decomposes at a higher temperature.

2(a)(i) Anthracene is a cyclic molecule. All carbon atoms of anthracene are sp^2 hybridised and are trigonal planar.

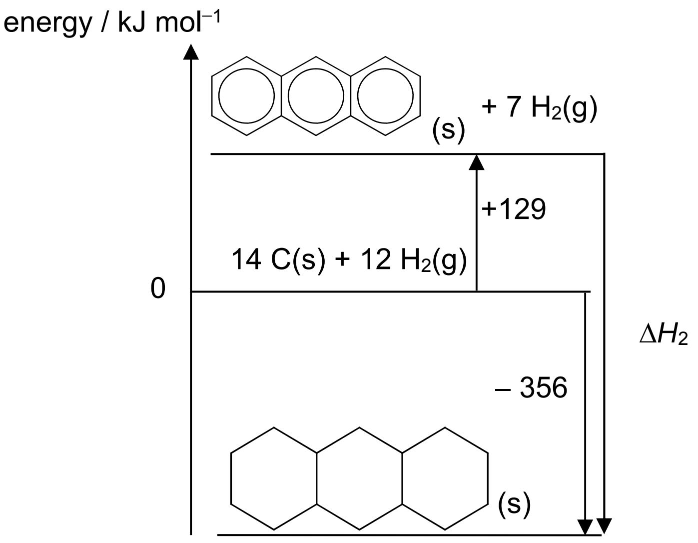
The unhybridised p-orbitals of the carbon atoms in anthracene can form a continuous p-orbital overlap, thus the π electrons are delocalised throughout the molecule.

Anthracene has 4(3) + 2 = 14 π electrons where or n = 3.



2(a)(ii) Enthalpy change of hydrogenation = 7(–118) = –826 kJ mol^{-1}

2(a)(iii)



Enthalpy change of hydrogenation = –356 –129 = $\underline{–485\ \text{kJmol}^{-1}}$

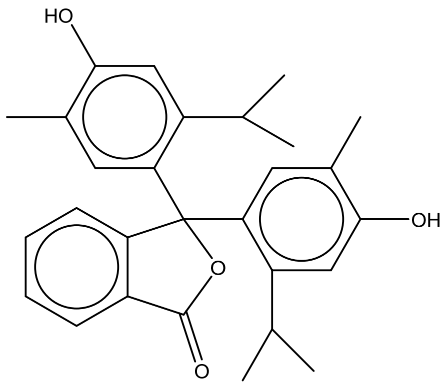
2(a)(iv) Resonance energy = 826 – 485 = $\underline{341\ \text{kJ mol}^{-1}}$

2(b)(i) TEQ = (0.029 x 0.01) + (0.135 x 0.01) + (0.204 x 1.00) = 0.20564 = $\underline{0.206}$

2(b)(ii) ECR = $\frac{0.20564}{70}$ x 1.37 x 10^{-3} = $\underline{4.00 \times 10^{-6}}$

Since the ECR from the consumption of smoked fish exceeds the value set by USEPA, it will be a cancer risk for the 70 kg person.

2(c)(i)



2(c)(ii) Thymol reacts more readily as the alkyl groups of thymol are electron donating and increase the electron density on the benzene ring making it more susceptible to electrophilic substitution.

2(d) The carboxylate anion in **A** is more stable than the phenoxide anion in **B** as the negative charge on oxygen is dispersed over the two highly electronegative oxygen atoms resulting in two equivalent resonance structures in **A** as compared to **B**.

3(a)(i) The stronger the base, the more available is its lone pair of electrons for donation to acid. Hence, a strong Lewis base will readily donate its lone pair to the electron deficient carboxyl C (Lewis acid) to reform the starting acid derivative. Thus, strong Lewis bases are poor leaving groups.

or

Strong Lewis bases donate electron pair more easily and are less likely to accept an electron pair. Thus, it is more difficult to break the C-Y bond to form Y^-.

3(a)(ii) Since pK_b of CH_3COO^- is more positive than NH_2^-, CH_3COO^- is a weaker base and is hence a better leaving group so that the reactivity of $(CH_3CO)_2O$ is higher than that of CH_3CONH_2. Reaction **1** will proceed with a faster rate than reaction **2**.

or

The pK_b of CH_3O^- is less positive than that of CH_3COO^- but more positive than that of NH_2^-. Hence the product CH_3COOCH_3 is less reactive than $(CH_3CO)_2O$ but more reactive than CH_3CONH_2. Thus, reaction **1** is likely to have a higher yield, as the product is less reactive than the reactant so that the backward reaction is less likely to occur, resulting in higher yield.

3(b)(i) Initial amount of $CH_3OH = \frac{20 \times 0.792}{32.0} = 0.495$ mol

3(b)(ii) $n_{CH3COOH}$ in 5.00 cm^3 of eqm mixture = $n_{NaOH} = \frac{16.80}{1000} \times 0.500 = 0.00840$mol

$n_{CH3COOH}$ in 40.00 cm^3 of eqm mixture = $0.0084 \times \frac{40.00}{5.00} = 0.0672$ mol

3(b)(iii) $K_c = \frac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$

3(b)(iv) $n_{CH3COOH}$ reacted = 0.350 – 0.0672 = 0.2828 mol

	$CH_3OH(l)$ +	$CH_3COOH(l)$ ⇌	$CH_3COOCH_3(l)$ +	$H_2O(l)$
Initial amt/ mol	0.495	0.350	0	0
Change in amt/ mol	–0.2828	–0.2828	+0.2828	+0.2828
Final amt/ mol	0.2122	0.0672	0.2828	0.2828

$$K_c = \frac{\left(\frac{0.2828}{V}\right)\left(\frac{0.2828}{V}\right)}{\left(\frac{0.2122}{V}\right)\left(\frac{0.0672}{V}\right)} = 5.61$$

3(b)(v) The mixture was added to a large amount of ice-cold water to quench it. Cooling and diluting the reaction mixture slows down the reaction so that the equilibrium position would not shift during the titration and the equilibrium concentration of CH_3COOH can be determined.

3(c) Warm the esters separately with aqueous alkaline iodine.
The ester that gives a yellow precipitate of CHI_3 is $HCOOCH_2CH_3$. No yellow precipitate for CH_3COOCH_3.

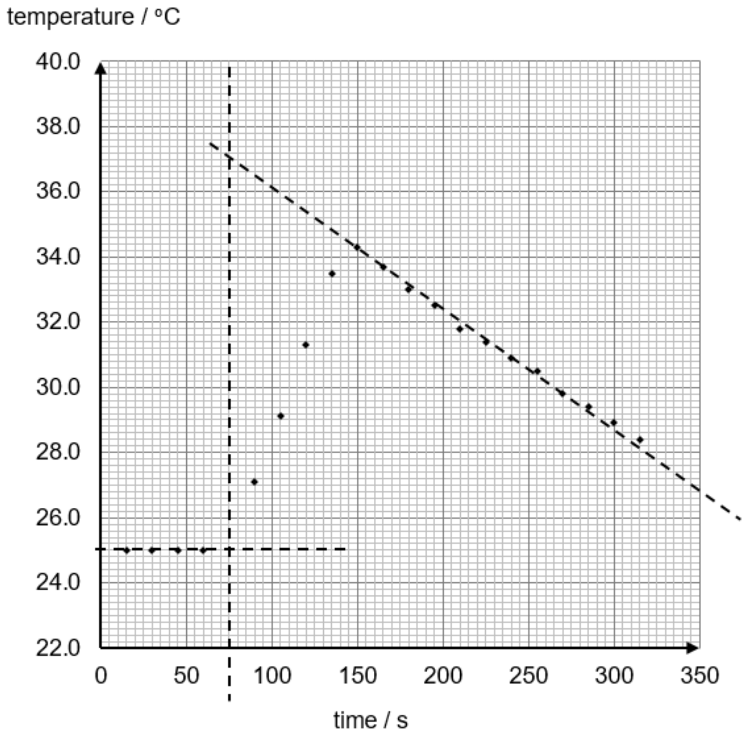
$HCOOCH_2CH_3 + OH^- \longrightarrow HCOO^- + CH_3CH_2OH$
$CH_3CH_2OH + 4I_2 + 6OH^- \longrightarrow HCOO^- + CHI_3 + 5I^- + 5H_2O$
[or $HCOOCH_2CH_3 + 4I_2 + 7OH^- \longrightarrow 2HCOO^- + CHI_3 + 5I^- + 5H_2O$]

3(d) Add dilute hydrochloric acid to the mixture. Stir and filter the mixture. **Q** is obtained as a salt in the filtrate while **P** is obtained as the residue.

Q is an amine and is basic. **Q** reacts with the acid to produce $(C_6H_5)_2NH_2^+$ (or salt) which forms strong ion–dipole interactions with water, resulting in its dissolution. Thus, **Q** dissolves in dilute hydrochloric acid and can be separated from **P** by filtration.

4(a)(i) It is the energy change when one mole of the substance is completely dissolved in a solvent to form an infinitely dilute solution at 298 K and 1 bar.

4(a)(ii) $\Delta T = 37.0 - 25.0 = +12.0\ ^\circ C$



4(a)(iii) Heat absorbed by water = $mc\Delta T = 100 \times 4.18 \times (12.0) = 5016$ J
Mr of anhydrous $MgSO_4 = 24.3 + 32.1 + 4(16.0) = 120.4$
Amt of anhydrous $MgSO_4$ used = $(7.500 / 120.4) = 0.06229$ mol
$\Delta H_{sol}^\ominus = -(5016 / 0.06229) = -80527\ J\ mol^{-1} = -80.5\ kJ\ mol^{-1}$

4(a)(iv) The experimental value is less exothermic than the actual value.

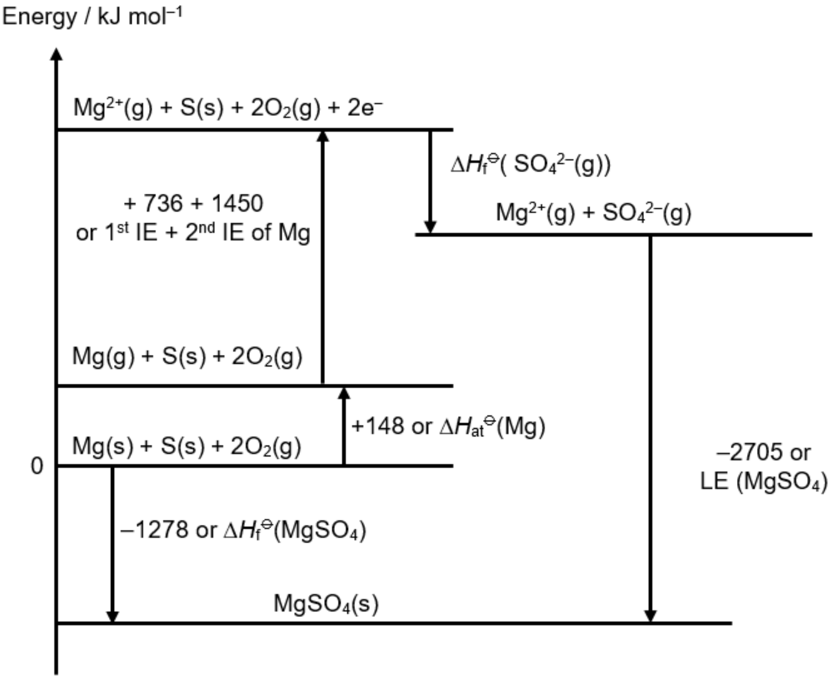
The heat capacity of cup/calorimeter was not taken into consideration. Account for the heat capacity of the cup/calorimeter by calibrating the calorimeter using a sample with known ΔH_{soln}.

or

The solution formed was not sufficiently dilute. Use a larger volume of water or use less solid.

4(a)(v) $\Delta H_r^\ominus = -88.0 - (+16.0) = \underline{-104 \text{ kJ mol}^{-1}}$

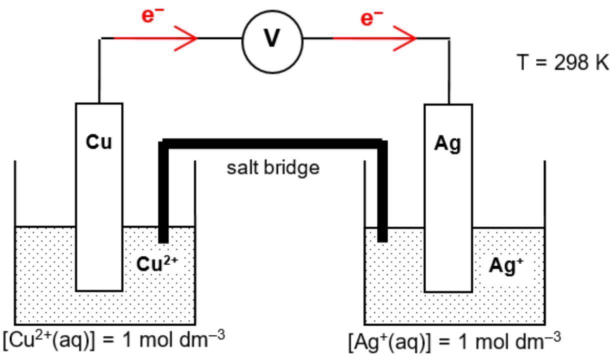
4(b)



$-1278 = +148 + 736 + 1450 + \Delta H_f^\ominus(SO_4^{2-}(g)) - 2705$

$\Delta H_f^\ominus(SO_4^{2-}(g)) = \underline{-907 \text{ kJ mol}^{-1}}$

5(a)(i)



5(a)(ii) $E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$

$= +0.80 - (+0.34)$

$= \underline{+0.46 \text{ V}}$

5(a)(iii) Upon addition of NH_3, <u>blue ppt forms</u>.
$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ blue ppt

Upon addition of excess NH_3, ppt dissolves and <u>deep blue solution</u> is formed.
$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$ deep blue complex

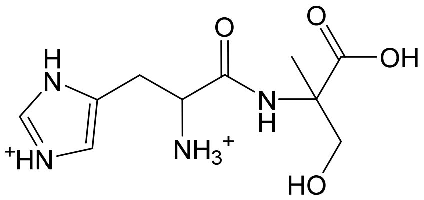
5(a)(iv) Upon addition of NH_3, <u>$[Cu^{2+}]$ decreases</u> such that it becomes less than 1 mol dm^{-3} (i.e. conditions are no longer standard). Position of equilibrium for $Cu^{2+} + 2e^- \rightleftharpoons Cu$ <u>shifts to the left</u>.

E_{anode} in **(a)(ii)** decreases and hence <u>E_{cell} becomes more positive.</u>

5(b) $\Delta G^\ominus = -nFE^\ominus_{cell} = -(2)(96500)(+1.60) = \underline{-309 \text{ kJ mol}^{-1}}$

6(a) <u>ams and msr</u> as they <u>do not follow the general formula $NH_2CH(R)COOH$</u>.

6(b)



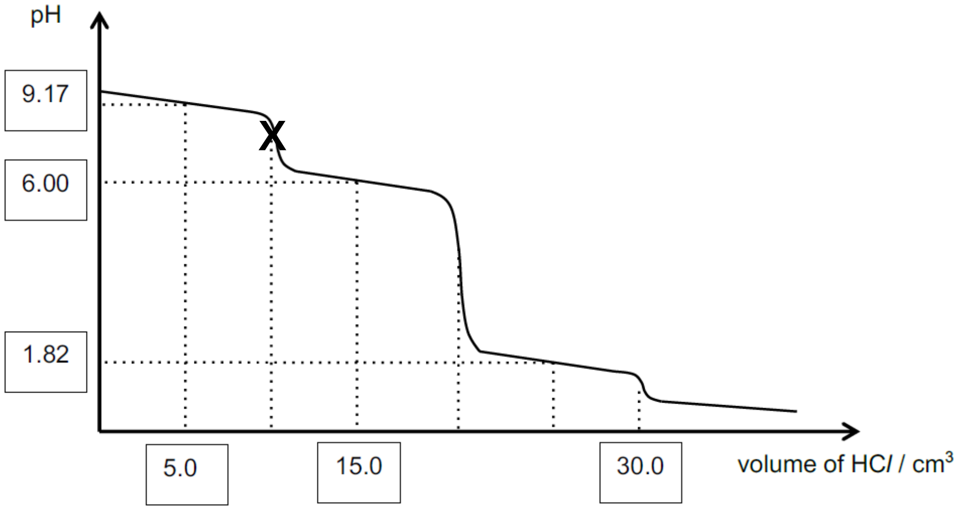
6(c)(i) pK_b of N① = 14 – 9.17 = <u>4.83</u>
pK_b of N③ = 14 – 6.00 = <u>8.00</u>

6(c)(ii) sp^3

6(c)(iii) The lone pair on N① is located in the sp^3 hybrid orbital which has <u>less s character</u> than the lone pair on N③ which is located in the sp^2 hybrid orbital. Therefore, N① lone pair is less strongly attracted to the nucleus and is <u>more available for coordination with a proton</u>.

6(c)(iv) The unhybridised p orbital on N② can overlap with the unhybridised p orbitals of the other atoms in the ring. Therefore the lone pair is <u>delocalised and unavailable for coordination with a proton.</u>

6(d) & 6(f)(ii)

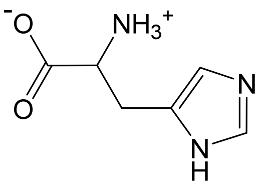


6(e) n(HC*l*) added = n(conjugate acid) formed = 6/1000 x 0.1 = 0.0006 mol
n(fully deprotonated *his*) remaining = (10/1000 x 0.1) – 0.0006 = 0.0004 mol

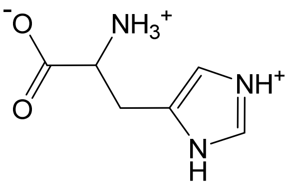
pH = pK_a + lg ([fully deprotonated *his*] / [conjugate acid])
= 9.17 + lg (0.0004 / 0.0006)
= <u>8.99</u>

6(f)(i)

point **Y**



point **Z**



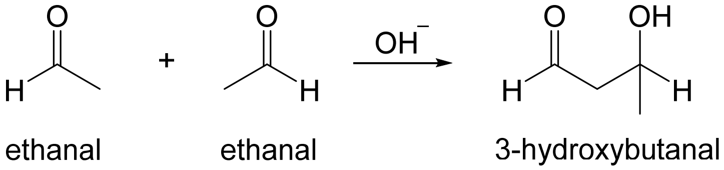
Section A

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

1 **(a)** In the aldol reaction, two carbonyl compounds react with each other in the presence of a base catalyst to form a hydroxy carbonyl compound.

The aldol reaction between two ethanal molecules, in the presence of OH^- ions, is shown below.

Reaction **1**



(i) A mixture of ethanal and propanone was subjected to the aldol reaction. Apart from 3-hydroxybutanal, suggest **three** other possible products formed. Ignore stereoisomers in your answer. [2]

To determine the kinetics of reaction **1**, two experiments, **I** and **II**, were carried out and the graphs of the concentration of ethanal against time were plotted.

The graphs on **page 13** show the results of experiments **I** and **II** with $[OH^-] = 1.0$ mol dm^{-3} and 2.0 mol dm^{-3} respectively. For **(a)(ii)** and **(a)(iii)**, draw clearly any construction lines on the graphs on **page 13**.

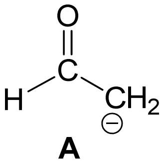
(ii) OH^- ions act as catalyst in the aldol reaction. Using the graph for Experiment **I**, determine the order of reaction with respect to ethanal. Explain your reasoning. [2]

(iii) By finding the initial rates, determine the order of reaction with respect to OH^-. [2]

(iv) Hence, write an overall rate equation for this reaction. [1]

(v) With reference to Experiment **I**, calculate a value for the rate constant and state its units. [2]

(b) **A** is an intermediate formed in reaction **1**.



A

In a separate reaction, **A** was used as a nucleophile to react with an optically active sample of 2-bromobutane. The product formed was found to rotate plane polarised light.

(i) Describe the mechanism of this reaction. In your answer, show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electrons. [3]

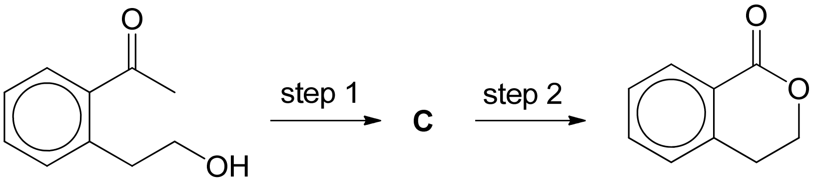
(ii) When conducted at a higher temperature, the same reaction occurred at a higher rate. With the aid of the Boltzmann distribution, explain why this is so. [3]

(iii) In another reaction with **A**, 2-chlorobutane was used instead of 2-bromobutane. With reference to the *Data Booklet*, predict and explain the effect on the rate of reaction. [1]

(iv) Instead of **A**, hydroxide ions were used to react with 2-bromobutane via the same mechanism in **(b)(i)**.

Suggest why the reaction between hydroxide ions and 2-bromobutane is faster than that between **A** and 2-bromobutane. [1]

(c) The following shows a reaction scheme to synthesise an ester **D** from compound **B**.



B **D**

(i) Suggest the structure of compound **C**. [1]

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

[Total: 20]

2 This question is about the halogens and their compounds.

Halogens react readily with lead to form lead halides. The melting points of some of the lead halides are given in Table 2.1.

Table 2.1

compound	melting point / °C
PbF_2	824
$PbCl_2$	501
$PbBr_2$	373
$PbCl_4$	–15

(a) **(i)** Explain, in terms of structure and bonding, why the melting points of the lead(II) halides decrease from PbF_2 to $PbBr_2$. [2]

(ii) Explain why $PbCl_4$ is a covalent compound and account for its low melting point. [2]

(iii) In an experiment, an excess of solid $PbCl_2$ was added to a solution of 0.050 mol dm^{-3} NaC*l* and allowed to reach equilibrium at 298 K. The mixture was then filtered. 25.0 cm^3 of the filtrate required the addition of 3.58×10^{-5} mol of NaI for the first trace of PbI_2 precipitate to appear.

Given that the solubility product of PbI_2 is 9.80×10^{-9} mol^3 dm^{-9}, calculate the solubility product of $PbCl_2$. [3]

When concentrated hydrochloric acid is added to a mixture containing the white precipitate of $PbCl_2$, the precipitate dissolves to form a colourless solution containing an ionic compound **E**.

(iv) **E** contains 0.6% H; 59.0% Pb; 40.4% C*l* by mass, and has a relative formula mass of 351.0. The ratio of the cation to anion in **E** is 2 : 1.

Suggest the identity of the **complex ion** present in **E**. [2]

(v) Hence, explain the above observation with relevant ionic equations. [2]

(b) Halogens react with hydrogen to form hydrogen halides which may decompose upon heating.

(i) Write an equation for the thermal decomposition of hydrogen iodide. [1]

(ii) In an experiment, three glass jars were filled with hydrogen chloride, hydrogen bromide and hydrogen iodide gases respectively. A red hot wire was inserted into each jar for a fixed period of time. The observations were recorded in Table 2.2.

Table 2.2

gas in glass jar	observations
hydrogen chloride	no observable change
hydrogen bromide	reddish brown vapour formed slowly
hydrogen iodide	purple fumes evolved vigorously

Explain these observations. [2]

(c) Interhalogen species are commonly formed between halogens, where the central atom is the less electronegative of the two halogens.

Draw the dot-and-cross diagram of the IF_4^- ion. In your diagram, use the symbols '•' and 'x' to distinguish the electrons from the iodine and fluorine atoms, and the symbol 'o' for any additional electron responsible for the overall negative charge.

State the shape and bond angle in IF_4^- ion. [2]

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

Halogens are strong oxidising agents which have important industrial applications. Chlorine, for example, is used as a disinfectant.

Show, with appropriate calculations, that manganese(IV) oxide is a product of the redox reaction between chlorine and manganese metal.

Hence, write the overall equation for the reaction. [3]

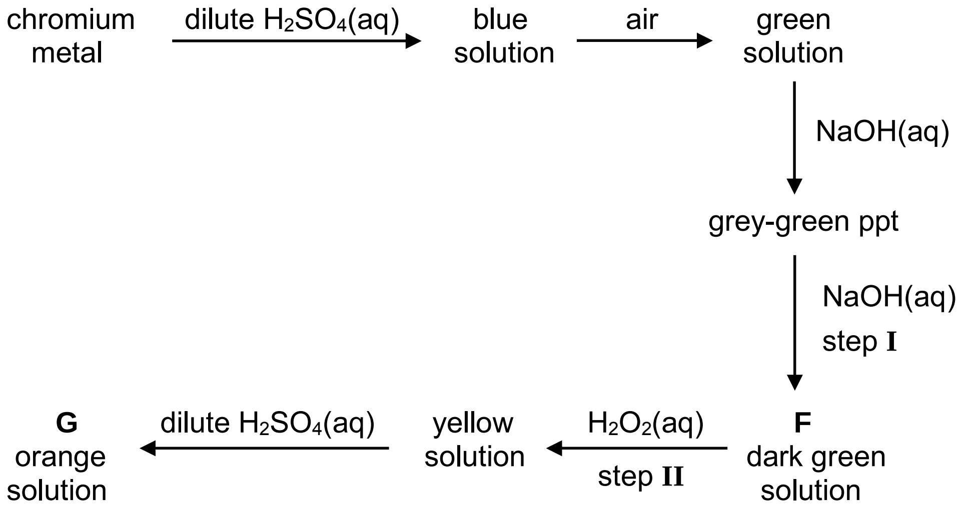
(e) Write a balanced equation for the reaction of PCl_5 with water. [1]

[Total: 20]

3 Chromium is a hard bluish–white metal that is extremely resistant to chemical attack at room temperature. Chromium metal is an important component in stainless steel.

(a) Write the electronic configuration of Cr. [1]

(b) The following sequence of reactions involving chromium illustrates many of the characteristic properties of transition metals.



(i) State the types of reaction in steps **I** and **II**.

Give the formula of the chromium-containing species, **F** and **G**. [3]

(ii) The variety of colours shown by chromium compounds in this reaction scheme is a typical property of transition metals.

State **one other** characteristic property of transition metals that is illustrated by this reaction scheme. Briefly explain why transition metals exhibit this property. [2]

(c) Chromium is said to be a d-block element as it contains d electrons.

(i) Draw the shape of d_{xy} and $d_{x^2-y^2}$ orbitals, showing clearly the axes. [1]

(ii) The five degenerate orbitals in the 3d subshell are split into two energy levels in the presence of ligands in an octahedral environment. Explain why this is so. [2]

(d) The complex ions formed from Cr^{3+}, most of which are octahedral, may exhibit isomerism.

Three compounds having the formula $CrCl_3(H_2O)_6$ are known. All three give a white precipitate when aqueous silver nitrate is added. However, they differ in the fraction of 'free' chloride present and in their electrical conductivities in aqueous solution. In addition, these three compounds exhibit different colours in aqueous solution.

(i) Identify the complex ion in each of the three compounds. [2]

(ii) Explain why aqueous solutions of these three compounds are coloured. [3]

(iii) Suggest why the aqueous solutions of these three compounds exhibit different colours. [2]

(iv) One of the three complex ions in **(d)(i)** can exhibit *cis-trans* isomerism. Draw the *cis* isomer of this complex ion. [1]

(e) Excess ethylenediamine is added to a solution of $[Cr(NH_3)_6]^{3+}(aq)$ ions according to the following equation.

$$[Cr(NH_3)_6]^{3+}(aq) + 3H_2NCH_2CH_2NH_2(aq) \rightleftharpoons \underset{\text{complex } \mathbf{H}}{[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}(aq)} + 6NH_3(aq)$$

(i) Predict, with reasoning, the sign of ΔS of the forward reaction. [1]

(ii) Suggest a reason why the ΔH value of the forward reaction is close to zero. [1]

(iii) By considering the $\Delta G^\ominus$ value of the forward reaction, suggest whether a higher or lower temperature will increase the yield of complex **H**. [1]

[Total: 20]

Section B

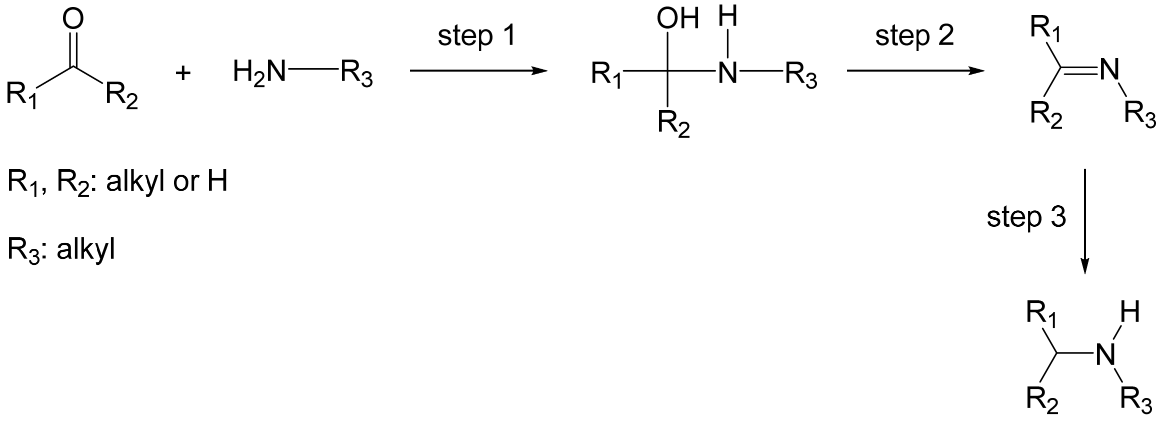
Answer **one** question from this section.

4 **(a)** **(i)** Describe the reactions, if any, of the oxides Na_2O, SiO_2 and P_4O_{10} with water. Write equations for any reactions that occur and include the approximate pH values of the resulting solutions. [5]

(ii) The acid-base behaviour of Al_2O_3 shows similarities to that of MgO and SO_3.

Describe and explain what these similarities are, and why Al_2O_3 occupies this in-between position. Write equations involving Al_2O_3 to illustrate your answer. [3]

In the Leuckart-Wallach reaction shown below, a carbonyl compound reacts with a primary amine to form a secondary amine.



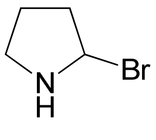
R_1, R_2: alkyl or H

R_3: alkyl

(b) **(i)** State the type of reaction in step 1. [1]

(ii) Unlike primary amines, primary amides cannot be used in the Leuckart-Wallach reaction. With reference to your answer in **(b)(i)**, explain why this is so. [1]

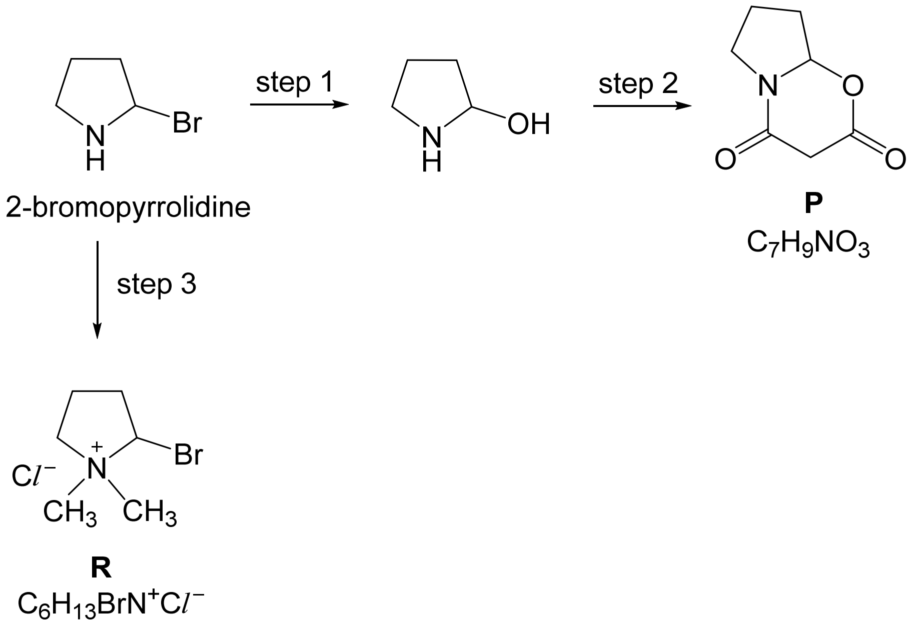
(iii) 2-bromopyrrolidine can be synthesised via the Leuckart-Wallach reaction.



2-bromopyrrolidine

Draw the displayed formula of the starting compound used in the synthesis of 2-bromopyrrolidine. [1]

(c) The following scheme shows the reactions involving 2-bromopyrrolidine.



2-bromopyrrolidine

P
$C_7H_9NO_3$

R
$C_6H_{13}BrN^+Cl^-$

(i) State the reagents and conditions for steps 1, 2 and 3. [3]

(ii) When compound **P** ($C_7H_9NO_3$) is reacted with $LiAlH_4$, compound **Q** ($C_7H_{15}NO_2$) is formed as the only organic product. 1 mole of **Q** reacts with 2 moles of Na but does not react with aqueous Na_2CO_3. Suggest the structure of **Q**. [1]

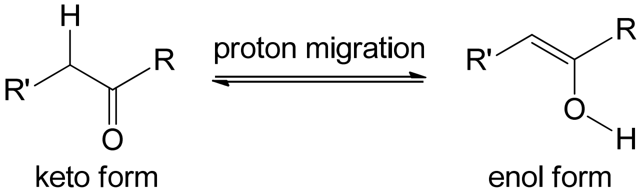
Under suitable conditions, compound **R** can undergo elimination to form two isomers **S** and **T** with the molecular formula $C_6H_{12}BrN$. Both **S** and **T** decolourise aqueous bromine and form salts in dilute acids. However, when heated with ethanolic $AgNO_3$, only **S** gives a pale cream precipitate.

(iii) Suggest the structures of **S** and **T** and state their isomeric relationship. [3]

(iv) Explain why **T** does not form a pale cream precipitate when heated with ethanolic $AgNO_3$. [2]

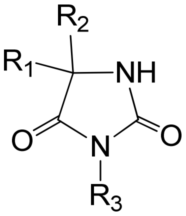
[Total: 20]

5 The stereochemistry of molecules plays a key role in their drug action. The conversion of the keto form to the enol form via proton migration often plays an important part in the orientation and effectiveness of drugs.



(a) State the isomeric relationship between the keto and enol forms. [1]

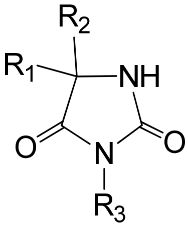
Hydantoins are a class of anti-epileptics that act against convulsions, tremors and seizures. The amide form of hydantoins has the general structure as shown.



(b) Similar to the keto-enol conversion, the molecule above can undergo proton migration to form another isomer under suitable conditions. Draw this isomer. [1]

(c) The most commonly used hydantoins include mephenytoin, phenytoin and derivative **X**.

	substituent		
	R_1	R_2	R_3
mephenytoin	C_6H_5	C_2H_5	CH_3
phenytoin	C_6H_5	C_6H_5	H
derivative **X**	C_6H_5	C_2H_5	C_6H_5



(i) Mephenytoin exists as a pair of stereoisomers.

State the type of stereoisomerism exhibited and draw the isomers. [2]

(ii) Suggest a simple chemical test to distinguish phenytoin from derivative **X**. [2]

(d) Compound **J** ($C_{10}H_{10}N_2O_2$) is neutral and exhibits optical activity. It does not react with 2,4-dinitrophenylhydrazine and does not contain the alkene functional group.

J reacts with H_2(g) in the presence of Ni catalyst at 150 °C and 1 bar to form **K** ($C_{10}H_{14}N_2O_2$). When **J** is heated with dilute sulfuric acid, carbon dioxide gas and NH_4^+ ions were formed. The resultant mixture was then distilled and **L** ($C_3H_6O_3$) was obtained as the distillate. To the residue from the distillation, a base was added and **M** was formed. **M** decolourises aqueous bromine to form a solid **N** ($C_6H_4NBr_3$). **L** reacts with hot alkaline aqueous iodine to give a pale yellow precipitate. **L** also turns hot orange acidified potassium dichromate(VI) green to produce **P**. **P** reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate **Q**.

(i) Calculate the volume of H_2(g) required for the complete reaction of 5.0 g of **J** to form **K**. [2]

(ii) Suggest possible structures for compounds **J** to **N**, **P** and **Q**, explaining the reactions involved. [12]

[Total: 20]

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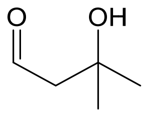
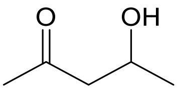
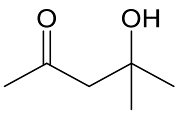
2018 Y6 H2 Chemistry Preliminary Exams Paper 3 (Suggested Solutions)

Section A

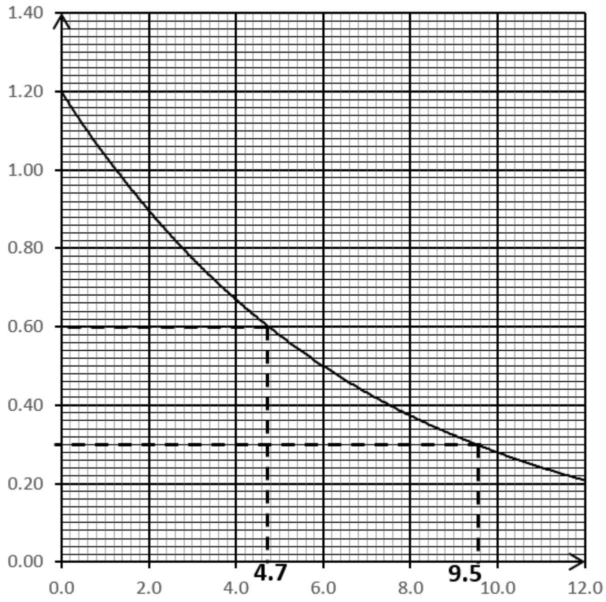
1 **(a)** **(i)**







(ii) Since OH^- is a catalyst, $[OH^-]$ is constant during each experiment and does not affect the reaction rate.



Using Experiment **I**,
First $t_{\frac{1}{2}}$ = <u>4.7 min</u>. Second $t_{\frac{1}{2}}$ = 9.5 – 4.7 = <u>4.8 min</u>.

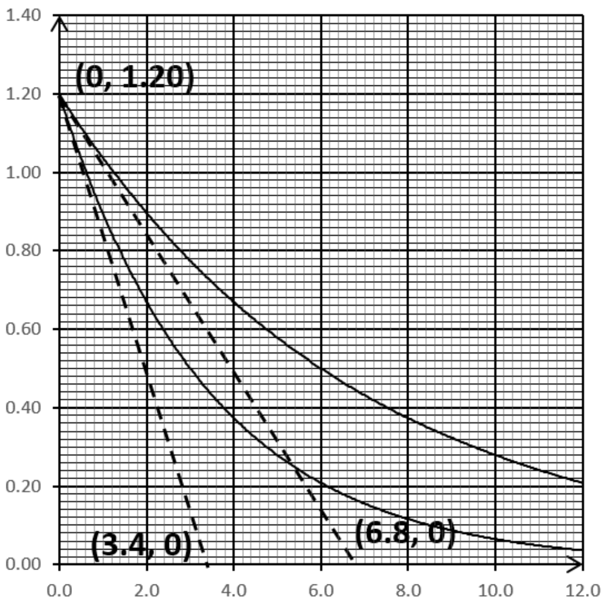
Since both $t_{\frac{1}{2}}$ are approximately the <u>same</u>, the reaction is <u>first order</u> w.r.t. ethanal.

(iii) By drawing tangents at t = 0 min,

For Experiment **I**, initial rate = $\left|\frac{1.20-0}{0-6.8}\right|$ = <u>0.176 mol dm^{-3} min^{-1}</u>

For Experiment **II**, initial rate = $\left|\frac{1.20-0}{0-3.4}\right|$ = <u>0.353 mol dm^{-3} min^{-1}</u>

When $[OH^-]$ doubles, rate doubles. Hence, reaction is <u>first order</u> w.r.t. OH^-.



(iv) rate = $k[OH^-]$[ethanal]

(v) Initial rate method

Using Experiment **I**, 0.1765 = $k(1.0)(1.2)$ → k = 0.147 $mol^{-1}\ dm^{3}\ min^{-1}$

OR

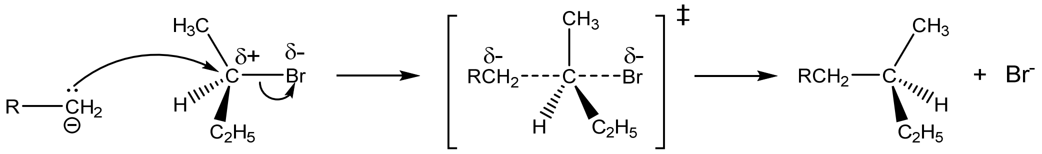
Half-life method

$$t_{½} = \frac{\ln 2}{k\,[OH^-]}$$

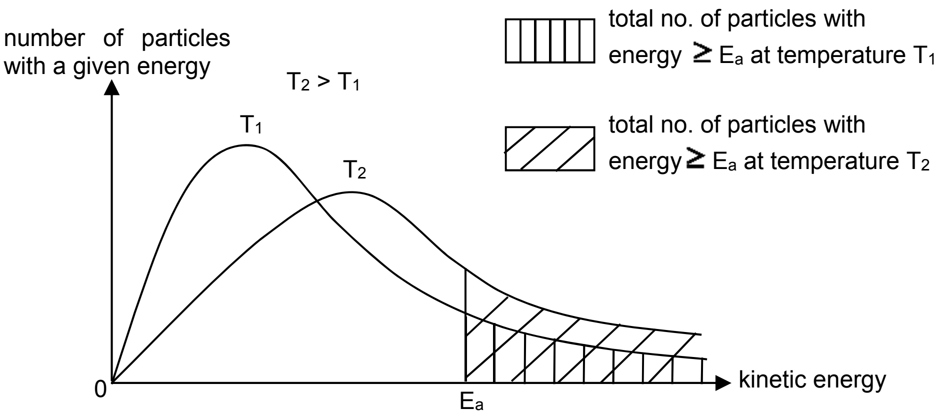
Using Experiment **I**, $4.75 = \frac{\ln 2}{k\,(1.0)}$ → k = 0.146 $mol^{-1}\ dm^{3}\ min^{-1}$

(b) **(i)** Mechanism: S_N2 (or bimolecular nucleophilic substitution)

Let RCH_2^- represent **A**.



(ii)



An increase in temperature from T_1 to T_2 increases the average kinetic energy of the reactant particles. More reactant particles have energy greater than or equal to the activation energy of the reaction.

This results in an increase in effective collision frequency and hence an increase in the rate of the reaction.

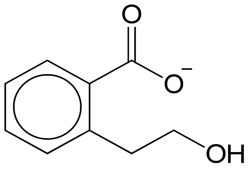
(iii) The C–C*l* bond (BE = 340 kJ mol^{-1}) is stronger than the C–Br bond (BE = 280 kJ mol^{-1}). Hence it is more difficult to break the C–C*l* bond, resulting in a slower reaction for 2-chlorobutane.

(iv) Hydroxide ions are less bulky and will experience less steric hindrance when attacking the electron deficient carbon atom.

OR

In **A**, the negative charge is delocalised into the adjacent C=O group. Hence, lone pair on **A** is less available, resulting in a slower reaction.

(c) **(i)**



(ii) Step 1: I_2(aq) with NaOH(aq), heat or warm
Step 2: (catalytic) conc H_2SO_4, heat

2 **(a)** **(i)** PbF_2, $PbCl_2$ and $PbBr_2$ have giant ionic structure with strong ionic bonds.

PbF_2, $PbCl_2$ and $PbBr_2$ have the same cation and the anions have the same charge. Since the ionic radius increases from F^- to Br^-, the interionic distance increases from PbF_2 to $PbBr_2$. Hence the strength of ionic bond and melting point decreases from PbF_2 to $PbBr_2$.

Or since $|LE| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$ and the ionic radius increases from F^- to Br^-, the LE become less exothermic, less energy is required to overcome the ionic bond and melting point decreases from PbF_2 to $PbBr_2$.

(ii) Due to its high charge and small size, Pb^{4+} has a high charge density and high polarising power, which causes it to distort the electron cloud of Cl^- to such an extent that $PbCl_4$ is predominantly a covalent compound.

Hence, $PbCl_4$, having a simple covalent/molecular structure, consists of discrete molecules held together by weak instantaneous dipole-induced dipole interactions which requires a small amount of energy to overcome. Thus, it has a low melting point.

(iii) $[I^-] = \dfrac{3.58 \times 10^{-5}}{25.0/1000} = 1.432 \times 10^{-3}$ mol dm^{-3}

$[Pb^{2+}]$ in filtrate $= \dfrac{9.80 \times 10^{-9}}{(1.431 \times 10^{-3})^2} = 4.779 \times 10^{-3}$ mol dm^{-3}

$[Cl^-]$ from $PbCl_2$ in filtrate $= 4.779 \times 10^{-3} \times 2 = 9.558 \times 10^{-3}$ mol dm^{-3}

Total $[Cl^-]$ in filtrate $= 9.558 \times 10^{-3} + 0.050 = 0.05956$ mol dm^{-3}

$K_{sp} = [Pb^{2+}][Cl^-]^2 = (4.779 \times 10^{-3})(0.05956)^2 = 1.70 \times 10^{-5}$ mol^3 dm^{-9}

(iv)

	H	Pb	Cl
mass	0.6	59.0	40.4
mole	0.6/1.0	59.0/207	40.4/35.5
	= 0.6	= 0.285	= 1.138
	≈ 2	≈ 1	≈ 4

Empirical formula = H_2PbCl_4
Actual formula = H_2PbCl_4
Complex ion = $[PbCl_4]^{2-}$

(v) The following equilibrium is established in the saturated solution:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \text{ -----(1)}$$

When concentrated hydrochloric acid is added and the mixture shaken, $[Cl^-]$ is greatly increased. Pb^{2+} ions react with Cl^- to form the soluble complex, $[PbCl_4]^{2-}$, as shown below.

$$Pb^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq) \text{ -----(2)}$$

The formation of $[PbCl_4]^{2-}$ decreases the $[Pb^{2+}]$ in the solution.
To counteract the decrease in $[Pb^{2+}]$, the equilibrium position of reaction (1) shifts to the right i.e. $PbCl_2$ dissolves.
or

$[Pb^{2+}]$ decreases due to the formation of $[PbCl_4]^{2-}$. When ionic product, $[Pb^{2+}][Cl^-]^2$ becomes less than the K_{sp}, all the $PbCl_2$ dissolves.

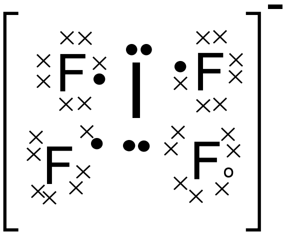
(b) **(i)** $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(ii) The thermal stabilities of HCl to HI, which is related to the H-X bond strength, increase in the order: HI < HBr < HC*l*

The stronger the H-X bond, the more thermally stable HX is. Since the bond strength of HI < HBr < HC*l*, the thermal stability of HI < HBr < HC*l*.

The energy supplied by the red hot wire was insufficient to decompose HC*l*, hence there is no observable change; was able to decompose some HBr, resulting in reddish-brown vapour of Br_2 formed slowly; and was able to decompose HI readily to result in purple fumes of I_2 evolved vigorously.

(c)



Square planar, 90˚

(d) $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^{\ominus} = +1.36$ V
$Mn^{2+} + 2e^- \rightleftharpoons Mn$ $E^{\ominus} = -1.18$ V
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$ $E^{\ominus} = +1.23$ V
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$ $E^{\ominus} = +1.67$ V

Considering the reaction between Cl_2 and Mn, $E^{\ominus}_{cell} = +1.36 - (-1.18)$
$= +2.54$ V (spontaneous)
Considering the reaction between Cl_2 and Mn^{2+}, $E^{\ominus}_{cell} = +1.36 - 1.23$
$= +0.13$ V (spontaneous)

Considering the reaction between Cl_2 and MnO_2, $E^{\ominus}_{cell} = +1.36 - 1.67$
$= -0.31$ V (not spontaneous)

Thus, Cl_2 will oxidise Mn to Mn^{2+} and further oxidise Mn^{2+} to MnO_2. (proven)

Overall eqn: $2Cl_2 + Mn + 2H_2O \longrightarrow 4Cl^- + MnO_2 + 4H^+$

(e) $PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$

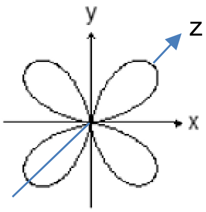
3 **(a)** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

(b) **(i)** Step **I**: acid-base (or complexation or complex formation)
Step **II**: oxidation / redox reaction
F: $[Cr(OH)_6]^{3-}(aq)$ or $[Cr(OH)_4]^-(aq)$
G: $Cr_2O_7^{2-}(aq)$

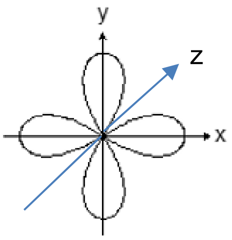
(ii) The ability to display variable oxidation states in their compounds. This is due to the close similarity in energy between the 3d and 4s electrons, which thus allows for different number of these electrons to participate in chemical bonding.

OR Ability to form complexes due to availability of low lying vacant orbitals.

(c) **(i)**



$3d_{xy}$



$3d_{x^2-y^2}$

(ii) In an octahedral environment, lone pairs on the ligands approach the central metal ion along the x, y and z axes.

$3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals have their greatest electron density along the co-ordinate axes on which the ligands are situated. Hence electrons in these orbitals are pointing towards the lone pairs of ligands, and will be repelled by them.

$3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals have their greatest electron density in between the co-ordinate axes. Hence the repulsion between electrons in these orbitals and those of the approaching ligands will be less compared to electrons in $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals.

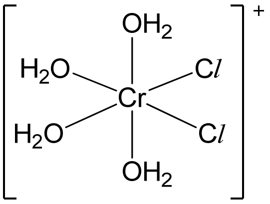
Hence the d-orbitals are split into two different energy levels.

(d) **(i)** $[Cr(H_2O)_4Cl_2]^+$
$[Cr(H_2O)_5Cl]^{2+}$
$[Cr(H_2O)_6]^{3+}$

(ii) The presence of ligands causes the splitting of the five 3d orbitals in Cr^{3+} into two sets of slightly different energy levels. Since the 3d subshell in Cr^{3+} are partially filled, electrons from the lower-energy d orbitals can absorb energy and get promoted to the higher-energy d orbitals (d-d transition). The energy absorbed corresponds to certain wavelength from the visible light spectrum and the colour observed is the complement of the colour absorbed.

(iii) Chloride and water are ligands of different strength. Different proportions of these ligands cause the d orbitals to be split to different extents, creating different energy gaps for different complexes, which in turn absorb energies of different wavelengths from the visible light spectrum, thus displaying different colours.

(iv)



cis-$[Cr(H_2O)_4Cl_2]^+$

(e) **(i)** Positive ($\Delta S > 0$). There is increase in disorder/entropy due to increase in number of particles / molecules / species formed.

(ii) ΔH value of the forward reaction is close to zero as the type (N→Cr coordinate bond) and the number of dative covalent bonds broken and formed are about the same.

(iii) $\Delta G = \Delta H - \mathrm{T}\Delta S$
Since ΔH is close to zero and ΔS is positive, ΔG (for the forward reaction) will be more negative at a higher temperature, hence increasing the yield of complex **H**.

Section B

4 **(a)** **(i)** Na_2O reacts with water to form a strongly alkaline solution (pH ≈ 13 – 14).
$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$

SiO_2 does not dissolve in water because of the strong Si–O covalent bonds in the giant molecular structure. Solution remains neutral (pH = 7).

P_4O_{10} reacts with water to form an acidic solution (pH ≈ 2).
$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$
(Note: H_3PO_4 is a weak acid)

(ii) (MgO is an ionic oxide which is basic and react with acids. SO_3 is a covalent oxide which is acidic and reacts with bases.)

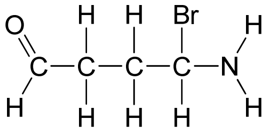
$\mathrm{A}l_2\mathrm{O}_3$ (an amphoteric oxide) reacts with both acids and bases as it is an ionic oxide with covalent character. The covalent character is due to the high charge density/polarising power of $\mathrm{A}l^{3+}$ that polarise and distort the electron cloud of O^{2-}.

With acid: $\mathrm{A}l_2\mathrm{O}_3(s) + 6H^+(aq) \rightarrow 2\mathrm{A}l^{3+}(aq) + 3H_2O(l)$
With base: $\mathrm{A}l_2\mathrm{O}_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[\mathrm{A}l(OH)_4]^-(aq)$

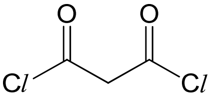
(b) **(i)** Step 1: nucleophilic addition

(ii) In primary amides, the lone pair of electrons on the nitrogen atom interacts with the π electron cloud of the adjacent C=O bond and is delocalised. Hence, the lone pair of electrons is not available for donation to the electrophilic carbonyl carbon atom /unable to act as a nucleophile in step 1.

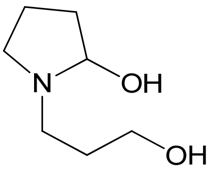
(iii)



(c) **(i)** Step 1: NaOH(aq), heat

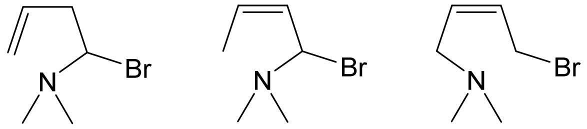
Step 2:  (anhydrous, rtp)
Step 3: excess $\mathrm{CH_3C}l$, heat

(ii)



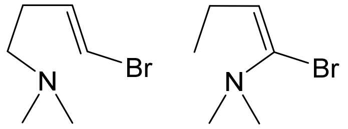
Q
$C_7H_{15}NO_2$

(iii) Possible structures for **S** ($C_6H_{12}BrN$):



(or the trans isomers)

Possible structures for **T** ($C_6H_{12}BrN$):



(or corresponding cis-trans isomer)

S and **T** are constitutional / structural / positional isomers.

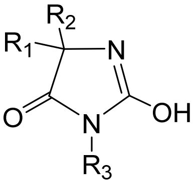
(iv) In **T**, the p orbital of Br overlaps with the π electron cloud of the adjacent C=C bond and the lone pair of electrons in the p orbital of Br delocalises into the C=C bond and results in partial double bond character in the C–Br bond.

Hence, **T** does not undergo nucleophilic substitution and no Br^- are present to react with Ag^+ to form pale cream ppt of AgBr.

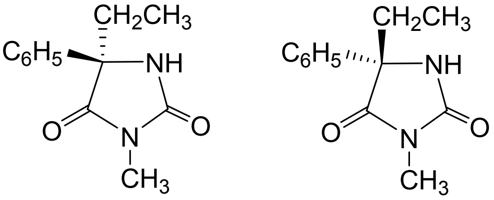
(**S** is an alkyl bromide that can undergo nucleophilic substitution when heated with ethanolic $AgNO_3$ to form alcohol and Br^-. Br^- then forms the pale cream ppt of AgBr with Ag^+.)

5 **(a)** Constitutional / Structural / Functional group isomerism

(b)



(c) **(i)** Enantiomerism



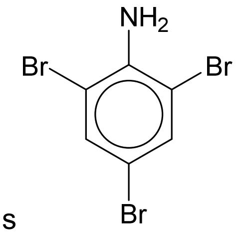
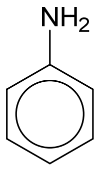
(ii) Test: To separate samples of **X** and phenytoin, add NaOH(aq) and heat strongly.

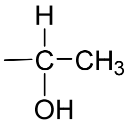
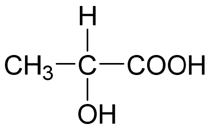
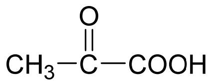
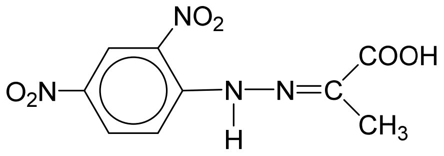
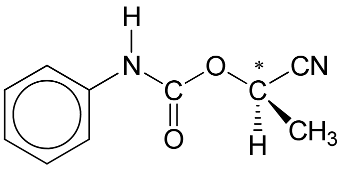
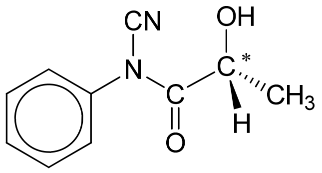
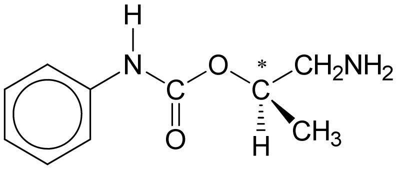
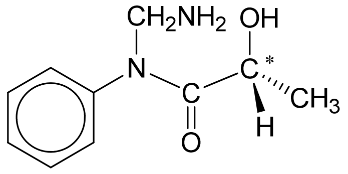
Observation: Pungent gas (NH_3) that turns moist red litmus blue is evolved for the sample containing phenytoin but no pungent gas is evolved for the sample containing **X**.

(d) **(i)** M_r (**J**) = 190
n(**J**) = 5/190 = 0.02632 mol; n(H_2) = 2(0.02632) = 0.05264 mol

$pV_{H2} = nRT$
$(1.0 \times 10^5)\ V_{H2} = (0.05264)(8.31)(273 + 150)$
$V_{H2} = 1.85 \times 10^{-3}\ m^3 = 1.85\ dm^3$

(ii)

Information / Reaction	**Deduction / Explanation**
J has molecular formula, $C_{10}H_{10}N_2O_2$	**J** is likely to contain a benzene ring due to the relatively high C to H ratio.
J exhibits optical activity	**J** contains a chiral centre and/or no plane of symmetry.
J is neutral**.**	**J** contains amide and/or –CN group. Or **J** is not carboxylic acid or amine or phenol.
J has no reaction with 2,4-DNPH	**J** is not aldehyde & ketone / carbonyl
$\mathbf{J} \xrightarrow[150\ ^\circ C]{H_2(g)\ /\ Ni} \mathbf{K}$	Reduction of nitrile. Since C=C is absent and there is increase of 4 H atoms from **J** to **K**, **J** contains –CN group.
$\mathbf{J} \xrightarrow[heat]{H_2SO_4(aq)} CO_2 + \text{resultant mixture} \xrightarrow{\text{distillation}} \text{residue} + \text{distillate } \mathbf{L}$ $\text{residue} \xrightarrow{base} \mathbf{M}$	**J** contains amide/ester/nitrile and undergoes acidic hydrolysis. Residue is an ionic salt. (**M** is a base.)
$\mathbf{M} \xrightarrow{Br_2(aq)} \mathbf{N}\ (C_6H_4NBr_3)$	**M** undergoes electrophilic substitution.  **N** is  Hence **M** is

<table>
<tr><td>L $\xrightarrow{\text{hot alkaline } I_2(aq)}$ yellow ppt</td><td>L contains the  $-\overset{H}{\underset{OH}{C}}-CH_3$ group</td></tr>
<tr><td>L decolourises acidified KMnO4(aq) to form P</td><td>L undergoes oxidation to form P. Hence, P is a methyl ketone / carbonyl compound.
(L cannot be a methyl ketone since J is not carbonyl compound and L is oxidised by $KMnO_4$ to form P.)</td></tr>
<tr><td>P $\xrightarrow{\text{2,4-DNPH}}$ Q (orange ppt)</td><td>Hence, L ($C_3H_6O_3$) is  $CH_3-\overset{H}{\underset{OH}{C}}-COOH$
P is  $CH_3-\overset{O}{\overset{\|}{C}}-COOH$
<u>Condensation</u>
Q is </td></tr>
<tr><td colspan="2">Combining the above deductions,
J can be:
 [or ]
K can be:
 [or ]</td></tr>
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