NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9746/03

Paper 3 **16 September 2009**

2 hours

Candidates answer on writing paper

Additional Materials:
Data Booklet
Graph paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **4 out of 5** questions.

Write your answers on the writing paper provided

Begin each question on a fresh piece of paper.

You are advised to show all working and calculations

1(a) **(i)** Element A [2]

The sharp drop in value from G to H indicates that G is from Group I where the second ionization energy involves the removal of an electron from the inner shell . Hence Element A is in Group III and is Aluminium.

(b) **(i)** $\mathbf{AB(CO_3)_2 \rightarrow AO + BO + 2\,CO_2}$ [1]

(ii) **Assume :** $\mathbf{AB(CO_3)_2 \rightarrow AO\ (s) + BO\ (aq) + 2\,CO_2}$

Masses given : 0.400 0.057 (0.275 – 0.057) x

Therefore, $x = 0.400 - 0.275 = 0.125$ g [1]

(iii) Soln : Let *Ar* of **A** be **a** and that of **B** be **b**

$$\mathbf{AB(CO_3)_2 \rightarrow AO\ (s) + BO\ (aq) + 2\,CO_2}$$

Mass / g : 0.400 0.057 0.218 0.125

Determining amts and using mol ratios

Amt of $\mathbf{CO_2}$ **=** 0.125/44 = 0.00284 mol

Amt of **AO** **=** 0.057/(a + 16) = 0.00284 /2 mol

Giving **a** = 24.1, Therefore **A** is **Mg**

Amt of **BO** **=** 0.218/(b + 16) = 0.00284 /2 mol

Giving **b** = 137.5, Therefore **B** is **Ba**

(c) $MgO > NaF > H_2O > CH_3NH_2 > CO_2$ [5]

- CO_2 have simple molecular structure consisting of CO_2 molecules held together by van der waals forces.
- CH_3NH_2 and H_2O have simple molecular structures consisting of CH_3NH_2 and H_2O molecules held together by stronger hydrogen bonds.
- H_2O has 2 lone pair hydrogen units while CH_3NH_2 has 1 thus H_2O has higher boiling point.
- NaF and MgO have ionic structures consisting of oppositely charged ions held together by strong electrostatic forces. MgO has higher boiling point because it has higher ionic charges than NaF.

(d) (i) For the amino acid residue to be found on the outer surface of a water soluble globular protein, the R group must be a hydrophilic group.

- Hence, Serine (ser) will be found on the outer surface

The OH group on serine can form hydrogen bonds with water hence soluble.

- Lysine (Lys) will also be found on the outer surface

The NH_2 group on lysine can form hydrogen bonds with water hence making it soluble.

[2]

(ii) For Phe, Pro, Leu : Hydrophobic or van der Waals forces

For Lys, Ser: hydrogen bonding

[1]

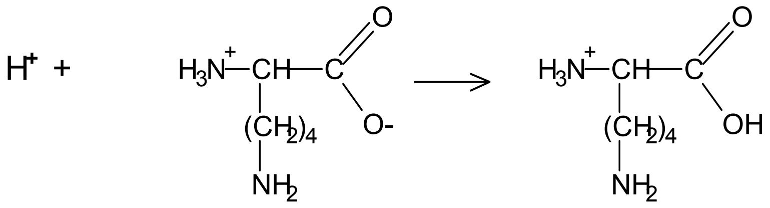
(iii) Denaturation of proteins.
When heated, the weaker R group interactions such as hydrogen bond and hydrophobic interactions stabilising the **tertiary structure** will be disrupted. Hence the polypeptide chain will uncoil itself and lose its shape. [3]

However, the primary structure will still be intact.

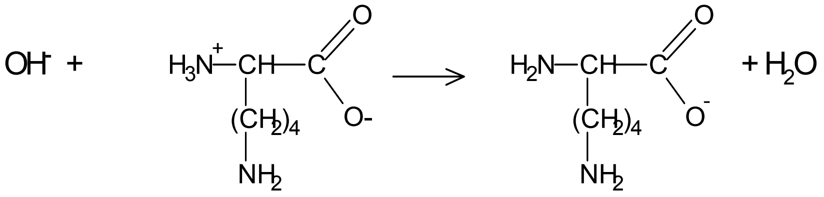
(iv) for Lys (the zwitterions for any other amino acid can also be drawn) [1]

(v) [2]

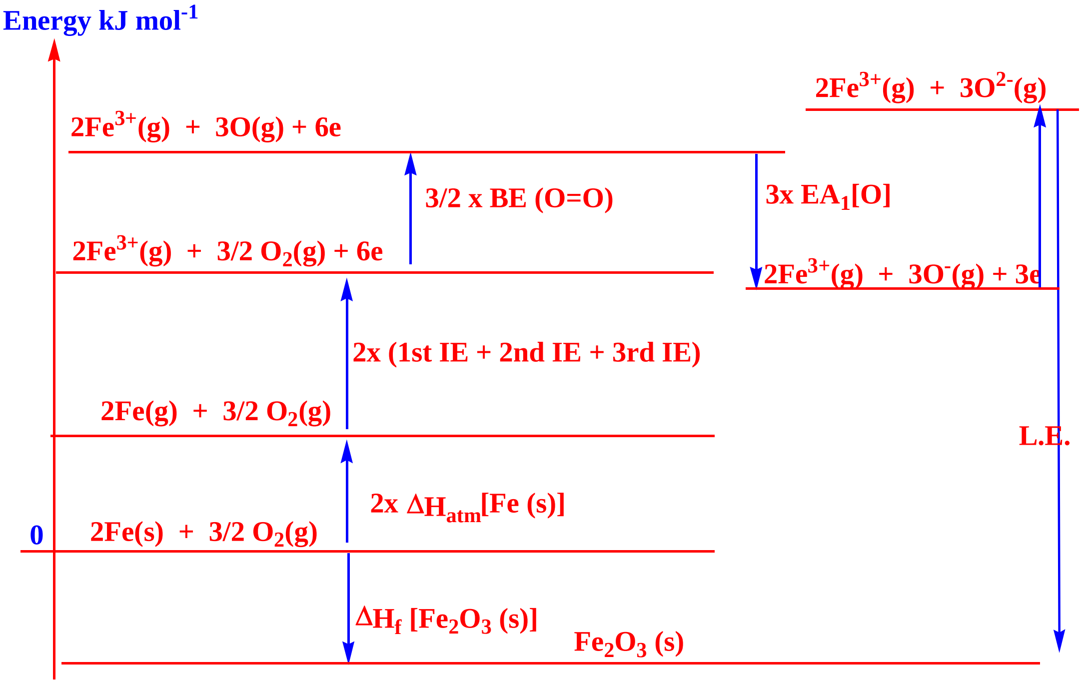
When a small amount of acid (H^+) is added,



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



2(a) (i)



[4]

By Hess' Law,

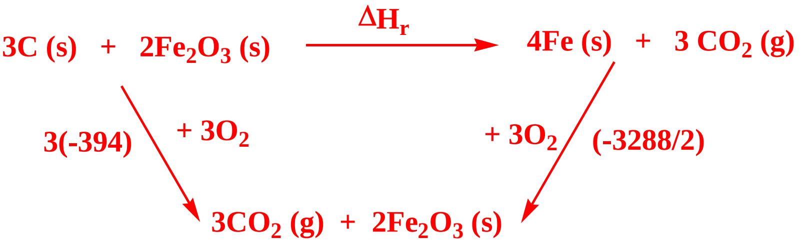
ΔH_f = 2(414) + 2(762 + 1560 + 2960) + 3/2 (496) + 3 (-141) + 3 (844) + L.E.

L.E. = - 1.51 x 10^4 kJ mol^{-1}

(ii) $O^-(g) + e \rightarrow O^{2-}(g)$ [1]

2^{nd} E.A. involves an electron added to negatively charged O^-. Energy needed to overcome repulsion between two negatively charged species, therefore ΔH is positive.

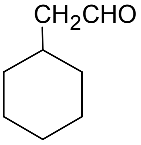
(iii) [4]



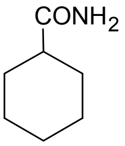
By Hess' Law

ΔH_r = 3(-394) - (-3288/2) = +462 kJ mol^{-1}

(b) (i) [2]



A &



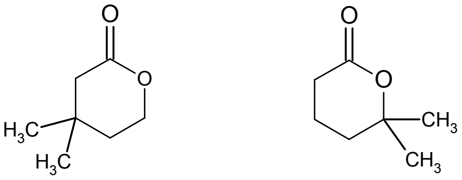
B

reagents and conditions: Add Fehling's reagent to A and B seperately, and warm.

Observations: For A, reddish brown precipitate formed. For B, no precipitate formed.

Other possible answers: (Write their observations)
Tollen's reagent, warm
$K_2Cr_2O_7$ with dil H_2SO_4 and heat
2,4-DNPH, warm

(ii) [2]



X **&** **Y**

reagents and conditions:

Step 1: Heat both X and Y separately with dil H_2SO_4.

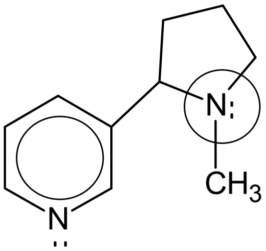
Step 2: To the resulting mixture from X and Y separately, add $K_2Cr_2O_7$ with dil H_2SO_4 and heat.

Observations: For X, orange $K_2Cr_2O_7$ turns green. For Y, orange $K_2Cr_2O_7$ remains.

Other possible answers: $KMnO_4$ with dil H_2SO_4 and heat

Or just use the oxidizing agent, with dil H_2SO_4, heat, since the acid present will hydrolyse the ester then immediately followed by oxidation of the alcohol

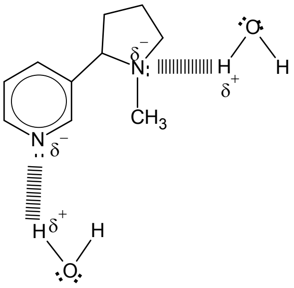
(c) (i)



The nitrogen atom (circled) is attached to the **three alkyl groups** which are **electro-donating**, making the **lone pair more available for bonding to H$^+$**/ hence **stabilizing the conjugate acid by dispersing the positive charge** on the nitrogen atom.

[3]

(ii)



[2]

(d)(i) $CH_3CH(NH_2)CH_2CONH_2$ [1]

(ii) $Cl^- NH_3^+CH_2CH_2CH_2COOH$ [1]

3(a) (i)

	N_2O (g) →	N_2 (g) +	½ O_2 (g)
Initial P/kPa	25.0	0	0
Change /kPa	-x	+x	+ ½ x
Final P / kPa	25.0-x	x	½ x

$P_T = 25.0 - x + x + ½ x = 25.0 + ½ x$

$x = 2(P_T - 25.0)$

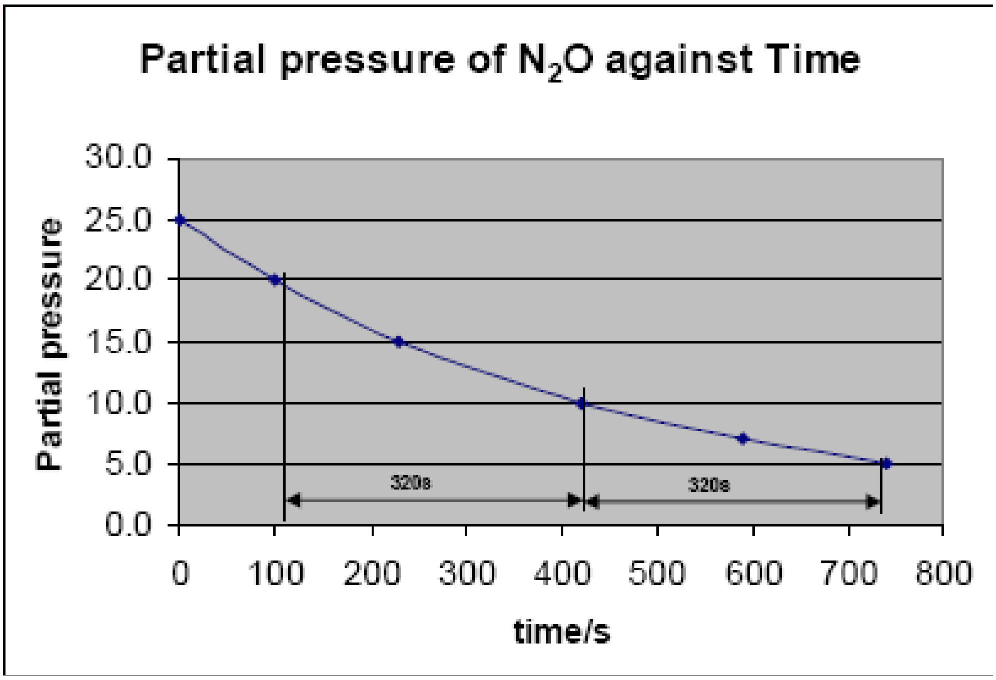
(where x = amt of N_2O decomposed at any given time)

$P_{N2O} = 25.0 - x = 75.0 - 2P_T$

At 230 s, $P_T = 30.0$, $P_{N2O} = 15.0$ kPa

At 590 s, $P_T = 34.0$, $P_{N2O} = 7.0$ kPa

(ii) [4]



(iii) At any time , $P_{N2} = x = 2(P_T - 25.0) = 25.0 - P_{N2O}$ 1m [3]

No. of half-lives	0	1	2
P_{N2O} / kPa	25.0	12.5	6.25
P_{N2} / kPa	0	12.5	18.75

setting up table (such as the one above) and some attempt to complete it…

Ans : 2 half lives

(b) **(i)** e^- config of cation of Y : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$ [2]

Identity of X : NH_3 or ammonia

(ii) [4]

(Y represents Cu)

$Cu(NO_3)_2 + 6\ H_2O \rightarrow [Cu(H_2O)_6]^{2+} + 2\ NO_3^-$

Blue

$[Cu(H_2O)_6]^{2+} + 2\ OH^- \rightarrow Cu(OH)_2(s) + 6\ H_2O$

light blue ppt.

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

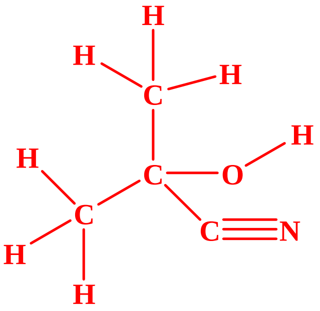
excess dark blue filtrate

$Mg(H_2O)_6^{2+} + 2\ OH^- \rightarrow Mg(OH)_2 + 6H_2O$

white residue, insoluble in excess NH_3

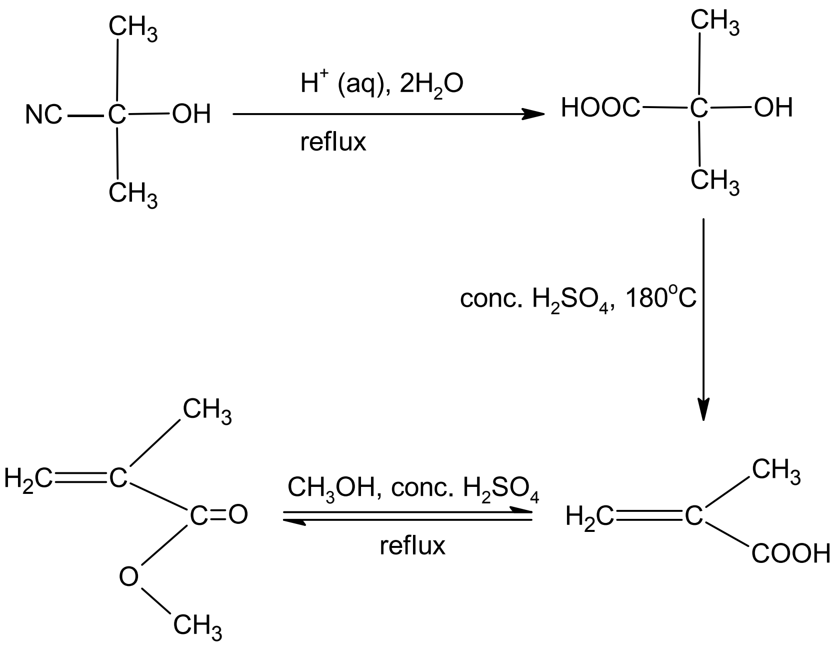
(c)

(i)



[1]

(ii) [3]



4(a) **(i)** $[OH^-] = \sqrt{5.6 \times 10^{-4}(0.200)} = 1.058 \times 10^{-2}\ \text{mol dm}^{-3}$ [1]

$\text{pOH} = -\lg 1.058 \times 10^{-2} = 1.98 \qquad \text{pH} = 12.02$

(ii) Using $\dfrac{0.200 \times V_{CH_3CH_2NH_2}}{0.120 \times 40.0} = \dfrac{1}{1} \Rightarrow V_{CH_3CH_2NH_2} = 24.0\ \text{cm}^3$ [1]

(iii) When vol = 48.0 cm^3, solution reached max buffering capacity [2]

(b) **(i)** $PbI_2 \rightarrow Pb^{2+} + 2I^-$ [2]

Let **x** be $[I^-]$

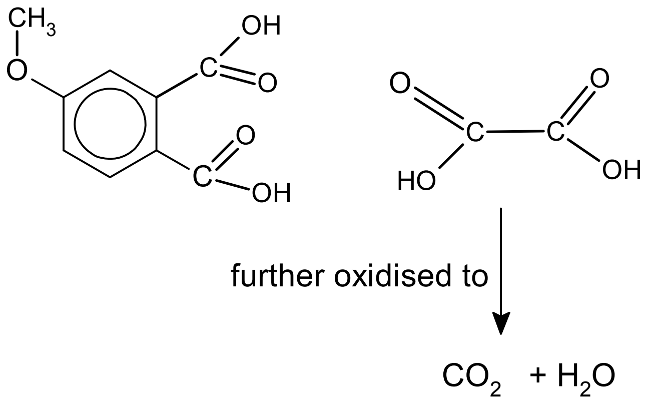
$$\boxed{\begin{aligned} &9.8 \times 10^{-9} = \tfrac{1}{2}\mathbf{x}\,(\mathbf{x})^2 \\ &\mathbf{x} = \sqrt[3]{2(9.8 \times 10^{-9})} = 2.696 \times 10^{-3}\ \text{mol dm}^{-3} \\ &\text{Solubility of } PbI_2 = \frac{2.696 \times 10^{-3}}{2}\ \text{mol dm}^{-3} \end{aligned}}$$

(ii) [2]

$$\boxed{\begin{aligned} &\text{Let } \mathbf{C} \text{ be } [Pb^{2+}] \text{ before mixing} \\ &[Pb^{2+}] \text{ after mixing} = \frac{\mathbf{C}}{2} \qquad [I^-] \text{ after mixing} = \frac{0.500}{2} \qquad [1m] \\ &\text{for ppt to appear, IP of } PbI_2 > K_{sp} \text{ of } PbI_2 \\ &\left(\frac{C}{2}\right)\left(\frac{0.500}{2}\right)^2 > 9.8 \times 10^{-9} \qquad [1m] \\ &\Rightarrow C > 3.136 \times 10^{-7}\ \text{mol dm}^{-3} \end{aligned}}$$

(c) Ester, alkene, primary alcohol [3]

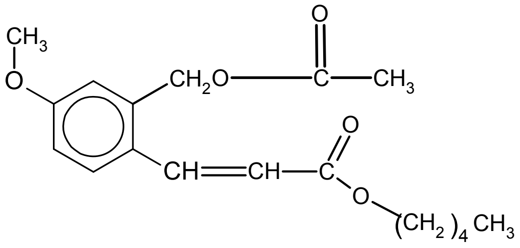
(d) **(i)**



$CH_3(CH_2)_3COOH$

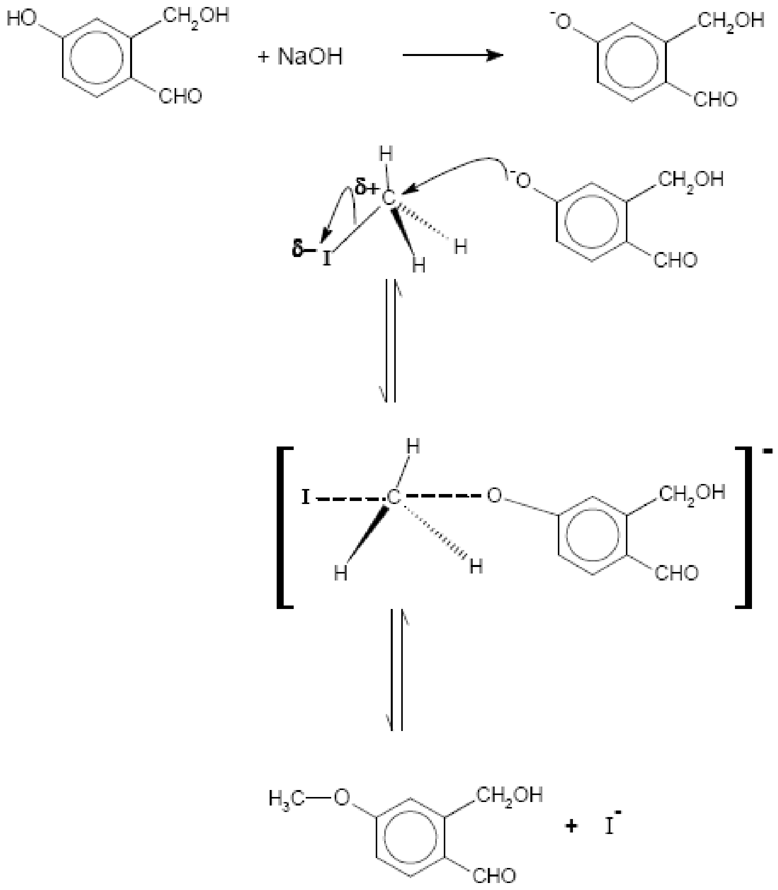
Accept ethandioic acid or CO_2 + H_2O

(ii) ethanoyl chloride [3]

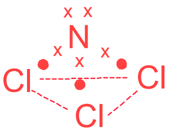


(e) **(i)** Condensation
Pentan-1-ol ($CH_3(CH_2)_3CH_2OH$)
Heat under reflux, with concentrated H_2SO_4 [3]

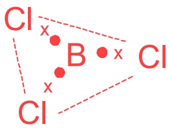
(ii) *Generation of nucleophile:* [3]



5(a)



3 bp 1 lp
Trigonal
pyramidal



3 bp 0 lp
Trigonal
plannar

each dot-cross diagram ½ m
each shape with reason ½ m

NCl_3 and BCl_3 have simple molecular structure but NCl_3 has a net overall dipole moment thus the molecules are held together by van der waals forces due to permanent dipoles.

BCl_3 has no overall dipole moment thus the molecules are held together by van der waals forces due to induced dipoles and therefore require less energy to break the bonds.

(b) **(i)** A nickel(II) sulphate solution contains $[Ni(H_2O)_6]^{2+}$ ions.

In the presence of **H_2O ligands,** the 3d orbitals are split into two groups with a **small** energy gap between them.

Electrons in the lower energy 3d orbital absorb energy as they move to a vacant and higher energy 3d orbital. The energy absorbed corresponds to **some wavelengths of visible light**.

The **unabsorbed complementary colours** are then emitted.

Such **d-d electron transitions** are responsible for the colour of the compounds.

(ii) The **NH_3 ligands** split the d orbitals of the Ni^{2+} ion into two sets of slightly different energies to a **different extent** from that of the **H_2O ligands**.(size of gap is different)

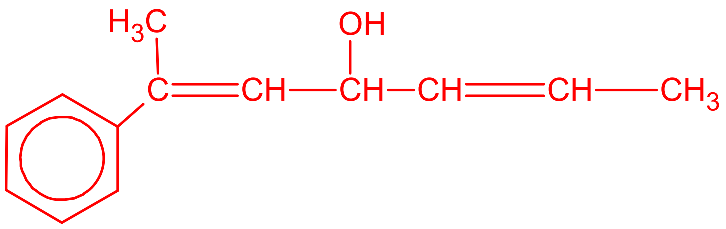
Hence, visible radiation of a **different wavelength** is **absorbed** and **emitted** for d-d transitions, giving rise to a different colour.

(iii) A bidentate ligand has 2 groups with **lone pairs of electrons** and hence can form **2 dative bonds** to the **central metal atom/ion**.

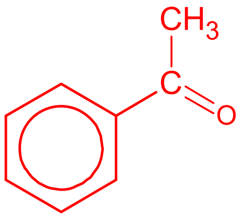
(Note : Ligands are groups that have lone pairs of electrons and are able to form dative bonds to the central metal atom/ion.)

(c) **STRUCTURES**

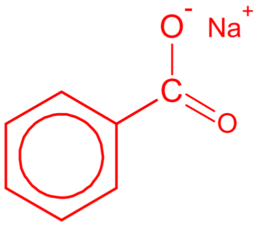
[1] M is



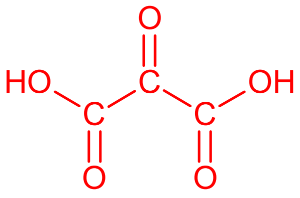
[1] N is



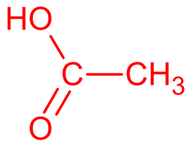
[1] R is



[1] P is



[10]

[1] Q is 

EXPLANATION OF THE REACTIONS DESCRIBED

[1] M decolourises aqueous bromine due to **electrophilic addition** across the **alkene (C=C)** functional group.

[1] M produces white fumes (of HCl) with PCl_5 due to a **substitution** reaction of the (secondary) **alcohol** functional group.

[1] M produced 3 compounds, N, P and Q with hot acidified potassium manganate (VII) due to **oxidative cleavage** of the (2) **alkene** functional groups present.

[1] N does not undergo **mild oxidation** with Fehling's reagent as it is **not an aldehyde**.

[1] N gives a yellow ppt (of CHI_3) and salt R with aq alkaline iodine due to the (mild) **oxidation** (and cleavage) of the **CH_3COR** group.

[1] P gives an effervescence (of CO_2) with Na_2CO_3(s) due to a **neutralization** reaction with the **carboxylic acid** functional group.

[1] P gives an orange precipitate with 2,4-DNPH due to **condensation** with the **ketone** functional group.

[1] Q gives an effervescence (of CO_2) with Na_2CO_3(s) due to a **neutralization** reaction with the **carboxylic acid** functional group.

[1] Q does not give an orange precipitate with 2,4-DNPH due to the **absence of a carbonyl** functional group for **condensation**.