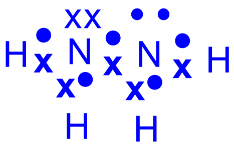
Answers for MJC 2008 H2 Chem Prelim Paper 3

1(a) Hydrazine, N_2H_4, has an ammonia-like odor, and is derived from the same industrial chemistry processes that manufacture ammonia. In some cases, hydrazine behaves like ammonia in chemical reactions. For example, hydrazine is able to form a product when it reacts with boron trifloride, BF_3, in a molar ratio of 1:1.

(i) Draw a 'dot-and-cross diagram' to show the electronic structure of a molecule of N_2H_4. Use the electron repulsion theory to pedict the shape of this molecule and state its bond angle.

[2]



- Bond angle is compressed to 107° and N_2H_4 is trigonal pyramidal about central N atom.

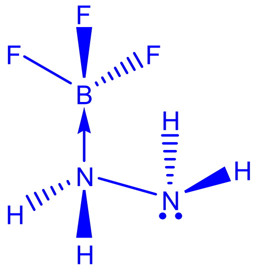
(ii) Explain why hydrazine form a product with BF_3 when they react in a molar ratio of 1:1.

[1]

In BF_3, B is electron deficient with only 6 electrons around it. Hence, B can accept the 1 lone pair of electrons from N in N_2H_4 via dative bonding to attain a stable octet configuration.

(iii) Draw a diagram to show the likely shape of the product formed.

[1]



(b) Hydrazine is used as rocket fuel and to prepare gas precursors used in air bags. Approximately 260 thousand tonnes of hydrazine are manufactured annually.

Liquid hydrazine undergoes combustion according to the following equation:

$$N_2H_4(l) \quad + \quad O_2(g) \quad \rightarrow \quad N_2(g) \quad + \quad 2H_2O(l)$$

A chemist conducted an experiment to determine the standard enthalpy change of combustion of hydrazine. In the experiment, 0.210g of hydrazine was burnt as fuel to heat up a beaker containing 200 cm^3 of water. The temperature of water rose by 4 ^oC. You may assume the process has 80 % efficiency.

(i) Explain what is meant by standard enthalpy change of combustion of hydrazine.

[1]

Standard enthalpy change of combustion (ΔH_c^θ) of hydrazine is the energy released when one mole of the hydrazine is completely burnt in oxygen at 298K and 1 atm.

(ii) Calculate the standard enthalpy change of combustion of hydrazine.

[2]

Amount of heat absorbed by water, Q = 200 x 4 x 4.18 = 3344 J

Amount of heat released by reaction, Q' = Q / 0.8 = 4180 J

No of moles of $N_2H_4 = 6.56 \times 10^{-3}$

Standard enthalpy change of combustion of hydrzaine

= $\underline{\mathbf{- 6.37 \times 10^2\ kJ\ mol^{-1}}}$

(iii) Given the following data:

enthalpy change of formation of steam = - 242 kJ mol^{-1}
enthalpy change of vapourisation of water = + 44 kJ mol^{-1}

and using the value you have calculated in ***b(ii),*** draw an appropriate energy cycle to determine the standard enthalpy of formation of hydrazine.

[3]

$$\begin{tikzcd}
N_2\ (g) + 2H_2\ (g) \arrow[r, "\Delta H_f(N_2H_4)"] \arrow[d, "2 \text{ x } \Delta H_f(H_2O(g))"'] & N_2H_4\ (l) \arrow[d, "\Delta H_c(N_2H_4)"] \\
N_2(g) + 2H_2O\ (g) & N_2(g) + 2H_2O\ (l) \arrow[l, "2 \text{ x } \Delta H_v(H_2O)"']
\end{tikzcd}$$

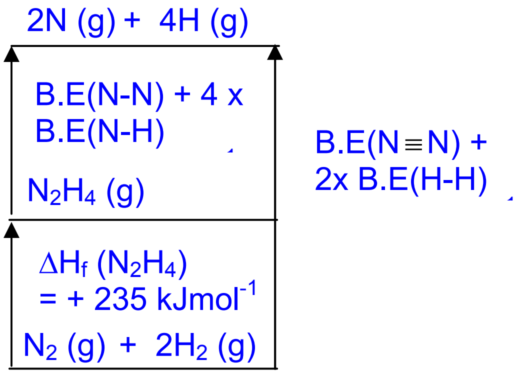
By Hess' law,

$\Delta H_f\ (N_2H_4) = 2(-242) - (-637) - 2(+44) =$ <u>**+ 65 $kJmol^{-1}$**</u>

The standard enthalpy change of formation of hydrazine gas is +235 kJ mol^{-1}.

(i) Using appropriate data from the *Data Booklet*, draw an energy level diagram to calculate the average bond energy of N-H bond in hydrazine.

[3]



By Hess Law,

160 + 4 x B.E(N-H) + 235 = 994 + 2(436)

B.E (N-H) = <u>368 kJ mol^{-1}</u>

(ii) Suggest a reason for the difference in the N-H bond energy value obtained from **(c)(i)** with the value given in the Data Booklet.

[1]

The bond energy values obtained from the Data Booklet are average values and would differ from the experimental values.

(d)(i) When sodium thiosulphate is reacted separately with bromine and iodine, different products are formed. Using the following data, and data from the Data Booklet, describe and explain the difference.

$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$ $E^\theta = +0.09V$
$4SO_2 + 4H^+ + 6e \rightleftharpoons S_4O_6^{2-} + 2H_2O$ $E^\theta = +0.51V$
$SO_4^{2-} + 4H^+ + 2e \rightleftharpoons SO_2 + 2H_2O$ $E^\theta = +0.17V$

[3]

Oxidising power of Br_2 is stronger than I_2.

$E_{cell} = +0.98V > 0 \Rightarrow$ Reaction is feasible.
Hence, bromine oxidizes $S_2O_3^{2-}$ to $S_4O_6^{2-}$.

$E_{cell} = +0.56V > 0 \Rightarrow$ Reaction is feasible.
Hence, bromine oxidizes $S_4O_6^{2-}$ to SO_2.

$E_{cell} = +0.90V > 0 \Rightarrow$ Reaction is feasible.
Hence, bromine oxidizes SO_2 to SO_4^{2-} .

$E_{cell} = +0.45V > 0 \Rightarrow$ Reaction is feasible.
Hence, iodine oxidizes $S_2O_3^{2-}$ to $S_4O_6^{2-}$.

Bromine can oxidize $S_2O_3^{2-}$ to SO_4^{2-} while iodine can only oxidize $S_2O_3^{2-}$ to $S_4O_6^{2-}$.

(ii) Describe and explain why the trend of boiling points of hydrogen halides differs from the trend of thermal stability of hydrogen halides down Group VII.

[3]
[Total : 20]

Thermal stability decreases from HCl to HI
while the boiling point increases from HCl to HI

Down the group,
Bond length of H-X increases
Bond strength of H-X decreases
Hence, bond dissociation energy of HX decrease

Down the group,
The molecular size of hydrogen halide molecules increases.

The greater the extent of distortion of the electron cloud, resulting in stronger van der Waal's forces of attraction between the molecules.

Hence, more energy is required to overcome these stronger van der Waals' forces.

2 An example of a gas-phase reaction is the decomposition of nitryl chloride NO_2Cl. At 700K, NO_2Cl decomposes according to the following equation.

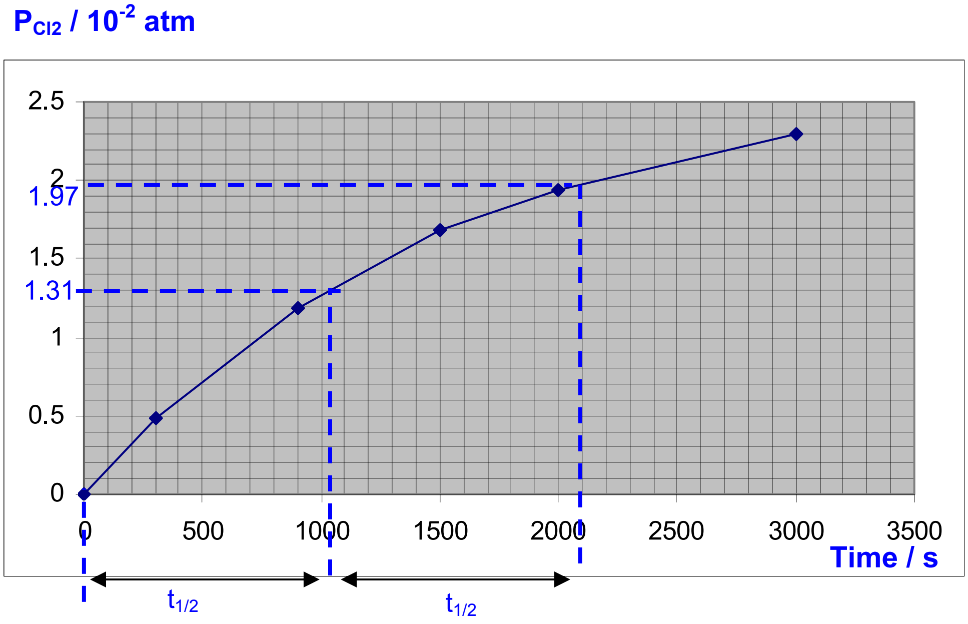
$$2\,NO_2Cl\,(g) \rightarrow 2\,NO_2\,(g) + Cl_2\,(g)$$

The initial pressure of NO_2Cl is 0.0524 atm. The rate of the reaction is followed by measuring the partial pressure of Cl_2 as it changes with time, t. In such as an experiment, the partial pressure of Cl_2 increased as follows.

Time, t /s	0	300	900	1500	2000	3000
Partial pressure of $Cl_2 \times 10^{-2}$ /atm	0	0.48	1.18	1.68	1.94	2.30

(a) (i) When the reaction is complete, the partial pressure of Cl_2 is 0.0262 atm. Plot a graph to show how the partial pressure of Cl_2 changes during the first 3000s of the reaction and determine the order of reaction with respect to NO_2Cl. Hence, write a rate equation for the decomposition of NO_2Cl.

[4]



Since half-life at 1050s and is a constant , the order of reaction with respect to $NOCl_2$ =1

(ii) Calculate the rate constant for the above reaction, stating its units.

[1]

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1050}$$

k = **$\underline{6.60 \times 10^{-4}\ s^{-1}}$**

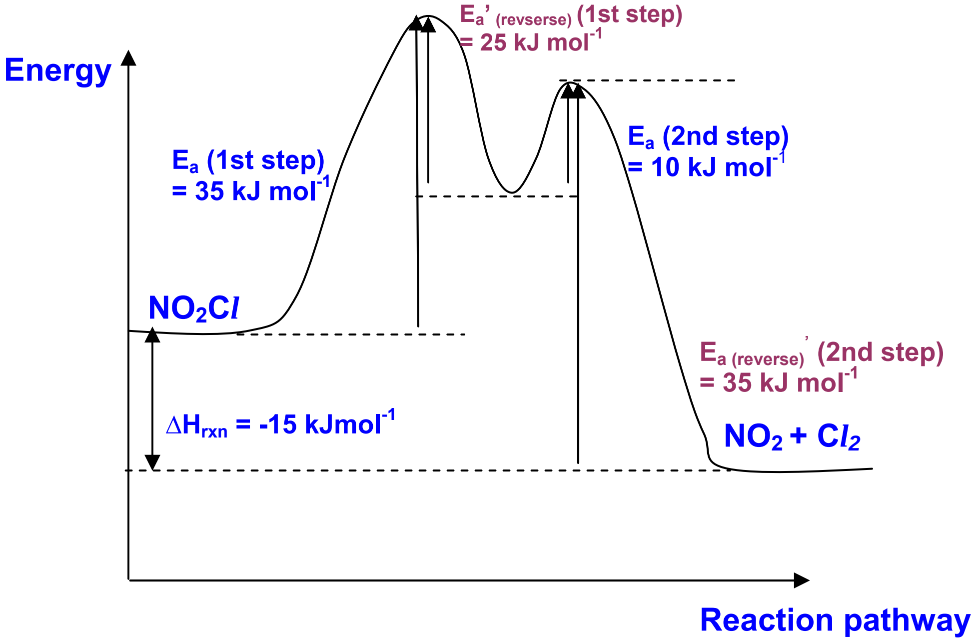
=

(iii) At a certain temperature, the decomposition of NO_2Cl follows a two-step mechanism as shown:

Step 1 : $NO_2Cl \rightarrow NO_2 + Cl$
Step 2 : $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$

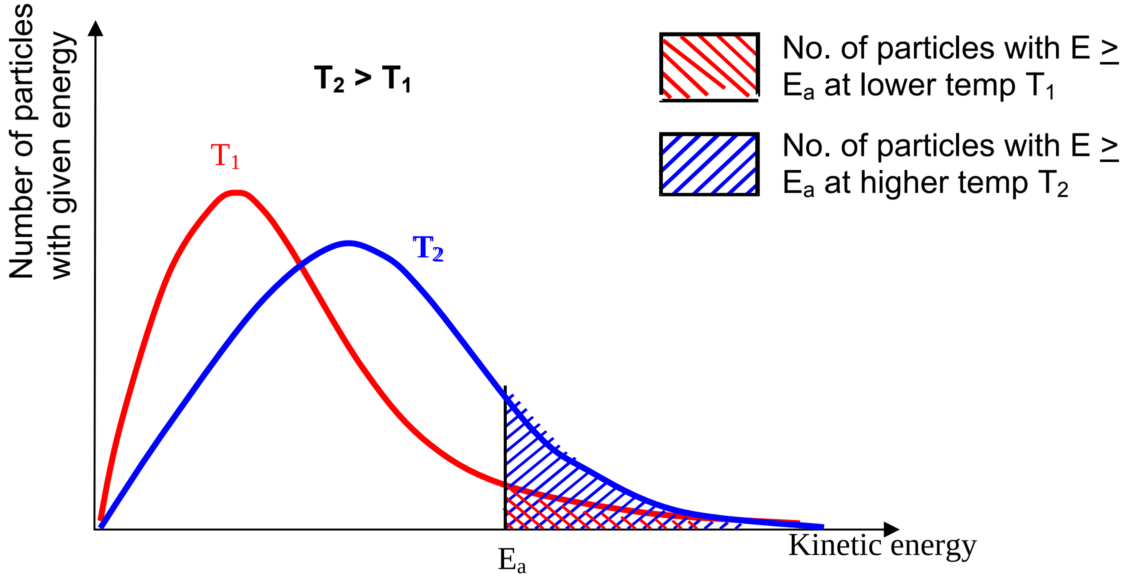
The enthalpy change for the overall process is -15 kJ mol^{-1}. For the first step, the activation energy for the forward reaction is 35 kJ mol^{-1} and that of a reverse reaction is 25 kJ mol^{-1}. The activation energy for the reverse reaction of the second step is 35 kJ mol^{-1}. Draw a labelled energy profile diagram based on the above given data.

[2]



(iv) The rate of decomposition of NO_2Cl is found to increase when temperature is raised. With the aid of a sketch of the Maxwell-Boltzmann distribution curve, explain how a small increase in temperature can lead to a large increase in the rate of decomposition.

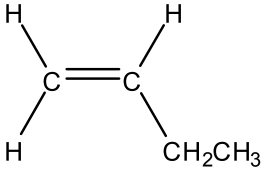
[3]



When temperature increases,

- kinetic energy of reactant particles increases
- Number of reactant particles with $E > E_a$ increases
- Number of effective collisions per unit time increases.
- Rate of reaction is proportional to number of effective collisions per unit time
- Hence, rate of reaction increases.

(b) C_4H_8 can exist in 4 non-cyclic isomers forms, **W**, **X**, **Y** and **Z**.
W has the structure as shown:



W reacts with chlorine under two different conditions.

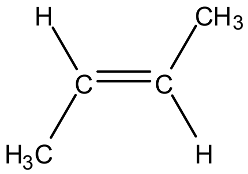
Reaction **I**:
In the absence of light, **W** reacts with Cl_2 dissolved in CCl_4 to give an equimolar mixture of two isomers **A** and **B**.

Reaction **II**:
W reacts with Cl_2 gas under ultraviolet light to give $H_2C{=}CH(CH_2CH_2Cl)$. However, the presence of trace amount of nitrogen monoxide may decrease the rate of reaction.

(i) Draw the isomeric structures of **X**, **Y** and **Z** and identify the types of isomerism present.

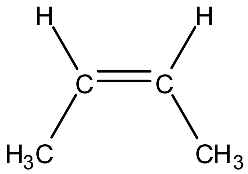
[3]

Geometric isomerism



X

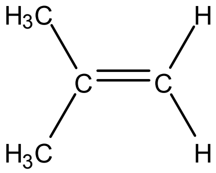
trans isomer



Y

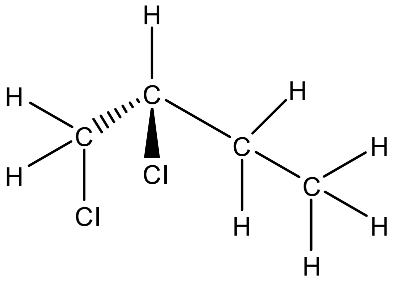
cis isomer

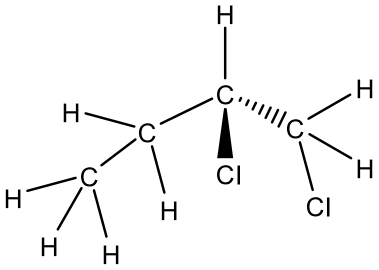
Structural isomerism (or chain isomerism)



(ii) Draw the displayed formulae of isomers **A** and **B** in reaction **I**.

[2]





(iii) Explain why the following step rarely occurs in reaction **II**.

$$H_2C{=}CH(CH_2CH_3) \;+\; Cl\bullet \;\rightarrow H_2C{=}CH(CH_2CH_2Cl) \;+\; H\bullet$$

[1]

H radical does not exist since it is highly reactive/unstable.

(iv) Suggest why the presence of nitrogen monoxide will slow down reaction **II**.

[1]

Nitrogen monoxide contains a lone electron on the nitrogen atom which can react with the Cl_2 gas to form NOCl.

This decreases the concentration of Cl_2 gas.

Hence, there is a decrease in the rate of the slow step of the free radical substitution reaction that generates Cl radicals.

(c)(i) Chlorine forms many compounds with different oxidation states. With the aid of balanced equations, explain how different chlorine-containing products are obtained when chlorine reacts with sodium hydroxide under different conditions.

[3]
[Total : 20]

With cold aqueous NaOH,

Cl_2 undergoes disproportionation to give a mixture of chloride and chlorate(I) ions.

$$2NaOH\ (aq) + Cl_2\ (aq) \rightarrow NaCl\ (aq) + NaClO\ (aq) + H_2O\ (l)$$

With hot aqueous NaOH,

ClO^- undergoes further disproportionation to give a mixture of chloride and chlorate(V) ions.

$$6\ NaOH\ (aq) + 3\ Cl_2\ (aq) \rightarrow 5\ NaCl\ (aq) + NaClO_3\ (aq) + 3\ H_2O\ (l)$$

3(a) Alloys are mixtures of two or more metals. Transition elements are usually alloyed with one another to enhance their properties. For instance, titanium is alloyed with iron to form a strong, light-weight and corrosion resistant material for aerospace and automobile.

(i) Explain what is meant by the term *transition element*.

[1]

A transition element (or transition metal) is a d-block element that forms at least one ion with incompletely filled d orbitals.

(ii) When 50g of the titanium-iron alloy is completely oxidized, 35.3g of FeO and a violet oxide of titanium, compound **A**, is obtained. The mass of oxygen measured in compound **A** is found to be 11.3g. Determine the molecular formula of this oxide. Hence calculate the oxidation number of titanium.

[2]

$2Fe + O_2 \rightarrow FeO$

No of mole FeO formed = 35.3 / 71.8
= 0.491

Mass of Fe in the alloy = 0.491 x 55.8
= 27.4g

No of mole of Ti in the alloy = 22.6 / 47.9
= 0.472

No of mole of O in the titanium oxide = 11.3 / 16
= 0.706

Ratio of Ti:O = 0.472 : 0.706
= 2 : 3

Molecular formula of the oxide of titanium is $\underline{\mathbf{Ti_2O_3}}$
Oxidation number of Ti in Ti_2O_3 = $\underline{\mathbf{+3}}$

(iii) On strong heating, compound **A** undergoes disproportionation to form two oxides. One of the oxide is a yellow solid and the other oxide is a white solid, compound **B.**

Write a balanced equation for the disproportionation reaction.

[1]

$Ti_2O_3 \rightarrow TiO + TiO_2$

(iv) State the full electronic configuration of Ti in compound **B**. Hence, explain why compound **B** is a white solid.

[1]

Electronic configuration of Ti in compound B: $1s^2 2s^2 2p^6 3s^2 3p^6$

Compound B is white since Ti in TiO_2 which has no 3d electrons.
Hence d-d transition does not occur.

(v) Explain why complexes of titanium are coloured. **[3]**

In the presence of ligands, the 3d orbitals are split into 2 groups with different energies. This effect is known as d orbital splitting.

d-d transition takes place when *d electrons* from the lower energy level are promoted to the higher energy level by absorbing a certain wavelength of light from the visible region of the electromagnetic spectrum.

The complex thus emits the remaining wavelength which appears as the colour of the complex observed.

(vi) $[Ti(H_2O)_6]^{3+}$ is violet in colour however $[TiF_6]^{3-}$ is pale green. Explain the difference in colour. **[2]**

Different ligands split the energy level of d orbitals to different extent, ΔE.

F^- is a stronger field ligandwhich results in a larger ΔE and shorter λ absorbed. Thus, the $[TiF_6]^{3-}$ is pale green.

H_2O is a weaker field ligand which results in a smaller ΔE and longer λ absorbed. Thus, the $[Ti(H_2O)_6]^{3+}$ is violet

(b) Use the *Data Booklet* to predict what will be formed when $FeCl_3$ (aq) is added to the following solutions. Write balanced equations and describe the observations.

[4]

(i) $Mn_2(SO_4)_3$

$Mn^{3+} + e \rightleftharpoons Mn^{2+}$ $E^{\theta} = +1.49$
$Cl_2 + 2e \rightleftharpoons 2Cl^-$ $E^{\theta} = +1.36$

$E^{\theta}_{cell} = +0.13V > 0$

$2Mn^{3+} (aq) + 2Cl^- (aq) \rightarrow 2Mn^{2+} (aq) + Cl_2 (g)$

Observation: A pale pink solution is formed.
A greenish yellow Cl_2 (g) is observed.

(ii) CuI

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^{\theta} = +0.77$
$Cu^{2+} + e \rightleftharpoons Cu^{+}$ $E^{\theta} = +0.15$

$E^{\theta}_{cell} = +0.62V > 0$

$Cu^{+} (aq) + Fe^{3+} (aq) \rightarrow Cu^{2+} (aq) + Fe^{2+} (aq)$

Observation: A blue (or blue-green) solution is formed.

(c) Aqueous Fe^{2+} is a good homogeneous catalyst for the decomposition of solution of aqueous hydrogen peroxide.

$2\,H_2O_2\,(aq) \rightarrow 2H_2O\,(l) + O_2\,(g)$

With reference to relevant E^{θ} in the *Data Booklet*, suggest a mechanism for the catalysis of this reaction by aqueous Fe^{2+}.

[3]

Step 1: Fe^{2+} reacts with H_2O_2

$2Fe^{2+}\,(aq) + H_2O_2\,(aq) + 2H^+\,(aq) \rightarrow 2\,Fe^{3+}\,(aq) + 2H_2O\,(l)$

$E^{\theta}_{cell} = +1.00\text{ V} > 0$ (feasible)

Step 2: Fe^{3+} intermediate reacts with H_2O_2

$2Fe^{3+}\,(aq) + H_2O_2\,(aq) \rightarrow 2\,Fe^{2+}\,(aq) + O_2\,(g) + 2H^+\,(aq)$

$E^{\theta}_{cell} = 0.77 - 0.68$

$E^{\theta}_{cell} = +0.09\text{ V} > 0$ (feasible)

(d) A white powder, anhydrous copper (II) sulphate is added and stirred into a beaker of water. Aqueous ammonia is added dropwise until excess to the solution. Describe and explain what will be observed in the above reactions.

[3]

When dilute ammonia is added gradually, a pale blue precipitate of $Cu(OH)_2$ is formed.

$$[Cu(H_2O)_6]^{2+} + \underset{\text{(from ammonia)}}{2OH^{-}} \rightleftharpoons Cu(OH)_2 + 6H_2O \qquad (1)$$

In excess ammonia,NH_3 ligands replace H_2O ligands to form a deep blue complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

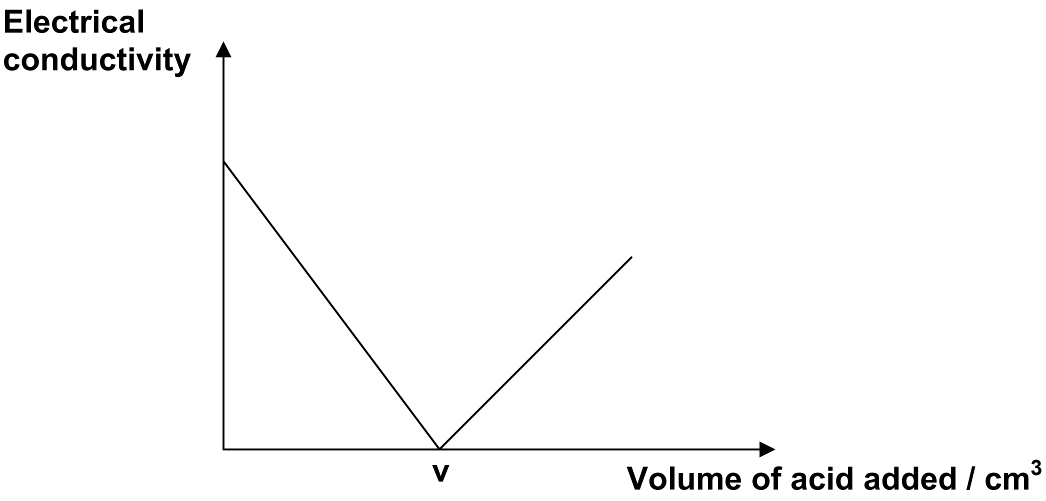
$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O \qquad (2)$$

Since concentration of $[Cu(H_2O)_6]^{2+}$ is decreased, by Le Chatelier's Prinicple, equilibrium position (1) shifts to the left to increase concentration of $[Cu(H_2O)_6]^{2+}$

Hence, pale-blue precipitate of $Cu(OH)_2$ dissolves.

4 This question is about the chemistry of group II compounds.

(a) 25 cm^3 of 0.50 mol dm^{-3} aqueous barium hydroxide was placed in a conical flask. 1.00 cm^3 of 1.00 mol dm^{-3} aqueous sulphuric acid were added at regular intervals, with stirring, from a burette. The electrical conductivity of the mixture was measured after each addition of acid. The following graph obtained shows the variation of electrical conductivity with volume of acid added.



(i) Write a balanced equation for the reaction of barium hydroxide and sulphuric acid, including the state symbols.

$Ba(OH)_2\ (aq) + H_2SO_4\ (aq) \rightarrow BaSO_4\ (s) + 2\ H_2O\ (l)$

(ii) Calculate the volume of acid added at point v.

$Ba(OH)_2 \equiv H_2SO_4 \equiv BaSO_4$

No. of moles of H_2SO_4 required to precipitate all $BaSO_4$ = 1.25×10^{-2}

Volume of H_2SO_4 required = **12.5 cm^3**

(iii) Explain the shape of the graph, stating clearly the species present before and after the addition of v cm^3 of sulphuric acid. **[4]**

Before acid is added, the free ions are $Ba^{2+}(aq)$ and $OH^-(aq)$.

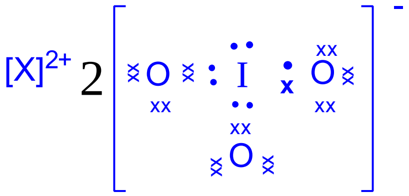
From 0 to v cm^3, the gradient of the slope is negative as the formation of solid $BaSO_4$ decreases the number of free ions in the solution.

When v cm^3 of acid is added, the conductivity reached zero (minimum) as there is only solid $BaSO_4$ and water with very little H^+ and OH^- ions.

When more acid is added that exceeds v cm^3 , the gradient of the slope is positive since there is an increased in number of $H^+(aq)$ and $SO_4^{2-}(aq)$ ions.

(b) **X, Y** and **Z** are Group II metals. They formed iodates (V) compounds as shown $X(IO_3)_2$, $Y(IO_3)_2$, $Z(IO_3)_2$. Upon heating, each of these iodates (V) compounds decomposes to yield a metal oxide, a purple gas and a colourless gas that rekindles a glowing splint.

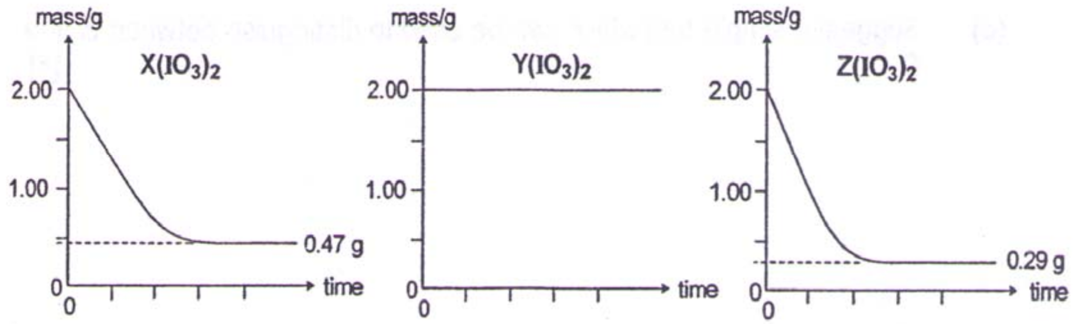
(i) Draw a dot-and-cross diagram of $X(IO_3)_2$. **[1]**



(ii) Write a balanced equation for the decomposition of $X(IO_3)_2$. **[1]**

$X(IO_3)_2\,(s) \rightarrow XO(s) + I_2(g) + 5/2\, O_2(g)$

(iii) The three graphs below show the change in mass when 2.00g of each iodates (V) compounds from Group II elements (Ca, Sr and Ba) are heated separately at a temperature of T°C. With the aid of the information from the graphs, state the identity of the $X(IO_3)_2$, $Y(IO_3)_2$ and $Z(IO_3)_2$..



$X(IO_3)_2$ is $Sr(IO_3)_2$
$Y(IO_3)_2$ is $Ba(IO_3)_2$
$Z(IO_3)_2$. is $Ca(IO_3)_2$

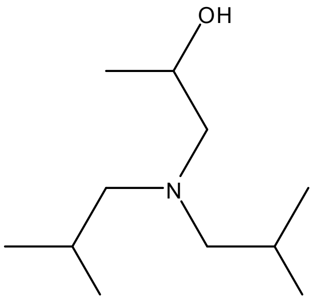
(iv) Arrange the three iodates (V) compound in order of increasing thermal stability and explain the trend as fully as you can.

[6]

The thermal stability of Group II iodates (V) increases in the following order:
$Z(IO_3)_2 < X(IO_3)_2 < Y(IO_3)_2$..

Down the group,
- size of Group II cations increases : $Z^{2+} < X^{2+} < Y^{2+}$
- charge of the cations is the same
- Charge density of M^{2+} decreases : $Z^{2+} > X^{2+} > Y^{2+}$
- Polarising power of M^{2+} decreases : $Z^{2+} > X^{2+} > Y^{2+}$
- Hence, cation is less able to distort electron cloud of IO_3^{2-} anion.
- Thermal stability of iodates increases and higher temperature required to bring about decomposition.

(c) Triisopropanolamine (TIPA), $N(C_3H_6OH)_3$, is a monoprotic base which is used as a neutralizing agent in agricultural products. The structure is as shown below.



TIPA

(i) Based on the structure of **TIPA**, explain how **TIPA** can act as a base in neutralizing excess acid in the soil.

TIPA has a lone pair on N which readily forms a dative bond with H^+ ions (or accept H^+) and hence neutralize the acid.

20 cm^3 of a solution of **TIPA** was exactly neutralized by 25.0 cm^3 of 0.05 $moldm^{-3}$ hydrochloric acid.

(ii) Calculate the concentration of the solution of **TIPA**.

No. of moles of $N(C_3H_6OH)_3 = 1.25 \times 10^{-3}$

$[N(C_3H_6OH)_3] = 6.25 \times 10^{-2}$ mol dm^{-3}

(iii) The pH of the solution of **TIPA** was found to be lower than 12.0, suggest with a reason, the strength of **TIPA** as a base.

pH = 12.0
$\Rightarrow$ $[OH^-]$ at pH 12.0 $= 10^{-2} = 0.0100$ mol dm^{-3}

Since $[OH^-] > [TIPA]$ TIPA is a weak base.

(iv) When 12.50 cm^3 of the same hydrochloric acid was added to the solution of **TIPA**, the resulting pH was 9.6. Calculate the value of K_b, base dissociation constant for TIPA.

pOH = pK_b
pH = 9.6

pOH = 4.4

Hence, $K_b = 10^{-4.4}$ **= <u>3.98×10^{-5} mol dm^{-3}</u>**

(v) Hence, determine the initial pH of the solution of **TIPA**.

[6]

Let x be the [OH-] at equilibrium

	$N(C_3H_6OH)_3$	+ H_2O	f $[HN(C_3H_6OH)_3]^+$	+ OH^-
Initial [ ] / mol dm^{-3}	6.25×10^{-2}	-	0	0
Change in [ ] / mol dm^{-3}	-x		+x	+x
Eqm [ ] / mol dm^{-3}	6.25×10^{-2} -x	-	x	x

$$K_b = \frac{[HN(C_3H_6O_H)_3]^+[OH^-]}{[N(C_3H_6OH)_3]}$$

$x = [OH-] = 1.58 \times 10^{-3}$ mol dm^{-3}

pOH = 2.8
pH = **<u>11.2</u>**

(d) It was found that besides the pH condition of soil, magnesium ion deficiency in the soil decreases the grain quality and protein content of the rice crop cultivated. Two soil samples with different amount of TIPA added were then analysed for their suitability in rice crop cultivation.

(i) In the first sample, the pH of the soil is 8.7 and the concentration of Mg^{2+} aqueous ions in the soil is found to be 0.0717 mol dm^{-3}. Write the K_{sp} expression of $Mg(OH)_2$ and calculate its K_{sp}, including the units.

$K_{sp} = [Mg^{2+}][OH^-]^2$

pH = 8.7 $\Rightarrow$ pOH = 5.3
$[OH^-] = 5.01 \times 10^{-6}$ mol dm^{-3}

$K_{sp} = [Mg^{2+}][OH-]^2 =$ **<u>1.80×10^{-12} mol^3 dm^{-9}</u>**

(ii) In the second sample, the pH of the soil is 12. Calculate the concentration of Mg^{2+} ions in the soil.

pH = 12
$\Rightarrow$ pOH = 2

$[OH^-] = 10^{-2}$ mol dm^{-3}

Ksp = $[Mg^{2+}][OH-]^2$
$[Mg^{2+}] =$ **<u>1.80×10^{-8} mol dm^{-3}</u>**

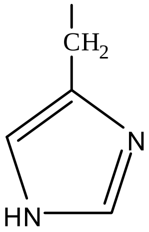
(iii) Deduce which soil samples, first or second, favours good cultivation of rice crop.

[4]
[Total : 20]

The first sample will favours good cultivation since its [Mg^{2+}] (0.0717 mol dm^{-3}) is higher than the second sample whereby [Mg^{2+}] = 1.80 x 10^{-8} mol dm^{-3} is very low.

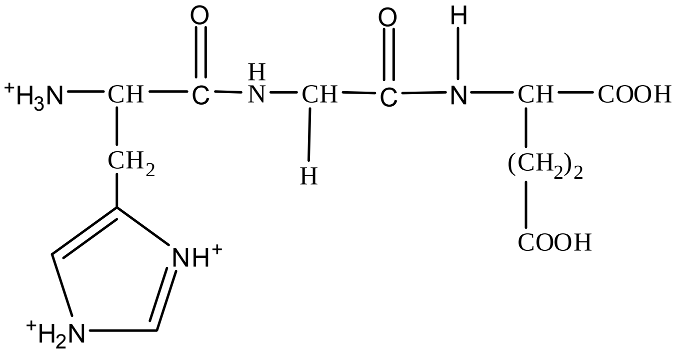
5(a) Amino acids are the basic structural building units of proteins. Beyond the amino acids that are found in all forms of life, many non-natural amino acids play vital roles in technology and industry.

Three amino acids with their R groups and isoelectric points are given in the table below.

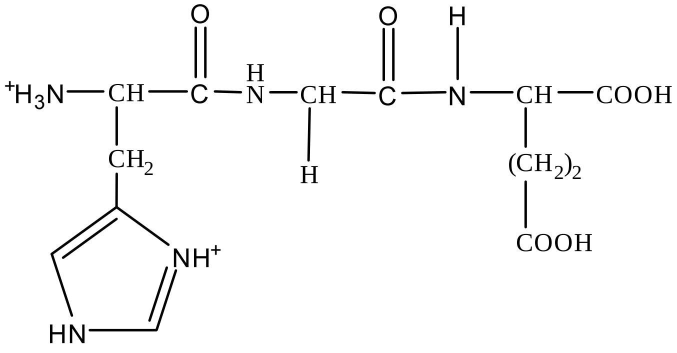
Amino acid	**R group**	**Isoelectric point**
Histidine		7.6
Glutamic acid	$-CH_2CH_2CO_2H$	3.2
Glycine	-H	6.0

(i) Draw the structural formula of a tripeptide with the sequence histidine-glycine-glutamic acid, showing the form in which it would exist at pH 2.

[1]



OR



(ii) Amino acids can act as buffer in solutions. By means of equations, show how glycine can act as a buffer when

- dilute hydrochloric acid and
- dilute NaOH

is added to separately into its solution.

[2]

When a small amount of acid (H^+) is added,

- $H^+ + {}^+NH_3CH_2COO^- \rightarrow {}^+NH_3CH_2COOH$
- H^+ added is removed by ${}^+NH_3CH_2COO^-$ to form ${}^+NH_3CH_2COOH$
- $[H^+]$ is slightly changed and pH of buffer solution remains fairly constant.

When a small amount of base (OH^-) is added,

- $OH^- + {}^+NH_3CH_2COO^- \rightarrow NH_2CH_2COO^- + H_2O$
- OH^- added is removed by NH_4^+ to form H_2O and NH_3
- $[OH^-]$ is slightly changed and and pH of buffer solution remains fairly constant.

(iii) Suggest with reasons a suitable pH which can be used to separate a mixture of histidine, glutamic acid and glycine using electrophoresis.

[2]

pH = 6.0

Glycine will have no net charge as the pH is at its isoelectric pH. Hence, it will remain stationary. Histidine will have a net positive charge and it will move towards the cathode (negative electrode). Glutamic acid will have a net negative charge and it will move towards the anode (positive electrode)

(iv) Crystals of the simplest amino acid, glycine, NH_2CH_2COOH, melt between 230°C and 235 °C. Suggest why the melting point of glycine is higher than that of 2-hydroxyethanamide, $HOCH_2CONH_2$ (m.p. 102-104°C).

[2]

Glycine exists as zwitterions whereas 2-hydroxyethanamide exists as simple molecules.

A larger amount of energy is required to overcome the stronger electrostatic forces of attraction between the zwitterions in 2-aminoethanoic acid than the hydrogen bonding between 2-hydroxyethanamide.

(b) Explain why phenylamine, $C_6H_5NH_2$ is a weaker base than benzylamine, $C_6H_5CH_2NH_2$ but reacts much more readily with aqueous bromine than benzylamine.

[3]

Phenylamine is a weaker base than benzylamine due to the delocalisation of the lone pair of electron on the nitrogen atom into the benzene ring.

Hence, the lone pair on N atom is less available to accept a proton.

The electron donating alkyl group ($C_6H_5CH_2$-) increases the electron density on the lone pair of N atom.

Hence, the lone pair on N atom is more available to accept a proton.

Phenylamine is more reactive than benzylamine towards electrophilic substitution.

For phenylamine, there is delocalisation of the lone pair of electron on the nitrogen atom into the benzene ring which increases the electron density in the ring which makes the benzene ring more susceptible to electrophilic substitution.

(c) The compounds **P** and **Q** are isomers with the molecular formula $C_9H_8O_2$.

P liberates carbon dioxide with sodium hydrogencarbonate but **Q** does not.

Upon reaction with hot acidified potassium manganate (VII), 1 mole of **P** gives 2 moles of carbon dioxide and $C_7H_6O_2$ while 1 mole of **Q** gives 1 mole of carbon dioxide and $C_8H_6O_4$.

P decolourises aqueous bromine in the dark to form **R**, $C_9H_9O_3Br$. **Q** reacts with aqueous bromine to form white precipitate of **S,** $C_9H_7O_3Br_3$.

Q can be obtained by reacting **T,** $C_9H_{10}O_3$, with excess concentrated sulphuric acid at 170°C. **T** gives a yellow precipitate on reaction with aqueous alkaline iodine solution.

When **Q** reacts with a mixture of NaCN and HCN, **U** is produced.

Suggest the structures of **P**, **Q**, **R**, **S**, **T** and **U**, explaining the chemistry of the reactions described.

[10]
[Total : 20]

P and Q have comparable number of C and H atoms and
no. of C atoms $\geq$ 6
$\Rightarrow$ P and Q contains benzene ring

P undergoes neutralization with sodium hydrogencarbonate.
$\Rightarrow$ P is a carboxylic acid

P undergoes oxidation with hot acidified $KMnO_4$ to form product with 2 carbon atoms less.
$\Rightarrow$ P is an alkene

Q undergoes oxidation with hot acidified $KMnO_4$ to liberate CO_2.
$\Rightarrow$ Q is a terminal alkene

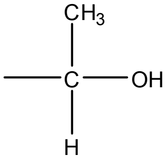
P undergoes electrophilic addition with aqueous Br_2 in the dark
$\Rightarrow$ P is an alkene

Q undergoes electrophilic substitution with aqueous Br_2
$\Rightarrow$ Q is a phenol

T undergoes elimination with excess concentrated H_2SO_4 to form Q
$\Rightarrow$ T is an alcohol

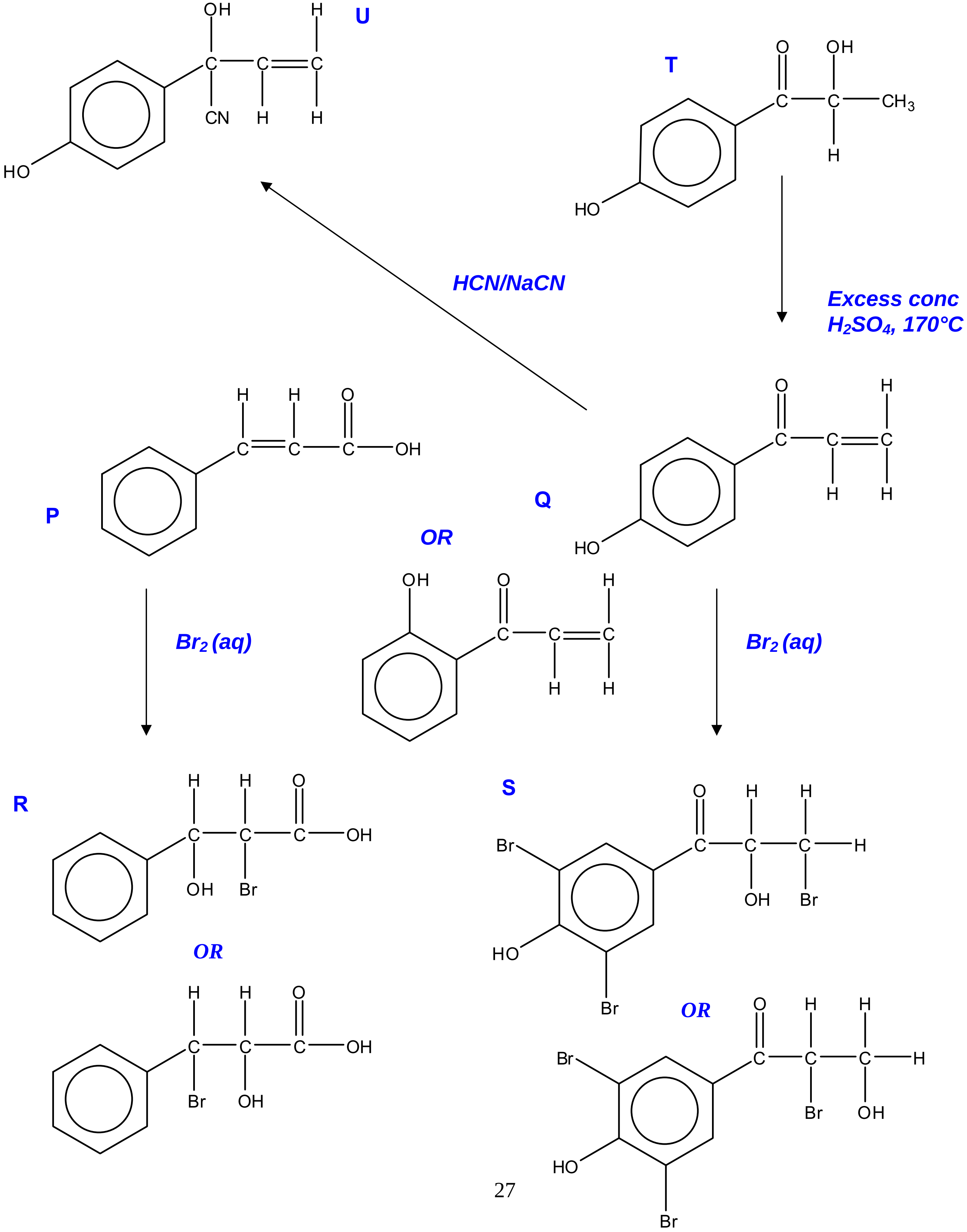
T undergoes oxidation with alkaline iodine

⇒ T contains



$$-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

Q undergoes nucleophilic addition with a mixture of NaCN and HCN to from U.
⇒ Q is carbonyl compound


U
T
HCN/NaCN
Excess conc
H2SO4, 170°C
P
Q
OR
Br2 (aq)
Br2 (aq)
R
OR
S
OR