Answer for Paper 3

1 The elements of Group VII of the Periodic Table are called halogens, which mean "salt formers". They lack only one electron to form a complete shell, and are extremely active chemically.

This question examines the chemistry of two reactions of halogens.

(a) In the first reaction, a 1:2 mixture of H_2 and I_2 gases was mixed at a constant temperature of 430 ^oC and a constant pressure of 2 atm. The following equilibrium was set up.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g) \qquad \Delta H = -11\ kJ\ mol^{-1}$$

(i) Given that degree of dissociation of H_2 is 86 %, calculate the equilibrium constant, K_p for the above reaction under these conditions.

	H_2 (g)	+	I_2 (g)	⇌	2 HI (g)
Initial amt / mol	X		2x		0
Change / mol	–0.86x		–0.86x		+1.72x
Equilbrium / mol	0.14x		1.14x		1.72x

.

n(total) = 1.14x + 0.14x + 1.72x = 3x

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{(\frac{1.72x}{3x}2)^2}{(\frac{0.14x}{3x}2)(\frac{0.14x}{3x}2)}$$

= 18.5

(ii) Suggest, with reasoning, a way to increase degree of dissociation of H_2 for the above reaction.

Decrease temperature.
By Le Chatelier's Principle, when temperature is decreased,
The forward exothermic reaction is favoured.
Hence POE shift to the right, and degree of dissociation of H_2 increases.

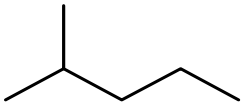
(iii) Deduce how K_p for the following system would be compared to your answer in **(i)**.

$$H_2\ (g) + Br_2\ (g) \rightleftharpoons 2HBr\ (g)$$

It will be larger since a stronger HBr bond is formed. Extent of equilibrium lies more to the right.

[7]

In another reaction, halogens can react with unreactive alkanes to form mono-substituted product. An example is the reaction of chlorine with 2-methylpentane shown below.



2-methylpentane

(b) **(i)** Explain why alkanes are generally unreactive.

The C-H bonds are non-polar and very strong

(ii) This reaction is seldom used for synthesis as there are many associated problems. Firstly, several isomeric products are formed. The relative ratio of the isomeric products may be more accurately determined if relative rates of abstraction of H atoms are taken into account.

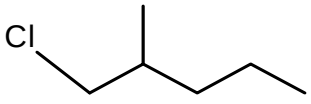
The relative rates of abstraction of H atoms are

Type of H atoms	Relative rate of abstraction
Primary	1
Secondary	4
Tertiary	6

By examining the difference in stability of the intermediates formed when different types of H atom are abstracted, explain the trend in relative rate of abstraction.

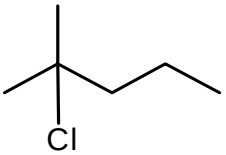
The tertiary radical is the most stable as it contains the most electron-donating alkyl groups which help to stabilise the electron-deficient radical centre. Hence, it is abstracted more easily/faster.

(iii) Predict the ratio of the following two products **A** and **B**, taking into account the relative rates of abstraction given in **(ii)**. Explain your reasoning.



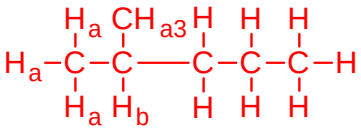
A

and



B

3



6 possible (primary) hydrogens (H_a) can be substituted to form **A**
1 possible (tertiary) hydrogens (H_b) can be substituted to form **B**
Assuming equal probability of abstraction,
Ratio of **A : B** = 6:1

However since a tertiary H is abstracted 6 times faster than a primary H,
Ratio of **A : B** = 6:1x6 = 1:1

(iv) Describe suitable chemical test(s) to distinguish compounds **A** and **B** in **(iii)**.

Add NaOH(aq) to both unknowns, heat (to form alcohols) **[1]** followed by $KMnO_4$, NaOH(aq), heat.

Observation for A: Purple $KMnO_4$ decolourised, Brown ppt of MnO_2 formed. (as 1^o alcohol formed is oxidised).

Observation for B: Purple $KMnO_4$ remains (as 3^o alcohol formed cannot be oxidised).

[7]

(c) Another problem of the reaction is multi-substitution.

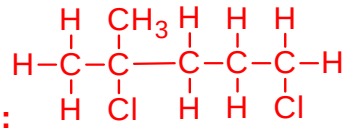
(i) Suggest the conditions that will give rise to formation of multi-substituted products.

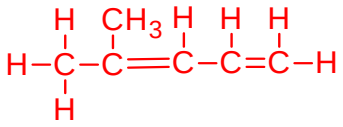
Excess Cl_2 or limited alkane. **[1]**

(ii) A di-substituted product **C** with molecular formula $C_6H_{12}Cl_2$ was obtained in the reaction of chlorine with 2-methylpentane.

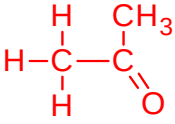
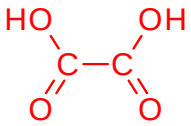
C does not exhibit optical activity. On warming with alcoholic KOH, a major product **D** is formed. When **D** is treated with hot acidified potassium manganate(VII) solution, effervescence was observed and the only organic product remaining gives a yellow precipitate with alkaline aqueous iodine.

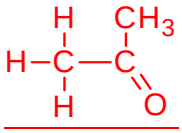
Use this information to deduce the structure of **C** and **D**, explaining your reasoning.

C: 

D: 

- **C** does not exhibit optical activity as it doesn't contain any chiral centre (no carbon with 4 different groups).
- Alkyl halide in **C** undergoes elimination with alcoholic KOH to form alkene in **D**.
- Alkene in **D** undergoes oxidative cleavage to form the following products:



CO_2



- undergoes oxidation to form yellow precipitate with alkaline aq iodine.
- The terminal alkene is oxidised to CO_2.
- Ethanedioic acid formed is also oxidised spontaneously to CO_2.

[6]

[Total: 20]

2 Precipitation plays an important function in growth of bones and teeth in our bodies.

5

Teeth and bones are largely composed of calcium phosphate salt $Ca_3(PO_4)_2$. In order for this precipitation to occur, the concentrations of the ions in blood must exceed the solubility product in the immediate region of deposition.

(a) Write an ionic equation with state symbols to show the formation of teeth and bones at the deposition region and hence an expression for the solubility product of the $Ca_3(PO_4)_2$ deposits. [2]

$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightleftharpoons Ca_3(PO_4)_2(s)$

Ksp of $Ca_3(PO_4)_2 = \left[Ca^{2+}\right]^3\left[PO_4^{3-}\right]^2$

(b) **(i)** At a temperature of 37 ^oC, the solubility product for calcium phosphate $Ca_3(PO_4)_2$ has a numerical value of 4×10^{-27}. In a sample of blood at a pH of 7.4, the concentrations of calcium and phosphate ions are found to be 1.2×10^{-3} mol dm^{-3} and 1.6×10^{-8} mol dm^{-3} respectively. State and explain if the above composition in blood will result in the growth or degeneration of teeth and bones.

ionic product = $\left[Ca^{2+}\right]^3\left[PO_4^{3-}\right]^2$ $= (1.2 \times 10^{-3})^3 \times (1.6 \times 10^{-8})^2$
$= 4.42 \times 10^{-25}$ $mol^5\ dm^{-15}$

Since IP > Ksp (4×10^{-27}), precipitation occurs resulting in growth.

(ii) Hence, state and explain if the pH environment of 7.4 in **(i)** is that for a growing child, a fully grown man or an old person.

At pH = 7.4, since there is deposition of calcium phosphate, it is the environment for a growing child.

[3]

(c) The pH at the area of growth may change due to metabolic processes in the body. The hydrogen ions that are present combine phosphate ions as hydrogen phosphate ions. This prevents growth of strong teeth and bones.

$$PO_4^{3-}(aq) + H^+(aq) \rightleftharpoons HPO_4^{2-}(aq)$$

Assuming that the $[HPO_4^{2-}]$ is maintained at 1.7×10^{-4} mol dm^{-3} by cell functions,

(i) calculate the pH that will result in neither growth nor degeneration at the teeth and bones deposition region when the concentration of calcium ions in blood is maintained at 1.2×10^{-3} mol dm^{-3}.
[K_a of $HPO_4^{2-} = 4.4 \times 10^{-13}$ mol dm^{-3}]

To prevent neither growth nor degeneration, the $[PO_4^{3-}(aq)]$ must be at saturation (or equilibrium with the $Ca_3(PO_4)_2(s)$,

$[PO_4^{3-}(aq)] = \sqrt{\frac{4\times10^{-27}}{(1.2\times10^{-3})^3}} = 1.52 \times 10^{-9}$ moldm^{-3}

$pH = -\log[H^+] = -\log\left(\frac{4.4\times10^{-13}\times1.7\times10^{-4}}{1.52\times10^{-9}}\right) = 7.3$

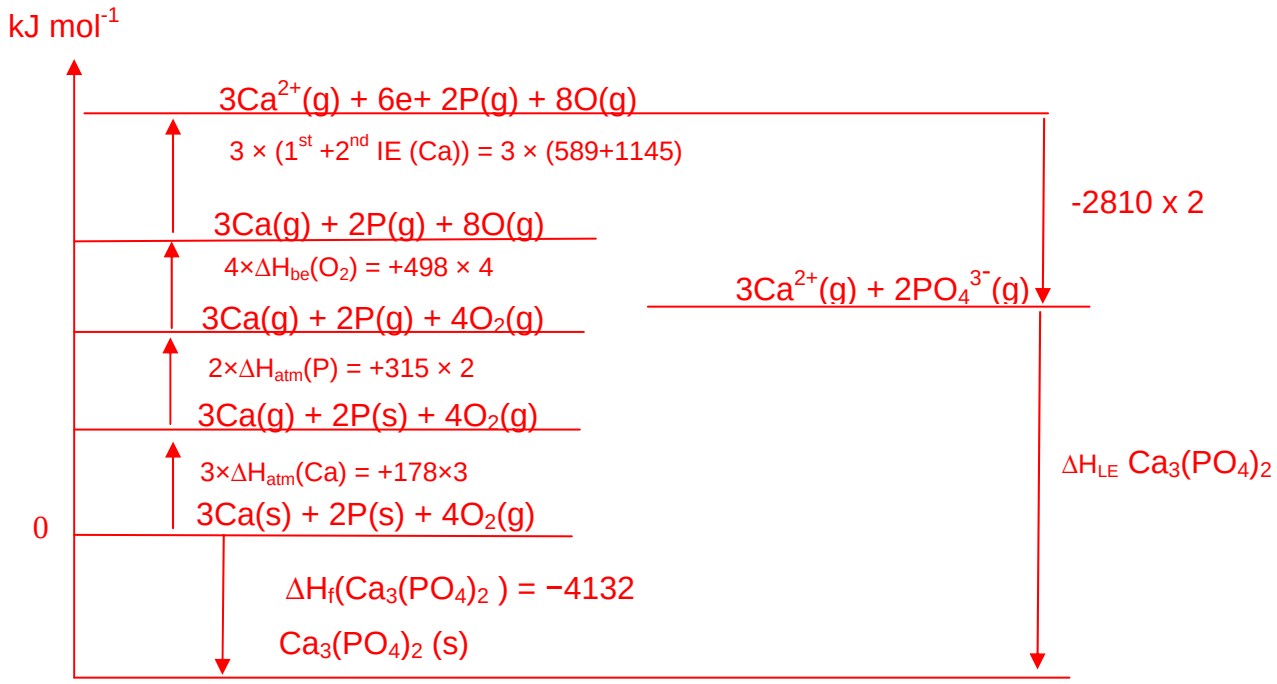
(ii) Suggest another acid–conjugate base equation that accounts for the constant supply of HPO_4^{2-} ions from cell functions.

$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq)$ [state symbols can be ignored].

[3]

(d) (i) Construct an energy level diagram for the formation of $Ca_3(PO_4)_2$ from its elements using relevant data from the table below and other appropriate values in the *Data Booklet*. Hence calculate the lattice energy of $Ca_3(PO_4)_2$.

Enthalpy	ΔH / kJ mol^{-1}
Standard enthalpy change of formation of $Ca_3(PO_4)_2$	−4132
Standard enthalpy change of atomisation of Ca	+178
Standard enthalpy change of atomisation of P	+315
$P(g) + 4O(g) + 3e \rightarrow PO_4^{3-}(g)$	−2810



By Hess' law,

$\Delta H_{LE}\ Ca_3(PO_4)_2$
= +2810 x 2 - 3 × (589+1145) - 498 × 4 - 315 × 2 - 178×3 – 4132
= -6870 kJmol^{-1}

7

(ii) Using your answers to **(i)** and other enthalpy change value if any, explain why $Ca_3(PO_4)_2$ is insoluble.

$\Delta H_{solution}$ $Ca_3(PO_4)_2$ = $-\Delta H_{LE}$ $Ca_3(PO_4)_2$ + $3\Delta H_{hydration}$ Ca^{2+} + $2\Delta H_{hydration}$ PO_4^{3-}

$-\Delta H_{LE}$ $Ca_3(PO_4)_2$ is very positive as seen in part **(d)** and both Ca^{2+}, PO_4^{3-} are have large radii, resulting in less negative $\Delta H_{hydration}$ values.

Hence $\Delta H_{solution}$ $Ca_3(PO_4)_2$ will likely to be positive. Making it insoluble.

[6]

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

Group VII elements exist as ions and play a vital role in bodily functions. The following observations are made about Group VII elements and their reactions. Explain the observations made.

(i) F_2 cannot be prepared by electrolytic oxidation of aqueous F^- solutions.

The electrode potential value of F_2 F^- is too electropositive, hence not favouring the backward reaction.

In an aqueous medium, H_2O will be preferentially oxidised to oxygen gas instead.

(ii) HI can be prepared by treating NaI with phosphoric acid, H_3PO_4 but not with concentrated sulfuric acid.

Phosphoric displaces HI from I^- and it does not further oxidise HI to I_2. H_2SO_4 on the other hand oxidises HI to I_2, itself being reduced to H_2S.

(iii) Interhalogen compounds such as IF_3, IF_5 and IF_7, BrF_3, BrF_5, ClF_3, ICl_3 exists. On the other hand, ClF_5 is not easily formed and $BrCl_3$ does not exists.

The large size of the I atom can accommodate up to seven small F atoms. As the central atom gets smaller from Br to Cl, it cannot accommodate as many F atoms.

As the surrounding atom gets bigger, the steric hindrance prevents too many of it from surrounding the central atom as well.

[6]

[Total: 20]

3 (a) Period 3 elements react with oxygen to form the corresponding oxides of varying acid-base nature. Using magnesium, aluminium and phosphorus as examples, describe the acid-base nature of the oxides across Period 3 with suitable equations. [4]

Magnesium oxide is a basic oxide and it reacts readily with acids to form salt and water.

$MgO\ (s) + 2H^+\ (aq) \rightarrow Mg^{2+}\ (aq) + H_2O\ (l)$

Aluminium oxide is an amphoteric oxide and it can react with both acids and alkali to give a salt.

$Al_2O_3\ (s) + 6H^+\ (aq) \rightarrow 2Al^{3+}\ (aq) + 3H_2O\ (l)$

$Al_2O_3\ (s) + 2OH^-\ (aq) + 3H_2O\ (l) \rightarrow 2[Al(OH)_4]^-\ (aq)$

Phosphorus trioxide / pentoxide is acidic and reacts with alkali to give a salt and water.

$P_4O_6\ (s) + 12OH^-\ (aq) \rightarrow 4PO_3^{3-}\ (aq) + 6H_2O\ (l)$

OR

$P_4O_{10}\ (s) + 12OH^-\ (aq) \rightarrow 4PO_4^{3-}\ (aq) + 6H_2O\ (l)$

(b) Aluminium is a reactive metal but its reactivity is limited due to a layer of inert aluminium oxide being formed. Both aluminium and its oxide react readily with aqueous sodium hydroxide to give similar products. Aluminium, however, produces another product which is a combustible gas.

(i) Write a balanced equation for the reaction when aluminium is heated in aqueous sodium hydroxide.

$2Al\ (s) + 2OH^-\ (aq) + 6H_2O\ (l) \rightarrow 2[Al(OH)_4]^-\ (aq) + 3H_2\ (g)$

(ii) Explain why a homogenous solution is obtained in **(i)**.

The aluminium hydroxide formed is amphoteric and can react with hydroxide to form $[Al(OH)_4]^-$.

The resulting product is charged and can form ion−dipole interaction with water thus becomes soluble.

[3]

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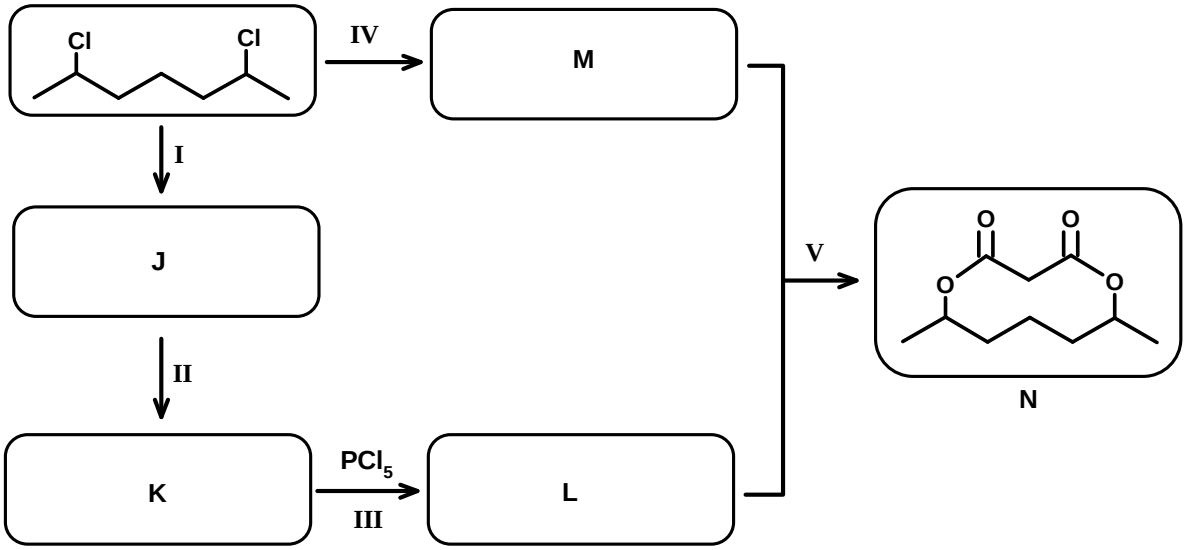
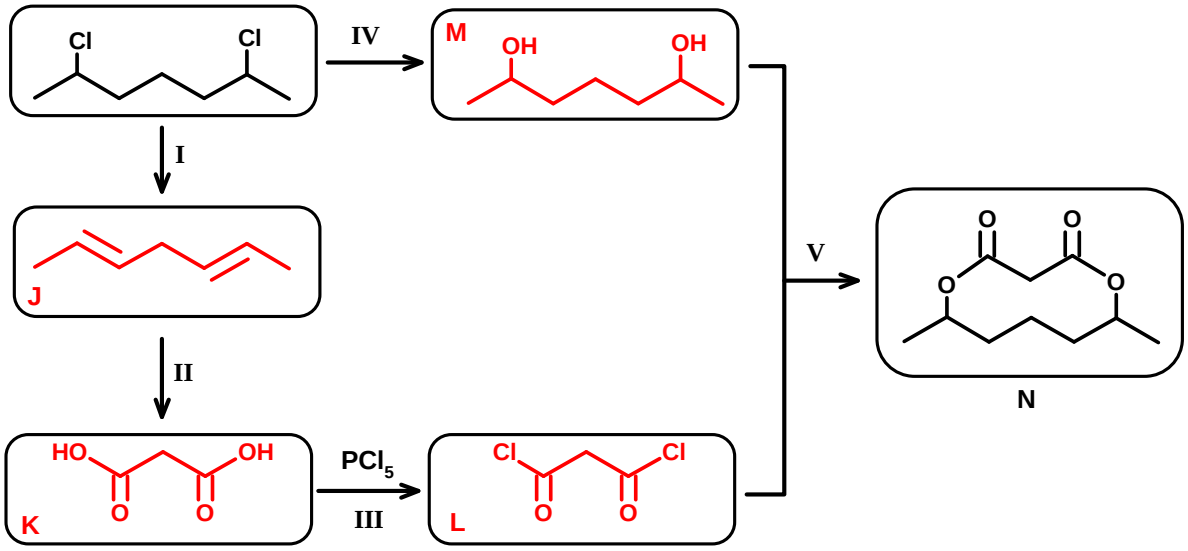
(c) Using 2,6−dichloroheptane as the starting compound, suggest the reagents and conditions for steps I, II and IV and the products **J** to **M** in the synthetic scheme below. [7]



Answer



Reagents and Conditions:

Step I: Ethanolic NaOH, heat under reflux

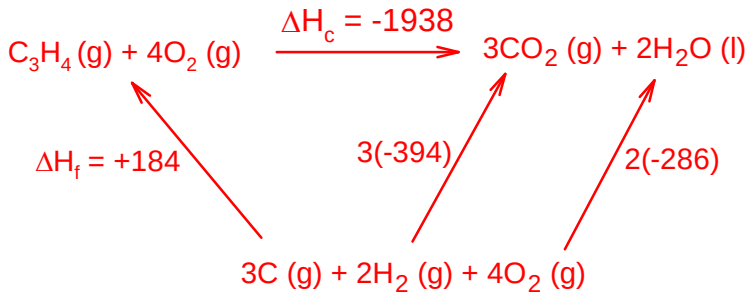
Step II: aq H_2SO_4, aq $KMnO_4$, heat under reflux

Step IV: aq NaOH, heat under reflux

(d) (i) Propyne, C_3H_4, like ethyne, C_2H_2, is commonly used for blow torches to cut metals in heavy metal industries.

By drawing an appropriate energy cycle, determine the enthalpy of combustion of propyne, given the following enthalpy values:

$\Delta H_f(C_3H_4) = +184$ kJ mol^{-1}
$\Delta H_c(C) = -394$ kJ mol^{-1}
$\Delta H_c(H_2) = -286$ kJ mol^{-1}



ΔH_c (propyne) = 3(−394) + 2(−286) − 184
= −1938 kJ mol^{-1}

(ii) Determine the enthalpy of combustion of propyne using bond energy values. Explain why the use of bond energy values to calculate the enthalpy of combustion is significantly less exothermic that those obtained in **(i)**.

$H_3C{-}C{\equiv}CH(g) + 4O_2(g) \longrightarrow 3\,O{=}C{=}O\,(g) + 2\,H{-}O{-}H\,(l)$

BD = 4(+410) + (+350) + (+840) + 4(+496)
BF = 6(+740) + 4(+460)

$\Delta H_c(C_3H_4) = +4814 + (-6280) = -1466$ kJ mol^{-1}

$\Delta H_{vap}(H_2O)$ is not taken into consideration.

[6]

[Total: 20]

4 Nickel is a typical transition element which is commonly used as a catalyst and metal for electroplating. Nickel also forms complex ions with ligands such as H_2O, NH_3 and $NH_2CH_2CH_2NH_2$ to give various coloured complexes.

(a) What do you understand by the terms *transition element*, *ligand* and *complex ion*? [3]

A transition element is a d-block element that can form one or more stable ions with a partially filled d-subshell.

A ligand is a molecule or anion with at least one lone pair of electrons that it can use to form coordinate bond to the central metal atom/ion in a complex ion.

A complex ion is a species that contains a central metal atom/ion surrounded by ligands which forms coordinate bonds to the metal centre.

(b) **(i)** Explain why transition metal complexes are coloured.

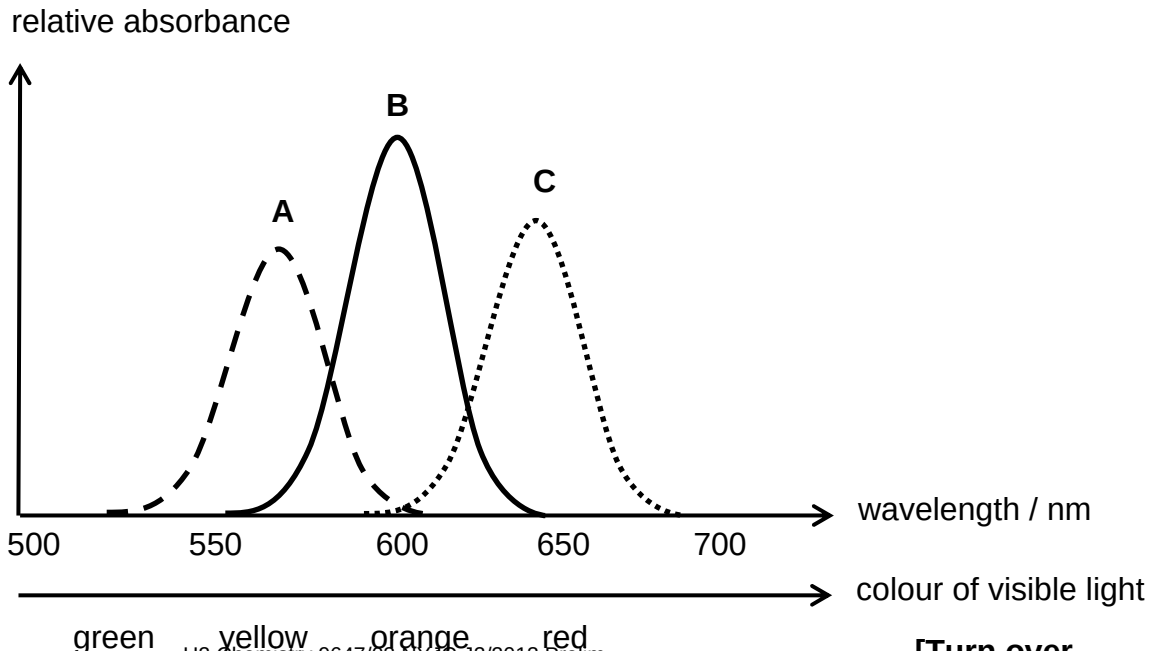
In the presence of ligands, the degenerate d orbitals of the transition metal split into 2 groups with an energy gap, ΔE.

When visible light passes through the solution of the transition metal ion, the wavelength of light corresponding to the energy gap is absorbed by the d electron in the lower energy level to promote to a vacant d orbital at the higher energy level./ for d-d transition**.**

The complementary colour corresponding to the unabsorbed wavelength is observed.

(ii) Complex ions of nickel such as $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ are green, blue and violet colour respectively.

The visible absorption spectra of the three complex ions of nickel are shown below:



Suggest an explanation for the difference in colour of the three complexes and using the colours of the complexes given, assign the peaks **A**, **B** and **C** to the three complex ions of nickel.

Due to the presence of different ligand, the d orbitals are split to different extent/ energy gap, ΔE. Light of different wavelength will be absorbed by the d electron of Ni(II) in the three complex ions and hence different complementary colours are observed.

A: $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ absorbs yellow and appears violet
B: $[Ni(NH_3)_6]^{2+}$ absorbs orange and appears blue
C: $[Ni(H_2O)_6]^{2+}$ absorbs red and appears green

[5]

(c) When Ni^{2+} (aq) is mixed with an excess of NH_3 (aq), each H_2O is replaced by a NH_3 at a time. The stepwise formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$ can be summarised by the following equations with their associated equilibrium constants:

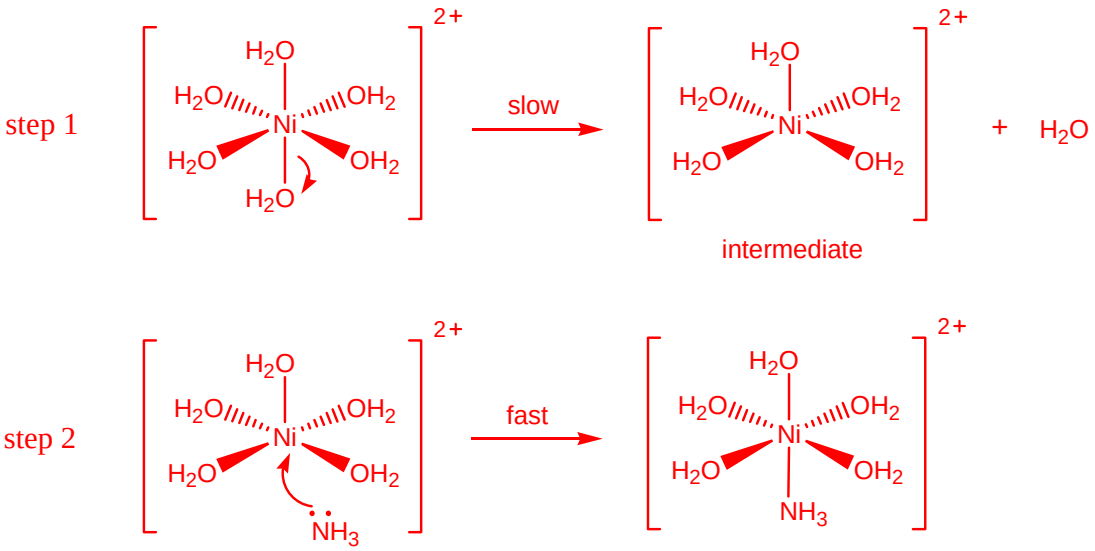
Step 1: $[Ni(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Ni(H_2O)_5(NH_3)]^{2+} + H_2O$ $K_1 = 630\ mol^{-1}dm^3$

Step 2: $[Ni(H_2O)_5(NH_3)]^{2+} + NH_3 \rightleftharpoons [Ni(H_2O)_4(NH_3)_2]^{2+} + H_2O$ $K_2 = 160\ mol^{-1}dm^3$

and so on for steps 3, 4 and 5.

Step 6: $[Ni(H_2O)(NH_3)_5]^{2+} + NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + H_2O$ $K_6 = 1.1\ mol^{-1}dm^3$

(i) The stepwise formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$ undergoes a dissociative mechanism which resembles a S_N1 mechanism in organic chemistry. Suggest a possible mechanism for Step 1 and show clearly how the shape of the complex ion changes.



Trigonal bipyramidal intermediate is accepted as well.

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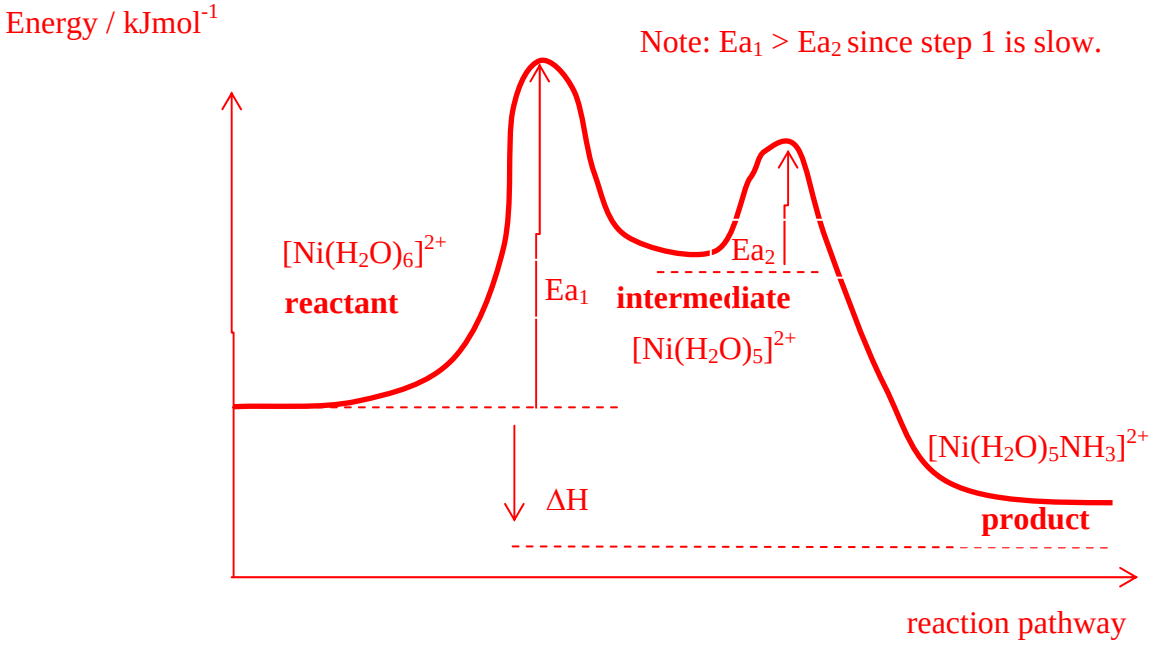
(ii) Sketch an energy profile diagram for the suggested mechanism in **(i)** given the reaction is exothermic.



(iii) Suggest a possible reason for the decrease in value of the equilibrium constant for each successive replacement of water by ammonia ligands.

For each successive substitution, the number of sites available for the ammonia ligands to replace decreases.

[6]

(d) $[Ni(H_2O)_6]^{2+}$ can also undergo ligand exchange reaction with $NH_2CH_2CH_2NH_2$ to form $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$. Using the signs of ΔG, ΔH and ΔS, explain how the formation of $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ would compare to that of $[Ni(NH_3)_6]^{2+}$. [3]

ΔH for formation of $[Ni(NH_3)_6]^{2+}$ and $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ is similar due to breaking of similar Ni–O bonds and forming of similar Ni–N bonds.

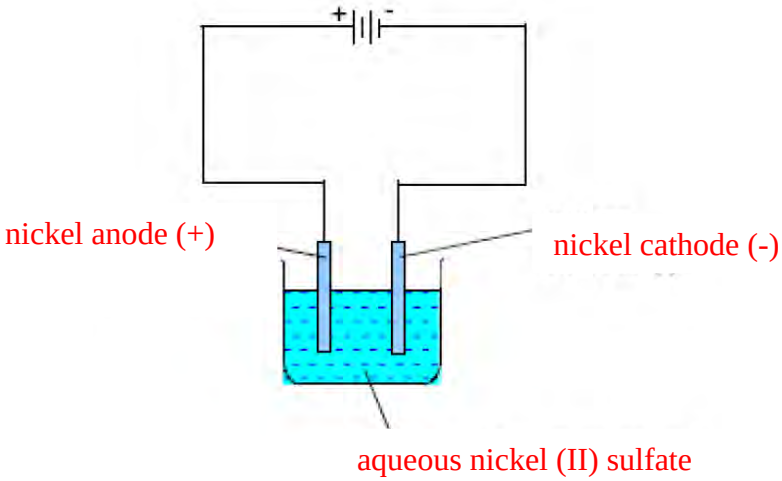
ΔS for formation of $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ would be more positive than that of $[Ni(NH_3)_6]^{2+}$ because there is an increase in number of aqueous particles as $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ is formed, allowing more ways of arranging the particles.

Since ΔH for formation of $[Ni(NH_3)_6]^{2+}$ and $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ are similar and ΔS for formation of $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ is more positive than that of $[Ni(NH_3)_6]^{2+}$, ΔG for formation of $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ would be more negative than that of $[Ni(NH_3)_6]^{2+}$ and hence more spontaneous.

(e) With the aid of a clearly labelled diagram, show the calculations you would carry out to determine a value for the Avogadro constant by the electroplating of nickel from nickel(II) ions.

You may assume that you are provided with the following data.

- mass of nickel deposited, m
- current used, I
- time taken, t



Calculations:

amount of nickel metal deposited = $\frac{m}{58.7}$ mol

amount of charge required to deposit 1 mol of Ni = $\frac{It}{\frac{m}{58.7}} = \frac{58.7It}{m}$ C

At the cathode: $Ni^{2+} + 2e \rightarrow Ni$

Quantity of charge per mol of electron passes = $\frac{58.7It}{m} \times \frac{1}{2} = \frac{58.7It}{2m}$

Given that the charge of an electron is 1.60×10^{-19} C,

Avogadro's constant = $\frac{\frac{58.7It}{2m}}{1.6 \times 10^{-19}} = \frac{58.7It}{2 \times 1.6 \times 10^{-19} m}$

[3]

[Total: 20]

5 (a) Amino acids play central roles both as building blocks of proteins and as intermediates in metabolism. The 20 amino acids that are found within proteins convey a vast array of chemical versatility and they have relatively high melting points and are soluble in water.

(i) Define the secondary structure of proteins.

The secondary structure refers to the **repeated coiling and folding** of a polypeptide chain in a regular arrangement.

The two common repeating structural patterns in proteins are**:** α**-helix** and β**-pleated sheets**. Both structures are stabilised by **hydrogen bonding** between the oxygen atom of the C=O group of a peptide bond and the hydrogen atom of the N-H group of another peptide bond.

(ii) What is meant by the term denaturation of proteins?

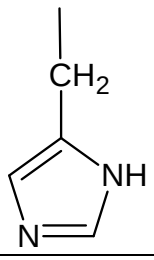
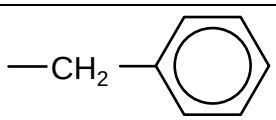
Denaturation is an irreversible process when the protein loses its biological activity. When proteins are denatured, the R–group interactions are destroyed, only the secondary, tertiary and quaternary structures are disrupted. This results in protein disintegrating to form random coils of polypeptide chains.

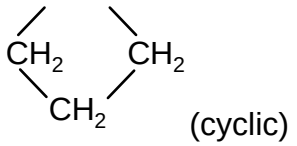
(iii) Suggest a brief outline of one method by which proteins may be denatured.

Proteins may be denatured by addition of acid to it. This will disrupt the ionic bonding originally present between the R groups.

[4]

(b) An octapeptide **A** was analyzed and contained the following amino acids:

Amino acid	abbreviation	R-group	Number of residues
Aspartic acid	Asp	$-CH_2CO_2H$	1
Glycine	Gly	– H	2
Histidine	His		1
Phenylalanine	Phe		1

Proline	Pro	 (cyclic)	2
Valine	Val	– $CH(CH_3)_2$	1

(i) Analysis showed that the C-terminus contained an amino acid which is optically inactive and partial hydrolysis gives the following fragments:

Val-Pro-His, Gly-Asp-Pro-Phe, Pro-Phe-Val

Use the above results to deduce the amino acid sequence of the octapeptide **A** and explain your reasoning.

Complete Sequence:

Gly-Asp-Pro-Phe

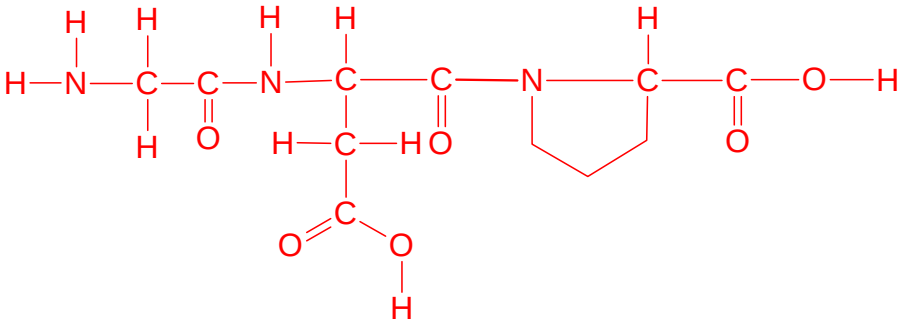
Pro-Phe-Val

Val-Pro-His

Gly

Octapeptide: Gly-Asp-Pro-Phe-Val-Pro-His -Gly

(ii) Draw the displayed formula of Gly-Asp-Pro which is part of the octapeptide chain in **A**.



[4]

(c) Histidine is utilized by your body to develop and maintain healthy tissues. It is especially important in the myelin sheath that coat nervous cells to ensure the transmission of messages from your brain to organs throughout your body. Histidine also stimulates the secretion of the digestive enzymes gastrin and is also required to manufacture both red and white blood cells.

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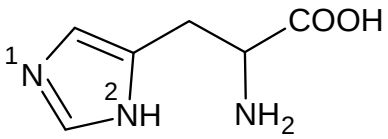


Structure of histidine

Histidine contains a total of 3 nitrogen atoms and each N atom exhibit different properties in aqueous solution.

(i) Considering the orbital arrangement of the atoms, explain why ^{2}N atom in histidine is less basic than ^{1}N atom.

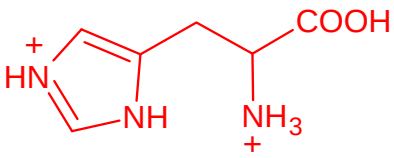
The lone pair of electrons on the ^{2}N atom is less available for donation to the proton via dative bonding because the lone pairs of electrons occupy an sp^3 orbital that can be delocalised into the ring.

While on the other hand, the lone pair of electrons on the ^{1}N atom is available for donation to the proton via dative bonding because the lone pairs of electrons occupy the sp^2 orbital.

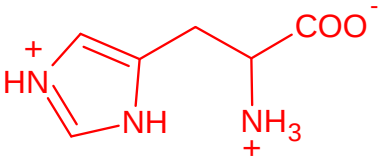
(ii) There are three pK_a values associated with the histidine: 1.8, 6.0, 9.2. Assuming that the ^{2}N atom does not exhibit any basic properties, make use of the three pK_a values to suggest the major species present in solutions of histidine with the following pH values.

- pH 1
- pH 5
- pH 7
- pH 11

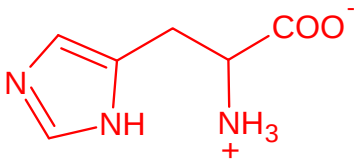
pH 1:



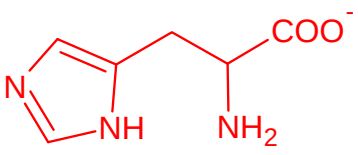
pH 5:



pH 7:



pH 11:



(iii) Consider the buffer solution at pH = 5, calculate what fraction of the histidine side chains will carry a positive charge at pH 5.

$$pH = pKa + \log \frac{[salt]}{[acid]}$$

$$5 = 6 + \log \frac{[salt]}{[acid]}$$

$$\frac{[salt]}{[acid]} = 10^{-1} = \frac{1}{10}$$

Since 10[salt] = [acid]

Therefore at pH 5, 10/11 of the histidine will be in the protonated form.

[8]

(d) 25.0 cm^3 of 0.150 mol dm^{-3} of diethylamine solution, $(CH_3CH_2)_2NH$, was placed in a conical flask and titrated against a solution of 0.200 mol dm^{-3} hydrochloric acid from a burette.

Given that the K_b of $(CH_3CH_2)_2NH$ is 8.60×10^{-4} mol dm^{-3},

(i) explain what is meant by the term base dissociation constant, K_b of diethylamine.

The base dissociation constant is defined as $K_b = \frac{[OH^-][(CH_3CH_2)_2NH_2^+]}{[(CH_3CH_2)_2NH]}$

(ii) Calculate the pH at equivalence point.

V(HCl) at neutralisation point = $\frac{(25.0)(0.150)}{(0.200)} = 18.75$ cm^3

At equivalence point, [salt] = $\frac{n_{salt}}{V_T} = \frac{(25.0)(0.150)}{(25.0 + 18.75)} = 0.08571$ mol dm^{-3}

Since salt is an acidic in nature, $[H^+] = \sqrt{\frac{1 \times 10^{-14}}{8.6 \times 10^{-4}} \times 0.08571} = 9.983 \times 10^{-7}$

$pH = -\log(9.983 \times 10^{-7}) = 6.00$

[4]

[Total: 20]