2009 H2 Chemistry 9746/3 Suggested Answers

1 Vanadium, a transition metal, is commercially important.

(a) **(i)** Write down the electronic configuration of V, hence, write down the electronic configuration of V^{2+} ion.

$_{23}\mathbf{V}$ $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2}$

$_{23}\mathbf{V^{2+}}$ $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6 3d^3}$

[1]

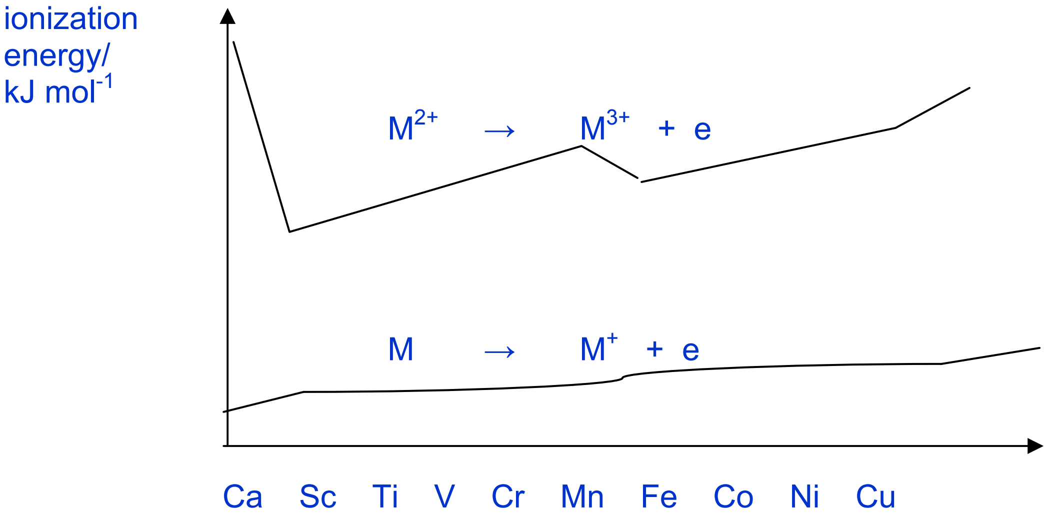
(ii) Explain why V^{2+}(aq) is coloured whereas Ca^{2+}(aq) is colourless.

In the presence of ligands, the 3d orbitals are split into two groups of slightly different energy levels. V^{2+} has a partially filled d orbitals, transition of electrons between the two different levels takes place with absorption of energy in the visible spectrum. The wavelengths that are transmitted correspond to the complementary colour observed.

In Ca^{2+}, there is no d-d transition due to absence of 3d electrons (or absence of partially filled 3d orbitals or electron transition takes place outside the visible region), hence it appears colourless.

[3]

(b) Sketch the general trends of the first ionization energy and the third ionization energy of the elements across the first series of transition metals; including Ca to Cu on the same axes. Explain the trends shown for these two properties.



The first ionization energy of the elements from scandium to copper remains relatively invariant as it involves the removal of 4s electrons. The significant screening effect of 3d electrons in the penultimate shell nullifies the increase in nuclear charge.

The transition elements have higher 1st ionization energy than Ca since they have higher effective nuclear charge than Ca due to the fact that d electrons are poorly shielding.
The increasing trend in third ionization energy is due to the increase in the effective nuclear charge and relatively constant shielding effect as 3d electrons are now in valence shell.

Third ionization energy of calcium is much higher than that of the other transition elements as the electron to be removed is from inner 3p orbital which is closer to the nucleus and has lower energy, held more strongly by the nucleus (or electron is removed from a full octet to form Ca^{3+}). Therefore, larger amount of energy is needed to remove it.

The 3rd electron from Fe^{2+} is removed from an orbital containing a pair of electrons, less energy is expected due to inter-electronic repulsion.

[5]

(c) Both Ca and Zn play an important role biologically in the body system. Vanadium ions are poisonous as they can cause bone porosity by replacing the calcium ions in bones. One treatment for vanadium poisoning involves administering a solution of edta, which forms hexacoordinate complexes with many divalent metal ions using the 4 donor oxygen and two donor nitrogen atoms.

Comment on the use of edta as a treatment for vanadium poisoning in the light of the following data:

Equilibrium	K_c /mol^{-1} dm^3
$Ca^{2+} + edta^{4-} \rightleftharpoons [Ca(edta)]^{2-}$	5×10^{10}
$Zn^{2+} + edta^{4-} \rightleftharpoons [Zn(edta)]^{2-}$	3×10^{16}
$V^{2+} + edta^{4-} \rightleftharpoons [V(edta)]^{2-}$	4×10^{16}

What problems might arise during the treatment and how could they be overcome?

As K_c of $[V(edta)]^{2-}$ is much higher than that of $[Ca(edta)]^{2-}$, V^{2+} will be removed in preference of Ca^{2+} when edta is used. Due to the close proximity in K_c between $[V(edta)]^{2-}$ and $[Zn(edta)]^{2-}$, Zn^{2+}, which is essential for health, will also be removed in addition to V^{2+}. Hence, limited amount of edta should be administered to prevent the loss of Ca^{2+}, removal of Zn^{2+} may be overcome by the administration of Zn ion supplements.

[2]

(d) Transition metals are often good homogeneous and heterogeneous catalysts.

V_2O_5 is used as catalyst to speed up the conversion of SO_2 into SO_3 in the Contact process for making sulfuric acid.

The key reaction in the contact process is as follows:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197\ \text{kJ mol}^{-1}$$

(i) For the reaction above, identify the type of catalyst involved and **explain clearly** how the catalyst works.

V_2O_5 acts as a heterogeneous catalyst, it is in a different phase from the reacting mixture. The reactant molecules readily adsorbed onto the catalyst surface. This allows for formation of weak bonds between reactants and the surface catalyst; weakens the intramolecular bonds in the reactants and helps to facilitate the reaction.

[2]

When a 2:1 ratio of sulfur dioxide and oxygen at a total initial pressure of 3 atm is passed over V_2O_5, the catalyst in a fixed volume steel vessel at 430°C, the partial pressure of sulfur trioxide at equilibrium is found to be 1.9 atm.

(ii) Calculate the percentage conversion of SO_2 to SO_3 and the equilibrium constant, K_p at 430°C.

	$2SO_2(g)$	**+**	**$O_2(g)$**	**$\rightleftharpoons$**	**$2SO_3(g)$**
Initial/atm	**2**		**1**		**0**
Change/atm	**-2x**		**-x**		**+2x**
Equilibrium/atm	**2-2x**		**1-x**		**2x**

Given $P_{\text{sulfur trioxide}} = 2x = 1.9$

$x = 0.95\text{atm}$

$P_{total} = 0.1 + 0.05 + 1.9 = 2.05\ \text{atm}$

% conversion $= 1.9/2 \times 1/100 = 95\%$

$$K_p = P^2_{SO3} / P^2_{SO2} \,.\, P_{O2}$$
$$= (1.9)^2 / (0.1)^2 (0.05)$$
$$= 7220\ \text{atm}^{-1}$$

[2]

(iii) According to Le Chatelier's Principle, the reaction will be favoured by a low temperature and a high pressure.

Give one other reason (other than cost factor) why a higher pressure is not applied?

At high pressures, however, sulfur dioxide liquefies and affects the catalytic reaction.

[1]

(iv) Comment on the effect on the percentage conversion if another unreactive but toxic gas was accidentally added to V_2O_5?

The catalyst is easily 'poisoned' by adsorbing the toxic gas on its surface. These take up the surface of the catalyst and impair its efficiency/slow down the process but no change in the perentage conversion.

[1]

(e) Given the following information on the colour of the aqueous vanadium ion of various oxidation states:

VO_2^+(yellow) VO^{2+}(blue) V^{3+}(green) V^{2+}(violet)

Use relevant $E^\ominus$ values from the *Data Booklet* to predict the colour observed upon mixing acidified aqueous ammonium polytrioxovanadate(V) solution with excess aqueous Sn^{2+} solution. Calculate the relevant $E^\ominus_{cell}$ values and write balanced equations.

Data	**$E^\ominus$/V**
(yellow)VO_2^+/VO^{2+}	**+1.00**
(blue)VO^{2+}/V^{3+}	**+0.34**
Sn^{4+}/Sn^{2+}	**+0.15**
(green)V^{3+}/V^{2+}(violet)	**-0.26**

E_{cell} = +1.00 – 0.15 = +0.85V > 0 feasible
E_{cell} = +0.34 – 0.15 = +0.19V > 0 feasible
E_{cell} = -0.26 – 0.15 = –0.41V < 0 not feasible

Sn^{2+}(aq) is powerful enough to reduce VO_3^- to V^{3+}. Hence, green solution is expected to form.

$$Sn^{2+} + 2VO_2^+ + 4H^+ \rightarrow Sn^{4+} + 2VO^{2+} + 2H_2O$$

[$Sn^{2+} + 2VO_3^- + 4H^+ \rightarrow Sn^{4+} + 2VO^{2+} + 2H_2O$ is acceptable]

$$Sn^{2+} + 2VO^{2+} + 4H^+ \rightarrow Sn^{4+} + 2V^{3+} + 2H_2O$$

[3]

[Total: 20]

2(a) The solubility products of some group II compounds at 25°C are shown in the following table.

Compound	K_{sp}
$Ba(OH)_2$	5.0×10^{-3}
$Ca(OH)_2$	?
$BaCO_3$	5.1×10^{-9}
$CaCO_3$	3.8×10^{-9}

With reference to the given data,

(i) Write an expression for the solubility product of $Ca(OH)_2$.

$Ca(OH)_2$ (s) $\rightleftharpoons$ Ca^{2+} (aq) + $2OH^-$ (aq)
K_{sp} of $Ca(OH)_2$ = $[Ca^{2+}][OH^-]^2$

[1]

(ii) Calculate the pH of a saturated solution of $Ca(OH)_2$ at 25°C given that its solubility is 0.830 g dm^{-3}.

M_r of $Ca(OH)_2$ = 74.1

Solubility of $Ca(OH)_2$ = $\frac{0.830}{74.1}$ = 1.12×10^{-2} mol dm^{-3}

$[OH^-] = 2 \times 1.12 \times 10^{-2} = 2.24 \times 10^{-2}$ mol dm^{-3}

pH = 14 – lg(2.24×10^{-2}) = 12.35

[2]

(ii) Determine the solubility product of $Ca(OH)_2$ at 25°C, stating its units.

$$K_{sp} \text{ of } Ca(OH)_2 = [Ca^{2+}][OH^-]^2 = (1.12 \times 10^{-2})(2.24 \times 10^{-2})^2 = 5.62 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$$

[1]

(iii) Explain and predict qualitatively the effect(if any) on the solubility and solubility product of $Ca(OH)_2$ when 25.0 cm^3 of 0.050 mol dm^{-3} solution of potassium hydroxide is added to the solution in (ii)

The common ion, OH^-, from the very soluble KOH would cause eqm in (i) to shift left, hence lowering the solubility of $Ca(OH)_2$.
K_{sp} of $Ca(OH)_2$ would not be affected as temperature is constant.

[2]

Barium hydroxide is also known as baryta water and just like limewater, may be used to detect the presence of carbon dioxide through the formation of a white precipitate.

(iv) Write a balanced equation to show the reaction between carbon dioxide and baryta water.

$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O$$

[1]

(v) Which solution, lime or baryta water,is more sensitive to the detection of carbon dioxide gas at 25°C? Explain your answer with reference to the data given in table in (a).

As the <u>K_{sp} of $CaCO_3$ is lower</u>, the <u>ionic product</u> of $[Ca^{2+}][CO_3^{2-}]$ would <u>exceed the K_{sp} of $CaCO_3$ more readily</u> hence <u>lime water would be more sensitive</u>.

[2]

(b) White lead, $Pb(OH)_2.PbCO_3$, used to be the primary white pigment used in paints but has since been replaced, largely by barium sulfate and titanium(IV) oxide due to the toxicity of lead.

(i) Assuming lead (II) compounds react in the same way as group II compounds, write a balanced equation, with state symbols, to illustrate the action of heat on 'white lead'.

$$Pb(OH)_2.PbCO_3(s) \longrightarrow 2\,PbO(s) + CO_2(g) + H_2O(g)$$

[1]

(ii) Calculate the percentage loss in mass on heating a sample of 'white lead' until no further change occurred.

Mr of $Pb(OH)_2.PbCO_3$ = 508

$$\text{\% loss in mass} = \frac{44.0 + 18.0}{508} \times 100 = 12.2$$

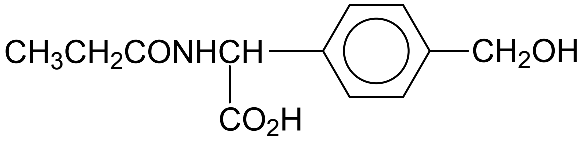
[1]

(iii) Would you expect the temperature required for the decomposition of white lead to be higher or lower than that of $Ca(OH)_2.CaCO_3$? Explain your answer.

The decomposition temperature for $Pb(OH)_2.PbCO_3$ is expected to be <u>higher</u>.
<u>Pb^{2+} ion is larger in size than Ca^{2+}</u> hence <u>charge density is</u> <u>lower</u> resulting in <u>lower polarizing power</u> which leads to <u>less distortion</u> on anionic charge clouds , hence white lead is more stable.

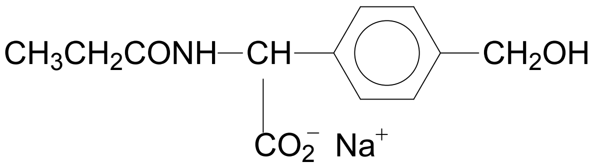
[3]

(c) Compound **P**, with the structure shown below, has two functional groups that may exhibit acidic properties.



(i) State and explain which of these two groups has a higher acid strength. Hence give the formula of the product formed when aqueous sodium carbonate is added to compound **P**.

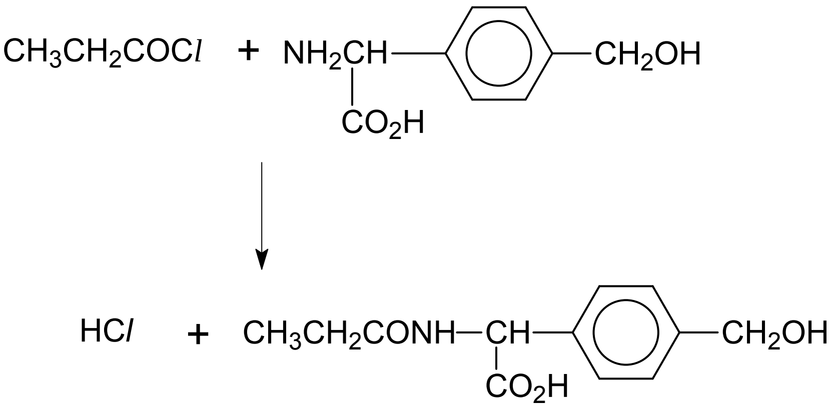
The carboxylic acid group has higher acid strength than alcohol. On dissociation, the carboxylate ion is more stable than the alkoxide ion due to resonance effect which disperses the negative charge on the ion, unlike alkoxide ion which does not have resonance effect.



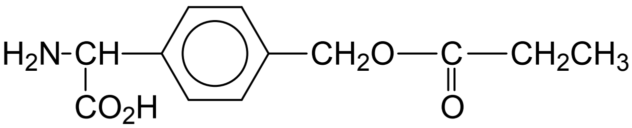
[4]

(ii) **P** can be synthesized by reacting an amino acid and an acyl chloride. Write an equation for its synthesis.

An isomer of **P** was also formed in the reaction. Give the structure of this isomer.



Isomer of P



[2]

[Total: 20]

3 This question is about Period 3 elements and their compounds.

(a) A sample of magnesium oxide is contaminated with some aluminium oxide. By making use of the fact that Period 3 oxides have different acid-base properties, describe a simple method by which a pure sample of magnesium oxide can be obtained. Include an equation for any reaction that is utilized.

Add excess NaOH(aq).
Only aluminium oxide will dissolve to form a soluble complex:
$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$
The mixture is then filtered and the MgO residue is washed with distilled water.

[2]

(b) Another Period 3 oxide, sulfur trioxide dissolves in water to form sulfuric acid, H_2SO_4 which can be converted into peroxodisulfuric acid, $H_2S_2O_8$ via the two-step process below, with chlorosulfonic acid, HSO_3Cl, as an intermediate:

$H_2SO_4 + HCl \rightarrow HSO_3Cl + H_2O$
$H_2O_2 + 2HSO_3Cl \rightarrow H_2S_2O_8 + 2HCl$

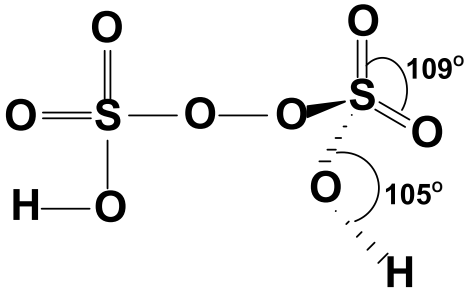
(i) The boiling point of H_2SO_4 is 290°C whereas that of HSO_3Cl is 152°C. By comparing the structures of the two compounds, explain the difference in the boiling points.

The molecular formulae suggest that the structure of chlorosulfonic acid is derived from that of sulfuric acid, with 1 –OH group being replaced by –C*l*.

Hence the extent of hydrogen bonding is less between chlorosulfonic acid molecules which explains its lower boiling point.

[2]

(ii) Give the displayed formula of the $H_2S_2O_8$ molecule, showing the spatial arrangement and estimated bond angle around any one sulfur atom and one oxygen atom.



Comments:
displayed formula with ALL bonds shown
bond angle and tetrahedral shape with wedge formula around any one S
bond angle and bent shape around any one O

[3]

(c) Chlorine forms an oxide, Cl_2O_7, with the structure $O_3ClOClO_3$ and a boiling point of 82°C. Its standard enthalpy change of formation is -546 kJ mol^{-1}.

(i) Write the equation which corresponds to the standard enthalpy change of formation of Cl_2O_7.

$Cl_2(g) + 7/2\ O_2(g) \rightarrow Cl_2O_7(l)$

[1]

(ii) Given that the bond energy of Cl–O bond is 269 kJ mol^{-1} and using relevant data from the *Data Booklet*, estimate the average bond energy of the Cl=O bond.

Bond energy of Cl - Cl = 244 kJ mol^{-1}, O=O = 496 kJ mol^{-1}
$-546 = 244 + 7/2(496) – [2\times269 + 6(Cl=O)]$
Bond energy of Cl =O = 331 kJ mol^{-1}

[2]

(iii) The bond energy calculated in **(ii)** could have been more accurate if the value of an additional enthalpy change is known. What process does this enthalpy change correspond to?

The enthalpy change required to change liquid Cl_2O_7 into its gaseous form OR enthalpy change of vaporization.

[1]

(d) (i) Define the term *lattice energy.*

Lattice energy is the heat evolved when one mole of an ionic solid is formed from its isolated gaseous ions from an infinite distance apart under standard conditions.

[1]

(ii) State and explain whether the oxide or fluoride ion is smaller.

F^- is a smaller ion.
Both O^{2-} and F^- are isoelectronic ions and hence shielding effect is similar for both ions.
However, F^- has a higher nuclear charge which causes its outermost electrons to experience a higher effective nuclear charge and be pulled closer to the nucleus.

[2]

(iii) Refractories are heat-resistant compounds used to line furnaces. Which compound, magnesium oxide or magnesium fluoride, is more suitable for use as a refractory? Explain your answer.

The higher charge of O^{2-} suggests that MgO has a higher LE while its bigger ionic size suggests otherwise.
The anionic charge is the more important factor.
OR Lattice energy α $q_+q_- / (r_+ + r_-)$. However, the higher charge of O^{2-} outweighs its larger ionic size.
Hence MgO should be used as a refractory as it has a higher melting point OR lattice energy.

[2]

(e) Magnesium fluoride, differs in its bonding from that of sulfur difluoride, SF_2, as reflected by the difference in their physical properties.

(i) Explain why the difference in bonding arises.

As Mg is less electronegative than S, the electronegativity difference between Mg and F is larger compared to that between S and F.
Hence MgF is ionic whereas SF_2 is covalent.

[1]

(ii) Suggest one difference in physical properties that is likely to ensue from the difference in bonding.

MgF_2 has a much higher melting point that SF_2.
OR MgF_2 conducts electricity in the molten state but SF_2 does not conduct electricity in any state.

[1]

(iii) The compound SF_2 readily reacts with fluorine to give SF_4. Suggest why MgF_2 does not react with more fluorine to give MgF_4.

To form MgF_4, Mg^{2+} has to lose two more electrons from the penultimate shell which results in a prohibitively high amount of energy required.
This cannot be compensated by the energy evolved from the formation of the ionic lattice of MgF_4.

[2]

[Total: 20]

4 Compound **P** is a sweet smelling substance extracted from a fern which grows in the tropical region. Acid hydrolysis of compound **P** yields three products, compounds **A**, **B** and **C**. Compound **C** was precipitated out as white solid and was filtered off the reaction mixture.

$$\longrightarrow$$

A series of tests were then performed on compound **A** and compound **B**.

(a) A gaseous sample of 0.146 g of compound **A** took up a volume of 80.1 cm^3 at a temperature of 400 K and a pressure of 1.01 x 10^5 Pa. In addition, effervescence of a colourless gas was observed when aqueous sodium carbonate is added to compound **A**.

Use these data to calculate the M_r of compound **A** and hence suggest a possible structure.

$$\begin{aligned} M_r &= \frac{mRT}{PV} \\ &= \frac{0.146 \text{ x } 8.31 \text{ x } 400}{1.01 \text{ x } 10^5 \text{ x } 80.1 \text{ x } 10^{-6}} \\ &= 60 \end{aligned}$$

Effervescence of a colourless gas was observed when aqueous sodium carbonate is added implies the presence of carboxylic acid functional group.

Compound **P**

i.e. A is RCOOH where R = CH_3.

[2]

(b) Reacting compound **A** and compound **B** with phosphorus pentachloride, PCl_5, yield compound **D** and compound **E** respectively. Effervescence of white fume was observed.

Both compound **D** and **E** are then hydrolysed with aqueous sodium hydroxide and the kinetics rate data are collected.

(i) The results for the hydrolysis of compound **D** is as shown.

Experiment	[**D**] / $moldm^{-3}$	$[OH^-]$ / $moldm^{-3}$	Initial rate/ mol $dm^{-3}s^{-1}$
1	0.0100	0.120	1.8 x 10^{-4}
2	0.0050	0.240	1.8 x 10^{-4}
3	0.0050	0.480	3.6 x 10^{-4}

Using the above data, deduce the order of reaction with respect to compound **D** and OH^-.

(i) **From experiments 2 and 3,**

When $[OH^-]$ doubles and [D] remains constant, the initial rate doubles. Hence, the reaction is first order with respect to OH^-.

Let the order of reaction with respect to compound D be a.

$$\frac{\text{rate }1}{\text{rate }2} = \frac{[\text{D}]^a[\text{OH}^-]}{[\text{D}]^a[\text{OH}^-]}$$

$$\frac{1.8 \times 10^{-4}}{1.8 \times 10^{-4}} = \frac{[0.0100]^a[0.120]}{[0.0050]^a[0.240]}$$

$$a = 1$$

(workings or statements)

Hence, the reaction is first order with respect to compound D.

[1.5]

(ii) Hence, construct a rate equation and use it to calculate a value of the rate constant, $k_{1,}$ including its units, for the hydrolysis of compound **D**.

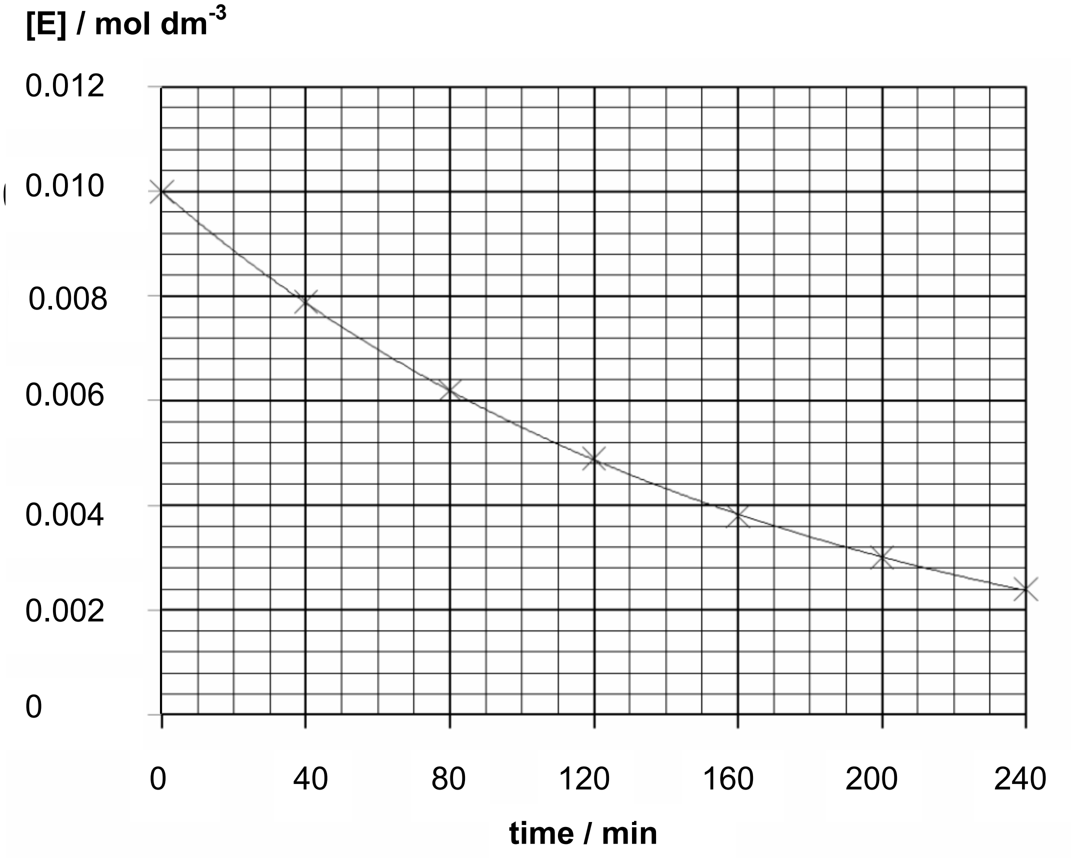
Rate = $k_1[D][OH^-]$

$1.8 \times 10^{-4} = k_1(0.0100)(0.120)$

$k_1 = 0.15$ $mol^{-1}dm^3s^{-1}$

[1.5]

(c) The results for the hydrolysis of compound **E** is shown in the form of graphical representation. The overall concentration of aqueous NaOH remained virtually constant at 0.120 mol dm^{-3}.



(i) Use the graph above to determine the following:

I Use the half life method to deduce the order of reaction with respect to compound **E**.

From 0.01 moldm^{-3} to 0.005 moldm^{-3}, half life = 115 min
From 0.005 moldm^{-3} to 0.0025 moldm^{-3}, half life = 115 min
[State two half life with values between 105 to 120 min.]
The two half life is (approximately) constant, thus the reaction is first order with respect to compound E.

[2]

II Given that the same plot was obtained when the experiment was repeated with 0.240 mol dm^{-3} of aqueous sodium hydroxide, calculate the value of the rate constant, k_2, including its units, for the hydrolysis of compound **E**.

Rate of reaction does not change when concentration of sodium hydroxide is doubled.
Order of reaction w.r.t OH$^-$ is zero.
Hence, overall order of reaction is first order.

rate constant, k_2 = $\frac{\ln 2}{116} = 5.98 \times 10^{-3}$ **min^{-1}**

[Value of rate constant must be within the range

$$5.78 \times 10^{-3} \le k_2 \le 6.60 \times 10^{-3}\,]$$

[2]

(ii) Using the initial rate data given in **b(i)** and the graph above, calculate the ratio of the initial rate of the hydrolysis of compound **D** : compound **E**. Hence, suggest the functional group which is likely to be present in compound **B**. Explain clearly your reasoning.

Initial rate of hydrolysis of compound E =

$$\frac{0.010 - 0.0088}{20 \times 60} = 1.0 \times 10^{-6}\,\text{moldm}^{-3}\text{s}^{-1}$$

[Answer ≈ 10^{-6} mol dm^{-3} s^{-1} are acceptable]
From the table in b(i), the initial rate when [D] = 0.010 mol dm^{-3} and [OH$^-$] = 0.012 mol dm^{-3} is 1.8 x 10^{-4} mol dm^{-3}s^{-1}.
Ratio of initial rate of D : E = 180 : 1
Since both compound A and compound B reacts with PC*l*$_5$ to evolve white fume of HC*l*, both compounds contain either an alcohol or a carboxylic acid functional group.
Compound D is ethanoyl chloride formed from the reaction of ethanoic acid and PC*l*$_5$.
Since the hydrolysis of compound D is much faster than that of compound E, we can deduce that an alcohol functional group is present in compound B since a chloroalkane undergoes hydrolysis slower than an acyl chloride.

[3]

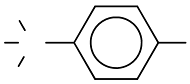
(d) Compound **B** has the molecular formula $C_9H_{12}O_2$ and is monobasic. Reacting compound **B** with aqueous bromine at room temperature produces compound **F** which is symmetrical. Compound **B** does not react with hot, acidified aqueous $Na_2Cr_2O_7$.

Using the data given above, suggest the structural formulae of compound **B** and compound **F**.

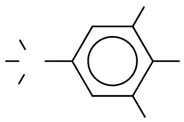
Compound B is monobasic (i.e. carboxylic acid or phenol) but cannot contain carboxylic acid functional group as deduced in c(ii). Thus, phenol functional must be present in compound B.

Reaction with aqueous bromine at room temperature causes electrophilic substitution of the benzene ring. Since the product is symmetrical, compound B must have a 1,4 disubstituted benzene ring.
Since compound B does not react with hot, acidified aqueous $Na_2Cr_2O_7$, the alcohol must be a tertiary alcohol.

Deducing from the molecular formula, the structure of compound B could only be

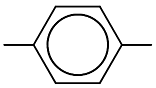


Hence, the structure of compound F could only be

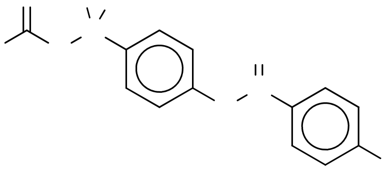


[2]

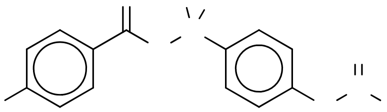
(e) Given that compound **C** is identified to be 4-methylbenzoic acid.



Draw a possible structural formula of compound **P**.

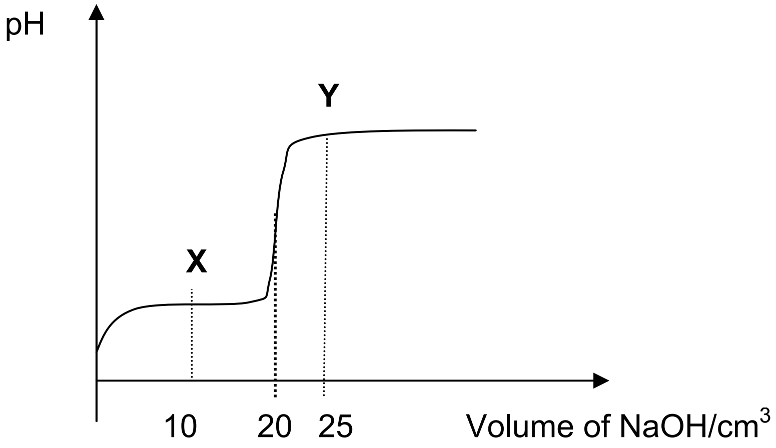


or



[1]

(f) Compound **A** can be converted to 2-chloroethanoic acid, $ClCH_2COOH$. 10.0 cm^3 of 0.100 mol dm^{-3} of 2-chloroethanoic acid is titrated against 0.0500 mol dm^{-3} of NaOH. The graph of pH against volume of NaOH added is shown:



(i) Given that the K_a of $ClCH_2COOH$ is 1.4×10^{-3} mol dm^{-3}, calculate the initial pH.

$$ClCH_3CO_2H\,(aq) \rightleftharpoons H^+\,(aq) + ClCH_3CO_2^-(aq)$$

$$K_a = \frac{[H^+]\,[ClCH_3CO_2^-]}{[ClCH_3CO_2H]}$$

$$1.4 \times 10^{-3} = [H^+]^2 \,/\, 0.100$$

$$[H^+] = 0.0118 \text{ mol dm}^{-3}$$

$$pH = -\lg[H^+] = 1.93$$

[2]

(ii) Calculate the pH at points **X** and **Y**.

At point X,

pH = pK_a

pH = -lg (1.4×10^{-3}) = 2.85

At point Y,

$$[OH^-] = \frac{0.0500 \times 5}{35} = 7.14 \times 10^{-3} \text{ moldm}^{-3}$$

pOH = -lg[OH^-] = 2.15

pH = 14 – pOH

= 11.9

[3]

[Total: 20]

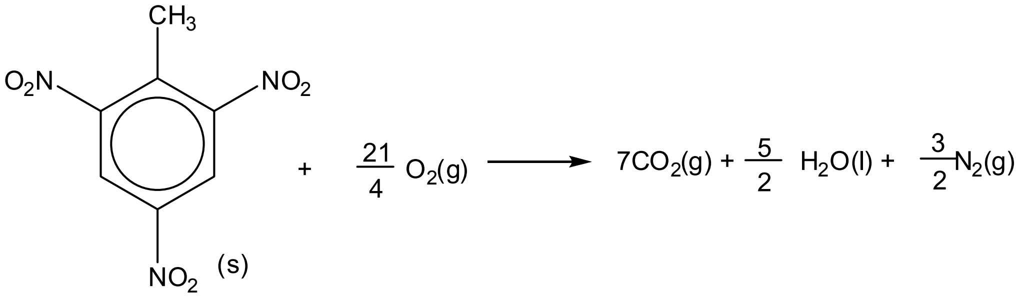
5 This question is about organic nitrogen compound.

TNT (2, 4, 6 – trinitromethylbenzene), a compound containing nitrogen atoms, was first prepared in 1863 by German chemist Joseph Wilbrand and originally used as a yellow dye. Its potential as an explosive was not appreciated for several years mainly because it was so difficult to detonate and because it was less powerful than alternatives. TNT is quite an explosive material. It can quickly destroy anything within its blast radius when detonated.

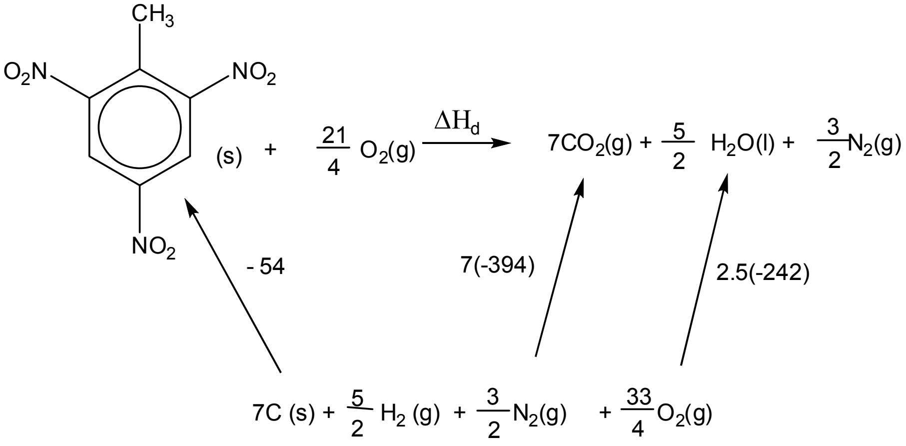
In the process of detonation, TNT is oxidised in the presence of excess oxygen into the stable products of CO_2, H_2O and N_2. The energy produced during the formation of these products from 1 mole of TNT is known as enthalpy of detonation, ΔH_d, in kJ mol^{-1}.

(a) **(i)** Write down a balanced equation showing the detonation of 1 mole of TNT. Using the data below, construct an energy cycle and use it to calculate the standard enthalpy change of detonation of TNT.

Standard enthalpy change of formation of TNT = –54 kJ mol^{-1}
Standard enthalpy change of formation of H_2O = –242 kJ mol^{-1}
Standard enthalpy change of combustion of carbon = –394 kJ mol^{-1}



$$C_7H_5N_3O_6(s) + \frac{21}{4}O_2(g) \longrightarrow 7CO_2(g) + \frac{5}{2}H_2O(l) + \frac{3}{2}N_2(g)$$



ΔH_d = – (–54) + 7(–394) + 2.5(–242) = – 3310 kJ mol^{-1} (3 sf)

[3]

(ii) The energy obtained from experimentally detonating TNT was – 2545 kJ mol^{-1}. Suggest a reason for the discrepancy from the value that was obtained in **b(i)**.

Experimental value is <u>less exothermic</u> than theoretical value due to <u>heat lost</u> to the surroundings.

[1]

(iii) Deduce the sign of ΔS for the detonation of TNT. Hence, or otherwise, explain why the detonation process is always spontaneous.

The number of <u>gaseous</u> molecules has <u>increased</u> after the reaction causing the system to become <u>more disordered</u>. Thus entropy <u>increases</u> and the sign of <u>ΔS is positive</u>.
$\Delta G = \Delta H - T\Delta S$. Since <u>$\Delta H$ is negative</u>, and the term <u>$-T\Delta S$ is negative</u>, thus <u>ΔG is always negative</u>, i.e. the reaction is always spontaneous.

[2]

(iv) Explain, in energy terms, why TNT is so explosive.

The forward reaction is <u>highly exothermic</u> as the formation of <u>stable products</u> containing <u>strong N-N triple bonds</u> and <u>C=O double bonds</u> releases a large amount of energy.

[1]

(b) TNT can be synthesized in the laboratory in a three-step nitration of methylbenzene.

(i) Name and describe the mechanism of the ***first*** step of the synthesis of TNT from methylbenzene.

Electrophilic Substitution mechanism

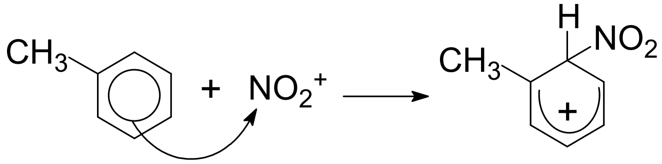
Step 1

Generation of strong electrophile NO_2^+:

$2H_2SO_4 + HNO_3 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$
(catalyst)

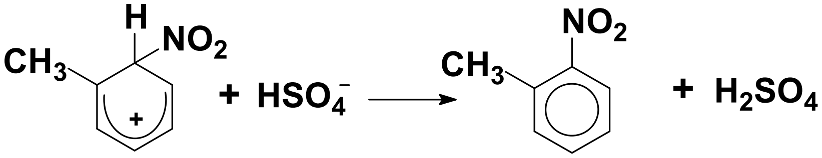
Step 2

Electrophilic attack of NO_2^+ on methylbenzene to form resonance-stabilised carbonium ion.



Step 3

HSO_4^- abstracts H^+ from carbonium ion to give 2-nitromethlybenzene and H_2SO_4 catalyst is regenerated.



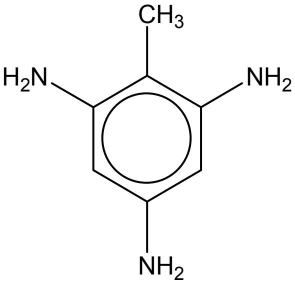
[3]

(ii) "Subsequent nitrations of the ring after the first one become more difficult". Comment on this statement.

The reactivity of the ring decreases for every nitro group added. This is because $–NO_2$ group is an <u>electron withdrawing inductive group</u> (or deactivating group) and will <u>decrease</u> the <u>electron density</u> of the benzene ring which makes it <u>less susceptible to electrophilic attack</u> of subsequent $-NO_2$ groups.

[1]

(iii) TNT can be converted into a non toxic form by reducing it to the amine as shown.

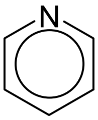
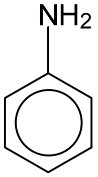


State the reagent(s) and conditions required for this conversion.

Reflux with Sn and concentrated HC*l*, followed by NaOH(aq)

[1]

(c) The pK_b values of some nitrogeneous bases are given below.

Methylamine	Trimethylamine	Ammonia	Hydroxylamine	Pyridine	Phenylamine
CH_3NH_2	$(CH_3)_3N$	NH_3	NH_2OH		
3.34	4.19	4.74	6.80	8.75	9.37

Explain the relative basicity of

(i) methylamine and trimethylamine;

Trimethylamine, is less basic than methylamine, due to presence of three bulky $-CH_3$ substituents which reduces the availability of the lone pair of electrons on nitrogen of trimethlyamine for donation to acid.

[1]

(ii) ammonia and hydroxylamine;

Hydroxylamine, is less basic than ammonia, due to electron-withdrawing inductive effect of the –OH group which makes the lone pair of electrons on its nitrogen less available for donation to acid.

[1]

(iii) pyridine and phenylamine.

Phenylamine is less basic than pyridine as the lone pair of electrons on nitrogen of phenylamine is delocalised into the aromatic ring, hence less available for donation to acid.

The lone pair on N of the heterocyclic aromatic ring is found in sp^2 orbital which is planar with the aromatic ring. Hence it is not delocalised into the aromatic ring.

[2]

(d) Explain the following observations:

(i) Alanine, $CH_3CH(NH_2)CO_2H$, extracted from silkworm is optically active whereas alanine synthesised via the following reaction scheme is optically inactive.

$$CH_3CH_2CO_2H \xrightarrow{Br_2\ /\ uv} CH_3CHBrCO_2H \xrightarrow{\text{excess } NH_3} CH_3CH(NH_2)CO_2H$$

Only one optical isomer is found naturally in silkworm and it rotates plane of polarised light due to presence of a chiral carbon.
When alanine is synthesised from the reaction scheme, a racemic mixture containing equal amount of both enantiomers is formed. Thus net optical activity is zero.

[2]

(ii) Egg white (which is originally colourless and transparent) turns white and opaque when an aqueous solution containing heavy metal ions such as Cu^{2+} is added to it.

Heavy metal ions such as Cu^{2+} will attract negatively charged R groups such as $\underline{-CO_2^-}$, hence <u>disrupting</u> the original <u>ionic bonds</u> holding the tertiary structure in egg white. This causes the protein chains to <u>unfold</u> and expose the <u>hydrophobic</u> R groups. Hence <u>solubility decreases</u> leading to precipitation and thus it turns white.

[2]

[Total: 20]