YISHUN JUNIOR COLLEGE
H2 CHEMISTRY 9647
JC2 INTENSIVE REVISION PACKAGE
Structured and Free Response Questions
(Extracted from 2010 Prelim Exams)

Name: ____ CTG: ________________

Contents

Section A: Physical Chemistry

Section B: Inorganic Chemistry

Section C: Organic Chemistry

DISCLAIMER

This publication is intended for your own personal revision purpose. As it contains the questions from the Preliminary Examinations (2010) of other colleges, **no part of this publication can be transmitted, in electronic means or otherwise, for other purposes**. This disclaimer is made in protection of the rights of all colleges who have shared their Preliminary Examination papers with us.

TOPIC 1: ATOMS, MOLECULES AND STOICHIOMETRY

1 CJC/2010/P2/Q2(a) Level of Difficulty: [☆]

In atmospheric pollution, nitrogen oxides commonly refer to a mixture of nitric oxide, NO, and nitrogen dioxide, NO_2, collectively represented as NO_x.

(a) Nitrogen dioxide, NO_2, a reddish-brown toxic gas with a characteristic sharp, biting odour is widely used as an intermediate in the Ostwald process for the industrial synthesis of nitric acid, as shown in the equation below:

$$3NO_2 + H_2O \rightarrow NO + 2HNO_3$$

Explain what is meant by *disproportionation* with reference to the reaction shown above, clearly stating the species and change in oxidation states involved.

2 HCI/2010/P2/Q2(d) Level of Difficulty: [☆]

A sample of copper contains the two isotopes ^{63}Cu and ^{65}Cu only. An experiment is conducted to find the relative atomic mass of this sample and is found to be 63.9.

(i) Explain why the value found is not a whole number.

(ii) Suggest why the relative atomic mass stated above differs from the value obtained from the periodic table.

[2]

3 NYJC/2010/P3/Q4(a) Level of Difficulty: [☆]

Silicon is found in Period 3 of the Periodic Table. It is the second most abundant element in the earth's crust after oxygen.

(i) Silicon has numerous known isotopes of which ^{28}Si, ^{29}Si and ^{30}Si are stable. Given that 3.1% of naturally occurring silicon is ^{30}Si, calculate the natural abundance of ^{28}Si.

4 PJC/2010/P3/Q3(b) Level of Difficulty: [☆]

One way to test for CO_2 gas is to bubble it into limewater, $Ca(OH)_2(aq)$. However, calcium hydroxide is only sparingly soluble.

An excess of solid calcium hydroxide is shaken in 0.010 mol dm^{-3} sodium hydroxide to reach equilibrium and then filtered. 25.0 cm^3 of the filtered solution is required to neutralise 20.0 cm^3 of 0.050 mol dm^{-3} hydrochloric acid.

(i) Calculate the total hydroxide ion concentration in mol dm^{-3} in the solution.

(ii) Calculate the concentration of hydroxide ions which is associated with the calcium ions.

(iii) Calculate the concentration of calcium ions in mol dm^{-3} in the solution.

20 HCI/2010/P3/Q5(a) Level of Difficulty: [✯✯✯]

Norsethite, $Ba_xMg_y(CO_3)_z$, is a mineral consisting of barium carbonate and magnesium carbonate. The decomposition temperatures of barium carbonate and magnesium carbonate are 1350 °C and 540 °C respectively.

(ii) A sample of pure norsethite was heated strongly at 1500 °C until no further change occurred. The gas evolved was collected and found to occupy a volume of 72 cm^3 at room temperature and pressure. The residue was a white powder which was dissolved in dilute nitric acid. On addition of aqueous sodium sulfate to the resulting solution, a white precipitate of barium sulfate was formed. The precipitate was dried and its mass was found to be 0.35 g.

Write an equation, with state symbols, to represent the decomposition of norsethite, giving your answer in terms of *x*, *y*, and *z*. Hence deduce the values of *x*, *y* and *z*.

[M_r of norsethite was found to be less than 300.]

21 PJC/2010/P3/Q4(b) Level of Difficulty: [✯✯✯]

When air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3, and the resultant solution is evaporated, crystals of a salt **X** are then isolated. **X**, which contains an octahedral complex ion, has the following composition by mass.

element	Co	N	H	C*l*
percentage by mass	25.2	24.0	5.1	45.7

On adding an excess $AgNO_3$(aq) to a solution containing 0.01 mol of **X**, 1.43 g of AgC*l*(s) is precipitated. Only free chloride ion is able to be precipitated as AgC*l*(s). Chloride ion bound as ligand in the complex ion with cobalt cannot be precipitated.

(i) Calculate the empirical formula of **X**.

(ii) Calculate the number of moles of AgC*l* precipitated.

(iii) Each of the cobalt complex ions contains 6 ligands. Hence, deduce the structural formula of **X**.

(iv) State the oxidation number of cobalt in **X**.

[6]

Suggested Answers

1 CJC/2010/P2/Q2(a) Level of Difficulty: [✯]

Disproportionation for the above reaction is the simultaneous reduction of N from +4 oxidation state in NO_2 to +2 oxidation state in NO as well as oxidation from +4 oxidation state in NO_2 to +5 oxidation state in HNO_3.

2 HCI/2010/P2/Q2(d) Level of Difficulty: [☆]

(i) Atomic mass is the weighted average of the mass of the isotopes

(ii) Percentage abundance of the isotopes in this sample differs from what is normally obtained OR There are more than 2 types of isotopes of copper.

3 NYJC/2010/P3/Q4(a) Level of Difficulty: [☆]

Let the abundance of ^{28}Si be x %

❶ $$\frac{x}{100}(28) + \frac{100-3.1-x}{100}(29) + \frac{3.1}{100}(30) = 28.1$$

$$x = 93.1\%$$

❶ for correct answer

4 PJC/2010/P3/Q3(b) Level of Difficulty: [☆]

(i) **Total no. of mol of hydroxide ions =** $\frac{20.0}{1000} \times 0.050$ **= 1.00×10^{-3} mol**

$[OH^-]$ = $\frac{1.00\times10^{-3}}{25.0} \times 1000$ **= 0.0400 mol dm^{-3}**

(ii) **No. of mol of OH^- from NaOH =** $\frac{25.0}{1000} \times 0.010$ **= 2.50×10^{-4} mol**

No. of mol of OH^- from $Ca(OH)_2$ = $1.00 \times 10^{-3} - 2.50 \times 10^{-4}$
= 7.50×10^{-4} mol

$[OH^-]$ from $Ca(OH)_2$ = $\frac{7.50\times10^{-4}}{25.0} \times 1000$ **= 0.0300 mol dm^{-3}**

(iii) **$[Ca^{2+}]$ = 0.0300 /2 = 0.0150 mol dm^{-3}**

5 VJC/2010/P2/Q5(a) Level of Difficulty: [☆]

(i)

Element	C	H	O
% by mass	63.2	8.7	28.1
No. of moles	63.2 / 12.0 = 5.27	8.7 / 1.0 = 8.7	28.1 / 16.0 = 1.76
Mole ratio	3	5	1

Empirical formula of **X** is C_3H_5O.

(ii)

No. of moles of Br_2 = $\frac{2.11}{2(79.9)}$ = 0.0132 mol

M_r of **X** = $\frac{1.50}{0.0132}$ = 113.6

(iii)

Let the molecular formula of **X** be $(C_3H_5O)_n$.
$(3 \times 12.0 + 5 \times 1.0 + 16.0)n = 113.6$
$n = 2$
Molecular formula of **X** is $C_6H_{10}O_2$.

6 YJC/2010/P2/Q4(a) Level of Difficulty: [☆]

	P	O
% by mass	**43.7**	**56.3**
No of moles	**1.410**	**3.519**
Ratio	**1.00**	**2.50**
	2	**5**

$$(31 \times 2 + 16 \times 5)n = 288$$
$$n = 2$$
molecular formula P_4O_{10}

7 ACJC/2010/P3/Q5(d) Level of Difficulty: [☆☆]

(i) Calculate the empirical formula of the red solid, and hence write the oxidation number of iron in the red solid.

	Ba	**Fe**	**O**
Mass/g	**53.4**	**21.7**	**24.9**
No of mol	**53.4/137**	**21.7/55.8**	**24.9/16**
	= 0.390	**=0.390**	**= 1.56**
simplest ratio	**1**	**1**	**4**

Empirical formula = $BaFeO_4$
oxidation number = +6

(ii) Construct a balanced ionic equation for the reaction between Fe_2O_3, OCl^- and OH^-.

$Fe_2O_3 + 10OH^- \longrightarrow 2FeO_4^{2-} + 5H_2O + 6e$ oxidation
$OCl^- + H_2O + 2e \longrightarrow Cl^- + 2OH^-$ reduction

$$\mathbf{Fe_2O_3 + 3OCl^- + 4OH^- \longrightarrow 2FeO_4^{2-} + 3Cl^- + 2H_2O}$$

8 CJC/2010/P2/Q3(c) Level of Difficulty: [☆☆]

Volume of air in the room = (5)(5)(3) = 75 m^3

600ppmv of CO_2 = 600 m^3 of CO_2 in 10^6 m^3 of air

$$\text{Volume of } CO_2 \text{ needed} = \frac{(75)(600)}{1 \times 10^6}$$
$= 0.045\ m^3$
$= 45000\ cm^3$
$= 45\ dm^3$

$$\text{Amount of } CO_2 \text{ required to reach the limit} = \frac{45}{24}$$
$=1.88$ mol

9 MI/2010/P3/Q1(b) Level of Difficulty: [☆☆]

(i) *1m for working ; 1m for answer – $Cu_2O_5CH_2$ / $CuCO_3 \bullet Cu(OH)_2$*

(ii) *$[Cu(H_2O)_6]^{2+}$*

(iii) *D is CuO / copper(II) oxide ; $Cu_2O_5CH_2 \rightarrow 2CuO + CO_2 + H_2O$*

$$\text{Amount of malachite} = \frac{10}{2 \times 63.5 + 5 \times 16.0 + 12.0 + 2 \times 1.0} = 0.04525\ mol$$

$$\text{Amount of } D = 2 \times 0.04525 = 0.09050\ mol$$

$$\text{Mass of } D = 0.09050 \times (63.5 + 16.0) = 7.19\ g$$

(iv) *E is copper; F is Fe^{2+} / $FeSO_4$; $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$*

(v) *blue ppt./solid formed ; dissolves in excess NH_3 to give dark blue colour*

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

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

10 MJC/2010/P2/Q3(c) Level of Difficulty: [☆☆]

(i) $4Br_2 + S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Br^-$

(ii) No. of moles of $S_2O_3^{2-}$ = 30/1000 x 0.100

= 0.00300 mol

$S_2O_3^{2-} \equiv 4Br_2 \equiv 6\ SiF_4$

No. of moles of SiF_4 = 6 x 0.003

= 0.018

Mass of SiF_4 = 0.018 x (28.1 +19.0 x 4)

= 1.9 g

(iii) Disproportionation

$3\ Br_2 + 6\ OH^- \rightarrow 5Br^- + BrO_3^- + 3\ H_2O$

11 NJC/2010/P2/Q2(c) Level of Difficulty: [☆☆]

(i) $Cr_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Cr$

(ii) 74.4 tons

12 RVHS/2010/P3/Q1(a) Level of Difficulty: [☆☆]

Amount of $MnO_2 = \frac{1.00}{54.9 + 2 \times 16.0}$

$= 0.0115$ mol

Amount of $Cl_2 = \frac{276}{24000}$

$= 0.0115$ mol

Therefore $MnO_2 \equiv Cl_2 \equiv 2e^-$ $(2Cl^- \rightarrow Cl_2 + 2e^-)$

Oxidation number of Mn in Mn-containing product = +4 – 2 = +2

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

$MnO_2(s) + 2HCl(aq) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$

13 RVHS/2010/P3/Q5(g) Level of Difficulty: [☆☆]

(i) Blue solution turns brown (with black ppt) and cream ppt formed.

$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(s/aq)$

(ii) Amount of $S_2O_3^{2-}$ needed $= 0.100 \times \frac{15.8}{1000}$

$= 0.00158$ mol

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ $(2S_2O_3^{2-} \equiv I_2)$

Amount of I_2 produced $= \frac{0.00158}{2}$

$= 0.000790$ mol

$2Cu^{2+} \equiv I_2$

Amount of Cu in sample $= 2 \times 0.000790$

$= 0.00158$ mol

Mass of Cu in sample $= 0.00158 \times 63.5$

$= 0.100$ g

$$\text{\% by mass of Cu in sample} = \frac{0.100}{2.0} \times 100\%$$
$$= 5.00\%$$

14 SAJC/2010/P2/Q2(a) Level of Difficulty: [☆☆]

(i) $NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O$

(ii) Moles of $S_2O_3^{2-}$ = 0.12 × 0.023 = 0.00276mol

$2S_2O_3^{2-} + Sn^{4+} \rightarrow Sn^{2+} + S_4O_6^{2-}$

Moles of Sn^{4+} = Moles of Sn^{2+} = 0.00276/2 = 0.00138mol

Moles of Sn^{2+} in 100 cm^3 solution = 0.00138 × 100/25 = 0.00552mol

Mass of Sn = 0.00552 × 119 = 0.657g

Percentage by mass = 0.657/5.00 × 100 = 13.1%

15 SAJC/2010/P3/Q5(d) Level of Difficulty: [☆☆]

(i) $2MnO_2(s) + 4OH^-(aq) + O_2(g) \rightarrow 2MnO_4^{2-}(aq) + 2H_2O(l)$

(ii) $3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(l)$

Disproportionation reaction has taken place.

Mn(VI) is oxidised to Mn(VII) and reduced to Mn(IV) at the same time.

16 SRJC/2010/P2/Q3(a) Level of Difficulty: [☆☆]

(i)

$\mathbf{TiO_2\ (s) + 2C\ (s) + 2Cl_2\ (g) \rightarrow TiCl_4\ (g) + 2CO\ (g)}$

$\mathbf{TiCl_4\ (g) + 2Mg\ (l) \rightarrow Ti\ (s) + 2MgCl_2\ (l)}$

(ii)

Amt of Ti = $\frac{100}{47.9} = 2.088 mol$

$Ti \equiv TiO_2$

Mass of TiO_2 required = 2.088 x (47.9 + 16 + 16) = **167 g**

17 SRJC/2010/P3/Q4(d) Level of Difficulty: [☆☆]

Analysis: $Mg + NH_3 \rightarrow$ **P** $+ H_2$
P $+ H_2O \rightarrow$ **Q**(white solid) + $\mathbf{NH_3}$
Element present in P is Mg and N

Amount of H^+ ion to neutralize ammonia = $2 \times \frac{20.00}{1000} \times 0.1$ = 0.00400mol

Amount of **P** reacted with water = $\frac{0.198}{100.9}$ = 0.00196 mol
Ratio P : NH_3
0.00196 : 0.00400
1: 2 (Since 1 mol of **P** forms 2 mol of NH_3)
Since there are 2 N, using M_r = 100.9, there will be 3 Mg
P = Mg_3N_2
Q = MgO
$3Mg + 2NH_3 \rightarrow Mg_3N_2 + 3H_2$
$Mg_3N_2 + 3H_2O \rightarrow 3MgO + 2NH_3$

18 TJC/2010/P3/Q3(e) Level of Difficulty: [☆☆]

(i)
- $6CrO_2 + 10H^+ \rightarrow 4Cr^{3+} + Cr_2O_7^{2-} + 5H_2O$
- $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

(ii) No of moles of Fe^{2+} = 10.0 x 0.02/1000 = 2.00 x 10^{-4}

$Cr_2O_7^{2-} \equiv 6Fe^{2+} \equiv 6CrO_2$

No of moles of CrO_2 = 2.00 x 10^{-4}

Mass of CrO_2 = 2.00 x 10^{-4} x 84 = 1.68 x 10^{-2} g.

19 AJC/2010/P3/Q1(c) Level of Difficulty: [☆☆☆]

(c)(i) The halogen is bromine.

	Cr	H_2O	Br
% mass	13.0	27.0	60.0
Moles	0.25	1.5	0.75
Ratio	**1**	**6**	**3**

Empirical formula is $\mathbf{Cr(H_2O)_6Br_3}$

(c)(ii) n(**A**) = 0.400 ÷ 399.7 = 0.001 mol
n(AgBr) = 0.188 ÷ 187.9 = 0.001 mol
1 mol of **A** contains 1 mol of free Br^- ion.

A is $[Cr(H_2O)_4Br_2]Br{\bullet}2H_2O$

(c)(iii) +3

20 HCI/2010/P3/Q5(a) Level of Difficulty: [☆ ☆ ☆]

$Ba_xMg_y(CO_3)_z(s) \rightarrow xBaO(s) + yMgO(s) + zCO_2(g)$

$$n_{CO2} = \frac{72}{24000} = 0.003 \text{ mol}$$

$BaO(s) + 2HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + H_2O(l)$

Similarly, $Mg(NO_3)_2$ is also formed.

$Ba(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HNO_3(aq)$

$$nBaSO_4 = nBaO = \frac{0.35}{(137+32.1+64)} = 0.001502 \text{ mol}$$

$x : z$
$= 1 : 2$

By balancing O atoms,
$3z = x + y + 2z$
$\Rightarrow z = x + y$
$\Rightarrow x = y$

$\therefore$ **$x = y = 1;\ z = 2$**

21 PJC/2010/P3/Q4(b) Level of Difficulty: [☆ ☆ ☆]

(i) **Let mass be 100 g.**

Element:	Co	N	H	Cl
Mass / g	25.2	24.0	5.1	45.7
Amt / mol	0.428	1.71	5.1	1.29
Mole ratio	1	4	12	3

Empirical formula is $CoN_4H_{12}Cl_3$.

(ii) **Amount of $AgCl$ precipitated = 9.97×10^{-3} mol**

(iii) **No. of free Cl^- ion from X that reacted with Ag^+ ions = $9.97 \times 10^{-3} / 0.01$**
= 0.997 ≈ 1

There are 4 NH_3 and 2 Cl^- ligands surrounding the cobalt ion.

Structural formula is $[Co(NH_3)_4Cl_2]^+\ Cl^-$. (reject $[Co(NH_3)_4Cl_2]^+$)

(iv) **Oxidation state of Co = +3**

TOPIC 2: ATOMIC STRUCTURE

1 ACJC/2010/P2/Q3(c) Level of Difficulty: [✮]

The use of the Data Booklet is relevant to the following questions.

(i) By comparing the first four Ionisation Energies of F and O, explain the common trend seen.

(ii) Briefly account for the difference in the Second Ionisation Energy values between F and O.

[4]

2 CJC/2010/P3/Q1(a) Level of Difficulty: [✮]

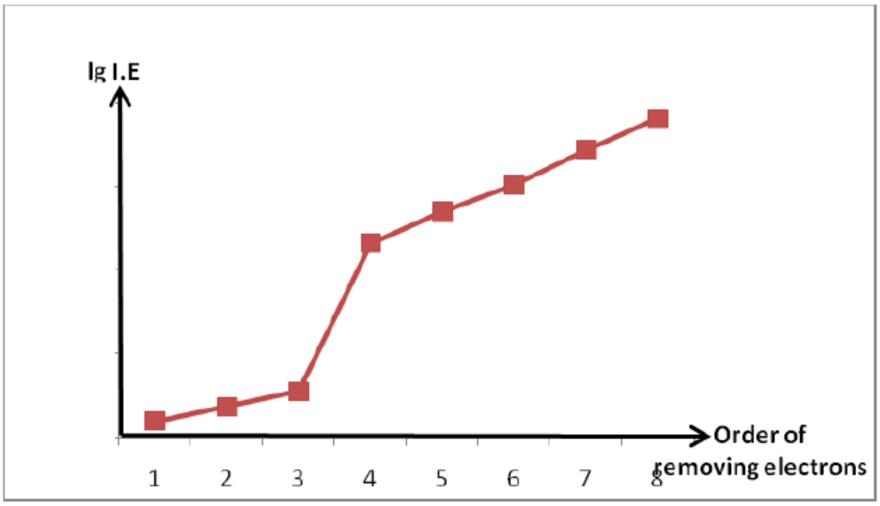
The first ionisation energy of aluminium is 577 kJ mol^{-1}, while that of magnesium is 736 kJ mol^{-1}. Explain this observation. [2]

3 PJC/2010/P3/Q4(a) Level of Difficulty: [✮]

(ii) Describe the cobalt atom, ^{59}Co, as fully as you can, including the nature and location of the sub-atomic particles.

4 SRJC/2010/P2/Q1(a),(b),(f) Level of Difficulty: [✮]

The graph below shows the first eight successive ionisation energies of **X** against the order of removal of electrons.



(a) From the graph, deduce which group of the periodic table does element **X** belongs to.

[2]

(b) Given that element **X** is from period 3, identify element **X**.

[1]

(f) Explain whether **X** or the element below **X** in the same group will have higher first ionisation energy.

[2]

7 MJC/2010/P2/Q1(b) Level of Difficulty: [☆☆]

Elements **K**, **L**, **M** and **N** are four consecutive Period 3 elements. The table below shows the first four ionisation energies of elements **K**, **L**, **M** and **N**.

Element	**First I.E**	**Second I.E**	**Third I.E**	**Fourth I.E**
K	577	1820	2740	11600
L	786	1580	3230	4360
M	1060	1900	2920	4960
N	1000	2260	3390	4540

(i) For element **K,** briefly explain why the energy difference between the removal of the 2nd and 3rd electrons is smaller than that between the removal of the 3rd and 4th electrons.

(ii) Explain why the first ionisation energy of element **N** is lower than that of element **M**.

(iii) Element **T** is a Period 2 element in the same group as element **M**. Suggest with reasoning why element **M** can form an oxo-anion of formula MO_4^{3-} but element **T** cannot.

Suggested Answers

1 ACJC/2010/P2/Q3(c) Level of Difficulty: [☆]

(i) By comparing the first four Ionisation Energies of F and O, explain the common trend seen.

As successive electrons are removed, Ionization Energy increases.

- This is because proton : electron ratio is increasing, since number of protons remains but number of electrons are decreasing (due to it being removed)

- The electrostatic attraction from the remaining electrons is greater and hence more energy is needed to remove subsequent electrons.

(ii) Briefly account for the difference in the 2nd Ionization Energy values between F and O.

F^+: $1s^2\,2s^2\,2p^4$
O^+: $1s^2\,2s^2\,2p^3$

- 2nd IE of F is of smaller value than that of O

- In removing the electron from F^+, it is a removing of one electron from a p orbital which has two electrons in it. There will be repulsion between the two electrons making it easier to be removed.

- Hence, causing the 2nd IE of F to be lower than that of O.

2 CJC/2010/P3/Q1(a) Level of Difficulty: [☆]

Mg $1s^2 2s^2 2p^6 3s^2$ **A*l*** $1s^2 2s^2 2p^6 3s^2 \underline{3p^1}$

- **Lower 1st I.E. of A*l* because less energy is needed to remove a 3p electron in A*l* than a 3s electron in Mg since the 3p electron is *further away* from the nucleus and it also experiences slightly better shielding (from the 3s electrons).**

3 PJC/2010/P3/Q4(a) Level of Difficulty: [☆]

(ii)

sub-atomic particles	**number**	**relative charge**	**location**
protons	**27**	**+1**	**in nucleus**
neutrons	**32**	**0**	**in nucleus**
electrons	**27**	**-1**	**in orbitals / outside the nucleus**

4 SRJC/2010/P2/Q1(a),(b),(f) Level of Difficulty: [☆]

(a)

Removing the 4th valence electron **requires a vast amount of energy**./
There is a **large jump** from the **3rd to 4th IE.**

The **4th electron** is removed from an **inner shell** / There are **3 valence electrons.**

Therefore, element **X** is from **group III**.

(b)

X is **aluminium**.

(f)

Electrons are added to the **next valence shell**.
The **distance** between the nucleus and the valence electrons **increases**.
Decrease in electrostatic forces of attraction between the nucleus and valence electrons.
Less energy needed to remove the valence electron, thus 1st I.E. decreases.
Element X will have a higher first ionization energy.

5 VJC/2010/P2/Q2(b) Level of Difficulty: [☆]

(i)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

(ii)

E is sulfur.
First I.E. of **E** is lower than that of **D** as less energy is required to remove the $\underline{3p^4}$ electron which experiences interelectronic repulsion.

6 HCI/2010/P2/Q2(e) Level of Difficulty: [☆☆]

(i) Correct direction and angle of deflection.

(ii) 1.7°

7 MJC/2010/P2/Q1(b) Level of Difficulty: [☆☆]

(i) 2nd and 3rd electrons occupy the same quantum shell while 3rd and 4th electrons are removed from the different quantum shell.

(ii)

$$\underset{1s^22s^22p^63s^23p^4}{\mathbf{N}} \rightarrow \underset{1s^22s^22p^63s^23p^3}{\mathbf{N}^+} + e$$

$$\underset{1s^22s^22p^63s^23p^3}{\mathbf{M}} \rightarrow \underset{1s^22s^22p^63s^23p^2}{\mathbf{M}^+} + e$$

OR

Element **N** is Group VI and Element **M** is Group V.

There is inter-electron repulsion between the paired electrons in the 3p orbital of element **N**.

Hence less energy is required to remove one valence 3p electron from **N**.

$\Rightarrow$ 1st ionisation energy of **M** > **N**.

(iii) **M**, being in Period 3, has empty and energetically accessible d orbitals to expand the octet configuration. Hence $\mathbf{M}O_4^{3-}$ can exist.

T, being in Period 2, does not have empty and energetically accessible d orbitals to accommodate the extra electrons and cannot expand the octet configuration. Hence $\mathbf{T}O_4^{3-}$ cannot exist.

TOPIC 3: CHEMICAL BONDING

1 <u>AJC/2010/P2/Q4(a),(b)</u> Level of Difficulty: [☆]

Methanethiol (CH_3SH) is a colourless gas with a smell like rotten cabbage. It is a natural substance found in the blood and brain of animals as well as in plant tissues. The boiling points and pK_a values of methanethiol, methanol, ethanol, tert–butanol and water are shown in the table below.

name	formula	boiling point / °C	solubility in water	pK_a at 25 °C
methanethiol	CH_3SH	6	immiscible	10.30
methanol	CH_3OH	65	miscible	15.54
ethanol	C_2H_5OH	78	miscible	15.90
tert–butanol	$(CH_3)_3COH$	82	miscible	18.00
water	H_2O	100	✕	15.74

(a) **(i)** Explain the differences in the boiling points of methanethiol, methanol and water.

(b) **(i)** All the compounds in the table are miscible with water except methanethiol. Draw a diagram to show the interaction between a molecule of ethanol and a molecule of water.

2 <u>MJC/2010/P2/Q2(a)</u> Level of Difficulty: [☆]

The melting points of the chlorides of the Period 3 elements magnesium to phosphorous, are given below.

Compound	Magnesium chloride	Aluminium chloride	Phosphorous pentachloride
Melting point / °C	714	178	162

(i) Account for the difference in the melting points of magnesium chloride and aluminium chloride, in terms of structure and bonding.

3 <u>MJC/2010/P2/Q6(c)</u> Level of Difficulty: [☆]

In gas phase, beryllium chloride exists as Be_2Cl_4, which is formed via dimerisation. Draw the displayed formula of Be_2Cl_4 and label all bond angles.

4 <u>NYJC/2010/P3/Q4(a)</u> Level of Difficulty: [☆]

(ii) Solid silicon melts at 1414 °C and is used widely industrially to manufacture computer chips. Describe the structure and bonding in solid silicon.

(iii) Account for its use in computer chips.

For each case, predict the other product formed and write an equation for its production. Suggest an explanation for the difference in behaviour of PCl_3 and NCl_3.

(ii) Draw a dot and cross diagram for the dibasic acid, H_3PO_3 and state the shape of the molecule.

[5]

Suggested Answers

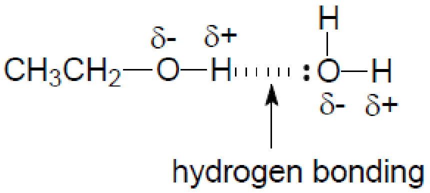
1 AJC/2010/P2/Q4(a),(b) Level of Difficulty: [☆]

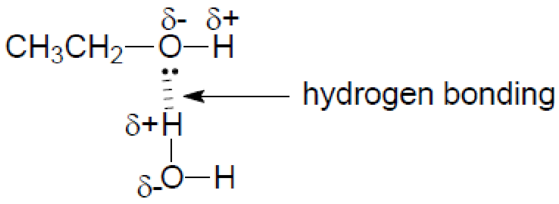
(a)(i) Both water and methanol have **stronger** hydrogen bonding between their molecules compared to **weaker** dipole–dipole attraction between methanethiol molecules.

Water has more extensive hydrogen bonding than methanol, accounting for its highest boiling point.

Methanethiol has the lowest boiling point as the least amount of energy is needed to overcome the weak dipole–dipole attractions.

(b)(i)





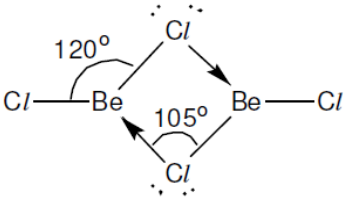
2 MJC/2010/P2/Q2(a) Level of Difficulty: [☆]

(i) $MgCl_2$ has a giant ionic lattice structure held by strong electrostatic forces of attraction between the oppositely charged Mg^{2+} and Cl^- ions. A large amount of energy is required to overcome the strong electrostatic forces of attraction, hence the melting point is high.

Aluminium chloride has a simple molecular structure.

The molecules are non-polar and held by which can be easily broken during melting weak induced dipole-induced dipole attractions/ Van der Waal's forces of attraction. A small amount of energy is required to overcome the weaker forces of attraction between the molecules, hence the melting point is low.

3 MJC/2010/P2/Q6(c) Level of Difficulty: [✯]



4 NYJC/2010/P3/Q4(a) Level of Difficulty: [✯]

(ii)

❶ Silicon has a giant covalent structure with strong covalent bonds between Si atoms.

(iii)

❶ Silicon has low electrical conductivity hence is used as a semi-conductor.

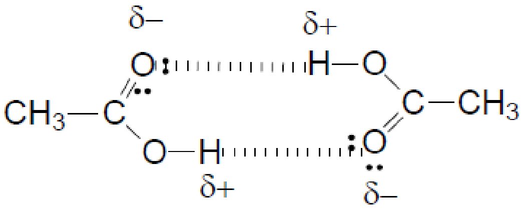
5 SRJC/2010/P2/Q2(b) Level of Difficulty: [✯]

(i) 2 bond pair and 2 lone pair → bent

(ii) 3 bond pair and 1 lone pair → Trigonal pyramidal

6 SRJC/2010/P2/Q4(b) Level of Difficulty: [✯]

In benzene, ethanoic acid forms **dimers.**



In vapour form, the acids exists as monomer as **sufficient energy has overcome** the hydrogen bonds between 2 ethanoic acid molecules

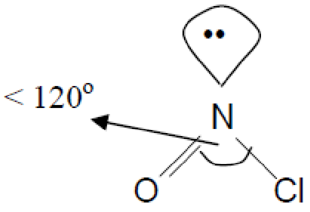
7 VJC/2010/P2/Q2(a) Level of Difficulty: [✯]

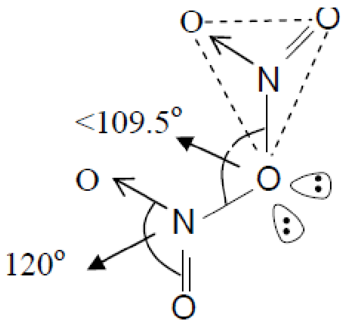
(i)

$MgCl_2$ has ionic bonding between Mg^{2+} and Cl^- ions.
$AlCl_3$ has dispersion forces between the molecules.
More energy is needed
to break the stronger ionic bonding in $MgCl_2$ leading to its higher melting point.

8 ACJC/2010/P3/Q4(a) Level of Difficulty: [☆☆]

(i)

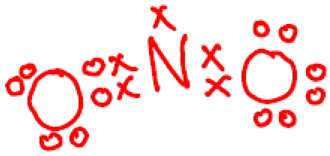


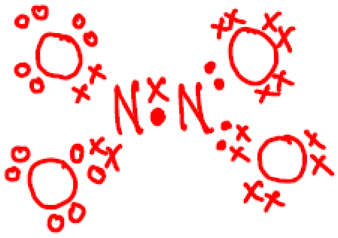


(ii)
- **Both have simple molecular structures and boiling involves breaking of intermolecular forces of attraction.**
- **HNO_3 has intermolecular hydrogen bonding which are stronger than the Van der Waals forces exist between NOCl molecules, hence more energy required to overcome, so higher boiling point.**

9 CJC/2010/P2/Q2(b) Level of Difficulty: [☆☆]

(i) Draw the dot-and-cross diagrams of NO_2 and N_2O_4.





10 HCI/2010/P2/Q2(a),(b) & (c) Level of Difficulty: [☆☆]

(a)(i) Copper: cation / Cu^{2+} ion
metallic bonding

(a)(ii) Iodine: molecule
van der Waals' forces / dispersion forces / id-id interactions

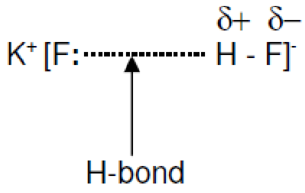
(b) The sea of delocalised electrons is able to accommodate any deformation to the cationic lattice OR The layers of cations can slide past each other while electrons hold them together.

(c) Electrical conductivity / solubility in organic solvent

Conductivity: Mobile electrons available to conduct electricity in copper but no mobile electrons or ions in iodine.
Solubility: Similar intermolecular forces of attraction for iodine and organic solvent, thus iodine is able to form favourable interactions with the organic solvent, but copper is unable to form favourable interactions with the organic solvent.

11 NJC/2010/P3/Q1(a) Level of Difficulty: [☆☆]

(i)

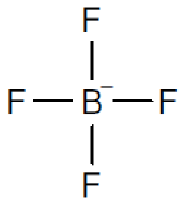


(ii) - CO_2 is a linear non-polar discrete molecule; hence only weak Van der Waals (VDW) forces exist between them. The kinetic energy possessed by CO_2 molecules at room temperature and pressure is sufficient to overcome these interactions, so the molecules are far apart and exist in the gaseous phase.

H_2O is a discrete molecule capable of having H-bonding between the molecules. These are much stronger than the weak VDW forces. The KE of the H_2O molecules under room conditions is not enough to overcome all the H-bonding interactions, thus resulting in them existing in small clusters as a liquid phase.

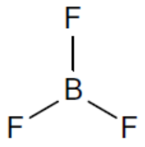
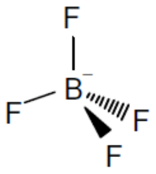
12 NYJC/2010/P2/Q2 Level of Difficulty: [☆☆]

(a)



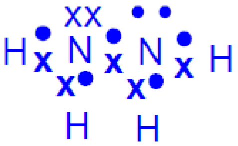
(1)

(b)

BF$_3$	anion of **S**
 (1)	 (1) do not penalise charge or lack of dative bond
Bond angle = 120°	Bond angle = 109.5° or 109° (1) for both bond angles

13 PJC/2010/P3/Q5(a),(b) Level of Difficulty: [☆☆]

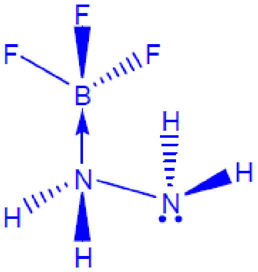
(a) **(i)**



107°

trigonal pyramidal about each N atom

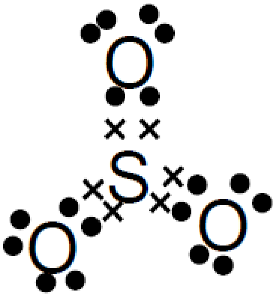
(ii)



(b) **Both ethene and hydrazine are covalent compounds with simple molecular structure. Hydrazine is a polar compound with hydrogen bonds as the intermolecular forces of attraction while ethene has van der Waals' (id-id interactions). More energy is needed to overcome the hydrogen bonds in hydrazine. Hence, the melting and boiling points of hydrazine are much higher than those in ethene.**

14 RVHS/2010/P3/Q2(a) Level of Difficulty: [☆☆]

(i)

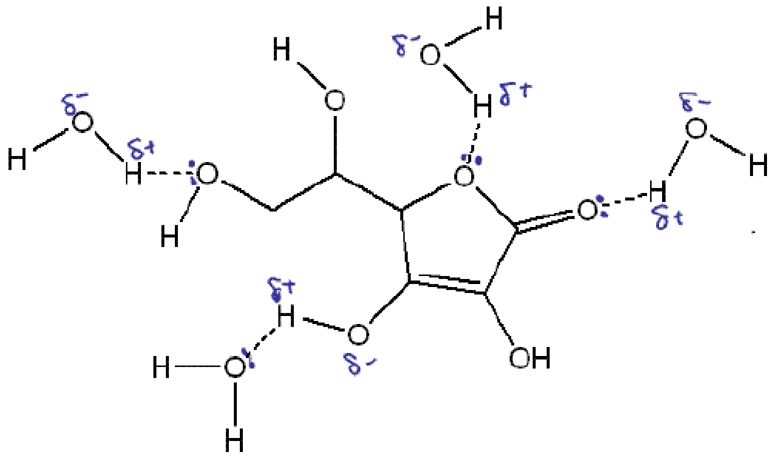


Trigonal planar

(ii) Both SO_2 and SO_3 have simple covalent/molecular structures. As SO_3 molecules have a larger number of electrons, more energy is required to overcome the stronger instantaneous dipole-induced dipole interactions between the non-polar SO_3 molecules than the weaker permanent dipole-permanent dipole interactions between the polar SO_2 molecules. Hence, SO_3 has a higher boiling point than SO_2.

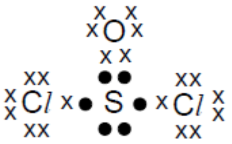
15 SAJC/2010/P2/Q7(a) Level of Difficulty: [☆☆]

(ii)



16 VJC/2010/P2/Q4(b) Level of Difficulty: [☆☆]

(i)



(ii)

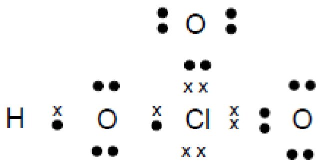
107^{o}

(iv)

CH_3OH molecules are held by hydrogen bonding.
$SOCl_2$ molecules are held by dipole–dipole interactions.
$SOCl_2$ molecules have more electrons than CH_3OH molecules.
Thus, dispersion forces between $SOCl_2$ molecules are stronger than hydrogen bonding between CH_3OH molecules.
More energy is needed to overcome the dispersion forces in $SOCl_2$ leading to its higher boiling point.

17 YJC/2010/P2/Q2(a) Level of Difficulty: [☆☆]

(iii)



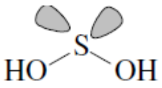
Shape – trigonal pyramidal ; bond angle - 107^0

18 MJC/2010/P2/Q6(d) Level of Difficulty: [☆☆☆]

(i) Be in BeF_2 is electron deficient and is able to accept 2 dative bonds from the fluoride ions to fulfill its stable octet configuration.

(ii)

19 NJC/2010/P2/Q6(c) Level of Difficulty: [☆☆☆]



has two lone pairs of electrons around S, which force the HÕŠOH bond angle to be much smaller than the tetrahedral angle. This result in the two O atoms brought very close together. Both of these O atoms carry considerable partial negative charge and each also possesses two lone pairs of electrons. The very strong repulsion between them makes the molecule highly unstable. Thus $S(OH)_2$ is unable to exist.

20 NJC/2010/P3/Q4(a) Level of Difficulty: [☆☆☆]

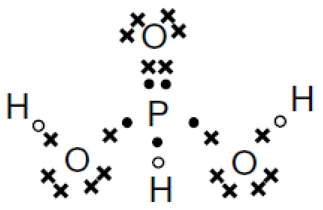
(i) P is less electronegative than Cl, hence H_2O attacks the partial positively charged P and displace Cl to form H_3PO_3 and HCl.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

N is more electronegative than Cl, hence H_2O attacks the partial positively charged Cl to form HOCl and NH_3.

$$NCl_3 + 3H_2O \rightarrow 3HOCl + NH_3$$

(ii)

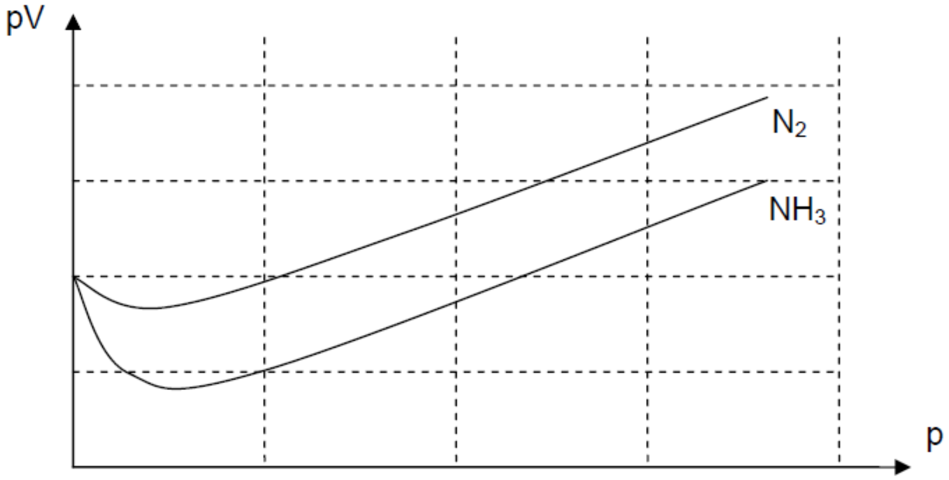


TOPIC 4: THE GASEOUS STATE

1 PJC/2010/P2/Q1(a) Level of Difficulty: [☆]

Ammonia is an important material in the production of various products, including nitric acid and fertilisers.

(a) Ammonia gas behaves less ideally than nitrogen gas. The following graphs show how the same amount of nitrogen gas and ammonia gas, at the same temperature, behave over a range of pressure.



(i) On the axes above, sketch a graph to show the behaviour of an ideal gas, of the same amount and with the same temperature as the nitrogen gas and ammonia gas.

(ii) Draw a diagram to show the intermolecular forces of attraction between ammonia molecules.

(iii) Explain why ammonia does not behave ideally.

(iv) A sample of ammonia gas in a vessel has a temperature of 250 °C and a pressure of 8.0×10^4 Pa. Assuming ideal gas behaviour, calculate the density of the ammonia gas in the vessel.

2 ACJC/2010/P2/Q3(b) Level of Difficulty: [☆☆]

The addition of F_2 to aqueous NaOH produces aqueous NaF and a triatomic gaseous molecule, **A**.

To produce a certain amount of **A**, a limited amount of F_2 gas is added into 150 cm^3 of 0.100 mol dm^{-3} of aqueous NaOH solution. At room temperature and pressure, the volume of **A** collected is 142 cm^3 and it weighs 0.324 g.

25.0 cm^3 of the resultant solution is titrated against 0.0500 mol dm^{-3} of aqueous H_2SO_4 solution using methyl orange as an indicator. 15.00 cm^3 of H_2SO_4 was needed for neutralisation.

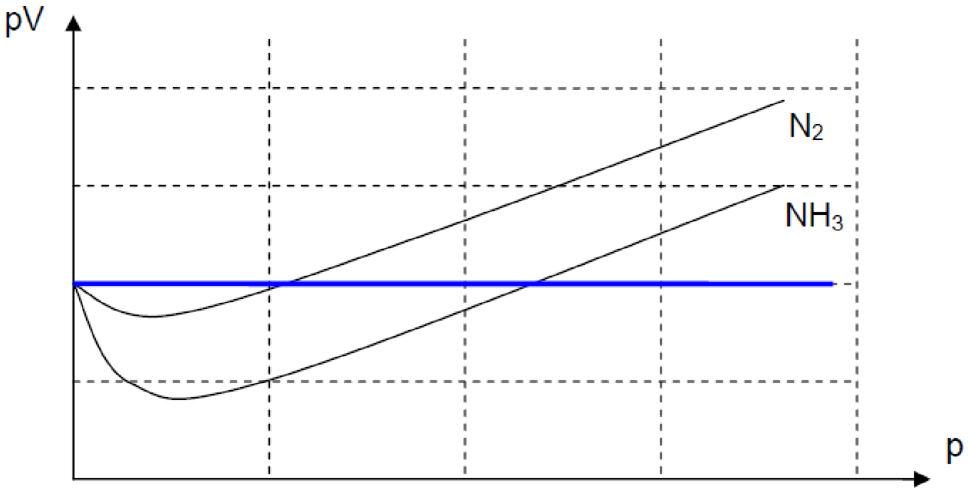
(i) Using the ideal gas equation, calculate the M_r of **A**.

(ii) Hence, deduce the molecular formula of **A**.

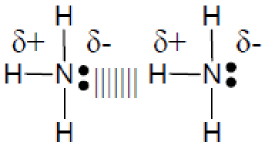
Suggested Answers

1 PJC/2010/P2/Q1(a) Level of Difficulty: [☆]

(a) **(i)**



(ii)



(iii)
- **<u>hydrogen bond</u> between NH_3 molecules**
- **inter-molecular forces of attraction is not negligible**

(iv) $pV = nRT \Rightarrow pV = (m/M_r)RT$

$pM_r = (m/V)RT = \rho RT$

$$\rho = \frac{pM_r}{RT} = \frac{8.0 \times 10^4 \times 17.0}{8.31 \times (250 + 273)} \Rightarrow \rho = 313 \text{ g m}^{-3}$$

2 ACJC/2010/P2/Q3(b) Level of Difficulty: [☆☆]

(i) Using the ideal gas equation, calculate the M_r of **A**.

$PV = nRT$

$$PV = \frac{mass}{Mr}RT$$

$$M_r = \frac{0.324}{1.01 \times 10^5 \times 142 \times 10^{-6}} \times 8.31 \times 298 = 55.9$$

(ii) Hence, deduce the molecular formula of **A**.

F_2O

(iii) This is because F_2O has permanent dipole – permanent dipole interactions and it is not negligible.

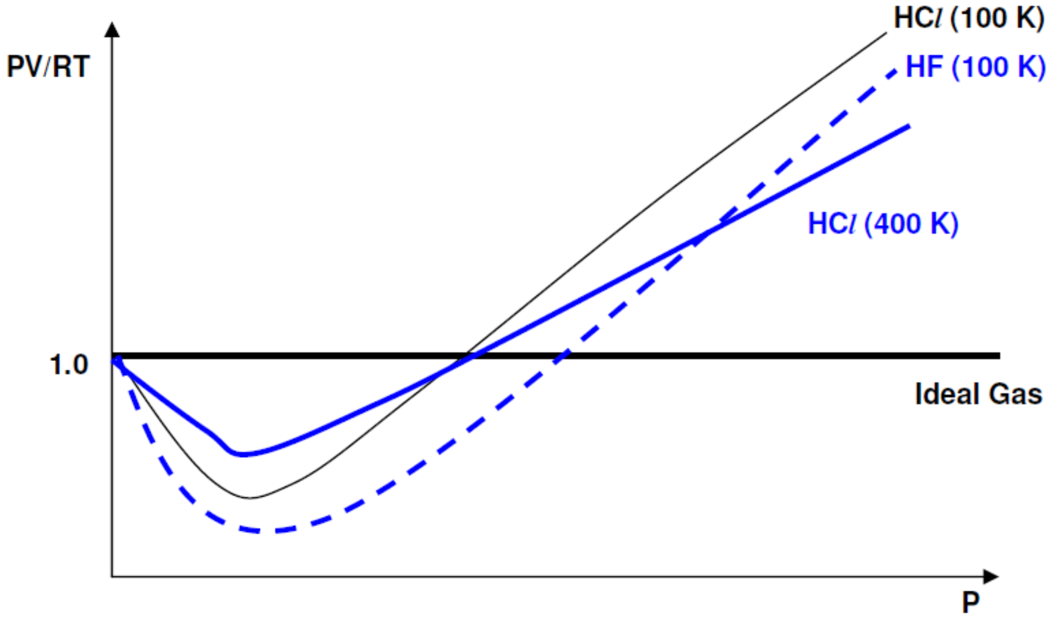
3 HCI/2010/P2/Q3(a) Level of Difficulty: [☆☆]

(i) Ammonia exerts strong Intermolecular forces (hydrogen bonding) between the gas molecules. (Do not accept large size of molecules as pressure is 1 atm)

(ii) Molecules of ammonia will not be close enough above 133 °C as the kinetic energy of molecules are very high; short range intermolecular forces will not operate.

4 MJC/2010/P2/Q3(a) Level of Difficulty: [☆☆]

3(a) (i)



(ii) HF is less ideal than HC*l* as HF has stronger intermolecular hydrogen bonding whereas HC*l* has weaker intermolecular Van der Waals forces of attraction.

(iii) At high temperature, there are negligible forces of attraction between the gas particles.

Hence, HC*l* gas will deviate less from ideal gas behaviour.

5 NJC/2010/P2/Q3(b),(c) Level of Difficulty: [☆☆]

b (i) P = 924 kPa

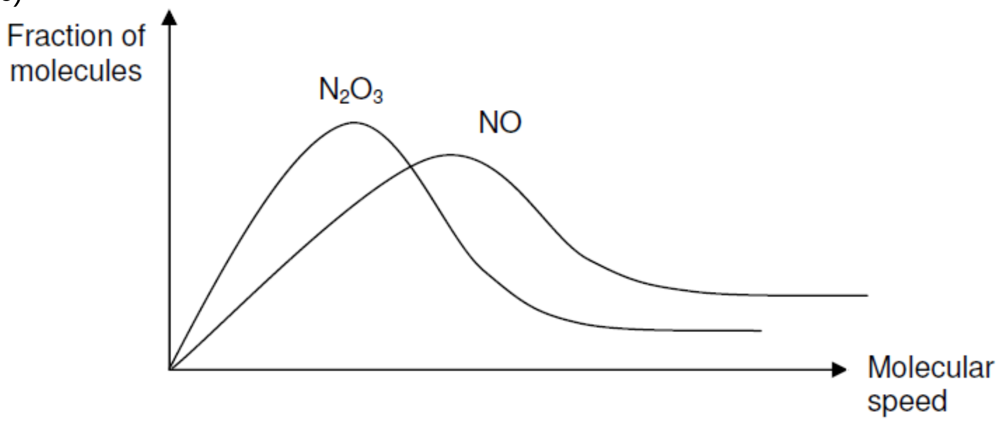
(ii)

In reality, there is presence of attractive forces between the gaseous molecules, resulting in a lower pressure exerted on the wall of the vessel.

OR

In reality, the volume occupied by the gaseous molecules cannot be considered to be negligible as compared to the size of the vessel.

(c)



NO has smaller molecular mass than N_2O_3, is lighter and thus has higher average molecular speed than N_2O_3.

6 SAJC/2010/P3/Q3(b) Level of Difficulty: [☆☆]

(i) $M_r = \frac{(mRT)}{pV} = \frac{1.56 \times 8.31 \times (273 + 180)}{(32.3 \times 10^3 \times 1 \times 10^{-3})}$

≈ 182

(ii) M_r of $AlCl_3$ = 133.5

M_r of Al_2Cl_6 = 267

Let y = % of dimer, (100 – y) = % of monomer

$\frac{267y + (100 - y) \times 133.5}{100} = 182$

% of dimer = 36.3%

7 TJC/2010/P3/Q5(b) Level of Difficulty: [☆☆]

(iv) pV = nRT

- number of moles of O_2 = $\frac{PV}{RT} = \frac{101\times10^3\times95\times10^{-6}}{8.31\times(30+273)}$ = 3.81×10^{-3} mol

(v) number of moles of $M(NO_3)_2.xH_2O$ = 0.00762 mol

number of moles of H_2O = $\frac{0.55}{18.0}$ = 0.0306 mol

- $x = \frac{0.0306}{0.00762} = 4$

- M_r of $M(NO_3)_2 = \dfrac{1.80-0.55}{0.00762} = 164.0$

  A_r of M = 164.0 – 2[14.0 + 3(16.0)] = 40.0
- *M* is calcium

  [the hydrate is $Ca(NO_3)_2.4H_2O$]

8 VJC/2010/P3/Q2(b) Level of Difficulty: [✮✮✮]

(i)

a is dependent on the strength of the attractive forces between molecules while *b* is dependent on the volume of the molecules.

(ii)

Attractive forces slow down the movement of a molecule approaching the wall of the container.
This causes the actual pressure to be lower than that of an ideal gas.
Hence, the term is added to *P*.
The volume of the molecules causes the free space within which molecules can move to be less than the entire volume of the container.
Hence, the *b* term is subtracted from *V*.

(iii)

Both helium and carbon dioxide are made up of non–polar molecules held by dispersion forces.
Dispersion forces in CO_2 are stronger due to the higher number of electrons present. Hence, CO_2 has a higher value of *a* than He.
Ammonia molecules are held by hydrogen bonding
which is stronger than dispersion forces. Hence, ammonia has the highest *a* value.

TOPIC 5: CHEMICAL ENERGETICS

1 AJC/2010/P3/Q4(d) Level of Difficulty: [☆]

When solid selenium dioxide undergoes sublimation, an equilibrium exists between the two phases.

$$SeO_2(s) \rightleftharpoons SeO_2(g)$$

The standard enthalpy change, $\Delta H^{\ominus}$, and the standard entropy change, $\Delta S^{\ominus}$, of sublimation are +111 kJ mol^{-1} and +183 J K^{-1} mol^{-1} respectively.

(i) Predict if the sublimation of solid selenium dioxide is spontaneous under room temperature.

(ii) Calculate the temperature at which solid selenium dioxide starts to sublime.

(iii) State *any* assumptions which you have made in the calculation in **(d)(ii)**.

[4]

2 HCI/2010/P3/Q1(b) Level of Difficulty: [☆]

The equation below shows how phosphorus pentachloride, PCl_5, reacts with a limited amount of water.

$$PCl_5(s) + H_2O(l) \rightarrow POCl_3(l) + 2HCl(g) \qquad \Delta H_r$$

The following data are given:

Standard enthalpy change of formation of $PCl_5(s)$ = –444 kJ mol^{-1}
Standard enthalpy change of formation of $POCl_3(l)$ = –1186 kJ mol^{-1}
Standard enthalpy change of formation of $HCl(g)$ = –92 kJ mol^{-1}
Standard enthalpy change of combustion of $H_2(g)$ = –286 kJ mol^{-1}

(i) What do you understand by the term *standard enthalpy change of formation of* $POCl_3(l)$?

(ii) Use the given data to draw a suitable energy cycle for the above reaction and use it to calculate ΔH_r.

[4]

3 MI/2010/P2/Q2(a),(b) Level of Difficulty: [☆]

Magnesium oxide, or magnesia, is a white solid mineral that occurs naturally as periclase and is a source of magnesium.

(a) Using the information given below and the Data Booklet, draw an energy level diagram for the formation of magnesium oxide and use it to determine the amount of energy required for the sublimation of one mole of magnesium. [3]

Suggested Answers

1 AJC/2010/P3/Q4(d) Level of Difficulty: [☆]

(d)(i) Using $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$,

$$\Delta G^\ominus = (111) - (298)(183/1000)$$
$$= \mathbf{+56.5\ kJ\ mol^{-1}}$$

Since $\Delta G^\ominus$ is positive, the sublimation process is not spontaneous at room temperature.

(d)(ii) During sublimation, $\Delta G^\ominus = 0$ kJ mol^{-1}

$$\Delta H^\ominus = T\Delta S^\ominus$$
$$T = \Delta H^\ominus / \Delta S^\ominus$$
$$= (111) / (0.183)$$
$$= 607\ K$$
$$= \mathbf{334\ °C}$$

(d)(iii) The assumption made is that both $\Delta H^\ominus$ and $\Delta S^\ominus$ remain constant at a higher temperature.

2 HCI/2010/P3/Q1(b) Level of Difficulty: [☆]

(i) It is the enthalpy change when **1 mol of $POCl_3(l)$** is **formed from its constituent elements in their standard states** (i.e., $P_4(s)$, $O_2(g)$ and $Cl_2(g)$) under standard conditions of 25 °C and 1 atm.

(ii)

$$\begin{tikzcd}
PCl_5(s) + H_2O(l) \arrow[rr, "\Delta H'_r"] & & POCl_3(l) + 2HCl(g) \\
& P(s) + 5/2\,Cl_2(g) + H_2(g) + \tfrac{1}{2}O_2(g) \arrow[ul, "\begin{array}{l}-444-286\\=-730\text{ kJ mol}^{-1}\end{array}"] \arrow[ur, swap, "\begin{array}{l}-1186-92\times2\\=-1370\text{ kJ mol}^{-1}\end{array}"] &
\end{tikzcd}$$

By Hess' law,
$\Delta H'_r = +730 + (-1370) = \mathbf{-640\ kJ\ mol^{-1}}$

3 MI/2010/P2/Q2(a),(b) Level of Difficulty: [☆]

(a)

1m for well – labeled diagram

1m for application of Hess Law

1m for final answer with correct units.

(b)

$$\text{L.E.} \; \alpha \; \frac{q^{+}q^{-}}{r^{+} + r^{-}}$$

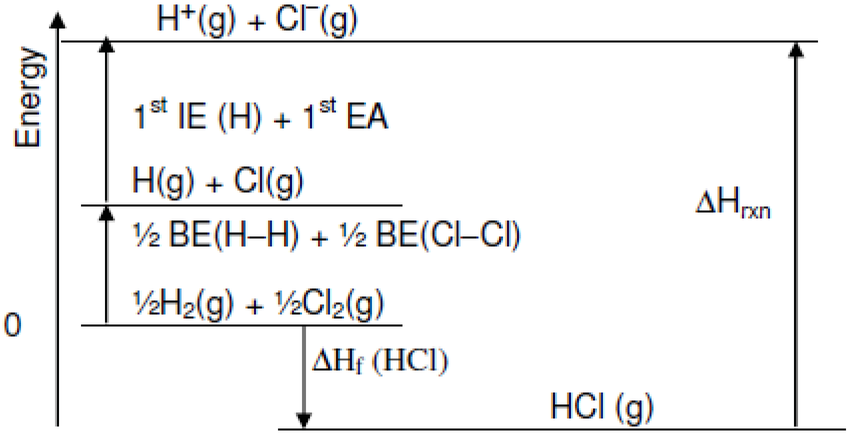
Charge on Mg^{3+} is two times that of Na^{+}

Size of Mg^{3+} is smaller than that of Na^{+}

Thus the LE of MgO should be more exothermic than Na_2O.

4 NYJC/2010/P3/Q1(c) Level of Difficulty: [☆]

(i)



$\Delta H_{rxn} = -\Delta H_f\,(HCl) + \frac{1}{2}\,BE(H\text{–}H) + \frac{1}{2}\,BE(Cl\text{–}Cl) + 1^{st}\,IE\,(H) + 1^{st}\,EA$

$\Delta H_{rxn} = -(-92) + \frac{1}{2}(436) + \frac{1}{2}(244) + 1310 + (-364)$

$\Delta H_{rxn} = +\,1378\ kJ\ mol^{-1}$

(ii)

Reaction 2 involves forming ion-dipole interactions between H^{+} and water molecules and Cl^{-} and water molecules. Energy is evolved in the formation of ion-dipole interactions which can more than compensate the heat absorbed to break the H–Cl bond in the gaseous state and to ionise the H atom, thus resulting in the enthalpy change of reaction 2 to be exothermic.

5 PJC/2010/P2/Q1(b),(c) Level of Difficulty: [☆]

(a)

(i) **ammonia is a weak base, does not dissociate completely**

(ii) ***(from dotted line added onto the graph)***

34.4 – 26.0 = 8.4 °C

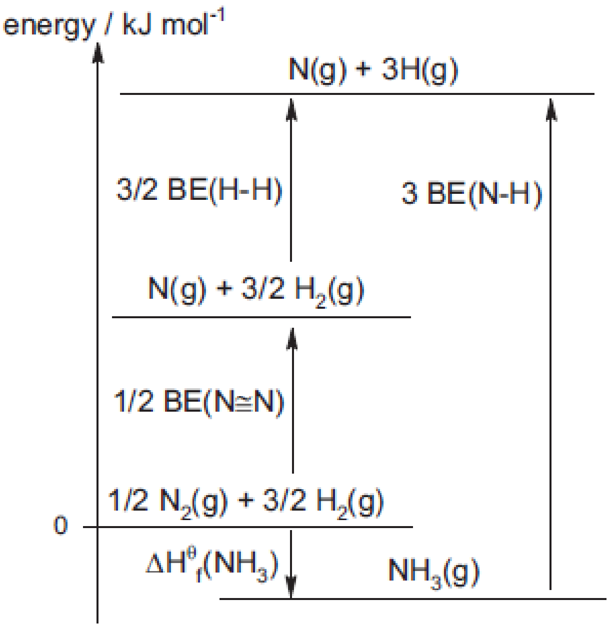
(iii)

$$\Delta H_n = \frac{-mc\Delta T}{n(H_2O)} = \frac{-60 \times 4.2 \times 8.4}{0.020 \times 2.0}$$
$$= -52920\ J\ mol^{-1}$$
$$= -52.9\ kJ\ mol^{-1}\ \text{(to 3 sf)}$$

(iv)

- **ethanoic acid is a weak acid, only dissociates partially**
- **$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$**
  during neutralisation, the O-H bonds break
- **some energy is absorbed for the bond breaking process which is endothermic**

(c)



By Hess' Law,

$3BE(N\text{-}H) = 3/2BE(H\text{-}H) + 1/2BE(N{\equiv}N) - \Delta H^\theta_f(NH_3)$

$= 3/2(436) + 1/2(994) - (-46) = 1197$

$BE(N\text{-}H) = 1197 / 3 = 399$ kJ mol^{-1}

6 PJC/2010/P3/Q5(c) Level of Difficulty: [☆]

(i) **$NO_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g)$**

(ii) **According to the equation in (b)(i), number of moles of gaseous products is more than the number of moles of gaseous reactants OR there is an increase in number of moles of gases.**

Thus, entropy increases since there are more particles moving randomly and more ways to distribute the particles and energy. Hence, $\Delta S > 0$.

(iii) **$NO_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g)$**

$\Delta H^\theta = \Sigma m\Delta H^\theta_f\text{(products)} - \Sigma n\Delta H^\theta_f\text{(reactants)}$

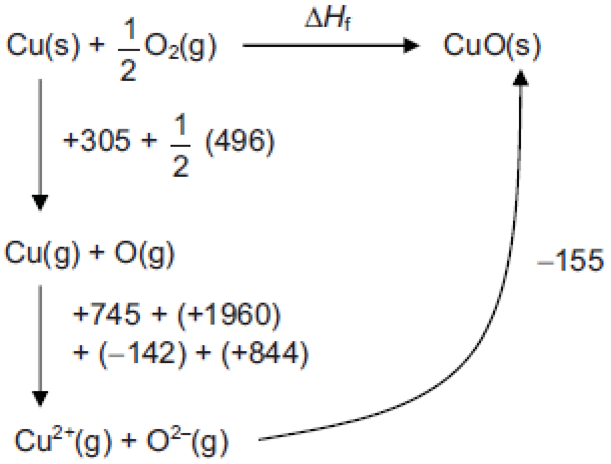
$= +90.3 - 33.2 = +57.1$ kJ mol^{-1}

$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$

$= +57.1 - 298(+73.3/1000) = +35.3$ kJ mol^{-1}

Since $\Delta G^\theta > 0$, the decomposition is not feasible.

7 RVHS/2010/P2/Q2(e) Level of Difficulty: [☆]



$$\Delta H_f(\text{CuO}) = 305 + \frac{1}{2}(496) + (+745) + (+1960) + (-142) + (+844) + (-155)$$

$$= 3805 \text{ kJ mol}^{-1}$$

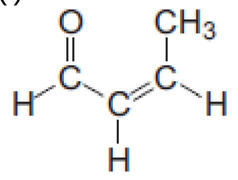
8 RVHS/2010/P2/Q4(a)(v) Level of Difficulty: [☆]

There is a decrease in the number of gaseous particles, hence decrease in disorder and $\Delta S < 0$.

Using $\Delta G = \Delta H - T\Delta S$, as temperature increases, the $-T\Delta S$ term increases/becomes more positive and, ΔG increases/becomes more positive.

9 SRJC/2010/P3/Q3(b)(i),(ii) Level of Difficulty: [☆]

(i)



(ii)

ΔH_{rxn} = BE(C=O) + 2BE(C-H) – [BE(C=C)] – 2BE(H-O)

= 740 + 2(410) – 610 – 2(460)

= **<u>+30 kJ mol^{-1}</u>**

10 SRJC/2010/P3/Q5(e) Level of Difficulty: [☆]

(i)

By Hess' Law, R = $-1224 - (-1212) = -12$ kJ mol^{-1}

At standard condition, T = 298K

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$+47 = -12 - (298)\,\Delta S^\ominus$

$\Delta S^\ominus = \dfrac{-12-47}{298} = -0.1980$ kJ mol^{-1}

(ii)

Sign of entropy change of solution of calcium carbonate is negative indicates that there is a **decrease in disorderliness / an increase in orderliness** after calcium carbonate is dissolved.

This is **out of expectation** because there is a change of state from solid to aqueous, increase in the randomness / disorderliness in the arrangement of the particles.

(iii)

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

Since $\Delta H^\ominus$ and $\Delta S^\ominus$ have negative values,

$\Delta G^\ominus = -\,|\Delta H^\ominus| + |T\Delta S^\ominus|$

Assuming $\Delta H^\ominus$ and $\Delta S^\ominus$ are constant, the **higher the temperature** in the water heater system, the **more positive $\Delta G^\ominus$** is. Calcium carbonate becomes **less soluble** and form scale in the water pipes, clogging them.

11 VJC/2010/P2/Q2(c) Level of Difficulty: [☆]

(c)(i)

$\Delta G_f^\ominus = \Delta H_f^\ominus - T\Delta S_f^\ominus \quad \Rightarrow \quad \Delta S_f^\ominus = (\Delta H_f^\ominus - \Delta G_f^\ominus) / T$

$\Delta S_f^\ominus(SO_2) = [-296.8 - (-300.2)] / 298 = 0.0114$ kJ mol^{-1} K^{-1} = 11.4 J mol^{-1} K^{-1}

$\Delta S_f^\ominus(SO_3) = [-395.7 - (-371.1)] / 298 = -0.0826$ kJ mol^{-1} K^{-1} = -82.6 J mol^{-1} K^{-1}

(ii)

$\Delta S_r^\ominus > 0$ as there are more gaseous products than gaseous molecules.

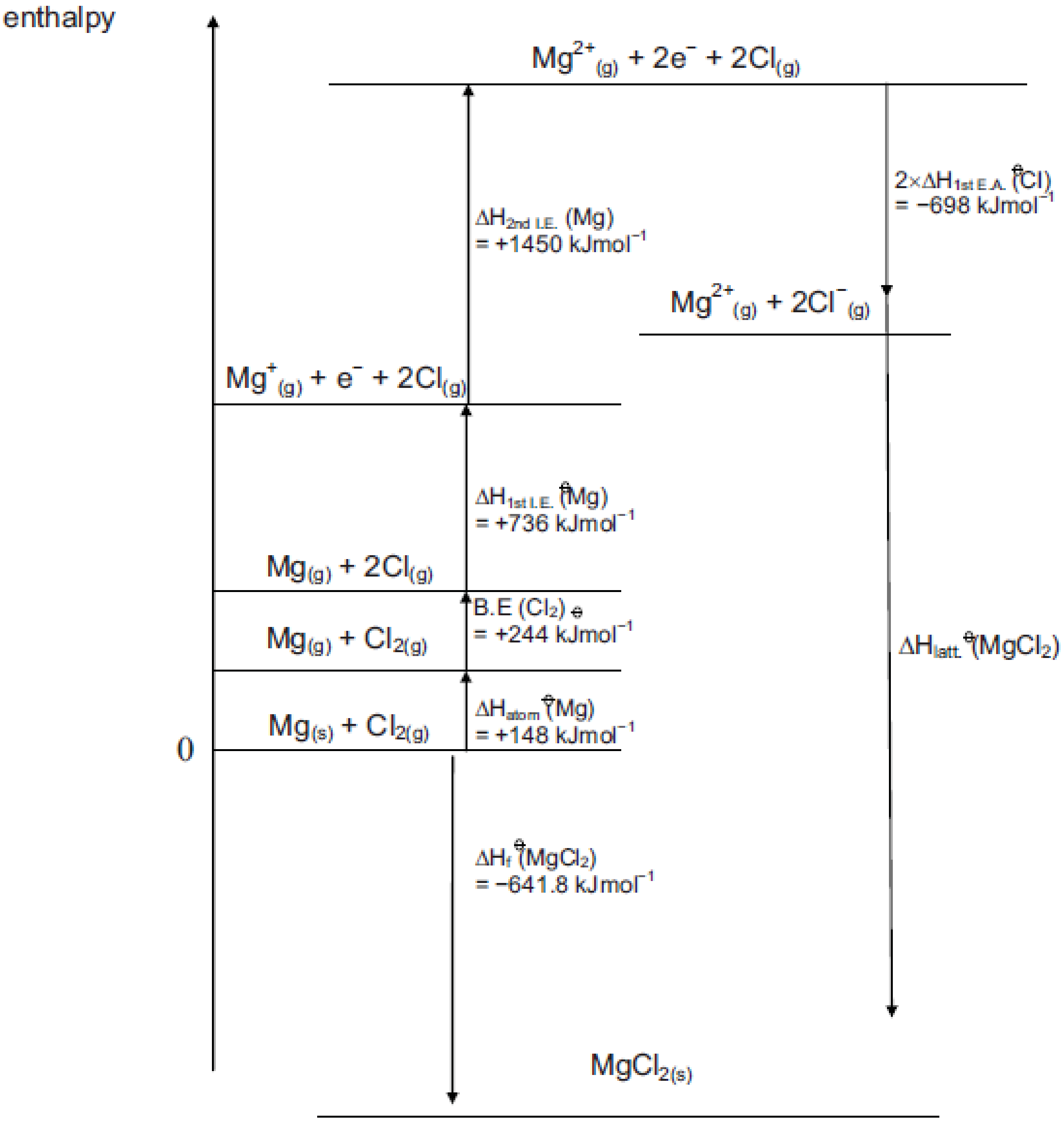
$\Delta G_r^\ominus < 0$ as $\Delta H_r^\ominus < 0$ and $\Delta S_r^\ominus > 0$. Hence, the reaction is feasible at all temperatures.

12 YJC/2010/P2/Q3(c)(i) Level of Difficulty: [☆]

$\Delta H(CO) = -2(460) - 41 + 2(740) + 436 = 955$ kJmol^{-1}

13 YJC/2010/P3/Q3(c) Level of Difficulty: [☆]

(i)



LE = -2521.8 kJ mol^{-1}

(ii)

The theoretical lattice energy is based on a pure ionic model, but $MgCl_2$ exhibits some covalent character due to the high polarizing power of Mg^{2+} which distorts the electron cloud of the Cl^- ion.

14 YJC/2010/P3/Q5(b) Level of Difficulty: [☆]

bi heat evolved, q = 80 x 4.2 x 6.5 = 2184 J
no of moles of water formed = 0.0400 mol
$\Delta H^{\theta}_{neut} = -2184/0.04 = -54.6\ kJmol^{-1}$

bii $\Delta G = \Delta H - T\Delta S = -54.6 - 298(80.6 \times 10^{-3}) = -78.6\ kJmol^{-1} < 0$
Since $\Delta G < 0$, the reaction is spontaneous.

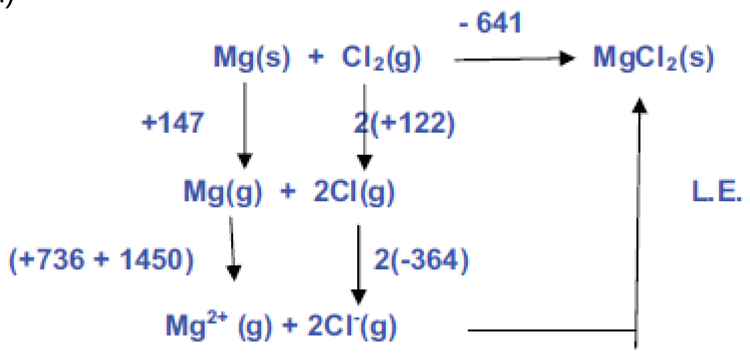
15 ACJC/2010/P2/Q2(b) Level of Difficulty: [☆☆]

(i)

Lattice energy of $MgCl_2$ is the heat evolved when one mole of solid $MgCl_2$ is formed from gaseous Mg^{2+} and Cl^- under standard conditions of 298K and 1 atm.

$$Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s)$$

(ii)



L.E. = - 2490 kJ mol^{-1}

(iii)

Magnitude of the lattice energy of $BaCl_2$ < $MgCl_2$.

This is because ionic radius of Ba^{2+} > Mg^{2+} / charge density of Ba^{2+} is smaller than that of Mg^{2+}, hence electrostatic forces of attraction are weaker between Ba^{2+} and Cl^-.

(iv)

$\Delta H_{reaction}$ = -641-2(-125) = - 391 kJ mol^{-1}

Reaction is exothermic which means that $MgCl_2(s)$ is more stable than $MgCl(s)$.

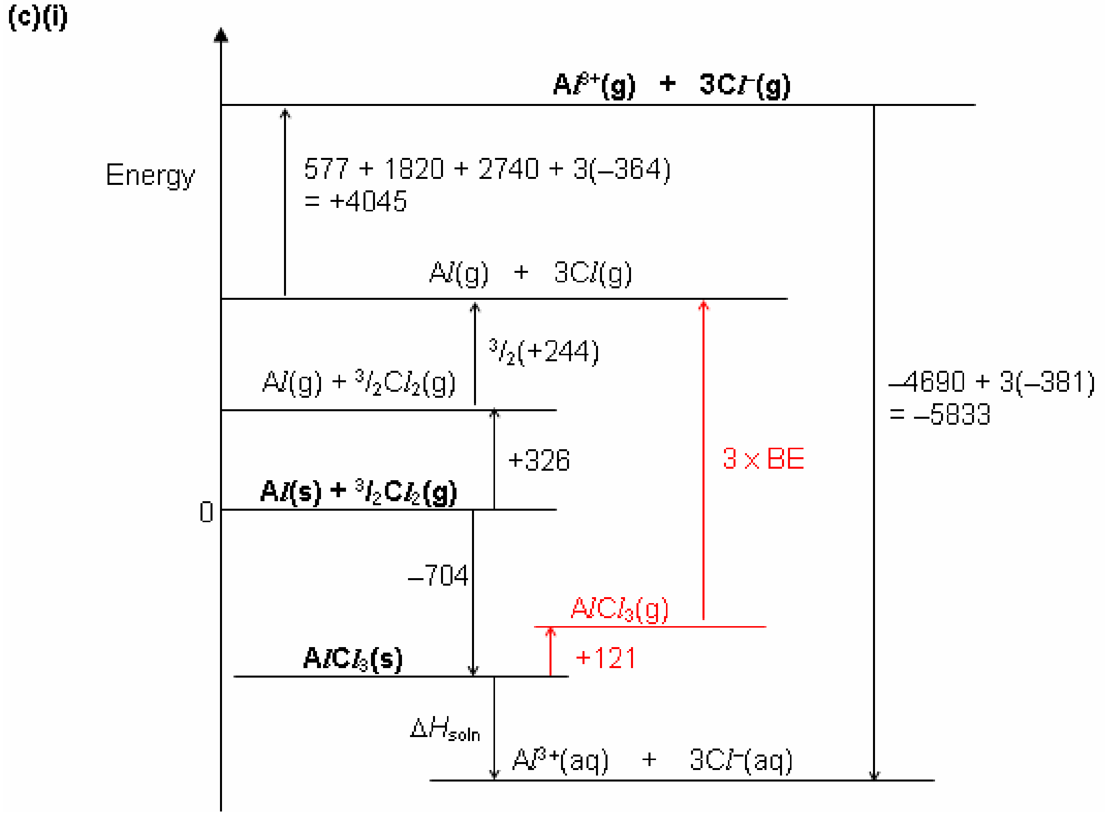
16 AJC/2010/P2/Q2(b),(c) Level of Difficulty: [☆☆]

(b)

ΔH_{hyd} of Cr^{3+} is less exothermic / smaller in magnitude than that of Al^{3+}.

Cr^{3+} is larger / has a smaller charge density than Al^{3+}, thus forms weaker ion–dipole interaction with water molecules.

(c)(i)



By Hess' Law,
ΔH_{soln} = <u>–392</u> kJ mol^{-1}

(c)(ii) By Hess' Law,
bond energy of Al–Cl = **<u>+425</u>** kJ mol^{-1}

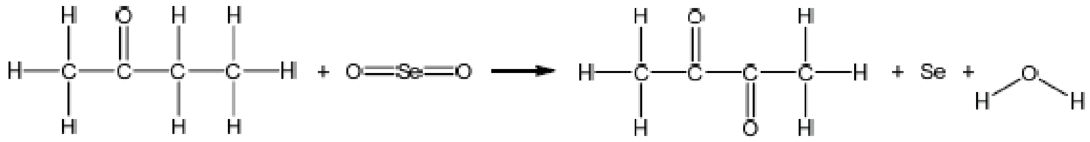
17 <u>AJC/2010/P3/Q4(b)</u> Level of Difficulty: [☆☆]

(b)(i) <u>Redox</u> reaction or <u>oxidation</u> of butanone.

SeO_2 is acting as the <u>oxidising agent</u>.

(b)(ii) $CH_3COCH_2CH_3 + SeO_2 \rightarrow CH_3COCOCH_3 + Se + H_2O$

(b)(iii)



<u>Bonds broken:</u>	<u>Bonds formed:</u>
C–H : 2(410)	C=O : 740
Se=O : 2(418)	O–H : 2(460)
Total: <u>1656 kJ mol^{-1}</u>	Total: <u>1660 kJ mol^{-1}</u>

$\Delta H^\ominus = \sum$ bonds broken – $\sum$ bonds formed
= 5906 – 5910 *(or 1656 – 1660)*
= **<u>–4 kJ mol^{-1}</u>**

(b)(iv)
- It is an approximation as the bond energies from the *Data Booklet* are only average values.

or
- Bond energies are for breaking of bonds in the gaseous phase. However, all the substances in the reaction are not in the gaseous phase under standard conditions.

18 CJC/2010/P2/Q2(b)(iii)-(v) Level of Difficulty: [☆☆]

(iii)

$\log_{10}15 - \log_{10}0.05 = [\Delta H\ (1/300 - 1/400)] / (2.30 \times 8.31)$

$\Delta H = 56814\ \text{J mol}^{-1}$ or $56.8\ \text{kJ mol}^{-1}$

Assumption is that ΔH remains constant at 300 K and 400 K

(iv)

ΔS is positive. Products contain a more number of moles of gas/ There is an increase in number of gaseous particles (i.e. 1 mole → 2 moles).

(v)

$\Delta G = \Delta H - T\Delta S$

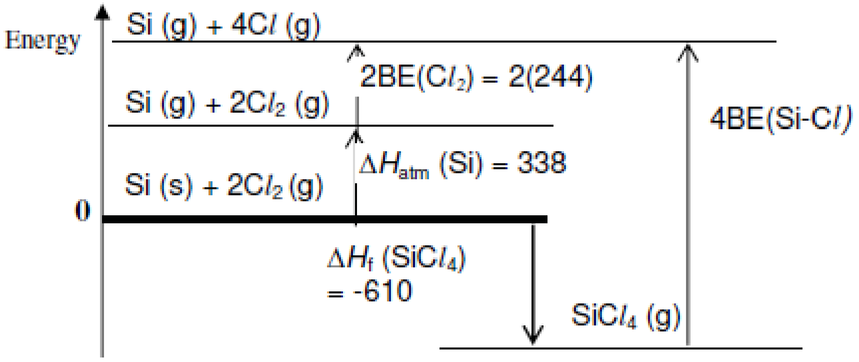
Since ΔH is positive and ΔS is positive ($-T\Delta S$ is negative)

Hence, ΔG is positive at low temperature and negative at high temperatures.

Reaction is non-spontaneous at low temperature & spontaneous at high temperature or reaction becomes more spontaneous with increasing temperature.

19 CJC/2010/P2/Q3(a),(b) Level of Difficulty: [☆☆]

(a)



-BE(Cl_2) = 244 [1, quote /use with the correct conversion]
-Includes (For correct and complete cycle):
1. Arrow pointing in the correct direction with the correct initial and final states,
2. Labeled arrows with correct coefficient,
3. Balanced correct element/compound with state symbols

By Hess' Law,
4BE (Si-Cl)= -(-610) + (338) + 2(244)
BE (Si-Cl) = +359 kJ mol^{-1}

(b)(i)

Energy required to heat 75 g of water from 15 °C to 75 °C
= 125 x 4.20 x (75-15)
= 3.15×10^4 J

Since the process is only 80% efficient,
Energy evolved from burning 1.50 g of cyclohexene

$= 3.15 \times 10^4 \times \frac{100}{80}$

$= 3.94 \times 10^4$ J

Amt of cyclohexene used $= \frac{1.50}{82.0} = 0.0183$ mol

Enthalpy change of combustion

$= -\frac{3.94 \times 10^4}{0.0183}$

$= -2150$ kJ mol^{-1}

(ii)

Heat loss to surroundings / Heat evolved to heat the container / Heat absorbed by container.

20 MI/2010/P3/Q3(a),(c),(d)(i) Level of Difficulty: [✩✩]

(a)

1m for cycle wth correct state symbols

1m for answer (=+11.3 kJ mol^{-1})

(c)

1m for working

1m for answer (= –212 kJ)

Bond energies are average values and differ when chemical environment is different.

(d)(i)

1m for answer for ΔG (= +12.5 kJ)

1m for concluding spontaneity based on sign of ΔG

21 MJC/2010/P3/Q4(a),(b),(d) Level of Difficulty: [✩✩]

(a) (i) Standard enthalpy change of neutralisation (ΔH_n^θ) is the energy released when an acid and a base react to form one mole of water at 298K and 1 atm (or standard conditions).

(ii) Actual quantity of heat evolved, Q' $= \frac{100}{80} \times (50+50) \times 4.2 \times 8.5$

$= 4462.5$ J

$2HCl(aq) + Sr(OH)_2(aq) \rightarrow SrCl_2(aq) + 2H_2O(l)$

n_{H2O} formed $= 2 \times n_{Sr(OH)2}$ reacted

$= 2 \times \frac{50}{100} \times 0.77 = 0.077$

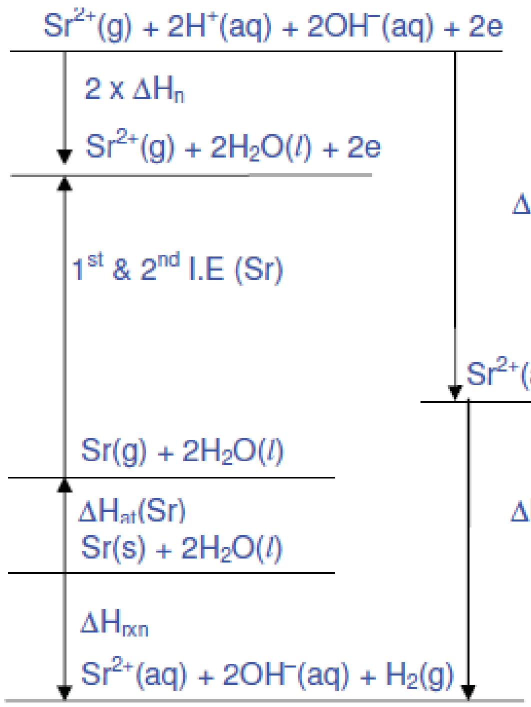
$\Delta H^{\theta}_n = -\frac{4462.5}{0.077}$

$= -58.0 \text{ kJ mol}^{-1}$

(iii) Aqueous ethanoic acid is a weak acid which dissociated slightly in aqueous solution.

Some of the energy evolved from the neutralisation process is used to further dissociate the weak acid completely .

(b)



$\Delta H_{rxn} - (164) - (548) - (1060) + 2(-58) = -1337 + (-850)$

$\Delta H_{rxn} = -299 \text{ kJ mol}^{-1}$

(d) **(i)** $\Delta G_{ppt}^{\theta} = 8.31 \times 298 \times \ln(3.2 \times 10^{-7})$

$= -3.70 \times 10^{4} \text{ J mol}^{-1}$

$= -37.0 \text{ kJ mol}^{-1}$

(ii) $-3.70 \times 10^{4} = -1453 \times 10^{3} - 298 \times \Delta S$

$\Delta S = -4750 \text{ J mol}^{-1} \text{ K}^{-1}$

(iii) ΔS is *negative*, as there is a change in phase from aqueous to solid state as Sr^{2+} and SO_4^{2-} ions forms solid $SrSO_4$ which results in a less disordered state / entropy decreases

22 NJC/2010/P3/Q1(b) Level of Difficulty: [☆☆]

(b) (i) $2K(s) + C(s) + 1\frac{1}{2}\ O_2(g) \rightarrow K_2CO_3(s)$ $\Delta H_{formation}$

(b) (ii) $\Delta H_{soln} = -1254/0.0362 \times 10^{-3} = -34.7\ kJ\ mol^{-1}$

(b) (iii)

$\Delta H_f = -1146.3\ kJ\ mol^{-1}$

23 NJC/2010/P3/Q3(e) Level of Difficulty: [☆☆]

Q at 75% efficiency = 759 kJ

24 RVHS/2010/P3/Q2(c) Level of Difficulty: [☆☆]

(i) The standard enthalpy change of combustion of mercaptopurine is the energy change when one mole of mercaptopurine is completely burnt in oxygen under standard conditions of 298 K and 1 atm.

$C_5H_4N_4S(s) + 7O_2(g) \rightarrow 5CO_2(g) + SO_2(g) + 2N_2(g) + 2H_2O(l)$

(state symbols required)

(ii) $\Delta H_c = [2E(N—H) + 2E(C—H) + 2E(C{=}N) + 6E(C—N) + E(C{=}C) + E(C{=}S) + E(C—C) + 7E(O{=}O)] - [10E(C{=}O) + 2E(S{=}O) + 2E(N{\equiv}N) + 4E(O—H)]$

$= [2(+390) + 2(+410) + 6(+305) + 2(+610) + (+610) + (+138) + (+350) + 7(+496)] - [10(+740) + 2(+128) + 2(+994) + 4(+460)]$

$= +9220 - (+11484)$

$= -2264\ kJ\ mol^{-1}$

(iii) Heat absorbed by water $= 100 \times 4.18 \times (87 - 25)$

$= 2.59 \times 10^4\ J$

Heat evolved by combustion $= \frac{100}{65} \times 2.59 \times 10^4$

$= 3.98 \times 10^4\ J$

Amount of mercaptopurine $= \frac{1.50}{5 \times 12.0 + 4 \times 1.0 + 4 \times 14.0 + 32.1}$

$= 0.00986\ mol$

$\Delta H_c = -\frac{3.98 \times 10^4}{0.00986}$

$= -4.04 \times 10^6\ J\ mol^{-1}$

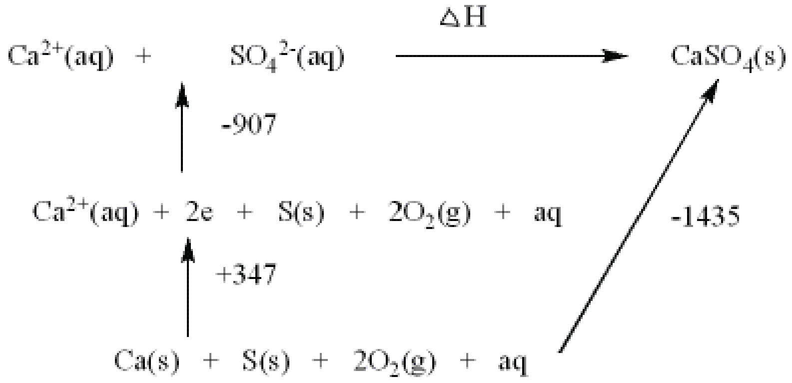
$= -4040\ kJ\ mol^{-1}$

(iv) The value for ΔH_c obtained from bond energies in (c)(ii) is not accurate as the bond energies quoted from the *Data Booklet* represent average bond energies derived from the full range of molecules that contain the particular bonds.

Mercaptopurine and H_2O are in the solid and liquid states respectively under standard conditions but the calculation in (c)(ii) makes use of bond energies which relate to breaking of covalent bonds in gaseous molecules. The enthalpy change of sublimation of mercaptopurine and enthalpy change of vapourisation of H_2O are not accounted for in the calculation of ΔH_c.

25 SAJC/2010/P2/Q3 Level of Difficulty: [☆☆]

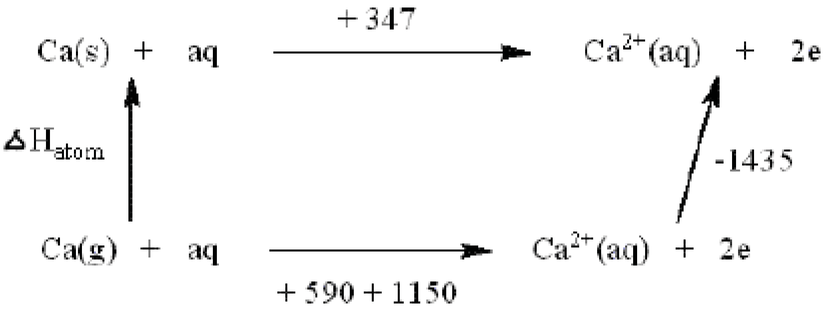
(a)



$\Delta H = +907 - 347 - 1435$

$= -875 \text{ kJmol}^{-1}$

(b)



$\Delta H = +347 + 1577 - 590 - 1150$

$= +184 \text{ kJmol}^{-1}$

26 SAJC/2010/P3/Q4(a),(b),(c)(i)-(iii) Level of Difficulty: [☆☆]

(a) $Ca(s) + C(s) + 3/2\ O_2(g) \rightarrow CaCO_3(s)$

The standard enthalpy change of formation of calcium carbonate is the enthalpy change when one mole of calcium carbonate is formed from its constituent elements in their standard states at 298K and 1 atmospheric pressure.

(b) (i) Heat evolved = (400 x 9.7) J

= 3.88 kJ

(ii) ΔH_r = (– 3.88 x 40.1) / 0.25

= – 622 kJ mol^{-1}

(iii) $Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$ ------- Eq.(1) – 622 kJ mo^{-1}

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$ ---- Eq.(2) – 95.0 kJ mol^{-1}

Eq.(1) + Reverse Eq.(2):

$Ca(s) + CO_2(g) + H_2O(l) \rightarrow CaCO_3(s) + H_2(g)$

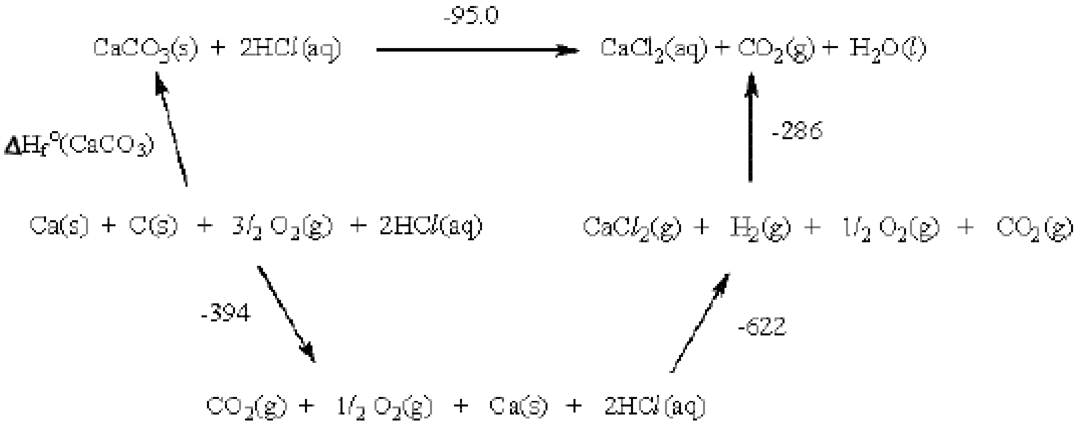
ΔH_r = – 622 + 95.0 = – 527 kJ mol^{-1}

$-527 = (\Delta H_f^\ominus(CaCO_3) + 0) - [0 + \Delta H_f^\ominus(CO_2) + (\Delta H_f^\ominus(H_2O)]$

$-527 = \Delta H_f^\ominus(CaCO_3) - [(-394) + (-286)]$

$\Delta H_f^\ominus(CaCO_3) = -1207$ kJ mol^{-1}

OR



$\Delta H_f^\ominus(CaCO_3) = -394 - 622 - 286 + 95.0 = -1207$ kJ mol^{-1}

(c) (i) The entropy increases due to <u>increase in the number of gaseous particles</u>, resulting in <u>more disorderliness</u> in the system.

(c) (ii) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$= +117 - (298 \times \frac{+175}{1000}) = +117 - 52.15$

$\approx$ + 64.9 kJ mol^{-1}

Since $\Delta G^\ominus$ is positive, the decomposition is not feasible, i.e. $MgCO_3$ is more stable than MgO and CO_2 at room temperature.

(iii) $\Delta G^\ominus = 0 = \Delta H^\ominus - T\Delta S^\ominus = +117 - (T \times \frac{+175}{1000})$

$T = 668K = 395^0C$

Above 668K, the decomposition reaction becomes feasible.

27 TJC/2010/P3/Q1(a) Level of Difficulty: [☆☆]

(i)
- Standard enthalpy change of combustion is the heat evolved when one mole of the substance is completely burnt in oxygen at 298 K and 1 atm.

(ii) •• (1 mark working, 1 mark answer)

$$\begin{tikzcd}
C_8H_{18}(l) + \frac{25}{2}O_2(g) \arrow[rr, "\Delta H_c"] & & 8CO_2(g) + 9H_2O(l) \\
& 8C(s) + 9H_2(g) + \frac{25}{2}O_2(g) \arrow[ul, "-269"] \arrow[ur, "8(-394) + 9(-286)"'] &
\end{tikzcd}$$

By Hess' Law,

$\Delta H_c = 269 + 8(-394) + 9(-286) = -5460 \text{ kJ mol}^{-1}$

- Heat evolved per gram of octane = $\frac{5460}{114}$ = 47.9 kJ g^{-1}

(iii) •• (1 mark working, 1 mark answer)

$CH_3OH(g) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

Bonds broken: 3C-H, C-O, O-H, $\frac{3}{2}$O=O

Bonds formed: 2C=O, 4O-H

$\Delta H_c = 3(410) + 360 + 460 + \frac{3}{2}(496) - 2(740) - 4(460) = -526 \text{ kJ mol}^{-1}$

- Heat evolved per gram of methanol = $\frac{526}{32}$ = 16.4 kJ g^{-1}

(iv)
- As weight considerations are usually important is racing car, one advantage of using petrol (octane) is that it produces more heat energy per gram of fuel.

28 VJC/2010/P2/Q3(a),(b) Level of Difficulty: [☆☆]

3(a)(i)

Heat evolved

$= 200 \times 4.18 \times 46.9 \times \frac{100}{80}$ [–½ m if missing 100/80]

$= 49000$ J or 49.0 kJ

Amount of cyclobutane used

$= \frac{1.00}{12.0 \times 4 + 1.0 \times 8}$

$= 0.0179$ mol

ΔH_c(cyclobutane)

$= -\frac{49.0}{0.0179}$

$= -2740 \text{ kJ mol}^{-1}$

[½ m for sign and unit. Ignore wrong computation, allow ecf.]

(ii)

$\Delta H_1 = \Delta H_c(\text{cyclobutane}) - 2\Delta H_c(CH_2{=}CH_2)$

$= -2740 - 2(-1422)$ (ecf)

$= +104 \text{ kJ mol}^{-1}$

(b)(i)

H_3PO_4 or concentrated H_2SO_4

(ii)

The heat change when **one mole of ethanol** is formed from **its constituent elements in their standard states** at 298 K and 1 atm.

$2C(s) + 3H_2(g) + ½O_2(g) \rightarrow CH_3CH_2OH(l)$

(iii)

$\Delta H = \Sigma BE(\text{reactants}) - \Sigma BE(\text{products})$

$= 3(436) + ½(496) - (350 + 5 \times 410 + 360 + 460)$

$= -1664 \text{ kJ mol}^{-1}$

(iv)

$$\begin{tikzcd}
2C(g) + 3H_2(g) + \tfrac{1}{2}O_2(g) \arrow[r, "-1664"] & CH_3CH_2OH(g) \\
2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \arrow[u, "2\Delta H_{at}"] \arrow[r, "-276"] & CH_3CH_2OH(l) \arrow[u, "+39"']
\end{tikzcd}$$

By Hess' Law,

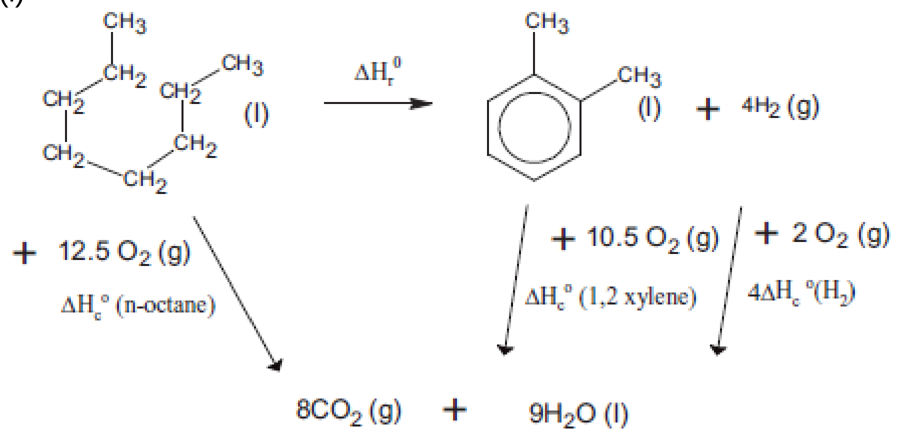
$2\Delta H_{at} = -276 + 39 - (-1664)$

$= +1427$ kJ

$\Delta H_{at} = +713.5 \text{ kJ mol}^{-1}$

29 ACJC/2010/P3/Q1(c) Level of Difficulty: [✩ ✩ ✩]

(i)



- **Complete cycle (state symbols + balanced + terms)**
- **ΔH_r^o = -5470 – [(-4540) + 4(-286)] = +214 kJ mol^{-1}.**

(ii)

Bond broken	Bonds formed
7 C - C	2 C – C
18 C – H	6 C⎓C
	10 C – H
	4 H – H

Picking the correct benzene double bond from Data Booklet

ΔH_r = 7(+350) + 18(+410) – [2(+350) + 6(+520) + 10(+410) + 4(+436)]
= (+9830) – (+9664) = +166 kJ mol^{-1}

The sum of enthalpy change of vaporization of the products is more endothermic than the enthalpy change of vaporization of the reactant.

(iii)

- **(c)(ii) is more accurate.**
- **Reforming take place at 500°C and pressure of 20 atm which are non-standard conditions. (Underline portion is necessary to get this mark. Must make reference to the passage.)**

(iv)

- **ΔG value will be more negative. Since, ΔG = ΔH - TΔS,**
- **ΔS > 0 because there is a production of 4 moles of H_2, which results in n(gas) to increase after the reaction.**

30 NJC/2010/P2/Q4(a),(b) Level of Difficulty: [✮✮✮]

(a)

Graph II.

Since $Sr(NO_3)_2(s) \rightarrow SrO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

$\Rightarrow \Delta n$ increases $\Rightarrow \Delta S$ is positive

$\therefore$ graph of ΔG against T should give a straight line with a negative gradient as

$\Delta G = \Delta H - T\Delta S$ (Gibbs eqn)

(b)

(i) $\Delta H = +600$ kJ mol^{-1}

(ii) Decomposition temp = 672 K

31 NYJC/2010/P2/Q9(a)(i),(ii) Level of Difficulty: [✮✮✮]

(i)

2-methyl-buta-1,3-diene is a conjugated diene. The extent of **overlap of the unhybridized p orbitals** of the 4 sp^2 C can overlap with each other causing the **π electrons to spread out, or delocalize** over the entire π framework (or over the 4 carbon atoms). Electron delocalization leads to a lower energy and hence leads to stability.

(ii)

The bond length will be **shorter** due to **sp^2-sp^2 overlap** that strengthens the bond between C2 and C3.

TOPIC 6: ELECTROCHEMISTRY

1 CJC/2010/P2/Q4c Level of Difficulty: [☆]

(c) Marine aquarists are generally very concerned about pH in aquariums because aquatic organisms can only thrive in a particular pH range. To measure the pH, one can use a pH meter. The probe on a pH meter has two electrodes, one is a glass electrode that responds to changes in [H^+(aq)] and the other a reference electrode that must have a stable electrode potential. The reference electrode is very often a silver electrode dipping in a saturated solution of 0.10 mol dm^{-3} KC*l* in contact with AgC*l*(s). The solubility product for AgC*l* is 2.0 x 10^{-10} mol^2 dm^{-6}.

(i) Calculate the [Ag^+(aq)] in the reference electrode.

(ii) The electrode potential, E, changes from the standard value, $E^\ominus$, if the concentration of the ions is non-standard. This change is given by the Nernst equation.

$$E = E^\ominus + 0.059 \log [Ag^+(aq)]$$

Calculate the electrode potential of the silver reference electrode at 298 K.

(iii) The potential of the glass electrode also changes according to the Nernst equation

$$E = E^\ominus + 0.059 \log [H^+(aq)]$$

If a pH meter operates over the range 0-14, what is the range of the voltage output of the pH meter?

[4]

2 PJC/2010/ P3 / Q2(a) Level of Difficulty: [☆]

(a) A cell consisting of two half-cells is used to power an electrolysis reaction.

The cell contains aqueous sodium hydroxide as the electrolyte with graphite as the electrodes. The reactants are hydrogen and oxygen gases.

(i) Draw a labelled diagram to show how you would measure the standard cell potential, E^θ_{cell}, of the cell. Indicate the direction of electron flow in your diagram.

(ii) Write the half-equations for the reactions taking place at the anode and cathode. Hence, calculate the E^θ_{cell} of the cell.

(iii) How will the E^θ_{cell} change when a small amount of acid is added to the electrode with oxygen gas?

(iv) The temperature under which the electrolysis is being carried out is increased but a constant current is maintained. State how the rate of the electrolysis would change.

[9]

1. The pattern of a window frame is drawn on the brass using a special ink.
2. The unprotected brass (not covered by ink) is removed by using dilute hydrochloric acid and the outline of the frame remains.

With the aid of the *Data Booklet*, identify the metal that dissolves in dilute hydrochloric acid. Explain your answer.

[3]

(d) A heart pacemaker consisting of zinc and platinum electrodes, is implanted into the body tissues. These electrodes in the oxygen-containing body fluid, with a pH of 7.4, form a cell in which zinc is oxidised and oxygen is reduced.

(i) Write a balanced equation for the overall reaction that takes place when a current flows.

(ii) How would the E^θ_{cell} value change if a human with the heart pacemaker undergoes a period of intense exercise? Explain your answer.

[4]

Suggested Answers

1 CJC/2010/P2/Q4c Level of Difficulty: [✩]

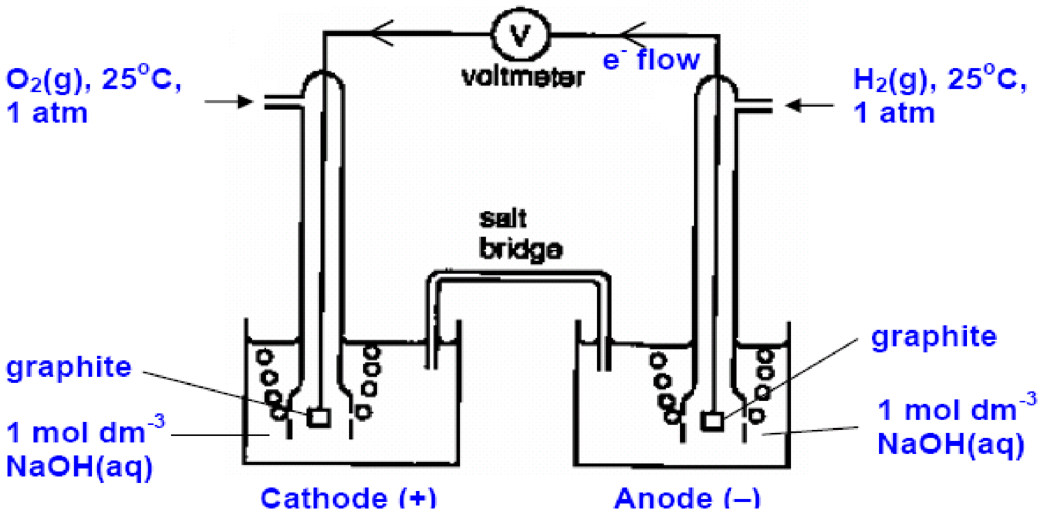
i. $[Ag^+] = 2.0 \times 10^{-10} / 0.1 = 2.0 \times 10^{-9}$ mol dm^{-3}

ii. $E = 0.80 + 0.059 \log 2.0 \times 10^{-9}$
$= 0.286$ V

iii. $E = 0 - 0.059$ pH
Min voltage = 0 V
Change in voltage output = $- 0.059 * 14 = - 0.826$V
Range of the voltage output: -0.826V to 0V

2 PJC/2010/P3 /Q2(a) Level of Difficulty: [✩]

i.



ii. **Anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ $E^{\ominus}_{oxd} = +0.83$ V**
Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ $E^{\ominus}_{red} = +0.40$ V
$E^{\ominus}_{cell} = +1.23$ V > 0, reaction is energetically feasible

iii.
- **When acid is added, the $[OH^-]$ decreases.**
- **Position of the equilibrium $O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$ shifts to the right.**
- **E_{red} increases.**
- **Hence, E_{cell} increases.**

iv. **constant rate**

3 SAJC/2010/ P2 / Q6(a) Level of Difficulty: [☆]

i. $8Ag + 2NO_3^- + 10H^+ \rightarrow 8Ag^+ + N_2O + 5H_2O$

$E^{o}_{cell} = +0.31V$

ii. Right to left

4 AJC/2010/P2/Q2(aiii) Level of Difficulty: [☆☆]

$Cr^{3+} + 3e \rightleftharpoons Cr$ $E^{\ominus} = -0.74$ V
$Mn^{2+} + 2e \rightleftharpoons Mn$ $E^{\ominus} = -1.18$ V
$Al^{3+} + 3e \rightleftharpoons Al$ $E^{\ominus} = -1.66$ V

Between Mn & Cr^{3+} : E^{θ}cell = E^{θ}red(cathode) - E^{θ}red(anode)
= (-0.74) - (- 1.18)
= **+ 0.44 V** > **0**

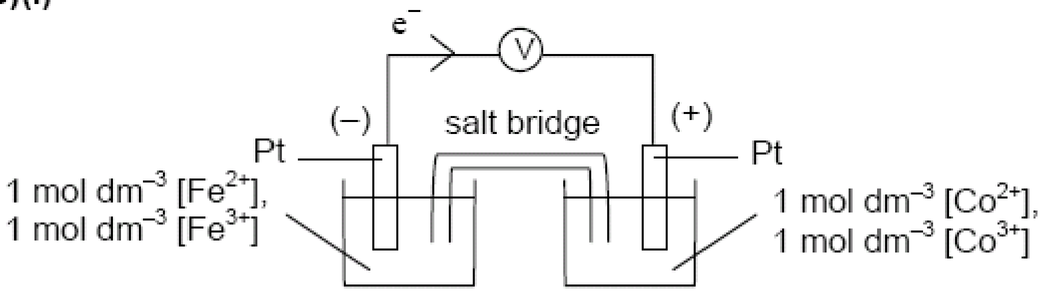
Hence, reaction is energetically feasible.

Between Mn & Al^{3+} : E^{θ}cell = E^{θ}red(cathode) - E^{θ}red(anode)
= (-1.66) - (- 1.18)
= **- 0.48 V** < **0**

Hence, reaction is energetically non-feasible.

5 AJC/2010/P3/Q3(b) Level of Difficulty: [☆☆]

(b)(i)



e.m.f. = (+1.82) – (+0.77) = **<u>+1.05V</u>**

(b)(ii) $E^{\ominus}$ $(Fe^{3+}/Fe^{2+}) = +0.77V$
$E^{\ominus}$ $(Fe(OH)_3/Fe(OH)_2) = -0.56V$

Addition of OH^- forms $Fe(OH)_2$ and $Fe(OH)_3$.
$E^{\ominus}$ value becomes more negative. Fe(II) is more easily oxidized.

(b)(iii) e.m.f. increases/ more positive than +1.05V.

(b)(iv) $4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + O_2 + 4H^+$

(b)(v) The reduction of Co(III) by water has a high activation energy / is slow.

(c) $n(Co)\text{ plated} = \frac{8.00}{58.9}$

$Q = \frac{8.00}{58.9} \times 2 \times 96500 = 26214\text{ C}$

$\text{Time needed} = \frac{26214}{5} = \underline{5240\text{ s}}\ (= 87.3\text{ min})$

6 ACJC/2010/P2/Q5(b), ci Level of Difficulty: [☆☆]

bi. **Fe^{3+}(aq) has high charge density and can undergo hydrolysis with water**

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+} + H_3O^+$$

ii.

$$Cu^{2+} + 2e \rightleftharpoons Cu \qquad E^\theta = +0.34V$$
$$2Fe^{3+} + 2e \rightleftharpoons 2Fe^{2+} \qquad E^\theta = +0.77V$$

$$2Fe^{3+} + Cu \longrightarrow Cu^{2+} + 2Fe^{2+} \qquad E^\theta = +0.43V > 0\text{, reaction is Feasible}$$

iii. **Green ppt of $Fe(OH)_2$**

ci.

$$I_2 + 2e \rightleftharpoons 2I^- \qquad E^\theta = +0.0.54V$$
$$2Fe^{3+} + 2e \rightleftharpoons 2Fe^{2+} \qquad E^\theta = +0.77V$$

$$2Fe^{3+} + 2I^- \longrightarrow I_2 + 2Fe^{2+} \qquad E^\theta = +0.23V > 0\text{, reaction is feasible.}$$

Fe^{3+} will oxidize I^- to I_2 while itself is reduced to Fe^{2+}

7 CJC/2010/P3/Q3(a)-(d) Level of Difficulty: [☆☆]

a When ligands are attached to the centre metal ion, they will cause the degenerate d-orbitals to **split into 2 energy levels**.
The d orbitals are **partially filled**. When electron from the lower d-orbitals **absorbs energy in the visible light** region, it will be **excited** to the higher d* orbital. Such transition is **d-d* electronic transition**.
Complementary colours which are not absorbed will the reflected as the colour of the compound.

b. (i) ‘red water’

$E_{Fe^{3+}/Fe^{2+}}$ will increase / more positive
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
Addition of red water will increase $[Fe^{3+}]$.
By LCP, position of equilibrium will shift to the right or more $[Fe^{2+}]$ is produced.

(ii) pure water

$E_{Fe^{3+}/Fe^{2+}}$ will not change
Addition of pure water will decrease $[Fe^{3+}]$ and $[Fe^{2+}]$ to the same extent

ci.

$E^\circ_{I_2/I^-} = +0.54$ V

$E^\circ = 0.77 - 0.54 > 0$ or $E^\circ_{Fe^{3+}/Fe^{2+}}$ is more positive than $E^\circ_{I_2/I^-}$ or I^- is oxidized by Fe^{3+} to I_2
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

cii.

$[Fe(H_2O)_6]^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-} + 6H_2O$

$E^\circ = 0.36 - 0.54 < 0$

or $E^\circ_{[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}}$ is less positive than $E^\circ_{I_2/I^-}$
or I^- is a weaker ligand than CN^-, ligand replacement cannot occur

di

$E^\circ = 0.77 - (-0.49) = 1.26 > 0$ Reaction is spontaneous/feasible
$2Fe^{3+} + C_2O_4^{2-} \rightarrow 2CO_2 + 2Fe^{2+}$

dii. Ethanedioic acid is a weak acid; partial dissociation of ethanedioic acid provides less $[C_2O_4^{2-}]$.

diii. $E^\circ_{O_2/H_2O_2} = +0.68$ V
$E^\circ = 0.77 - (0.68) = 0.09$V
E° value is small; reaction will not go to completion, not effective

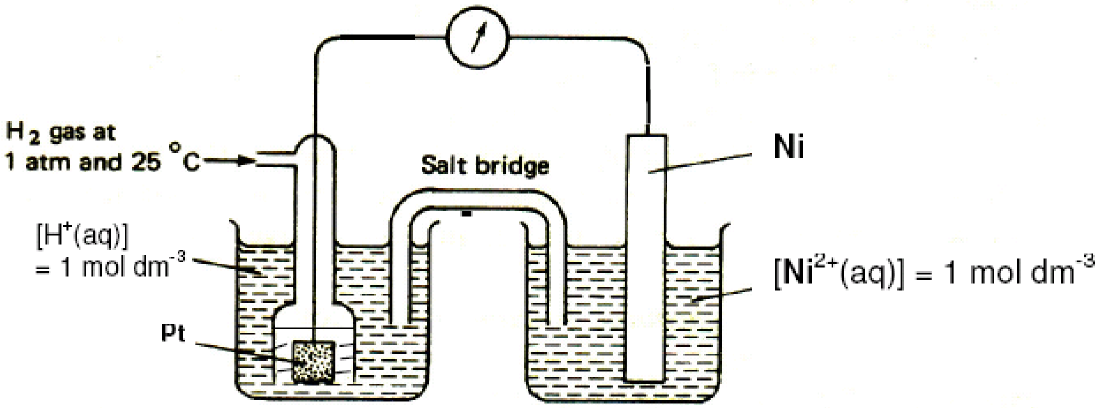
8 MJC/2010/P3/Q2a),(b) Level of Difficulty: [☆☆]

a (i) Metal **X** is the anode (oxidation)
$Ni^{2+} + 2e \rightleftharpoons Ni$ $E^\circ = -0.25$ V
$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxid} = -0.25 - E^\circ_{oxid} = +0.51$ V

$E^\circ_{oxid} = -0.76$V (for $Zn^{2+} + 2e \rightleftharpoons Zn$)

X is Zn.

(ii)



(iii) $Ni^{2+} + 2e \rightleftharpoons Ni$ $E^{\ominus}_{Ni2+/Ni}$

On adding NaOH, $[Ni^{2+}]$ will decrease due to the formation of $Ni(OH)_2$ precipitate. By Le Chatelier's Principle, position of equilibrium will shift left to increase $[Ni^{2+}]$ so $E_{Ni2+/Ni}$ becomes less positive and E_{cell} will be less positive.

b. $Ni^{2+} + 2e \rightarrow Ni$

No of moles of Ni $= \frac{m}{A_r} = \frac{I \times t}{n_e \times 96500}$

$$\frac{15}{58.7} = \frac{12 \times t}{2 \times 96500}$$

t= 4110 s = 1.14 hrs

9 NJC/2010/P3/Q2(d) Level of Difficulty: [☆☆]

i. $E^{\theta}cell = E^{\theta}red(cathode) - E^{\theta}red(anode)$
$= (+1.33) - (+0.68)$
$= \mathbf{+0.65\ V} \quad > \mathbf{0}$

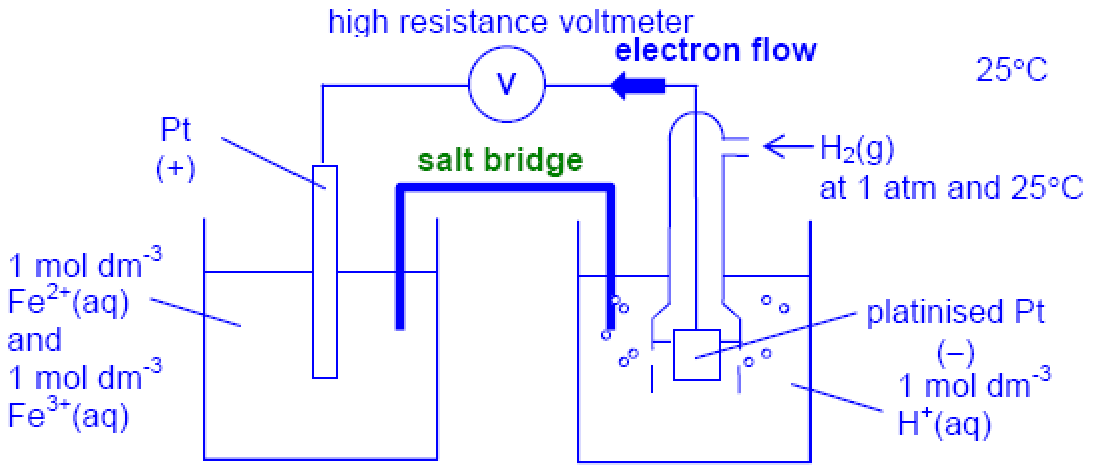
Orange dichromate solution turned yellow.

ii. $E^{\theta}cell = E^{\theta}red(cathode) - E^{\theta}red(anode)$
$= (+1.24) - (-0.13)$
$= \mathbf{+1.37\ V} \quad > \mathbf{0}$

Grey green solution turned yellow.

10 NYJC/2010/P3/Q3a),(b) Level of Difficulty: [☆☆]

ai



aii. $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^{\ominus} = +0.77$ V reaction (1)

$E^{\ominus}_{cell} = E^{\ominus}(Fe^{3+}/Fe^{2+}) - E^{\ominus}(H^{+}/H_2) = +0.77V$

When H^{+}/MnO_4^{-} is added dropwise to the Fe^{2+}/Fe^{3+} half cell, Fe^{2+} will be oxidised to Fe^{3+}.

$[Fe^{2+}]$ decreases.

By Le Chatelier's Principle, the position of equilibrium for reaction (1) shifts right.

Hence $E^{\ominus}(Fe^{3+}/Fe^{2+})$ becomes more positive. [1]

$E^{\ominus}_{cell}$ increases. [1]

aiii.

x = + 1.52 V

MnO_4^{-}/Mn^{2+} system.

bi.

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^{\ominus} = +0.77$ V

$I_2 + 2e \rightleftharpoons 2I^{-}$ $E^{\ominus} = +0.54$ V

$E^{\ominus}_{cell} = +0.77 - (+0.54) = 0.23$ V [1]

$2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_2$

- Hence the solution turns brown due to the formation of aqueous iodine. [1]

bii. Ligand exchange occurs. **[1] for stating.**

CN^{-} ligands displace water ligands from, Fe^{3+} to form the more stable complex $[Fe(CN)_6]^{3-}$ which is orange-red in solution.

- $[Fe(H_2O)_6]^{3+} + 6CN^{-} \rightleftharpoons [Fe(CN)_6]^{3-} + 6H_2O$
  Brown orange-red

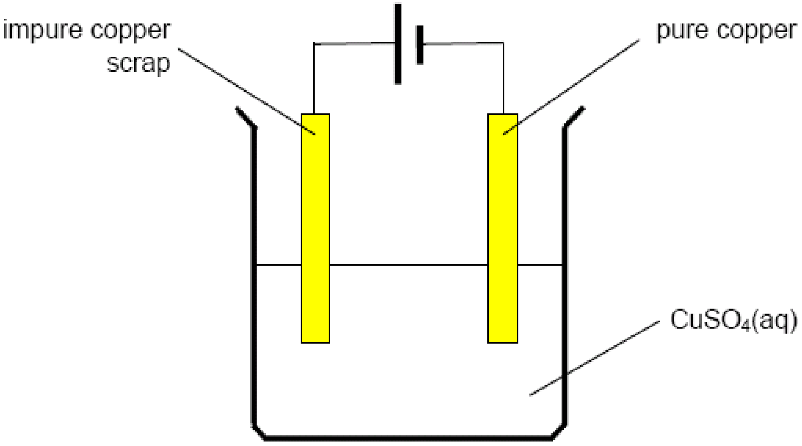
- $I_2 + 2e \rightleftharpoons 2I^{-}$ $E^{\ominus} = +0.54$ V
  $[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^{\ominus} = +0.36$ V

$E^{\ominus}_{cell} = +0.36 - (+0.54) < 0$ [1]

- Since the $E^{\ominus}_{cell} < 0$, $[Fe(CN)_6]^{3-}$ will not be able to oxidise I^-. Hence the solution remains orange-red.

11 RVHS/2010/P2/Q2 Level of Difficulty: [☆☆]

(a) (i)



(ii) $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

(state symbols not required)

Cu^{2+} is continuously replenished by the dissolving copper scrap.

(b) $n_{Cu} = \dfrac{800}{63.5}$

$= 12.6$ mol

$Cu \equiv 2e^-$

n_{e^-} required $= 2 \times 12.6$

$= 25.2$ mol

Total charge passed $= 25.2 \times 96500 = 2.43 \times 10^6$ C

$Q = It \Rightarrow t = \dfrac{Q}{I}$

Time required for extraction $= \dfrac{2.43 \times 10^6}{10.0}$

$= 2.43 \times 10^5$ s

$= 2.81$ days

(c) $E(Fe^{2+}(aq)/Fe(s)) = -0.44$ V

$E(Cu^{2+}(aq)/Cu(s)) = +0.34$ V

$E(Cu^{2+}(aq)/Cu(s))$ is more positive than $E(Fe^{2+}(aq)/Fe(s))$, hence Cu^{2+} is preferentially reduced over Fe^{2+}.

(d) **(i)** Al^{3+}, Pb^{2+}

(ii) Any one of the following:

- Add any soluble chloride or sulfate (e.g. HC*l*, H_2SO_4) to the filtrate. The formation of a white ppt indicates presence of Pb^{2+}(aq), while Al^{3+}(aq) does not give any ppt.
- Add any soluble carbonate (e.g. Na_2CO_3) to the filtrate. The formation of a white ppt with effervescence (of colourless odourless gas which gives a white ppt with limewater) indicates presence of Al^{3+}(aq), while Pb^{2+}(aq) gives a white ppt only. (Recall that a solution of Al^{3+} is acidic due to hydrolysis.)
- Add any soluble chromate(VI) (e.g. K_2CrO_4) to the filtrate. The formation of a yellow ppt indicates presence of Pb^{2+}(aq), while Al^{3+}(aq) turns the yellow solution of chromate(VI) to orange.
- Add any soluble iodide (e.g. KI) to the filtrate. The formation of a yellow ppt indicates presence of Pb^{2+}(aq), while Al^{3+}(aq) does not give any ppt.

12 SAJC/2010/P3/Q3a Level of Difficulty: [☆☆]

(a) (i) The high charge density of Fe^{3+} ion causes hydrolysis, producing acidic solution with H_3O^+.

$Fe(H_2O)_6^{3+}(aq) + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$

(a) (ii) $Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$ $E^0 = +0.77V$

$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$ $E^0 = +0.34V$

Overall equation: $2Fe^{3+}(aq) + Cu(s) \rightleftharpoons 2Fe^{2+}(aq) + Cu^{2+}(aq)$

$E^o_{cell} = +0.43V$

Since E^o value is positive, reaction is feasible**.**

The pale greenish blue solution observed is due to the mixture of Cu^{2+}(aq) and Fe^{2+}(aq) formed.

(iii) E^o remains unchanged.

13 SRJC/2010/P3/Q1(b), (c) Level of Difficulty: [☆☆]

b

When a M^{3+}/M^{2+} half-cell was connected to a standard hydrogen electrode, electrons flowed from the standard hydrogen electrode to the M^{3+}/M^{2+} half-cell →
It implies that hydrogen is undergoing oxidation and M^{3+} is undergoing reduction. Thus the E^θ value of M^{3+}/M^{2+} half-cell is positive (greater than zero V)

E^θ of $Ni^{2+}/Ni = -0.25V$

When M^{3+}/M^{2+} half-cell was connected to Ni^{2+}/Ni half-cell, half-cell with a more positive $E^{\ominus}$ value underwent reduction (cathode) and the one with more negative E^{θ} value underwent oxidation (anode). Thus, **M^{3+}/M^{2+} half-cell is the cathode**

$E^{o}_{cell} = E^{o}_{red} - E^{o}_{ox}$
E^{θ} of M^{3+}/M^{2+} = +1.08 – 0.25 = **$+0.83V$**

ci. Anode : $Ni \rightarrow Ni^{2+} + 2e$
Cathode : $Ni^{2+} + 2e \rightarrow Ni$

cii. $Ni^{2+} + 2e \rightarrow Ni$

Volume of Ni formed = (30) x (0.20 x 10^{-1}) = 0.6 cm^3
Mass of Ni formed = 0.06 x 8.91= 5.346 g

$$\text{amt of Ni} = \frac{I \times t}{n_e\ F}$$

$$\frac{5.346}{58.7} = \frac{0.2 \times t}{2 \times 96500}$$

$$= 87886s$$

$$= 87900s$$

14 TJC/2010/P3/Q2(e) Level of Difficulty: [☆☆]

(e) $E^{\theta}_{BrO_3^-/Br_2} = +1.48\ V$
$E^{\theta}_{Zn^{2+}/Zn} = -0.76\ V$
$E^{\theta}_{Br_2/Br^-} = +1.07\ V$
$E^{\theta}_{H^+/H_2} = 0.00\ V$

- Since $E^{\theta}_{BrO_3^-/Br_2}$ is more positive than $E^{\theta}_{Zn^{2+}/Zn}$, BrO_3^- will reduced to Br_2 and Zn will be oxidised to Zn^{2+}.
OR
E^{θ}_{cell} = 1.48 – (-0.76) = +2.24 V
Since $E^{\theta}_{cell} > 0$, reaction is feasible

- $2BrO_3^- + 12H^+ + 5Zn \rightarrow Br_2 + 6H_2O + 5Zn^{2+}$

- Zinc will be oxidized to form Zn^{2+} while colourless BrO_3^- will be first reduced to brown Br_2. Zinc metal gets smaller/thinner as it is being oxidised.

- Since $E^\theta_{Br_2/Br^-}$ is more positive than $E^\theta_{Zn^{2+}/Zn}$, Br_2 will reduced to Br^- and Zn will be oxidised to Zn^{2+}.
  OR
  $E^\theta_{cell} = 1.07 - (-0.76) = +1.83$ V
  Since $E^\theta_{cell} > 0$, reaction is feasible

  $Br_2 + Zn \rightarrow 2Br^- + Zn^{2+}$

  Brown Br_2 is further reduced to colourless Br^-.

- Since $E^\theta_{H^+/H_2}$ is more positive than $E^\theta_{Zn^{2+}/Zn}$, H^+ will reduced to H_2 and Zn will be oxidised to Zn^{2+}.
  OR
  $E^\theta_{cell} = 0.00 - (-0.76) = +0.76$ V
  Since $E^\theta_{cell} > 0$, reaction is feasible

  $H^+ + Zn \rightarrow H_2 + Zn^{2+}$

  Effervescence of H_2 gas observed.

15 VJC/2010/P3/Q1(b) Level of Difficulty: [☆☆]

(b)(i)

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
$E^\ominus_{cell} = 1.47 - (-0.13) = +1.60V$
E.m.f of a series of 6 cells = +(6 x 1.60) = +9.60V

(ii)

Both **electrodes** are coated with the product, **$PbSO_4$(s)**.
Hence, when an **external source of direct current** is applied, it will recharge the battery by driving the cell reaction in the **reverse** direction.

(iii)

Sulfuric acid is consumed during discharging to form solid $PbSO_4$ and water.
Hence, measuring density of **sulfuric acid** in the electrolyte provides a quick check on the state of discharge of the battery.

(iv)(I)

During charging, species that can undergo reduction are **$PbSO_4$** and **M^{2+}**.
Since $E^\ominus(M^{2+}|M)$ is **more positive** than $E^\ominus(PbSO_4|Pb)$,
M^{2+} will be reduced to **M** preferably.

(II)

During discharging, species that can undergo reduction are **PbO_2** and **M^{2+}**.
Since $E^\ominus(PbO_2|Pb^{2+})$ is **more positive** than $E^\ominus(M^{2+}|M)$, PbO_2 will be reduced to Pb^{2+} preferably.
There is no effect on the discharging process.

16 HCI/ 2010/ P3/ 4(b),(c) Level of Difficulty: [☆ ☆ ☆]

(b) **(i)** SO_4^{2-}

[R] $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ $E^\ominus$ +1.52 V
[O] $SO_4^{2-} + 2H^+ + 2e \rightarrow SO_3^{2-} + H_2O$ $E^\ominus$ < +1.52 V

(ii) From the titration results,

$$\frac{n_{MnO_4^-}}{n_{SO_3^{2-}}} = \frac{25.0 \times 0.020}{12.5 \times 0.10} = 0.4 \text{ or } \frac{2}{5}$$

Each mol of MnO_4^- accepts 5 mol of electrons when reduced to Mn^{2+}.

This means 2 mol of MnO_4^- accepts 10 mol of e^- from 5 mol of SO_3^{2-};
or each SO_3^{2-} ion loses $\frac{10}{5}$ = 2 electrons.
Hence oxidation state of S increases by 2 units from +4 (in SO_3^{2-}) to + 6 (in SO_4^{2-})

(c) **(i)** When $[Fe^{2+}] = [Fe^{3+}]$, $ln\frac{[Fe^{3+}]}{[Fe^{2+}]} = 0$.

Hence, $E = E^\ominus(Fe^{3+}/Fe^{2+}) = +0.77$ V.

(ii) Vol of $KMnO_4$ = 50.0 cm^3

(iii) The equivalence point is reached between 80 and 120 cm^3 (precisely at 100 cm^3). This means that the E value switches from a calculation based on Fe^{3+}/Fe^{2+} to one based on MnO_4^-/Mn^{2+}.

(iv) The *E* value of MnO_4^-/Mn^{2+} (and hence, the oxidizing power of MnO_4^-) is dependent on $[H^+]$;
or changes in $[H^+]$ affects the value of the measured *E*, because of
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$.

(b) **(i)** SO_4^{2-}

[R] $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ $E^\ominus$ +1.52 V
[O] $SO_4^{2-} + 2H^+ + 2e \rightarrow SO_3^{2-} + H_2O$ $E^\ominus$ < +1.52 V

(ii) From the titration results,

$$\frac{n_{MnO_4^-}}{n_{SO_3^{2-}}} = \frac{25.0 \times 0.020}{12.5 \times 0.10} = 0.4 \text{ or } \frac{2}{5}$$

Each mol of MnO_4^- accepts 5 mol of electrons when reduced to Mn^{2+}.

This means 2 mol of MnO_4^- accepts 10 mol of e^- from 5 mol of SO_3^{2-};
or each SO_3^{2-} ion loses $\frac{10}{5}$ = 2 electrons.

Hence oxidation state of S increases by 2 units from +4 (in SO_3^{2-}) to + 6 (in SO_4^{2-})

(c) (i) When $[Fe^{2+}] = [Fe^{3+}]$, $ln \frac{[Fe^{3+}]}{[Fe^{2+}]} = 0$.

Hence, $E = E^{\ominus}(Fe^{3+}/Fe^{2+}) = +0.77$ V.

(ii) Vol of $KMnO_4$ = 50.0 cm^3

(iii) The equivalence point is reached between 80 and 120 cm^3 (precisely at 100 cm^3). This means that the E value switches from a calculation based on Fe^{3+}/Fe^{2+} to one based on MnO_4^-/Mn^{2+}.

(iv) The *E* value of MnO_4^-/Mn^{2+} (and hence, the oxidizing power of MnO_4^-) is dependent on $[H^+]$;
or changes in $[H^+]$ affects the value of the measured *E*, because of
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$.

17 MJC/ 2010/ P3/ 2(c) Level of Difficulty: [☆☆☆]

(c) (i) Anode: $CH_3CH_2OH + 3\ H_2O \rightarrow 2\ CO_2 + 12\ H^+ + 12\ e$

Cathode: $O_2 + 4\ H^+ + 4\ e \rightarrow 2\ H_2O$

Overall eqn: $CH_3CH_2OH\ (l) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O\ (l)$

(ii) Ethanol produces twice as many electrons per mole of alcohol than methanol

OR

$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12\ H^+ + 12e$
$CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6e$

18 NJC/ 2010/ P3/ 3(d) Level of Difficulty: [☆☆☆]

3 (d) (i) Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$
Cathode: $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

Overall: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

3 (d) (ii) Phosphoric acid can act as a charge carrier.

3 (d) (iii) Carbon paper is porous. Platinum acts as catalyst for oxidation of ethanol.

3 (d) (iv) High costs involved in maintaining the high temperature.
High costs involved as platinum catalyst is expensive.

19 NYJC/2010/P3/Q3 (d) Level of Difficulty: [☆☆☆]

i.

Y Cathode , *Z* Anode **[1] for correct identification**
Oxidation occurs at ***Z*** rather than ***Y*** because there is a higher concentration of dissolved oxygen present at the air/electrolyte interface.

ii.

Y Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
Z Anode: $Fe \rightarrow Fe^{2+} + 2e$
[1] x2 for each equation. No ecf.

iii.

Mass = density x volume = $7.3 \times 0.5 \times (1.0 \times 10^{-5}) \times 10^6 = 36.5$ g **[1]**

$n_{Cr} = \frac{36.5}{52} = 0.7019$ mol

$Cr^{+6} + 6e \rightarrow Cr$

$Q = n_eF = It$

$6 \times 0.7019 \times 96500 = 40 \times t$ **[1]**

t = 10160 s = **2.82 h** **[1]**

20 SRJC/ 2010/ P2 / 2 (c),(d) Level of Difficulty: [☆☆☆]

c.

$Zn^{2+} + 2e \rightleftharpoons$ **Zn** -0.76 V (E_{oxd})
$Cu^{2+} + 2e \rightleftharpoons$ **Cu** +0.34 V (E_{oxd})
H^+ $+ 2e \rightleftharpoons H_2$ 0.00V (E_{red})

For HC*l*, H^+ undergoes reduction.
$2H^+ + 2e \rightarrow H_2$ $E^\theta = 0.00V$

For Copper, it undergoes oxidation.

E^θcell = 0.00 – 0.34 = -0.34 V
E^θcell < 0, thus Cu will not dissolves in acid.

For Zinc, it undergoes oxidation.

E^θcell = 0.00 – (-0.76) = +0.76 V
E^θcell > 0, thus Zn will dissolve in acid.

Zinc metal will dissolve in dilute hydrochloric acid.

di. Anode: $Zn \rightarrow Zn^{2+} + 2e$
Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
Overall:
$\underline{\mathbf{2Zn + O_2 + 2H_2O \rightarrow 2Zn^{2+} + 4OH^-}}$
OR
$2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2$

dii. E^{θ}_{cell} value will **increase**.

During exercising, lactic **acid** is produced. Thus, it results in the **decrease of the pH**.

When pH drops, $[H^+]$ increases, thus the equilibrium position in

$$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$$

shifts to the right, **favouring reduction**. (as OH^- is neutralised by H^+) Therefore, **E^{θ} value will become more positive** and E^{θ}_{cell} value will increase.

TOPIC 7.1: CHEMICAL EQUILIBRIUM

1 CJC/2010/P2/Q2(b) Level of Difficulty: [☆]

(b) Nitrogen dioxide, which can be classified as a free radical, exists in equilibrium with dinitrogen tetroxide, N_2O_4, a powerful oxidiser which is highly toxic and corrosive.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

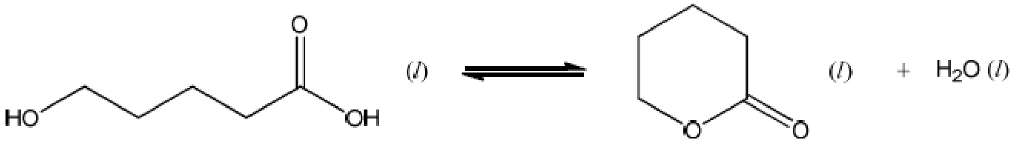
(i) Draw the dot-and-cross diagrams of NO_2 and N_2O_4.

(ii) A mixture of the two gases are allowed to reach equilibrium in a gas syringe. State and explain how an increase in the volume occupied by the gases in the syringe would affect the equilibrium position and hence the composition of the mixture at equilibrium under constant temperature.

2 HCI/2010/P3/2(a) Level of Difficulty: [☆]

2 (a) Esterification is commonly carried out using acids as catalysts.

5-hydroxypentanoic acid can undergo intramolecular esterification to form a cyclic ester.



5-hydroxypentanoic acid

This esterification system exists in a *dynamic equilibrium*.

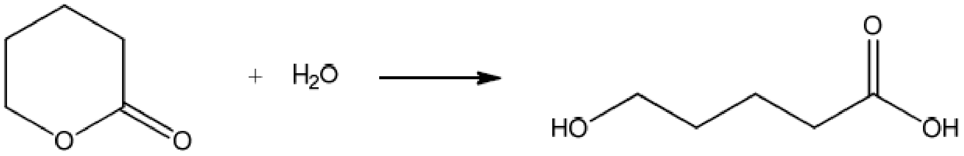
(i) Explain what is meant by the term *dynamic equilibrium*.

(ii) Write an expression for the equilibrium constant, K_c, for this esterification reaction.

(iii) In an experiment, 2.0 mol of 5-hydroxypentanoic acid was allowed to undergo esterification.

Given that 5% of 5-hydroxypentanoic acid remained at equilibrium and the total volume of the mixture remained constant at 200 cm^3, calculate the K_c for this reaction.

(iv) In the reverse reaction, i.e. the hydrolysis of the cyclic ester,



the rate of the reaction gradually increases at first, but then decreases.

Explain why this is so.

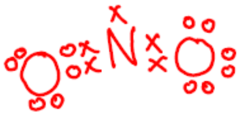
[6]

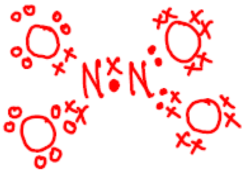
(ii) On the same graph, sketch a curve to show how the fraction of N_2 changes at a higher pressure, P_2.

(b) An initial 5 moles of NH_3 and 3 moles of O_2 are mixed in a 2 dm^3 vessel. At 450° C, an equilibrium mixture shows 80% of ammonia has reacted . Calculate a value for the equilibrium constant, K_c and give its unit.

Suggested Answers

1 CJC/2010/P2/Q2(b) Level of Difficulty: [✰]





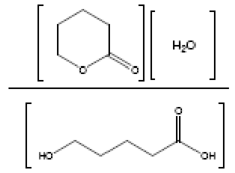
When volume occupied by gases in syringe increase, pressure decreases, According to Le Chatelier's Principle, POE shifts right to favour reaction with greater number of moles of gas to increase pressure

Eqm mixture contains more NO_2 and less N_2O_4

2 HCI/2010/P3/2(a) Level of Difficulty: [✰]

2 (a) (i) A system is said to be in dynamic equilibrium when the rate of forward reaction is equal to the rate of backward reaction.

(ii) $K_c =$



(iii)

$$K_c = \frac{\left(\frac{1.90}{0.2}\right)^2}{\left(\frac{0.10}{0.2}\right)} = 180.5\ mol\ dm^{-3}$$

(iv) The rate increases at first when the carboxylic acid is first formed because it partially dissociates to give H^+ which catalyses the hydrolysis of ester.

The rate decreases as the reaction proceeds due to decrease in the concentration of the ester, leading to decrease in frequency of effective collisions.

3 MJC/2010/P2/Q2(c) Level of Difficulty: [✰]

(c) (i) $2\,NOCl\,(g) \rightleftharpoons 2\,NO\,(g) + Cl_2\,(g)$

Initial moles	1	0	0
Δ in moles	- 0.4	+ 0.4	+ 0.2
Eqm moles	0.6	0.4	0.2

$$K_p = \frac{(P_{NO})^2 \cdot P_{Cl_2}}{(P_{NOCl})^2}$$

$$= \frac{\left(\frac{0.4}{1.2}(2)\right)^2 \left(\frac{0.2}{1.2}(2)\right)}{\left(\frac{0.6}{1.2}(2)\right)^2}$$

$$= 0.148 \text{ atm}$$

(ii) The forward reaction is endothermic.

At a higher temperature, K_p value is larger, which means that more products are formed. Hence by Le Chatelier's Principle, the equilibrium position should shift right towards the endothermic reaction to lower the temperature by absorbing the heat.

(iii) When the total pressure is halved, by Le Chatelier's Principle, the equilibrium position will shift right to produce more number of moles of gas molecules to increase pressure. The mass of the mixture remains constant, so since the no of moles of gas molecules increases, the apparent molar mass of the mixture decreases.

4 RVHS/2010/P2/Q4(a) Level of Difficulty: [✯]

4 **(a)** **(i)** $N_2(g) + 3H_2(g) = 2NH_3(g)$

(state symbols not required)

(ii) $$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

(iii) $$K_c = \frac{\left(\frac{1.6}{2}\right)^2}{\left(\frac{14.0}{2}\right)\left(\frac{18.0}{2}\right)^3}$$

$$= 1.25 \times 10^{-4} \text{ mol}^{-2} \text{ dm}^6$$

(iv) The activation energy of the reaction is very high as the N%N (triple) bond is very strong / has a high bond energy.

(Finely divided) iron /iron(III) oxide / ruthenium

5 SAJC/2010/P2/Q4 Level of Difficulty: [✯]

4. **(a)** Large amount of energy required to break N≡N.

(b) High temperature in car engines causes the equilibrium to favour endothermic reaction in order to absorb/remove excess heat. Equilibrium position for the given reaction shifts to the right, resulting in higher composition of NO in car engine.

(c) K_C remains constant.

$$K_C = \frac{(\frac{0.24}{0.2})^2}{(\frac{0.42}{0.2})^2(\frac{0.52}{0.2})}$$

K_c = 0.1256 $mol^{-1}\ dm^3$

$$0.1256 = \frac{(\frac{1.88}{V})^2}{(\frac{1.56}{V})^2(\frac{5.78}{V})}$$

V = 0.5 dm^3 ; x = 500 cm^3

6 SAJC/2010/P3/Q3(b) Level of Difficulty: [☆]

(b) (i) $M_r = \frac{(mRT)}{pV} = \frac{1.56 \times 8.31 \times (273 + 180)}{(32.3 \times 10^3 \times 1 \times 10^{-3})}$

≈ 182

(ii) M_r of $AlCl_3$ = 133.5

M_r of Al_2Cl_6 = 267

Let y = % of dimer, (100 – y) = % of monomer

$\frac{267y + (100 - y) \times 133.5}{100} = 182$

% of dimer = 36.3%

(iii) Dimerisation involved bond formation.

(iv) **I** $2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g)$

The system tries to increase the pressure by increasing the no. of moles of gaseous molecules.

Equilibrium shifts to the left and the proportion of dimer would decrease.

II $2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g)$

The system tries to increase the temperature by favouring the exothermic process to produce more heat energy.

Thus, the equilibrium shifts to the right and proportion of dimer increases.

7 ACJC/2010/P3/Q3(a)-(c) Level of Difficulty: [☆☆]

To determine the initial partial pressure of water,

$P_{H_2O} = n_{H_2O}RT/V$ = (0.100)(8.31)(1073)/1.00 x 10^{-3} = 891663 Pa = 891663/1.01 x 10^5
= 8.83 atm **[1]**

	C(s) +	$H_2O(g)$	CO(g)	+ $H_2(g)$
Initial Pressure / atm		**8.83**	**0**	**0**
Change		**-*x***	**+*x***	**+*x***
Equilibrium		**8.83 - *x***	***x***	***x***

$$K_p = \frac{P_{CO_2}\,P_{H_2}}{P_{H_2O}} = \frac{(x)(x)}{(8.83 - x)} = 14.1$$

Solving quadratic equation $x^2 = 14.1\,(8.83 - x)$

$x^2 + 14.1x - 124.5 = 0$

$x = 6.15$ **atm**

$P_{CO_2} = 6.15$ **atm**

$P_{H_2} = 6.15$ **atm**

$P_{H_2O} = (8.83 - 6.15) = 2.68$ **atm**

6.15 atm of $H_2O(g)$ must react for the system to achieve equilibrium. Using ideal gas equation to convert this partial pressure into amount of $H_2O(g)$.

$P_{H_2O} = n_{H_2O}RT/V$

$n_{H_2O} = P_{H_2O}V / RT = 6.15 \times (1.01 \times 10^5) \times 1.00 \times 10^{-3} / 8.31\,(1073) = 0.0697$ **mol**

Hence 0.0697 mol of H_2O and the same amount of C must react to achieve equilibrium.
As a result there must be at least 0.0697 mol of C present among the reactants at the start of the reaction.

$P_{Total} = P_{H_2O} + P_{CO} + P_{H_2} = 2.68 + 6.15 + 6.15 = 14.98 = 15.0$ **atm**

There is **an increase in K_p value with increasing temperature**. Hence the forward reaction is **endothermic** reaction favouring an absorption of heat.

According to Le Chatelier's Principle, a decrease in pressure causes a gaseous equilibrium to **shift towards the side with greater number of moles of gas**. In this case, there are 2 moles of gas on the product side and only 1 mole on the reactant side. Therefore the **pressure should be reduced** to maximise the yield of CO and H_2.

8 AJC/2010/P3/Q5(a) Level of Difficulty: [☆☆]

5 (a)(i)

	CH_4	+	H_2O	$\rightleftharpoons$	$3\,H_2$	+	CO
Initial P/atm	1.0		1.0		0.0		0.0
Eqm P/atm	0.60		0.60		3(0.40)		0.40

$$K_p = \frac{(1.2)^3(0.40)}{(0.6)^2} = \underline{1.92\ \text{atm}^2}$$

(a)(ii) When temperature increases (from 550°C to 850°C),

I Percentage of H_2 increases (from 1.68% to 11.9%), thus forward reaction is favoured.

By L.C.P, endothermic reaction is favoured.
Hence, production of H_2 is endothermic.

II When volume changes from **Z** to **X**,

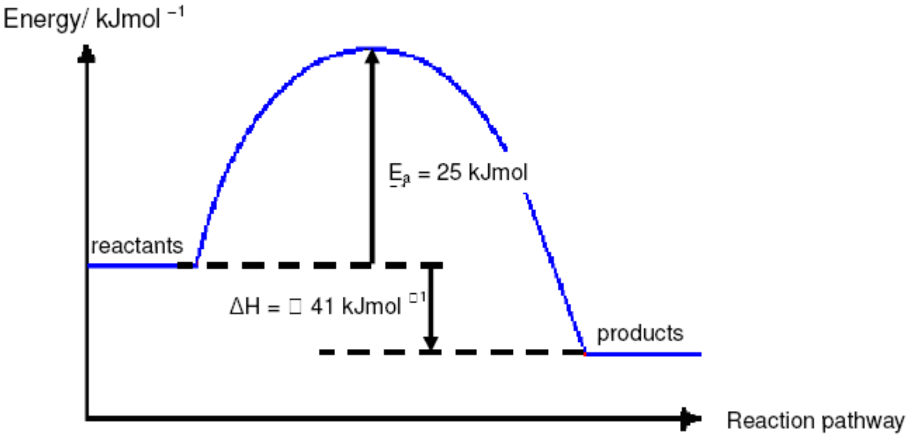
Percentage of H_2 increases (from 0.009% to 1.68%) thus forward reaction is favoured.

When equilibrium shifts to the right, the number of moles of gas increases. By L.C.P. pressure has decreased / volume has increased.

Hence, increasing order: **Z** < **Y** < **X**

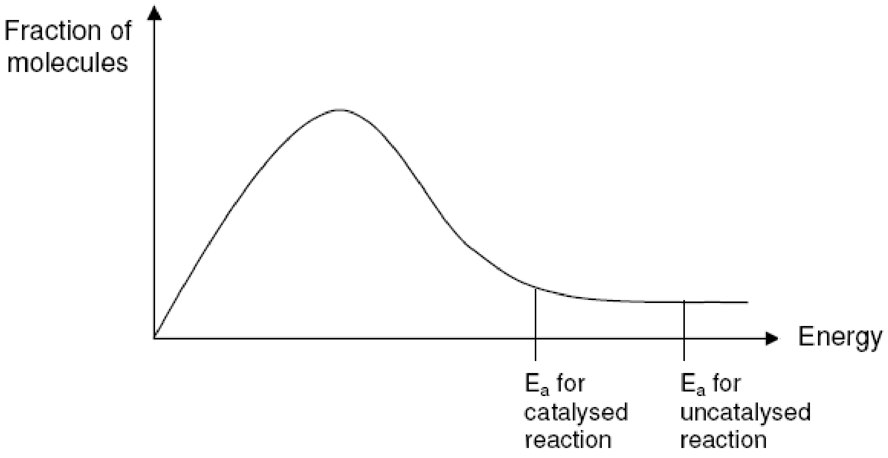
9 NJC/2010/P3/Q1(c) Level of Difficulty: [☆☆]

1 (c) (i)



1 (c) (ii) Fe_3O_4 functions as a **heterogeneous catalyst**. The reactant molecules are **adsorbed onto the surface area** of Fe_3O_4. This weakens the existing bonds in the reactant molecules. Thus, Fe_3O_4 **lowers the activation energy** of the reaction, allowing rate of reaction to increase.

1 (c) (iii) When a catalyst provides an alternative pathway with a lower activation energy for the reaction to take place, there is a **larger proportion of molecules with energy greater than activation energy**. Thus rate of reaction increases.



1 (c) (iv)

$$\text{Kp} = \frac{P_{CO_2}.P_{H_2}}{P_{CO}\ .P_{H_2O}}$$
$$= \frac{(1.5)(1.5)}{(0.5)(2.5)}$$
$$= 1.8$$

1 (c) (v) When aqueous sodium hydroxide is added, CO_2 is removed. Thus by Le Chatelier's Principle, position of equilibrium shifts right to produce more CO_2.

10 NYJC/2010/P3/Q1(b) Level of Difficulty: [☆☆]

$$\text{Q} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

A: Q = 0

B: $\text{Q} = \dfrac{(0.4/\text{V})^2}{(0.2/\text{V})(0.2/\text{V})} = 4$

C, D & E:

$$\text{Q} = \frac{(0.6/\text{V})^2}{(0.1/\text{V})(0.1/\text{V})} = 36$$

From the calculation above, it can be seen that Q approaches a constant value as the reaction progress to scene **E**. [1] Thus the reaction mixture has reached equilibrium at scene **E**.

36

	$I_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial amt/mol	0.1		0.1		0.6
Change in amt/mol	+0.15		+0.15		-0.3
Equim amt/mol	0.25		0.25		0.3

$$\text{K}_\text{C} = \frac{(0.3/\text{V})^2}{(0.25/\text{V})(0.25/\text{V})} = 1.44$$

As temperature increases, K_c decreases. By LCP, an increase in temperature favored the endothermic reaction. Since K_c decreases, POE lies to the left. The backward reaction is endothermic, thus the reaction between hydrogen and iodine which is the forward reaction is exothermic. The sign of the enthalpy change of reaction of hydrogen and iodine is negative.

The amount of hydrogen iodide will remained unchanged. As the mole ratio of the reactants to the products is 1:1, the equilibrium is not affected by changes in pressure.

11 PJC/2010/P3/Q1(a) Level of Difficulty: [☆☆]

1 (a) (i)
- **Low temperature favours forward reaction which is exothermic. This gives high yield of SO_3.**
- **But equilibrium is attained at a lower rate at low temperature.**
- **A moderately high temperature is used to achieve equilibrium more rapidly (together with a catalyst to increase the rate).**

(ii)

	$2SO_2(g)$ +	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
Initial partial pressure / atm	**1.0**	**0.5**		**–**
Change in partial pressure / atm	**-0.94**	**-0.47**		**+0.94**
Eqm partial pressure / atm	**0.06**	**0.03**		**0.94**

$$Kp = \frac{(0.94)^2}{(0.06)^2(0.03)}$$

$= 8180\ \text{atm}^{-1}$ **(3 sf)**

(iii)
- **when volume is reduced, pressure is increased**
- **by Le Chatelier's Principle, equilibrium position shifts right to the side with fewer gaseous molecules**
- **percentage conversion of SO_2 into SO_3 increases**

12 TJC/2010/P3/Q2(a)-(b) Level of Difficulty: [☆☆]

2 (a) (i) • Le Chatelier's Principle states that when system at dynamic equilibrium is subjected to a change which disturbs the equilibrium, the system will respond in such a way so as to counteract the effect of the change (to re-establish equilibrium).

(ii) • Catalyst is added to speed up the reaction and to achieve equilibrium at a shorter time.

• Only atmospheric pressure (or low pressure) is used as by Le Chatelier's principle, a low pressure would favour the forward reaction as to produce more number of moles of gaseous products thus improving the yield.

• A high temperature of 300 °C is used as the forward reaction is endothermic and by Le Chatelier's principle, a high temperature would favour the forward reaction as to absorb heat, thus increasing the yield of the products.

(b) (i)

• $K_p = \dfrac{P_{C_7H_8} \,.\, P_{H_2}{}^4}{P_{C_7H_{16}}}$

(ii) Let x be the initial pressure of C_7H_{16} and P be the total pressure at equilibrium.

	C_7H_{16} (g)	$\rightleftharpoons$	C_7H_8 (g) +	$4H_2$ (g)
Initial pressure/ atm	x		0	0
Change in pressure/atm	-0.9x		+0.9x	+3.6x
Final pressure/ atm	0.1x		0.9x	3.6x

$$0.1x + 0.9x + 3.6x = P$$

$$4.6x = P$$

$$x = \frac{P}{4.6}$$

- Partial pressure of C_7H_{16} = $0.1\left(\frac{P}{4.6}\right)$

  = 0.0217P atm

- Partial pressure of C_7H_8 = $0.9\left(\frac{P}{4.6}\right)$

  = 0.196P atm

- Partial pressure of H_2 = $3.6\left(\frac{P}{4.6}\right)$

  = 0.783P atm

$$K_p = \frac{(0.196P)(0.783P)^4}{(0.0217P)} = 1$$

- P = 0.737 atm

13 VJC/2010/P3/Q2(a) Level of Difficulty: [☆☆]

2(a)(i)

$$P_{CO} = \frac{1}{3} \times \frac{6}{298} \times 500$$

$$= 3.36 \text{ atm}$$

(ii)

$$K_p = \frac{P_{CH_3OH}}{P_{CO}P_{H_2}{}^2}$$

(iii)

$$P_{H2} = \frac{2}{3} \times \frac{6}{298} \times 500 \text{ (ecf)}$$

$$= 6.71 \text{ atm}$$

	$CO(g)$	+	$2H_2(g)$	$\rightleftharpoons$	$CH_3OH(g)$
Initial / atm	3.36		6.71		0
Change / atm	–3.2		–6.4		3.2
Equilibrium / atm	0.16		0.31		3.2

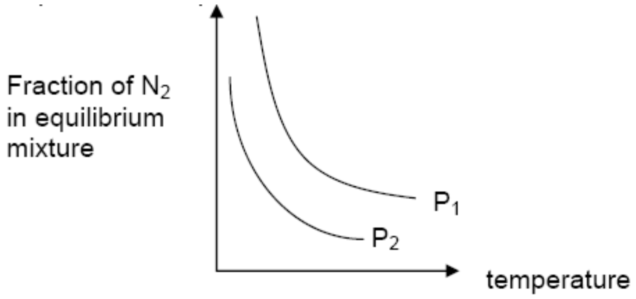
(iv)

$$K_p = \frac{3.2}{0.16 \times 0.31^2} \text{ (ecf)}$$

$$= 208 \text{ atm}^{-2} \text{ (ecf)}$$

14 YJC/2010/P2/Q3(a)-(b) Level of Difficulty: [✯✯]

As temperature increases, amount of N_2 decreases. Therefore the equilibrium position has shifted to the left since ΔH is exothermic.



$$K_c = \frac{(0.5/2)^2\,(1.5/2)^6}{(4/2)^4\,(2.25/2)^3}$$

$$= 4.88 \times 10^{-4}\ \text{mol dm}^{-3}$$

TOPIC 7.2: IONIC EQUILIBRIUM

1 CJC/2010/P2/Q4(d) Level of Difficulty: [✯]

(d) Before use, a pH meter is calibrated using a buffer solution of pH 4.00. It contains 0.0113 mol dm^{-3} methanoic acid and 0.0200 mol dm^{-3} sodium methanoate.

Calculate the K_a for methanoic acid.

2 CJC/2010/P2/Q6(a) Level of Difficulty: [✯]

6 (a) Limewater is a saturated solution of $Ca(OH)_2$, and is often used to test for the presence of CO_2 formed during experiments. A positive test is indicated by the formation of white precipitate, $CaCO_3$.

(i) Write an equation, with state symbols, to represent the reaction between limewater and CO_2.

(ii) The solubility of $Ca(OH)_2$ is 1.73 g dm^{-3}. Calculate the concentration of Ca^{2+} in mol dm^{-3}, in limewater (saturated $Ca(OH)_2$ solution).

(iii) Calculate the K_{sp} of $CaCO_3$ given that its solubility is 1.5×10^{-4} mol dm^{-3}.

(iv) Hence, calculate the minimum volume of CO_2 at r.t.p., that must be bubbled through 1 cm^3 of limewater in order to give a white precipitate, $CaCO_3$.

3 HCI/2010/P2/Q3(b) Level of Difficulty: [✯]

(b) Ammonium ion is acidic in aqueous solution.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

(i) Which feature of this equation tells you that the ammonium ion is a **weak** acid?

(ii) Write the expression for the acid dissociation constant, K_a, of the ammonium ion.

(iii) Calculate the pH of a 0.30 mol dm^{-3} solution of NH_4Cl.
State any assumptions you have made.
[K_b for the ammonia is 1.78×10^{-5} mol dm^{-3} at 25 °C]

(iv) Use the data in the following table to suggest a suitable indicator for the titration of ammonia solution with hydrochloric acid. Justify your answer.

Indicator	pK_{In}
Thymol blue	1.7
Bromocresol green	4.7
Bromothymol blue	7.0
Phenol red	7.9
Thymolphthalein	9.7

4 HCI/2010/P3/Q1(d) Level of Difficulty: [✯]

(d) Phosphates have an amazing array of applications in home and industry. For example, sodium hydrogenphosphate, Na_2HPO_4, is a laxative ingredient and is used to adjust the acidity of boiler water.

A buffer solution is made by mixing 500 cm^3 of 0.30 mol dm^{-3} NaH_2PO_4 with 100 cm^3 of 0.20 mol dm^{-3} Na_2HPO_4.

(v) A student wishes to simulate the blood plasma buffer by mixing 25.0 cm^3 of 0.20 mol dm^{-3} H_2CO_3 solution with 0.30 mol dm^{-3} NaOH solution. The neutralisation that takes place is represented by

$$NaOH + H_2CO_3 \rightarrow NaHCO_3 + H_2O$$

Using your answer in **(c)(ii)**, calculate the volume of NaOH that should be added. [8]

Suggested Answers

1 CJC/2010/P2/Q4(d) Level of Difficulty: [☆]

$4 = pK_a + \lg (0.0200 / 0.0113)$

$K_a = 1.77 \times 10^{-4}$ mol dm^{-3}

2 CJC/2010/P2/Q6(a) Level of Difficulty: [☆]

$Ca(OH)_2 (aq) + CO_2 (g) \rightarrow CaCO_3(s) + H_2O(l)$

$[Ca^{2+}]$ of saturated solution $= \dfrac{1.73}{40.1 + 2(16.0 + 1.0)} = 2.33 \times 10^{-2}$ mol dm^{-3}

$K_{sp} = (1.5 \times 10^{-4})(1.5 \times 10^{-4}) = 2.25 \times 10^{-8}$ mol^2 dm^{-6}

$2.25 \times 10^{-8} = (2.33 \times 10^{-2}) [CO_3^{2-}]$

$[CO_3^{2-}] = 9.66 \times 10^{-7}$ mol dm^{-3}

Number of moles of $CO_2 = 9.66 \times 10^{-7} \times 1/1000 = 9.66 \times 10^{-10}$ mol

Volume of $CO_2 = 9.66 \times 10^{-10} \times 24 = 2.32 \times 10^{-8}$ dm^3 at r.t.p.

3 HCI/2010/P2/Q3(b) Level of Difficulty: [☆]

3(b)(i) The equilibrium sign suggest an incomplete ionisation, thus a weak acid.

3(b)(ii) $$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

3(b)(iii) $5.62 \times 10^{-10} = [H^+]^2 / (0.30 - x)$

$[H^+] = 1.298 \times 10^{-5}$ mol dm^{-3}

pH = 4.89

Assumption: Ammonium ion is a weak acid and amount dissociated is negligible.

3(b)(iv) The weak base-strong acid titration has equivalence point at the acidic range from the hydrolysis of the ammonium ion / pKin value is the pH value the indicator changes color. {pH = pKin ±1}

Thus the correct indicator is bromocresol green.

4 HCI/2010/P3/Q1(d) Level of Difficulty: [☆]

(d) **(i)**

$$K_a = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{[H^+][\text{salt}]}{[\text{weak acid}]}$$

$$\Rightarrow [H^+] = K_a\frac{[\text{weak acid}]}{[\text{salt}]} = 6.30\times10^{-7}\times\frac{\frac{500\times0.3}{600}}{\frac{100\times0.2}{600}} = 4.725\times10^{-6}\text{ mol dm}^{-3}$$

$\therefore$ pH = –lg [H^+] = <u>5.33</u>

(ii) When a small amount of H^+(aq) ions are added,

$$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$$

When a small amount of OH^-(aq) ions are added,

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$$

5 HCI/2010/P3/Q5(c) Level of Difficulty: [☆]

(c) **(i)** $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

pH = 10.5, pOH = 14 – 10.5 = 3.5

$[OH^-] = 10^{-3.5} = 3.162 \times 10^{-4}$ mol dm^{-3}

$[Mg^{2+}] = \frac{1}{2} \times 3.162 \times 10^{-4} = 1.581 \times 10^{-4}$ mol dm^{-3}

M_r of $Mg(OH)_2$ = 58.3

Solubility of $Mg(OH)_2$ = $[Mg(OH)_2(aq)]$
= $[Mg^{2+}]$
= $1.581 \times 10^{-4} \times 58.3 = 9.217 \times 10^{-3}$ g dm^{-3}
= **<u>9.22×10^{-3} g dm^{-3}</u>**

(ii) K_{sp} of $Mg(OH)_2$ = $[Mg^{2+}][OH^-]^2$
= $(1.581 \times 10^{-4})(3.162 \times 10^{-4})^2$
= 1.581×10^{-11} mol^3 dm^{-9}
= **<u>1.58×10^{-11} mol^3 dm^{-9}</u>**

6 NYJC/2010/P3/Q3(c) Level of Difficulty: [☆]

$[Ca(OH)_2] = \frac{0.160 \times 10}{74.1} = 0.0216$ mol dm^{-3} [1]

$K_{sp} = [Ca^{2+}][OH^-]^2 = (0.0216)(2\times0.0216)^2 = 4.02 \times 10^{-5}$ mol^3 dm^{-9}

[1] for correct Ksp value and units

$[Ca^{2+}]$ in mixture = 0.100

$K_{sp} = [Ca^{2+}][OH^-]^2 = 4.02 \times 10^{-5}$

$[OH^-] = 0.0200$ mol dm^{-3} **[1] correct calculated $[OH^-]$. Allow ecf**

$[Ca(OH)_2] = \frac{1}{2}[OH^-] = 0.0100$ mol dm^{-3} **[1] for correct answer. Ecf**

7 SRJC/2010/P2/Q4(c)(ii) Level of Difficulty: [☆]

$CH_3COO^-Na^+ \rightarrow CH_3COO^- + Na^+$
$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
Salt hydrolysis occurs
$[H^+]$ is lesser than $[OH^-]$
End point pH is greater than 7.

8 SRJC/2010/P3/Q2(b) Level of Difficulty: [☆]

$[H^+] = \sqrt{K_a \times c} = \sqrt{(10^{-4.75} \times 1)} = 0.004217$ mol dm^{-3}
pH = -log 0.004217 = **2.38**

Ethanoic acid is a **weak acid** which **dissociates partially**.
Heat released during the neutralisation process is **absorbed to bring about complete dissociation** of ethanoic acid molecules.

---

(1) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
(2) $HCl \rightarrow H^+ + Cl^-$

(3) $2H^+ + Zn \rightarrow Zn^{2+} + H_2$

Same volume of H_2 gas will be produced in both cases
Reason: Since H^+ reacts with zinc, for (1), $[H^+]$ will decrease and by LCP, equilibrium position of (1) will shift right, hence all CH_3COOH will be reacted eventually producing the same amount of H_2 gas.

9 SRJC/2010/P3/Q4(b) Level of Difficulty: [☆]

$Ag_2CO_3\ (s) \rightleftharpoons 2Ag^+\ (aq) + CO_3^{2-}\ (aq)$
$K_{sp} = [Ag^+]^2[CO_3^{2-}] = 8 \times 10^{-12}$

$CH_3COO^-Ag^+\ (s) \rightleftharpoons Ag^+\ (aq) + CH_3COO^-\ (aq)$
$K_{sp} = [Ag^+][CH_3COO^-] = 2 \times 10^{-3}$

$[Ag^+] = 1 \times 10^{-4}$ mol dm^{-3}
$[CO_3^{2-}] = 1$ mol dm^{-3}
$[CH_3COO^-] = 1$ mol dm^{-3}

Ionic Product of $Ag_2CO_3 = (1 \times 10^{-4})^2 (1) = 1 \times 10^{-8}$ mol^3 dm^{-9} (> Ksp)
⇨ Precipitation

Ionic Product of $AgCH_3COO = (1 \times 10^{-4})(1) = 1 \times 10^{-4}$ mol^2 dm^{-6}
(< Ksp)

⇨ NO Precipitation

10 SRJC/2010/P3/Q5(f) Level of Difficulty: [☆]

Small amount of CO_2 is to be detected; only a small amount of CO_3^{2-} is formed. Amount of $CaCO_3$ formed is too little to form ppt.

Since $BaCO_3$ is less soluble / has lower K_{SP} than $CaCO_3$, small amount of $BaCO_3$ will form ppt, thus able to detect small amount of CO_2.

11 TJC/2010/P2/Q3(a) Level of Difficulty: [☆]

- **Solubility of $AgCl$ = $\sqrt{1.6\text{x}10^{-10}}$ = 1.26×10^{-5} mol dm^{-3}**

- $$\left\{\begin{array}{l} AgCl \rightleftharpoons Ag^+ + Cl^- \quad \text{------ (1)} \quad K_{sp} = [Ag^+][Cl^-] \\ Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \quad \text{------ (2)} \end{array}\right.$$
- **When NH_3(aq) is added, it react with Ag^+ to form a complex ion as shown in equilibrium (2), hence lowering the concentration of Ag^+ in solution.**
- **By LCP, the position of equilibrium (1) shifts right when the concentration of Ag^+ decrease, hence the solubility of $AgCl$ increases.**

OR

The ionic product of $AgCl$, $[Ag^+][Cl^-]$, decreases to a value lower than its K_{sp} hence $AgCl$ will dissolve.

12 TJC/2010/P2/Q5(a)(iii) Level of Difficulty: [☆]

- **Yellow**

13 ACJC/2010/P3/Q3 Level of Difficulty: [☆☆]

BaF_2

Solubility = $\sqrt[3]{(1.7 \times 10^{-6} / 4)} = 7.5 \times 10^{-3}$ mol dm^{-3}

F^- ions from KF solution will decrease the solubility of BaF_2(s) due to common ion effect

---

$[Ba^{2+}]$ diluted = (25/1000 x 0.100) / (0.050 + 0.025) = 0.0333 mol dm^{-3}

To precipitate BaF_2

$[Ba^{2+}][F^-]^2 \geq K_{sp}$

$(0.0333)\ [F^-]^2 \geq 1.7 \times 10^{-6}$

$[F^-] \geq \sqrt{(1.7 \times 10^{-6})} / 0.0333 = 7.14 \times 10^{-3}$ mol dm^{-3}

minimum $[F^-] = 7.14 \times 10^{-3}$ mol dm^{-3}

CaF_2 ppted first; followed by BaF_2

For BaF_2 to appear as ppt, minimum $[F^-] = 7.14 \times 10^{-3}$ mol dm^{-3}

$[Ca^{2+}][F^-]^2 = K_{sp}$
$[Ca^{2+}]\ (7.14 \times 10^{-3})^2 = 3.9 \times 10^{-11}$
$[Ca^{2+}]$ remaining = 7.65×10^{-7} mol dm^{-3}

14 AJC/2010/P2/Q3 Level of Difficulty: [☆☆]

3 (a)(i) $K_{a1} \approx \dfrac{(10^{-pH})^2}{0.100} = 4.3 \times 10^{-7}\ \text{mol dm}^{-3}$

$\therefore$ pH = $-\lg(4.3 \times 10^{-7} \times 0.100)^{1/2}$ = **3.68**

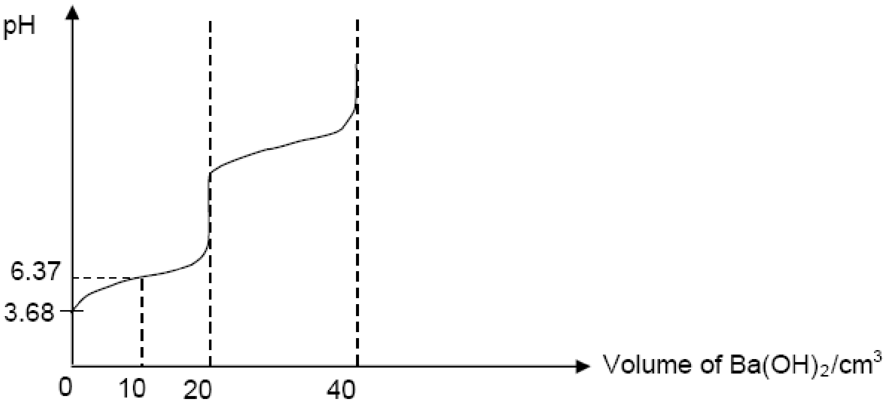
(a)(ii) $H_2CO_3 + Ba(OH)_2 \rightarrow BaCO_3 + 2H_2O$

$n(Ba(OH)_2) = n(H_2CO_3)$
$0.0625 \times V = 0.100 \times 25$

volume of $Ba(OH)_2$ required = **40 cm^3**

(a)(iii) $K_{a1} = \dfrac{[HCO_3^-][H^+]}{[H_2CO_3]} \Rightarrow pH = pK_{a1}$ = **6.37**

(a)(iv)



(b)(i) On addition of H$^+$, $HCO_3^- + H^+ \rightarrow H_2CO_3$

On addition of OH$^-$, $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$

(b)(ii) $pH = pK_{a1} + \lg\dfrac{[HCO_3^-]}{[H_2CO_3]}$

$\lg\dfrac{[HCO_3^-]}{[H_2CO_3]} = 7.4 - 6.37 = 1.03 \quad \Rightarrow \dfrac{[HCO_3^-]}{[H_2CO_3]} =$ **10.7**

(b)(iii) $\dfrac{[HCO_3^-]}{[H_2CO_3]} = 10.7$

$\therefore [HCO_3^-] = 10.7 \times 2.4 \times 10^{-2} = 0.257\ \text{mol dm}^{-3}$

$H_2CO_3 + 2OH^- \rightarrow CO_3^{2-} + 2H_2O$
$2 \times 2.4 \times 10^{-2}$

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$
0.257

$\therefore$ n(OH^-) needed = $(2 \times 2.4 \times 10^{-2} + 0.257) \times \frac{10}{1000}$

$= \mathbf{3.05 \times 10^{-3}}$ mol

Volume of $Ba(OH)_2$ needed = $\frac{3.05 \times 10^{-3} / 2}{0.0625}$

$= \mathbf{0.0244}$ dm^3 (24.4 cm^3)

(b)(iv) $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

$CO_2(g)$ dissolves to form $H_2CO_3(aq)$.
Increasing the concentration of H_2CO_3 shifts the equilibrium to the right to increase $[H_3O^+]$.

Thus the pH of blood is restored to 7.4.

15 MI/2010/P2/Q3 Level of Difficulty: [☆☆]

$$K = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{[H^+][HS^-]}{[H_2S]} \times \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$= 5.7 \times 10^{-8} \times 1.3 \times 10^{-13}$$

$$= 7.41 \times 10^{-21} mol^2 dm^{-6}$$

$$7.41 \times 10^{-21} = \frac{[0.010]^2[S^{2-}]}{[0.10]}$$;

$$[S^{2-}] = 7.41 \times 10^{-18} moldm^{-3}$$

$$[Bi^{3+}]^2[S^{2-}]^3 = (0.0015)^2(7.41 \times 10^{-18})^3$$

$$= 9.15 \times 10^{-58} mol^5 dm^{-15}$$

$$[Mn^{2+}][S^{2-}] = (0.0015)(7.41 \times 10^{-18})$$;

$$= 1.11 \times 10^{-20} mol^2 dm^{-6}$$

$\therefore$ Bi_2S_3 will precipitate first since ionic product exceeds K_{sp} of the compound. ;

$$K_{sp}=\left[Mn^{2+}\right]\left[S^{2-}\right]$$
$$3.0\times10^{-11}=(0.0015)\left[S^{2-}\right]$$
$$\left[S^{2-}\right]=\frac{3.0\times10^{-11}}{0.0015}$$
$$=2.00\times10^{-8}\,mol\,dm^{-3}$$

$$K=\frac{\left[H^{+}\right]^{2}\left[S^{2-}\right]}{\left[H_2S\right]}$$
$$7.41\times10^{-21}=\frac{\left[H^{+}\right]^{2}\left(2.00\times10^{-8}\right)}{(0.10)}$$
$$\left[H^{+}\right]=\sqrt{\frac{7.41\times10^{-21}\times0.10}{2.00\times10^{-8}}}$$
$$=1.92\times10^{-7}\,mol\,dm^{-3}$$

$$pH=-\lg[H+]=-\lg\left(1.92\times10^{-7}\right)=6.72$$

16 MI/2010/P3/Q4 Level of Difficulty: [✩✩]

$$K_1=\frac{\left[H^{+}\right]\left[HCO_3^{-}\right]}{\left[H_2CO_3\right]}\qquad 4.2\times10^{-7}=\frac{\left[H^{+}\right]^{2}}{(0.033)}\qquad \left[H^{+}\right]=1.2\times10^{-4}$$;

pH = -lg [H$^+$] = 3.93 ;

$$CO_3^{2-}(aq)+H_2O(l)\rightleftharpoons HCO_3^{-}(aq)+OH^{-}(aq)$$

$$\left[OH^{-}\right]=\sqrt{\frac{K_w}{K_a}\times\left[CO_3^{2-}\right]}$$;

$$\left[OH^{-}\right]=\sqrt{\frac{1.0\times10^{-14}}{4.7\times10^{-11}}\times0.125}$$

$$\left[OH^{-}\right]=\sqrt{2.7\times10^{-5}}\qquad \left[OH^{-}\right]=0.0052$$;

pOH = 2.28 pH = 14 – 2.28 = 11.7 ;

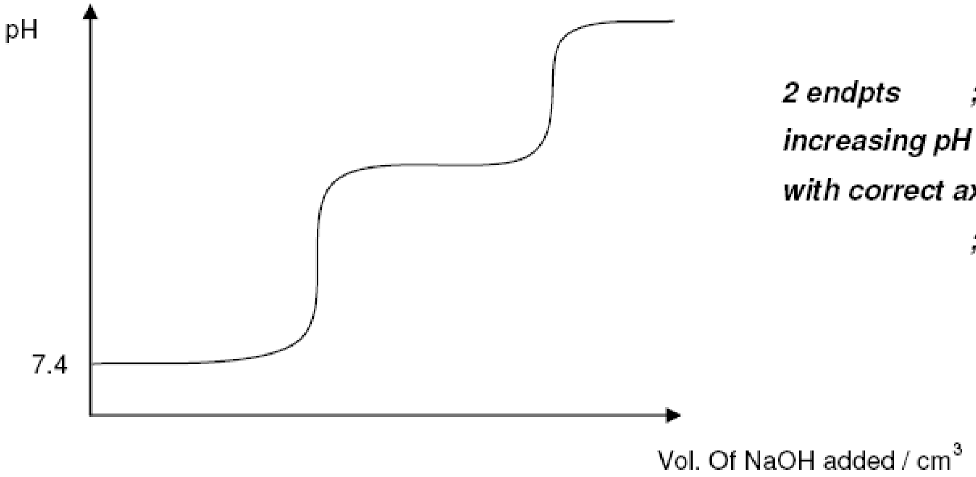
Components of the best buffer: H_2CO_3 and HCO_3^- ;

$$pH=pK_a+lg\frac{[conjugate\ base]}{[acid]}$$

.: Ratio of HCO_3^- to H_2CO_3 = 10.5 ;

$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$

$HCO_3^- + H^+ \rightarrow H_2CO_3$



2 endpts ;
increasing pH
with correct axes
;

17 MJC/2010/P3/Q1 Level of Difficulty: [☆☆]

1(a) (i) For the amide, the electron-withdrawing effect of the carbonyl group reduces the electron density on the N atom, making the lone pair less available to accept a proton, hence it is a weaker base compared to the amine.

(ii)
$$K_b = \frac{[BH^+]\,[OH^-]}{[B]}$$
$$= \frac{[OH^-]^2}{[B]}$$

By approximation method,

$$[OH^-] = \sqrt{10^{-6.1} \times 0.025}$$
$$= 1.41 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pH = 10.1$$

(iii) Let x be the number of moles of HC*l* required, and v be the total volume.

$$pOH = pK_b + \lg \frac{[BH^+]}{[B]}$$

$$14 - 7 = 6.1 + \lg \frac{x/v}{(0.025 - x)/v}$$

$$x = 2.23 \times 10^{-2}$$

Volume of HC*l* required $= \dfrac{2.23 \times 10^{-2}}{0.5}$

$= 4.46 \times 10^{-2}$ dm^3
$= 44.6$ cm^3

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

$OH^- + BH^+ \rightarrow H_2O + B$

In the buffer solution, $[OH^-]$ is slightly changed and pH of buffer solution remains fairly constant.

18 MJC/2010/P3/Q4(c) Level of Difficulty: [✯✯]

(c) **(i)** $SrF_2\ (s) \rightleftharpoons Sr^{2+}\ (aq) + 2F^-\ (aq)$

$K_{sp}(SrF_2) = [Sr^{2+}][F^-]^2$

$2.5 \times 10^{-9} = (s)(2s)^2$
$s = 8.55 \times 10^{-4}\ mol\ dm^{-3}$

$SrSO_4\ (s) \rightleftharpoons Sr^{2+}\ (aq) + SO_4^{2-}\ (aq)$

$K_{sp}(SrSO_4) = [Sr^{2+}][SO_4^{2-}]^2$

$3.2 \times 10^{-7} = (s)^2$
$s = 5.66 \times 10^{-4}\ mol\ dm^{-3}$

Based on the calculated solubilities, SrF_2 is more soluble than $SrSO_4$.

(ii) $SrF_2\ (s) \rightleftharpoons Sr^{2+}\ (aq) + 2F^-\ (aq)$
$NaF\ (s) \rightarrow Na^+\ (aq) + F^-\ (aq)$

There will be common ion effect due to the presence of F^-. By Le Chatelier's Principle, position of equilibrium will shift to the left to decrease $[F^-]$. The solubility of SrF_2 is reduced. The solubility product of SrF_2, K_{sp}, is not affected as it is only dependent on temperature.

(iii) **(1)** When $BaCl_2$ and $SrCl_2$ are mixed,

$$[Ba^{2+}] = \frac{\frac{50}{1000} \times 0.1}{(\frac{50}{1000} + \frac{50}{1000})} = 0.0500\ mol\ dm^{-3}$$

In the saturated solution of BaF_2,

Ionic pdt (BaF_2) = K_{sp}
$(0.05)[F^-]^2 = 1.7 \times 10^{-6}$
$[F^-] = 5.83 \times 10^{-3}\ mol\ dm^{-3}$

(2) For Sr^{2+} remaining in saturated solution of SrF_2,

Ionic pdt (SrF_2) = K_{sp}
$[Sr^{2+}][5.83 \times 10^{-3}]^2 = 2.5 \times 10^{-9}$
$[Sr^{2+}]_{remaining} = 7.36 \times 10^{-5}\ mol\ dm^{-3}$

19 NJC/2010/P3/Q2(d) Level of Difficulty: [☆☆]

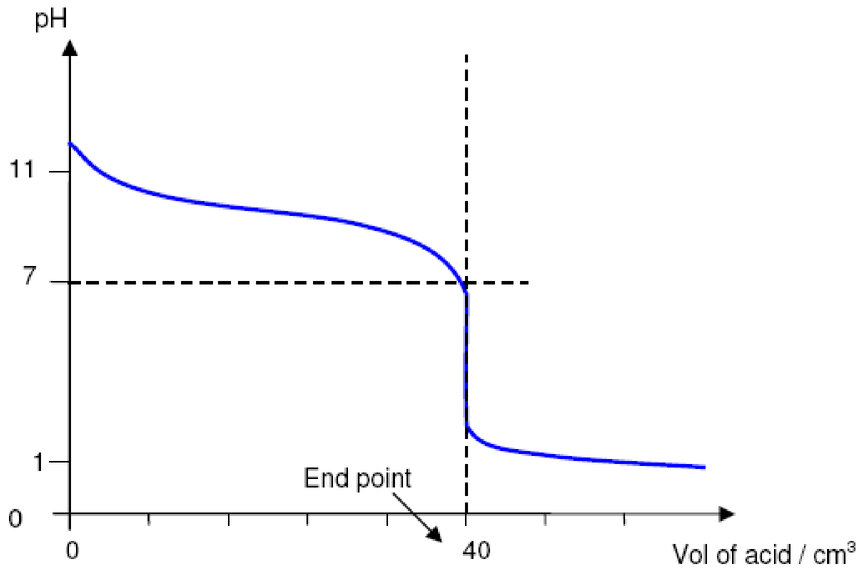
2 (d) (i) Mg^{2+} has a higher charge over ionic radius ratio than Cu^{2+}
$\Delta H_{hydration}$ of Mg^{2+} is more exo than $\Delta H_{hydration}$ of Cu^{2+}
L.E is approximately constant in both compounds
$\Delta H_{solution}$ of $Mg(OH)_2$ is more exo than $\Delta H_{solution}$ of $Cu(OH)_2$

Hence $Mg(OH)_2$ is more soluble than $Cu(OH)_2$.

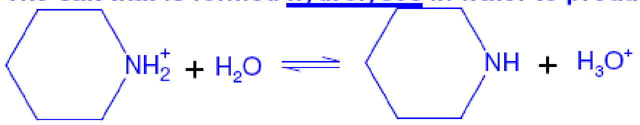
2 (d) (ii) 7.2×10^{-20} mol dm^{-2}

2 (d) (iii) Higher due to the absence of common ion effect.

20 NYJC/2010/P3/Q2(c) Level of Difficulty: [☆☆]



The salt that is formed <u>hydrolyses</u> in water to produce H^+ ions



An **<u>ionic</u>** salt is formed which has **<u>low volatility</u>** and does not give off a smell.

21 PJC/2010/P3/Q3(a)-(b) Level of Difficulty: [☆☆]

3 (a) (i) A buffer solution is one which tends to <u>resist</u> changes in pH (on dilution or) on addition of <u>small</u> quantities of acid or alkali.

(ii)
$$K_a = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

$pH = 7.4 \Rightarrow [H^+] = 10^{-7.4}$ mol dm^{-3}

$$7.90 \times 10^{-7} = \frac{[HCO_3^-](10^{-7.40})}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{7.90 \times 10^{-7}}{3.98 \times 10^{-8}} = 19.8$$

(iii) **$H^+(aq)$ + $HCO_3^-(aq)$ → $H_2CO_3(aq)$**

(iv) **When lactic acid is released, $H^+(aq)$ + $HCO_3^-(aq)$ → $H_2CO_3(aq)$**

$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l)$ ----- (1)
When $[H_2CO_3]$ increases, equilibrium position in (1) shifts right, forming more $CO_2(aq)$.

$CO_2(aq) \rightleftharpoons CO_2(g)$ ----- (2)
Increase in $[CO_2(aq)]$ will result in equilibrium position in (2) to shift to the right, forming more $CO_2(g)$ and thus resulting in higher rate of breathing.

(b) **(i)** **Total no. of mol of hydroxide ions =** $\frac{20.0}{1000} x0.050$ **= 1.00×10^{-3} mol**

$[OH^-]$ = $\frac{1.00x10^{-3}}{25.0} x1000$ **= 0.0400 mol dm^{-3}**

(ii) **No. of mol of OH^- from NaOH =** $\frac{25.0}{1000} x0.010$ **= 2.50×10^{-4} mol**

No. of mol of OH^- from $Ca(OH)_2$ = $1.00 \times 10^{-3} - 2.50 \times 10^{-4}$
= 7.50×10^{-4} mol

$[OH^-]$ from $Ca(OH)_2$ = $\frac{7.50x10^{-4}}{25.0} x1000$ **= 0.0300 mol dm^{-3}**

(iii) **$[Ca^{2+}]$ = 0.0300 /2 = 0.0150 mol dm^{-3}**

(iv) **K_{sp} = $[Ca^{2+}]_{eqm}\ [OH^-]_{eqm}^2$**
= $(0.0150)\ (0.0400)^2$ = 2.40×10^{-4} $mol^3\ dm^{-9}$

22 SAJC/2010/P2/Q6(b) Level of Difficulty: [☆☆]

Let the solubility of $Ag_2Cr_2O_7$ be x mol dm^{-3} before adding $Na_2Cr_2O_7$

$$Ag_2Cr_2O_7\ (s) \rightleftharpoons \underset{2x}{2Ag^+(aq)} + \underset{x}{Cr_2O_7^{2-}(aq)}$$

K_{sp} = $[Ag^+(aq)]^2\ [Cr_2O_7^{2-}\ (aq)] = 4x^3$

$2 \times 10^{-7} = 4x^3$

$x = 3.68 \times 10^{-3}$ mol dm^{-3}

Thus in 1 dm^3 of saturated $Ag_2Cr_2O_7$ solution,

$[Cr_2O_7^{2-}] = 3.68 \times 10^{-3}$ mol dm^{-3}

$[Ag^+] = 7.36 \times 10^{-3}$ mol dm^{-3}

No of moles of $Cr_2O_7^{2-}$ from $Na_2Cr_2O_7$ = 0.02 mol

The new conc. of $Cr_2O_7^{2-}$ = $(0.02 + 3.68 \times 10^{-3})$ = 0.02368 mol dm^{-3}

Let no of moles of $Ag_2Cr_2O_7$ precipitated after adding $Na_2Cr_2O_7$ be y mol.

$$2Ag^+ (aq) \quad + \quad Cr_2O_7^{2-} \ (aq) \rightleftharpoons Ag_2Cr_2O_7 \ (s)$$

Conc before ppt$_n$ /M	7.36×10^{-3}	0.02368	0
Change in conc/ M	– 2y	– y	+ y
Conc after ppt$_n$ /M	$7.36 \times 10^{-3} - 2y$	0.02368 – y	y

Since K_{sp} of $Ag_2Cr_2O_7 = 2 \times 10^{-7}$ mol^2 dm^{-6}

$2 \times 10^{-7} = (7.36 \times 10^{-3} - 2y)^2 (0.02368 - y)$

$0.02368 - y \approx 0.02368$

$2 \times 10^{-7} = (7.36 \times 10^{-3} - 2y)^2 (0.02368)$

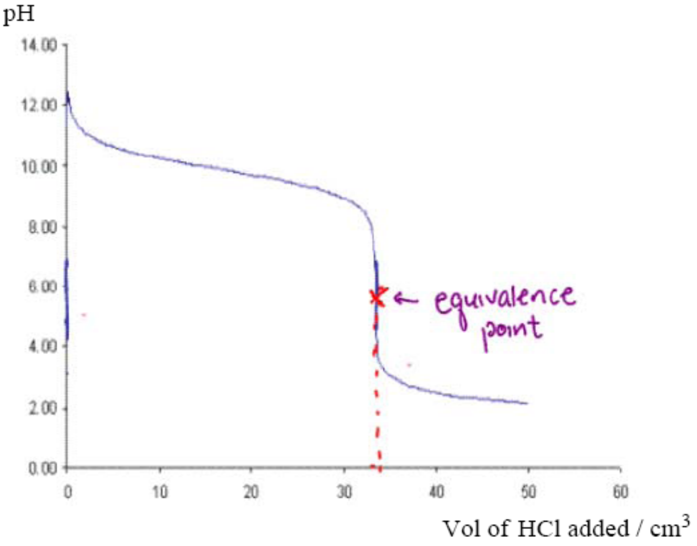
$y = 2.23 \times 10^{-3}$ mol

Mass of $Ag_2Cr_2O_7$ precipitated $= 2.23 \times 10^{-3} \times 432$

$= 0.963$ g

23 SAJC/2010/P3/Q2(b) Level of Difficulty: [☆☆]

(i)



When HC*l* is added, trimethylamine is neutralised and pH decreased.

The rate of decrease in pH was slowed down due to the formation of buffer.

(b) (i) As more HC*l* was added, the buffer broke down as more trimethylamine was neutralised.

The pH decreased rapidly and trimethylamine was completely neutralised at 33 cm^3.

The pH at equivalence point is less than 7 due to the hydrolysis of the acidic salt, producing excess H_3O^+.

OR $(CH_3)_3NH^+ + H_2O \rightleftharpoons (CH_3)_3N + H_3O^+$

After neutralisation, the pH decreased slowly until constant due to addition of excess HC*l*.

(b) (i) Adding a <u>small</u> amount of H^+:

$H^+ + HCO_3^- \rightarrow H_2CO_3$

Adding a <u>small</u> amount of OH^-:

$OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O$

A <u>small amount</u> of H^+ and OH^- added is removed by a <u>large reservoir</u> of HCO_3^- and H_2CO_3. Thus, pH is remains almost constant.

(b) (ii)

$$7.4 = pK_{a1} + \lg \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\lg \frac{[HCO_3^-]}{[H_2CO_3]} = 7.4 - 6.38 = 1.02$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 10.5$$

25 <u>TJC/2010/P3/Q4(a)</u> Level of Difficulty: [☆☆]

4 **(a)** **(i)** • A buffer solution is one that can **<u>resist changes in pH</u>** upon additions of **<u>small</u>** amounts of acid or alkali.

(ii) • On adding H^+, $C_5H_7O_4CO_2^-$ mainly from the salt reacts with it to form $C_5H_7O_4CO_2H$. This helps to remove the excess H^+ and hence maintain pH.

$C_5H_7O_4CO_2^- + H^+ \longrightarrow C_5H_7O_4CO_2H$

• On adding OH^-, $C_5H_7O_4CO_2H$ reacts with it to form water. This helps to remove the excess OH^- and hence maintain pH.

$C_5H_7O_4CO_2H + OH^- \longrightarrow C_5H_7O_4CO_2^- + H_2O$

(iii) $pH = pK_a + \lg \frac{[salt]}{[acid]} = -\log(7.4 \times 10^{-4}) + \lg \frac{(0.002/0.050)}{(0.001/0.050)} = 3.43$

(• correct substitution in formula; • final answer)

26 <u>VJC/2010/P2/Q4(c)</u> Level of Difficulty: [☆☆]

(c)(i)

$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$

Let *s* be the solubility of AgC*l* in the given $AgNO_3$ solution.
$(s + 5.0 \times 10^{-3})(s) = 1.8 \times 10^{-10}$
Assume $s \ll 5.0 \times 10^{-3}$,
$s = 3.6 \times 10^{-8}$ mol dm^{-3}

Maximum mass of AgC*l* that could dissolve
$= 3.6 \times 10^{-8} \times 0.300 \times 143.5$
$= 1.55 \times 10^{-6}$ g

(ii)

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
$Ag^+(aq)$ from $AgNO_3$
caused the above equilibrium to shift left by Le Chatelier's Principle.
Thus, the solubility of AgC*l* is suppressed due to common ion effect.

(iii)

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
$S_2O_3^{2-}$ forms a complex with Ag^+.
This decreases $[Ag^+]$.
Hence, the above equilibrium shifts right which causes more AgC*l* to dissolve.

27 VJC/2010/P2/Q5(b)(iii) Level of Difficulty: [☆☆]

(iii)

$-\lg [H^+] = 5.0$
$[H^+] = 1.0 \times 10^{-5}$ mol dm^{-3}
$$K_a = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]}$$
$10^{-9.95} = (1.0 \times 10^{-5})^2 / [C_6H_5OH]$
$[C_6H_5OH] = 0.891$ mol dm^{-3}

Solubility of $C_6H_5OH = 0.891$ mol dm^{-3}

28 YJC/2010/P3/Q3(e) Level of Difficulty: [☆☆]

e $MgCl_2 (aq) + 2NaOH (aq) \rightarrow Mg(OH)_2 (s) + 2 NaCl (aq)$
pH = 10.2 ⇒ pOH = 3.8
$[OH^-] = 1.58 \times 10^{-4}$ mol dm^{-3}
Ionic product = $K_{sp} = [Mg^{2+}][OH^-]^2$
$$= \left(\frac{1.58 \times 10^{-4}}{2}\right)(1.58 \times 10^{-4})^2$$
$$= \mathbf{2.0 \times 10^{-12}\ mol^3dm^{-9}}$$

29 YJC/2010/P3/Q5(a) Level of Difficulty: [☆☆]

5 ai $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$
$HPO_4^{2-} + H_3O^+ \rightarrow H_2PO_4^- + H_2O$

aii $[NaH_2PO_4]$ in buffer = 0.0625 moldm^{-3}
$[Na_2HPO_4]$ in buffer = 0.0375 moldm^{-3}
pH = 7.2 + lg{0.0375/0.0625} = 6.98

aiii [HCl] = 0.00244 mol dm^{-3}
Decrease in concentration of Na_2HPO_4 = (30X0.1/1000)-(2X0.1/1000)
=2.8 X10^{-3} X1000/82 = 0.0342 moldm^{-3}
Increase in concentration of NaH_2PO_4 = (50X0.1/1000)+(2X0.1/1000)
=5.2 X 10^{-3} X1000/82 = 0.0634
pH =6.93 ; change in pH = 0.05

30 AJC/2010/P3/Q1(b) Level of Difficulty: [☆☆☆]

(b)(i) White solid of AgC*l* turns yellow.

AgI is precipitated as AgI is less soluble than AgC*l*

(b)(ii) To precipitate AgC*l*, $[Ag^+][Cl^-] > K_{sp}\ (AgCl)$

$$[Ag^+] > \frac{2.02 \times 10^{-10}}{0.1}$$

$\therefore$ minimum $[Ag^+]$ = **2.02×10^{-9}** mol dm^{-3}

To precipitate Ag_2CrO_4, $[Ag^+]^2\,[CrO_4{}^{2-}] > K_{sp}\ (Ag_2CrO_4)$

$$[Ag^+] > \sqrt{\frac{3.01 \times 10^{-12}}{0.01}}$$

$\therefore$ minimum $[Ag^+]$ = **1.73×10^{-5}** mol dm^{-3}

(b)(iii) At the end–point, a red precipitate of Ag_2CrO_4 is seen.

(b)(iv) When Ag_2CrO_4 is first precipitated,
$[Ag^+]$ in the solution = 1.73×10^{-5} mol dm^{-3}

$\therefore$ $[Cl^-]$ in the solution

$$= \frac{K_{sp} \text{ of AgCl}}{[Ag^+]} = \frac{2.02 \times 10^{-10}}{1.73 \times 10^{-5}} = \mathbf{1.17 \times 10^{-5}\ mol\ dm^{-3}}$$

(b)(v) % of Cl^- precipitated out as AgC*l*

$$= \frac{0.1 - (1.17 \times 10^{-5})}{0.1} \times 100\% = 99.988\% \approx 100\%$$

Hence, Ag_2CrO_4 is only precipitated when all the AgC*l* has been formed.

31 NJC/2010/P3/Q3(a)-(c) Level of Difficulty: [☆☆☆]

3 (a) (i) The pH value of 2.2 represents the maximum buffer capacity.

3 (a) (ii) pH = 1.65

3 (a) (iii) NaH_2PO_4.

3 (b) (i) $H_2PO_4^- + OH^- \rightarrow HPO_4^- + H_2O$

3 (b) (ii) Mass of NaOH = 0.366 grams

3 (c) The NH_3 gas that is formed dissolves in the water present in soil to give OH^- ions, thus increasing the soil pH temporarily.
Over time, the NH_3 gas escapes and $NH_4H_2PO_4$ dissociates to give NH_4^+ and $H_2PO_4^-$, which will hydrolyse in water to give H_3O^+, therefore the soil becomes more acidic than before.

32 NYJC/2010/P2/Q4 Level of Difficulty: [✯ ✯ ✯]

$H_2PO_4^-$/ HPO_4^{2-} or HF/ F^- [1]

The equilibrium constant will be less than 1.
HF has a larger K_a than $H_2PO_4^-$ and will donate proton more readily.
HPO_4^{2-} has a larger K_b than F^- and will accept proton more readily.
Thus the reaction between HF and HPO_4^{2-} takes place more readily, favouring the backward equation.

Solution **A**

$n(HCl) = \frac{0.0500}{1000} \times 1.000 =$ 5.00 x 10^{-5} mol [1st]

n(salt) left

$= (\frac{100}{1000} \times 0.0200) - 5.0 \times 10^{-5}$

= 0.00195 mol [2nd]

new n(acid)

$= (\frac{100}{1000} \times 0.0113) + 5.0 \times 10^{-5}$

= 0.00118 mol [3rd]

New pH

$= -\lg(1.8 \times 10^{-4}) + \lg \frac{0.00195}{0.00118}$ [4th: correct buffer equation used]

= 3.96

Change in pH = 4.00 – 3.96 = 0.0371

Solution **B**

$n(HCl) = \frac{0.0500}{1000} \times 1.000 =$ 5.00 x 10^{-5} mol

n(salt) left

$= (\frac{100}{1000} \times 0.00200) - 5.0 \times 10^{-5}$

= 1.50 x 10^{-4} mol [6th]

new n(acid)

$= (\frac{100}{1000} \times 0.00113) + 5.0 \times 10^{-5}$

= 1.63 x 10^{-4} mol [7th]

New pH

$= -\lg(1.8 \times 10^{-4}) + \lg \frac{1.5 \times 10^{-4}}{1.63 \times 10^{-4}}$

= 3.71

Change in pH = 4.00 – 3.71 = 0.291

(ii) Equivalence point indicated on graph

Any indicator except for phenolphthalein

Working pH for indicator falls within the region of rapid pH change in the titration curve.

24 SAJC/2010/P3/Q5(a)-(b) Level of Difficulty: [☆☆]

(a) (i) $K_{a1} = \frac{[H^+]^2}{[H_2CO_3]}$

$4.2 \times 10^{-7} = \frac{[H^+]^2}{0.1}$

$[H^+] = \sqrt{(4.2 \times 10^{-7} \times 0.10)} = 2.05 \times 10^{-4}$ mol dm^{-3}

pH = 3.69

Assumptions (any one):

- Since the weak carbonic acid dissociate slightly, $[H_2CO_3]$ at eqm $\approx$ initial $[H_2CO_3]$
- HCO_3^- does not dissociate further as $K_{a2} << K_{a1}$

(ii) $H_2CO_3 + NaOH \rightarrow NaHCO_3 + H_2O$

No. of mole of NaOH required = 0.100 x 20/1000 = 2×10^{-3} mol

No. of mole of $NaHCO_3$ salt formed = 2×10^{-3} mol

$[HCO_3^-] = \frac{2 \times 10^{-3} \text{ mol}}{40 \times 10^{-3} \text{ dm}^3} = 0.05$ mol dm^{-3}

HCO_3^- hydrolyses in water producing OH^-:

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

$K_{b1} = \frac{[OH^-]^2}{[salt]}$

$\frac{10^{-14}}{4.2x10^{-7}} = \frac{[OH^-]^2}{0.05}$

$[OH^-] = 3.45 \times 10^{-5}$ mol dm^{-3}

pH = 14 – 4.46 = 9.54

(iii) pH at **B** = 10.3

pH at **B** = pK_{a2} at max buffer capacity OR when $[CO_3^{2-}] = [HCO_3^-]$

Solution A has a higher buffering effect than solution B. The components of the buffer in solution B are more diluted (or less concentrated). As such the addition of HCl to solution B changes the concentration of the components in solution B more than in A, resulting in a larger change in pH.

33 RVHS/2010/P3/Q3(c)-(d) Level of Difficulty: [☆☆☆]

(c) **(i)**

$$\text{pH} = \text{p}K_a + \lg \frac{[CH_3COO^-]}{[CH_3COOH]} = -\lg(1.8 \times 10^{-5}) + \lg\left(\frac{\frac{1.0}{2}}{\frac{1.0}{2}}\right)$$

$$= 4.74$$

(ii) $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Each dip will remove 0.0500 mol of CH_3COOH and introduce 0.0500 mol of CH_3COO^-.

Let number of dips be n.

Amount of CH_3COOH left $= (1.0 \times 1) - 0.0500n$

$= (1 - 0.05n)$ mol

Amount of CH_3COO^- in resultant solution $= (1.0 \times 1) + 0.0500n$

$= (1 + 0.05n)$ mol

$$\text{pH} = -\lg(1.8 \times 10^{-5}) + \lg\left(\frac{\frac{1+0.05n}{2}}{\frac{1-0.05n}{2}}\right) < 5$$

$n < 5.71 \Rightarrow$ therefore maximum number of dips = 5

(d) **(i)** $K_{sp} = [Ag^+][X^-]$

(ii) Let solubility of AgX be x mol dm^{-3}.

$$AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq)$$

Equilibrium conc x x

$1.0 \times 10^{-10} = x^2$

$x = 3.16 \times 10^{-5}$ mol dm^{-3}

Amount of $Ag^+(aq)$ in 1 dm^3 of saturated solution $= 3.16 \times 10^{-5}$ mol

(iii) From (d)(ii), AgX dissociates partially to give a small amount of Ag^+ and X^- ions in solution. As $S_2O_3^{2-}$ is added, Ag^+ forms a very stable $[Ag(S_2O_3)_2]^{3-}$ complex with the $S_2O_3^{2-}$ ions as seen from the large value of $K_c(1)$ and $[Ag^+]$ in the solution decreases. As a result, the equilibrium position of the reaction for the dissociation of AgX shifts to the right, causing AgX to dissolve.

34 VJC/2010/P3/Q2(c) Level of Difficulty: [✮✮✮]

(c)(i)

A buffer solution is one that resists changes in pH
when a small amount of acid or base is added.

(ii)

$7.90 \times 10^{-7} = [H^+][HCO_3^-] / [H_2CO_3]$
$= 10^{-7.4} [HCO_3^-] / [H_2CO_3]$

$[HCO_3^-] / [H_2CO_3] = 19.8$

(iii)

$HCO_3^- + RCO_2H \rightarrow H_2CO_3 + RCO_2^-$

(iv)

As more H_2CO_3 is formed,
position of equilibrium **I** shifts left.
This increases $[CO_2(aq)]$
and in turn causes the position of equilibrium **III** to shift right, i.e. breathing rate increases.

(v)

Let the volume of NaOH added be V cm^3.
Initial moles of H_2CO_3 $= 0.20 \times 25.0 \times 10^{-3}$
$= 5.0 \times 10^{-3}$ mol

Moles of H_2CO_3 left after neutralisation $= 5.0 \times 10^{-3} - 0.30 V \times 10^{-3}$
$= 0.005 - 3 \times 10^{-4} V$ mol

Moles of HCO_3^- formed = moles of NaOH used = 3×10^{-4} V mol
$3 \times 10^{-4} V / [0.005 - 3 \times 10^{-4} V] = 19.8$ (ecf from **(c)(ii)**)
V = 15.9 cm^3

TOPIC 8: REACTION KINETICS

1 CJC/2010/P3/Q2(b) Level of Difficulty: [☆]

The decomposition of hydrogen peroxide to form water and oxygen follows **first order** kinetics. It was found that a certain solution of hydrogen peroxide undergoes complete decomposition to liberate 96 cm^3 of oxygen gas.

(i) Given that 48 cm^3 of oxygen gas was collected in 46 minutes, calculate the time taken for 72 cm^3 of the gas to be evolved. (All volumes of oxygen gas are measured at the same temperature and pressure).

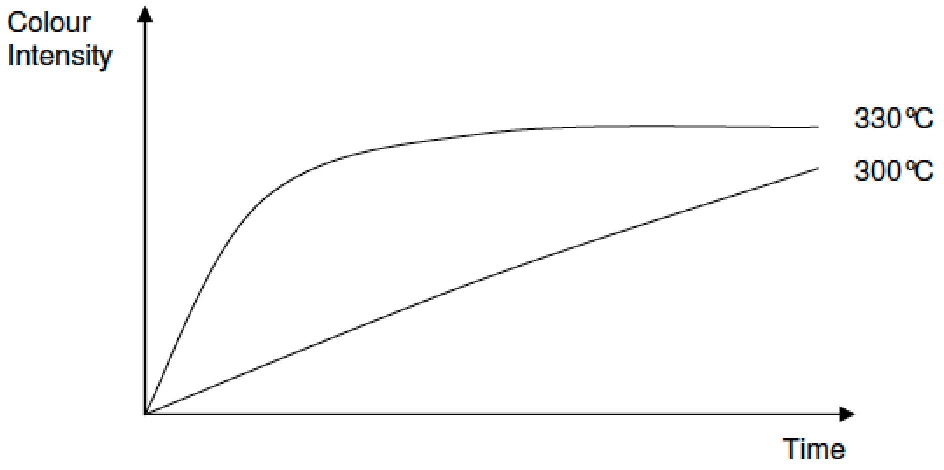
(ii) Find the rate constant, *k*, for the reaction.

2 MI/2010/P2/Q4 Level of Difficulty: [☆]

Iodide ion, I^-(aq), reacts with peroxydisulfate ion, $S_2O_8^{2-}$(aq), according to the equation below.

$$3I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_3^-(aq) + 2SO_4^{2-}(aq)$$

Equal volumes of I^-(aq) and $S_2O_8^{2-}$(aq) are mixed at two different temperatures of 300°C and 330°C, and the variation in colour intensity was monitored over a period of time. The graphs below show the variation of the colour intensity with time.



(a) What is the significance of the colour intensity in this reaction?

(b) State the significance of the initial slope of the graph and hence explain, with the aid of a Maxwell–Boltzmann distribution curve, the difference in the initial slopes of the two graphs. [4]

(c) A heterogeneous catalyst is usually used for this reaction.
Write equations to show how Fe^{2+}(aq) can act as a suitable catalyst for the above reaction. [2]

(v) The rate constant for this reaction has units of $mol^{-1} dm^3 min^{-1}$.

Experiment 1 was repeated using propanone of concentration 0.8 mol dm^{-3}. Without doing any calculation, sketch on the same axes in **(iii)**, the graph you would expect to obtain.

[10]

Suggested Answers

1 CJC/2010/P3/Q2(b) Level of Difficulty: [✯]

(i) $2H_2O_2 \rightarrow 2H_2O + O_2$

The half-life of the reaction, $t_{½}$ is 46 minutes (2760s).

Two half-lives would have elapsed when the total volume of gas collected is 72 cm^3.

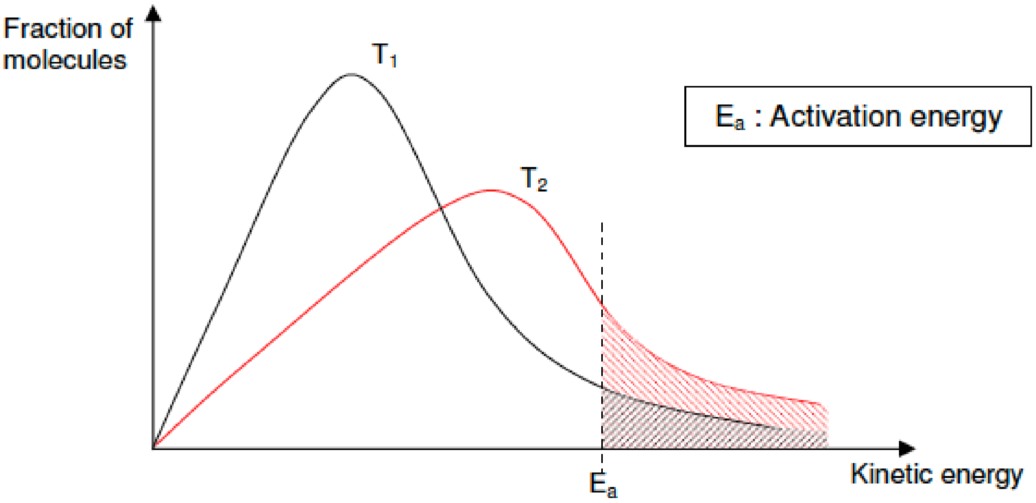
Time taken = 46 x 2 = 92 minutes.

(ii) $k = \ln 2 / t_{½} = \ln 2 / 46 = 0.0151\ min^{-1}$ or $2.51 \times 10^{-4}\ s^{-1}$

2 MI/2010/P2/Q4 Level of Difficulty: [✯]

(a) ***Colour intensity is proportional to concentration of I_3^-** in mixture, since it is the only coloured component in the mixture.* ;

(b) ***The initial slope of the graph is proportional to the initial rate of reaction.** A greater slope for the graph at 330°C means a faster initial rate.* ;



Increase in temperature increases the energy that the molecules possess, resulting in a greater proportion of molecules having energy greater than or equal to activation energy and an increase in molecular movement. ;

Hence rate of reaction increases due to the increase in the frequency of effective collisions. ;

(c) $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$
$3I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_3^-(aq) + 2Fe^{2+}(aq)$

3 MJC/2010/P2/Q5(a)(ii) Level of Difficulty: [☆]

At low concentration of peptide **Y**,

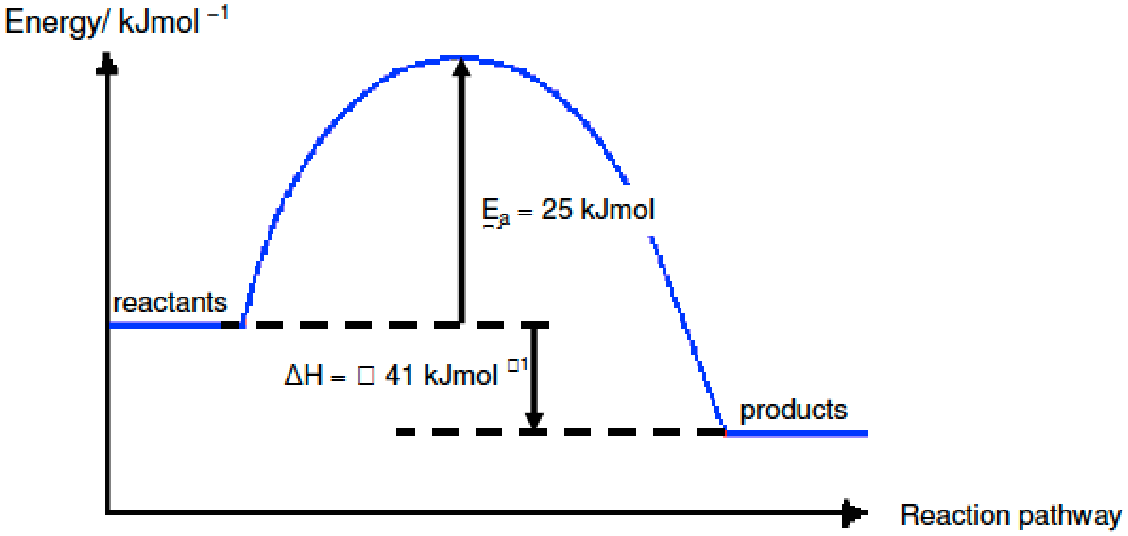
- Rate of reaction increases linearly as active sites of the enzyme are not fully occupied
- Reaction is approximately first order wrt the concentration of peptide **Y**.

However, at high concentration of peptide **Y**,

- Rate of reaction is constant
- Rate is independent of concentration of peptide **Y** as all active sites occupied
- Reaction is zero order wrt the concentration of peptide **Y**.

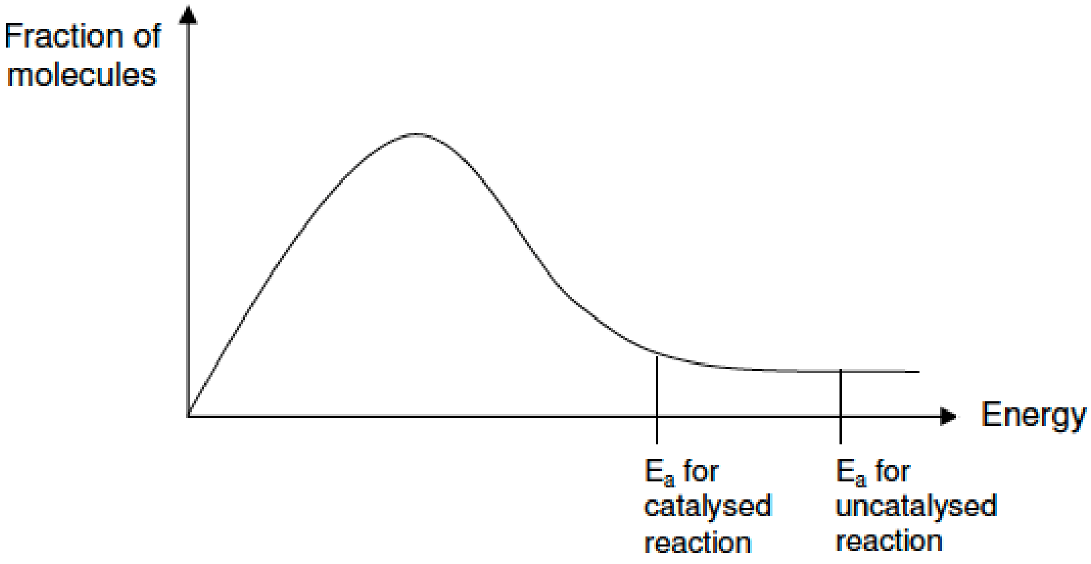
4 NJC/2010/P3/Q1(c)(i),(ii),(iii) Level of Difficulty: [☆]

(i)



(ii) Fe_3O_4 functions as a **heterogeneous catalyst**. The reactant molecules are **adsorbed onto the surface area** of Fe_3O_4. This weakens the existing bonds in the reactant molecules. Thus, Fe_3O_4 **lowers the activation energy** of the reaction, allowing rate of reaction to increase.

(iii) When a catalyst provides an alternative pathway with a lower activation energy for the reaction to take place, there is a **larger proportion of molecules with energy greater than activation energy**. Thus rate of reaction increases.



5 SRJC/2010/P3/Q1(a) Level of Difficulty: [☆]

Experiment	Relative time for colour of iodine to disappear	$Rate = \frac{k}{time}$ Relative rate
A	1	1
B	2	0.5
C	2	0.5
D	1	1

Comparing experiments A and C,
When [propanone] doubles, rate doubles too.
Therefore, order of reaction wrt to propanone is **one**.

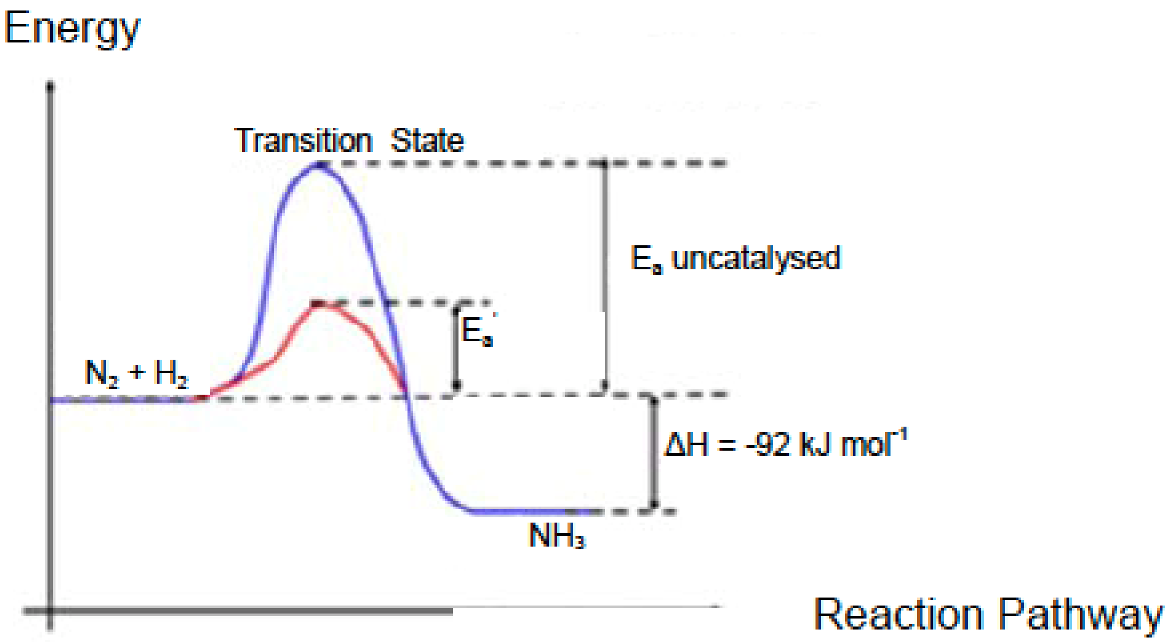
Comparing experiments A and D,
When [iodine] doubles, rate remains the same.
Therefore, order of reaction wrt to iodine is **zero**.

Comparing experiments A and B,
When [H^+] doubles, rate doubles too.
Therefore, order of reaction wrt to H^+ is **one**.

Rate=k[propanone][H^+]

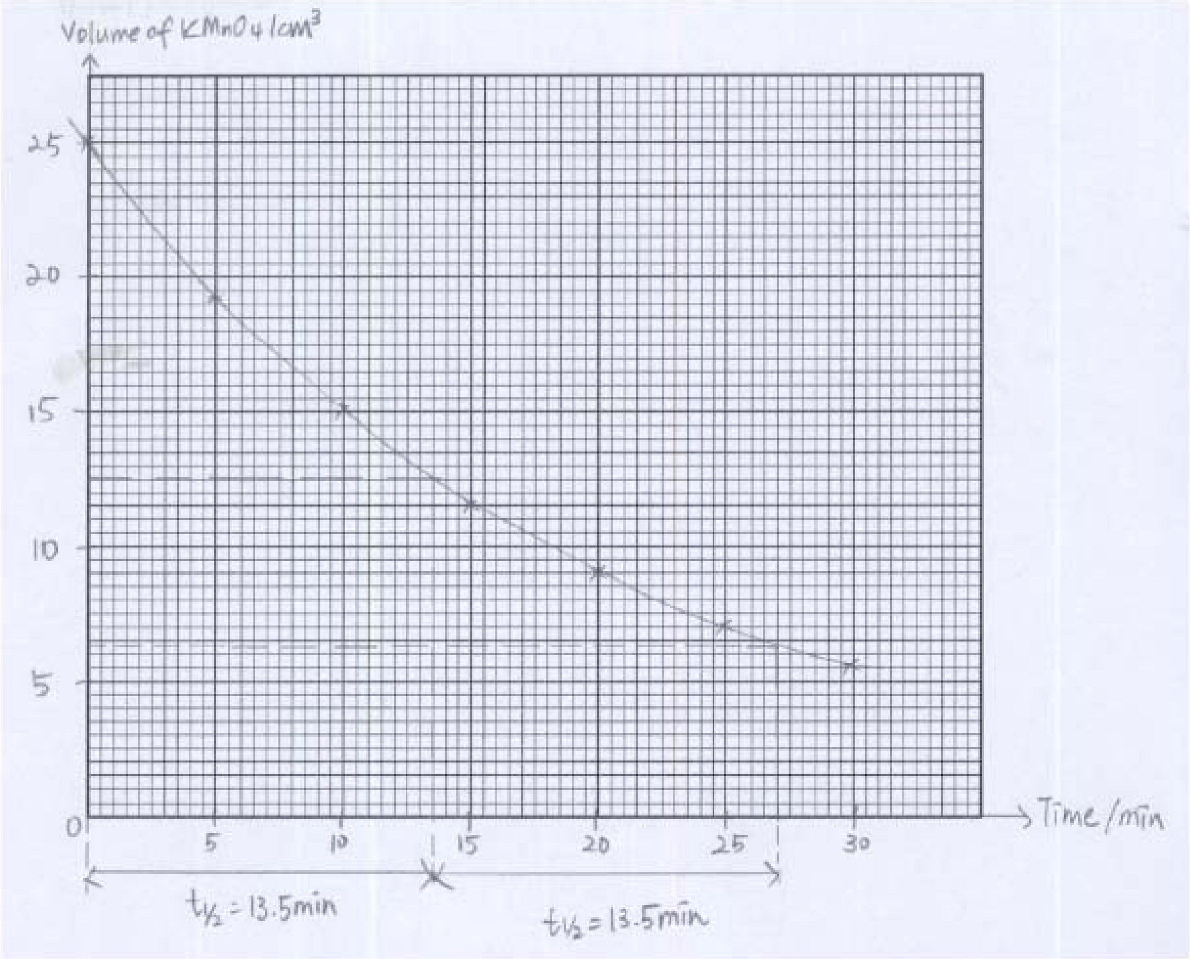
6 SRJC/2010/P3/Q2(d) Level of Difficulty: [☆]

Formation of nitrogen dioxide is an endothermic process. Thus **high temperature** is required to obtain higher yield of nitrogen dioxide.
Since high temperature is used, the **rate** of formation of nitrogen dioxide is **fast**. Hence, a catalyst is not required.



7 TJC/2010/P2/Q2(b) Level of Difficulty: [☆]

(i)



(ii) Calculate the rate constant and state its units.

Half-life obtained from graph = $\frac{13.5+13.5}{2}$ **= 13.5 min**

- **k =** $\frac{\ln 2}{t_{\frac{1}{2}}}$ **= 0.0513 min^{-1}**
- **1 mark for correct units**

(iii) What effect will the presence of the catalase have on the rate constant for the reaction? Explain your answer.

Rate = k[reactants]

- **Since all concentration remains constant yet rate increases, thus the value of k must also increase.**

(iv) Calculate the concentration of the hydrogen peroxide at the time the first portion was withdrawn. Hence estimate how long the solution had been in the contaminated bottle. [8]

$5H_2O_2 \equiv 2MnO_4^-$

- **No of moles of H_2O_2 at time when first portion withdrawn**
  $= \frac{25}{1000} x 0.2 x \frac{5}{2}$ **= 0.0125 mol**

- **Concentration of H_2O_2 =** $\frac{0.0125 x 1000}{10}$ **= 1.25 mol dm^{-3}**

  Concentration of H_2O_2 by the time first portion is one quarter of the original amount (5 → 2.5 → 1.25). Thus 2 half-lives passed.

- **Length of time solution has been contaminated = 13.5 x 2 = 27.0 min**

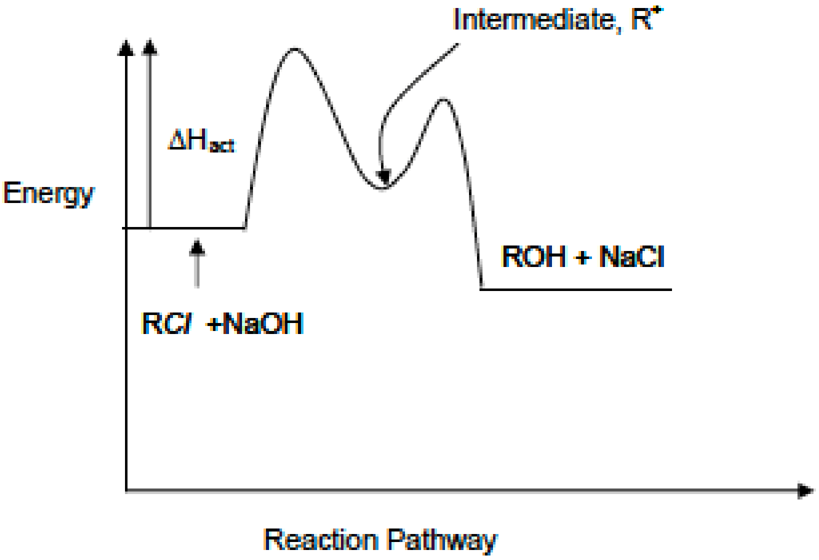
8 ACJC/2010/P3/Q2(c) Level of Difficulty: [☆☆]

(i) Gradient for [R*Cl*] = x mol dm^{-3} is half that for [R*Cl*] = 2x mol dm^{-3} . Hence first order wrt to R*Cl*. Both graphs are straight lines with a negative gradient, hence zero order wrt to NaOH

Rate = k [R*Cl*]

(ii) Tertiary alkyl halide.

(iii)



(iv) **Pipette out 10 cm^3 (can accept 25 cm^3 even though it is wasteful and time consuming) of the reaction mixture at regular intervals, chill immediately and titrate with HCl(aq) or H_2SO_4(aq) of known concentration to calculate the [NaOH] remaining.**

(v) **Aqueous hydrochloric acid is a strong acid and is completely ionized in water. The neutralization reaction is <u>immediate</u>.** (1m)

The rate of reaction of $(CH_3)_2CCHCl$ is much slower. (1/2m)$(CH_3)_2CCHCl$ contains a C=C.(1/2m) The C-Cl bond shows double bond characteristics(1m) and hence difficult to break it.

9 ACJC/2010/P3/Q5(a) Level of Difficulty: [☆☆]

(i) Rate – $k[S_2O_8^{2-}][I^-]$

Since total volume of solution is constant,

concentration of a reactant ∝ volume of reactant

∗ rate ∝ 1/time

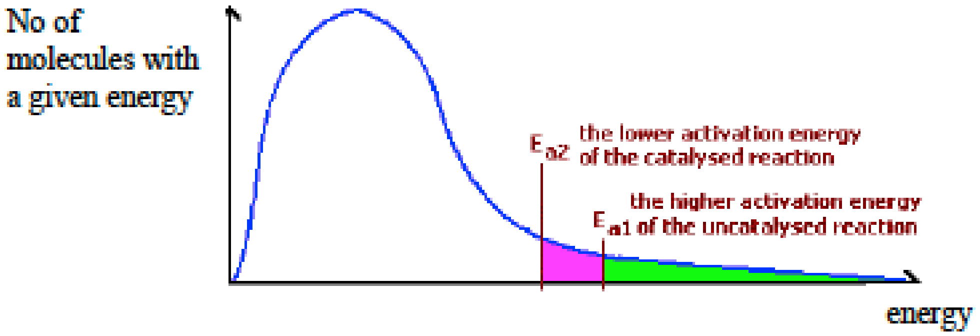
1/time = k (volume of $S_2O_8^{2-}$)(volume of I^-)

(volume of $S_2O_8^{2-}$)(volume of I^-) x time = constant

time for expt 3 = 96 s

(ii) **Heterogeneous catalysis**

The catalyst (Fe) provides an alternative pathway with lower activation energy, E_{a2}



As shown by the Maxwell-Boltzmann Distribution curve, the fraction of molecules with energy ≥E_{a2} (catalysed) is greater. Hence there are more effective collisions, leading to an increase in rate of reaction.

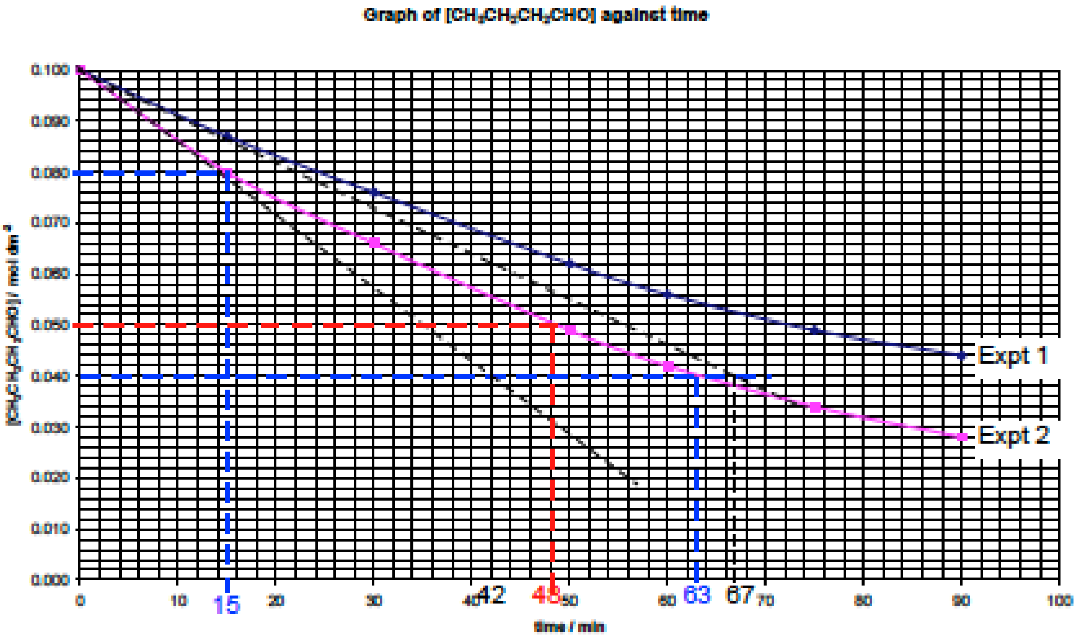
10 AJC/2010/P3/Q2(a) Level of Difficulty: [☆☆]

(a)(i) Order of reaction is the power to which the concentration of reactant is raised in the rate equation.

(a)(ii) $NaBH_4$ is in large excess, so that [$NaBH_4$] is kept relatively constant throughout the experiment.

[$CH_3CH_2CH_2CHO$] will therefore be the only variable and its order of reaction can be determined.

(a)(iii)



From the graph of experiment 2,
$t_{1/2}$ for $[CH_3CH_2CH_2CHO]$ to drop from 0.100 to 0.050 mol dm^{-3} = **48 min**
$t_{1/2}$ for $[CH_3CH_2CH_2CHO]$ to drop from 0.080 to 0.040 mol dm^{-3} = 63 – 15
= 48 min

Since $t_{1/2}$ is constant, reaction is <u>1^{st} order</u> with respect to butanal.

For experiment 1, initial rate = $\dfrac{0.100 - 0.040}{67}$ = 8.96×10^{-4} mol dm^{-3}

For experiment 2, initial rate = = $\dfrac{0.100 - 0.040}{42}$ = 1.43×10^{-3} mol dm^{-3}

From the data, when initial $[NaBH_4]$ increases by 1.5 times, the rate increases by approximately 1.5 times. Therefore, reaction is <u>1^{st} order</u> with respect to $NaBH_4$.

(a)(iv) Rate = $k\,[CH_3CH_2CH_2CHO][NaBH_4]$

Since $[NaBH_4]$ is relatively constant during expt. 2,
rate = $k'\,[CH_3CH_2CH_2CHO]$ where $k' = k[NaHB_4]$

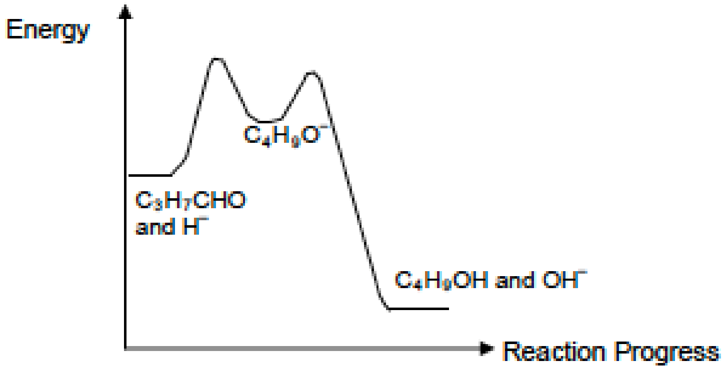
Using $t_{½} = \dfrac{\ln 2}{k'}$ and average $t_{½}$ = 48 min

$k' = \dfrac{\ln 2}{t_{1/2}} = 0.01444\ min^{-1}$

$\therefore k = \dfrac{k'}{1.50}$ = <u>$9.63 \times 10^{-3}\ mol^{-1}\ dm^{3}\ min^{-1}$</u>

(a)(v) The proposed mechanism is <u>consistent</u> with the observed kinetics since 1 mole of $CH_3CH_2CH_2CHO$ and 1 mole of H^- are involved in the slow step.

(a)(vi)



(a)(vii) In ketones, the 2 electron donating alkyl_groups attached to the carbonyl carbon makes the carbon less electron deficient and less susceptible to the attack by the H^- nucleophile.
or
H^- nucleophile experiences a larger steric hindrance in the reaction with ketones due to 2 alkyl groups attached to the carbonyl carbon.

11 CJC/2010/P3/Q2(c) Level of Difficulty: [☆☆]

(i) Comparing experiments 1 & 2, when [2-bromobutane] was increased by 2.5 times, initial rate also increased by 2.5 times. Hence, rate α [2-bromobutane], order of reaction wrt 2-bromobutane = 1.

Comparing experiments 1 & 3, both [2-bromobutane] & $[OH^-]$ were increased by 6 times & initial rate increased by only 6 times. Since order of reaction wrt 2-bromobutane is already found to be 1, the increase in rate was due to the increase in [2-bromobutane] while increase in $[OH^-]$ has no effect on rate. Hence, order of reaction wrt NaOH = 0
OR
Comparing experiment 1 and 3, Rate = $[2\text{-bromobutane}]^m[OH^-]^n$

$$\frac{0.024}{0.144} = \frac{k(0.0012)(0.10)^n}{k(0.0072)(0.60)^n}$$

$$\frac{1}{6} = \frac{(1)(1)^n}{(6)(6)^n}$$

$$1 = (\frac{1}{6})^n$$

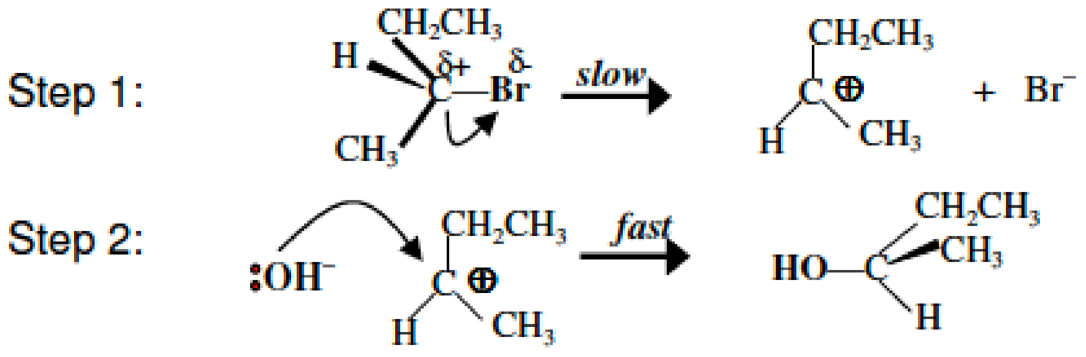
$$n = 0$$

Hence, order of reaction wrt NaOH = 0

Rate = k [2-bromobutane]

(ii) $$k = \frac{0.024}{0.0012} = 20\ \text{min}^{-1}$$

(iii) Nucleophilic substitution (S_N1)



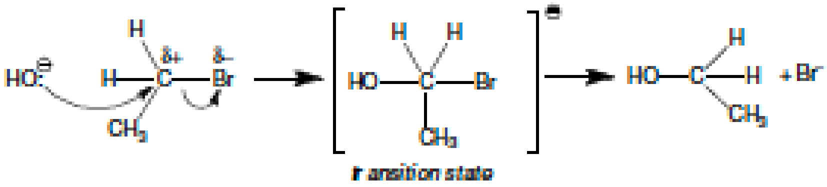
12 HCI/2010/P2/Q5 Level of Difficulty: [☆☆]

5(a)(i) $t_{1/2}$ is constant ~3min.
Reaction is first order wrt aqueous sodium hydroxide.

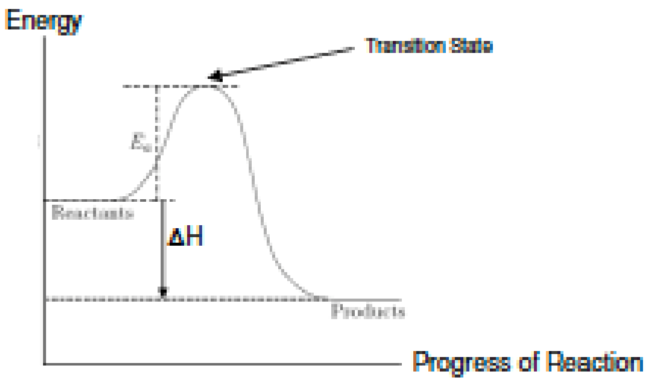
5(a)(ii) When concentration of the bromoethane double, the gradient of the graph doubles.
Therefore reaction is first order wrt to the bromoethane.

5(a)(iii) Rate = $k[C_2H_5Br][OH^-]$

5(b)(i) Name: Nucleophilic substitution, S_N2



5(b)(ii)



5(b)(iii) Iodoethane has a faster rate of hydrolysis.
Iodine is bigger hence the C–I bond is longer and therefore weaker.

13 MJC/2010/P3/Q3(a),(b),(c) Level of Difficulty: [☆☆]

3 (a) (i) From the plot of P_{N2} against time,
Half life is almost constant at 19 min

Hence, order of reaction wrt N_2O = 1.

(ii) Rate = $k[N_2O]$

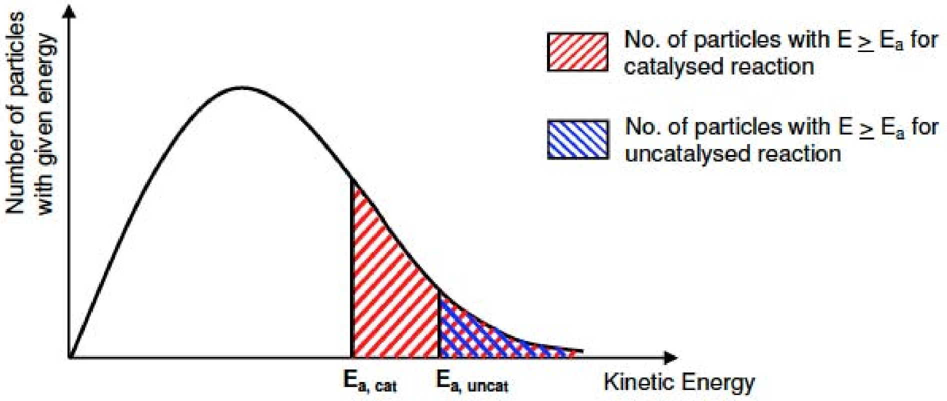
$t_{1/2} = \frac{\ln 2}{k} = 19$

$k = 0.0365\ \text{min}^{-1}$

(b) Rate = $k[NO]^2[H_2]$

(c) (i) Iron can act as a heterogeneous catalyst because of the availability of 3d and 4s electrons for temporary bond formation with reactants.

(ii)



The iron catalyst increases the rate of reaction by providing an alternative reaction pathway of lower activation energy. Number of reactant particles with E ≥ E_a increases, Frequency of effective collisions increases. Since rate of reaction is proportional to the frequency of effective collisions, rate of reaction increases.

14 NYJC/2010/P2/Q3 Level of Difficulty: [☆☆]

Experiment 1

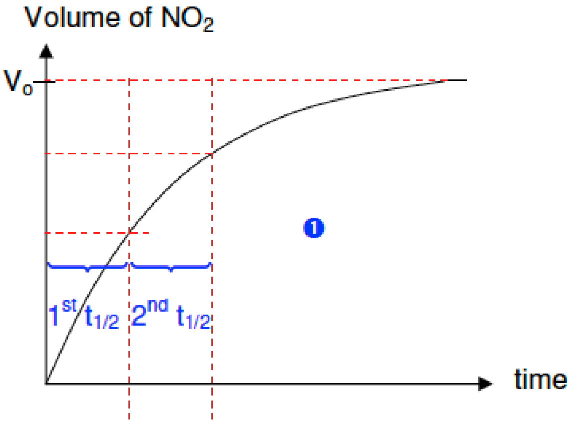
[NO] = 0.100 mol dm^{-3}

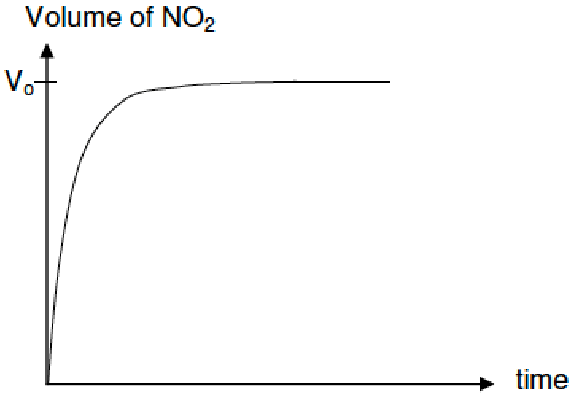
[O_2] = 0.001 mol dm^{-3}

Experiment 2

[NO] = 0.200 or (any value > 0.100) mol dm^{-3}

[O_2] = 0.001 mol dm^{-3}





(a) The results of *experiment 1* allowed the order of reaction with respect to *one* of the reagents to be found.

(i) State which reagent and explain your reasoning.

❶ O_2. In Expt 1, a huge excess of NO is used. Hence [NO] remain relatively constant as reaction proceeds. The apparent overall order of reaction depends only on the order with respect to O_2, which will determine the shape of the graph.

(ii) Deduce the order of reaction with respect to the reagent, showing your working on the graph for *Experiment 1*.

❶ 1st order

The reactants molecules are chemically adsorbed on neighbouring active sites on the catalyst, increasing the surface concentration of the reactant molecules. ❶ The activation energy decreases due to the weakening of the covalent bonds within the reactant molecules ❶ and aid in the formation of the product molecules.

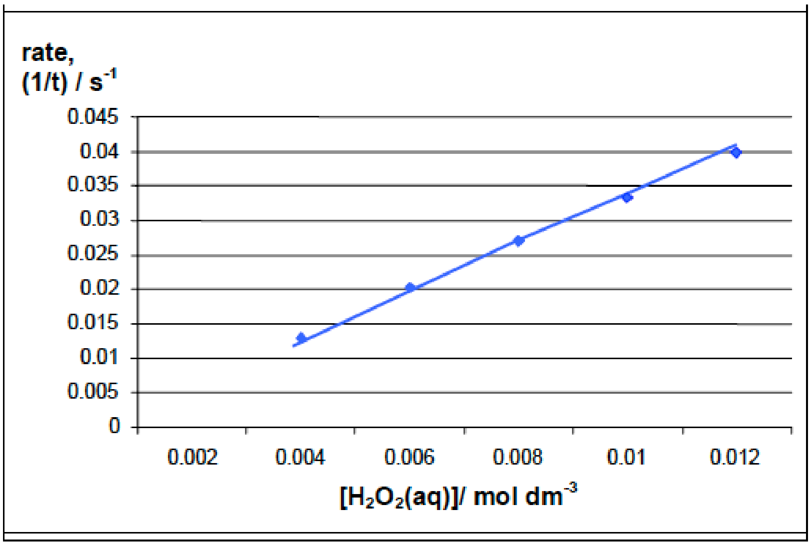
---

15 PJC/2010/P2/Q2 Level of Difficulty: [☆☆]

(a) (i) **rate ∝ 1/time**

experiment	**[H^+] = [I^-] = 0.500 mol dm^{-3}**		
	[H_2O_2] / mol dm^{-3}	**time / s**	**rate**
1	0.004	74	**0.0135**
2	0.006	49	**0.0204**
3	0.008	37	**0.0270**
4	0.010	30	**0.0333**
5	0.012	25	**0.0400**

(ii)



(iii) **first order, because the graph is upward-sloping / straight line <u>with positive gradient</u> / rate is proportional to [H_2O_2]**

(iv) **So that the concentration of I^- and H^+ remain relatively constant (OR change in concentration of I^- and H^+ is negligible) throughout the experiment. Hence, any change in the time taken for deep blue colour to appear is solely due to H_2O_2.**

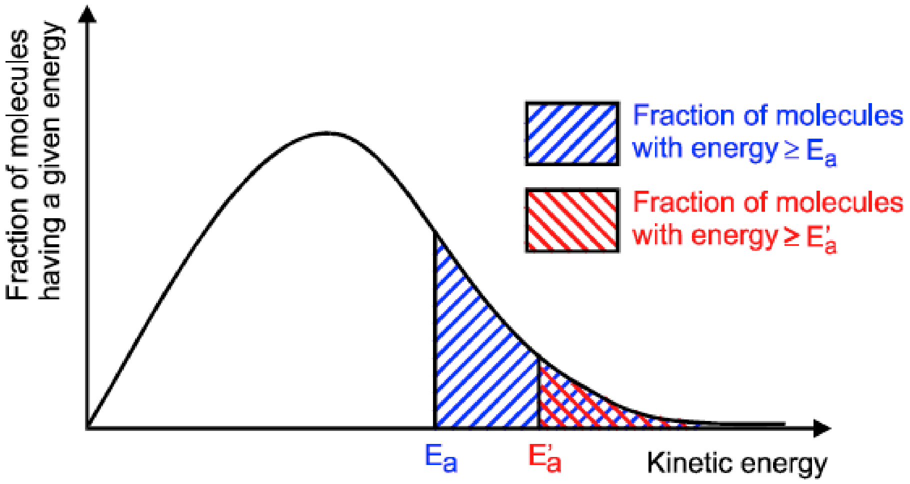
(b) (i) **Total volume is constant so that volume of reactant is directly proportional to the concentration of reactants.**

(ii) **Comparing experiment 1 and 2, [H_2O_2] and [H^+] are constant,**
[I^-] doubles, time taken for colour to change is approximately halved / rate doubled.
$\therefore$ order of reaction with respect to I^- = 1 or rate $\propto$ [I^-]

(iii)

Expt	Volume / cm^3						Time / s
	0.10 M H_2O_2	1.00 M KI	0.10 M HC*l*	0.10 M $Na_2S_2O_3$	starch	water	
1	5	10	10	2	3	70	100
2	5	20	10	2	3	60	48

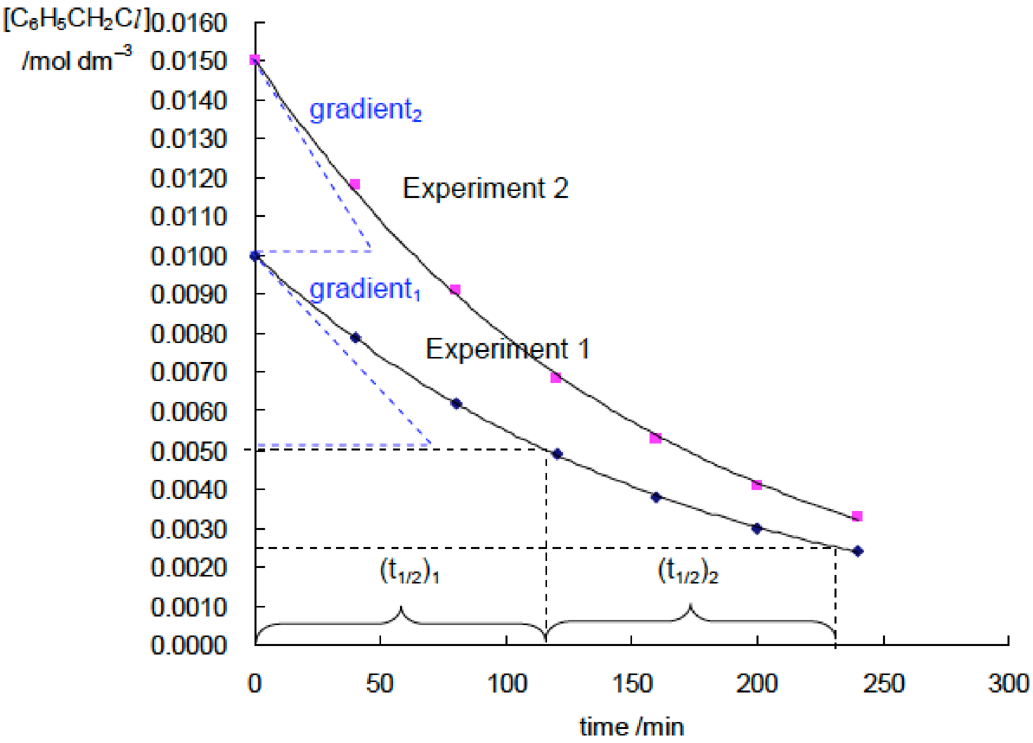
(c) **A catalyst increases the rate of a chemical reaction by providing an <u>alternative reaction pathway</u> with a <u>lower activation energy.</u>**



$E_{a,catalysed}$ is lower than $E_{a,uncatalysed}$ and, fraction of particles with energy ≥ $E_{a,catalysed}$ increases.
Frequency of effective collisions increases.
Rate of reaction increases.

16 <u>RVHS/2010/P3/Q4(b)</u> Level of Difficulty: [✩✩]

(b) **(i)**



(ii) As successive half-lives are the approximately the same ($(t_{1/2})_1 \approx (t_{1/2})_2$), the reaction is 1st order with respect to $C_6H_5CH_2Cl$.

gradient$_2$ = 1.5 × gradient$_1$, this shows that when **both** [NaOH] and [$C_6H_5CH_2Cl$] are increased to 1.5 times, the initial rate also increased to 1.5 times.

As order of reaction with respect to $C_6H_5CH_2Cl$ is 1, the rate of reaction is independent of [NaOH]. Hence, reaction is 0th order with respect to NaOH.

(iii) Rate = $k[C_6H_5CH_2Cl]$

k = gradient ÷ [$C_6H_5CH_2Cl$]

= (value) min^{-1}

or $k = \dfrac{\ln 2}{t_{1/2}}$

17 SAJC/2010/P2/Q5 Level of Difficulty: [☆☆]

(a) Rate = k[A]

Rate = k[B][NaOH]

(b) **(i)** Compound A: Graph 2

Compound C: Graph 1

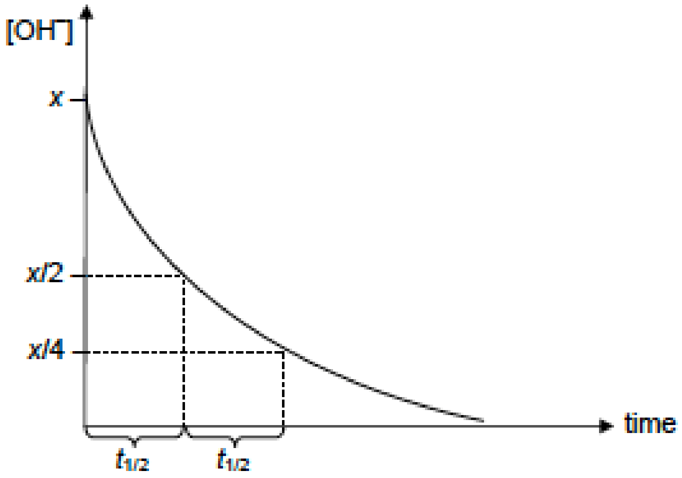
(ii) Since I atom is larger, there is less effective overlap between the atomic orbitals. C – I bond is longer. Hence C – I bond is weaker and rate of hydrolysis for compound C is faster.

18 VJC/2010/P3/Q3(b),(c) Level of Difficulty: [☆☆]

(b)(i)

rate = $k\,[OH^-]\,[NR_4^+]$
Units of k: $mol^{-1}\ dm^3\ s^{-1}$

(ii)



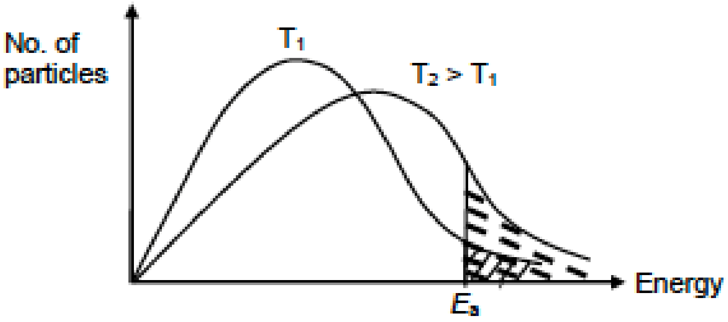
(iii)(I)

Half–life remains unchanged.

(II)

Half–life is halved.

(iv)



Both curves sketched correctly.
As temperature increases, molecules possess greater kinetic energy.
Hence, the number of molecules with energy greater or equal to activation energy is larger
as shown by the two shaded areas in the diagram above.
This results in higher frequency of effective collisions and hence higher rate of reaction.

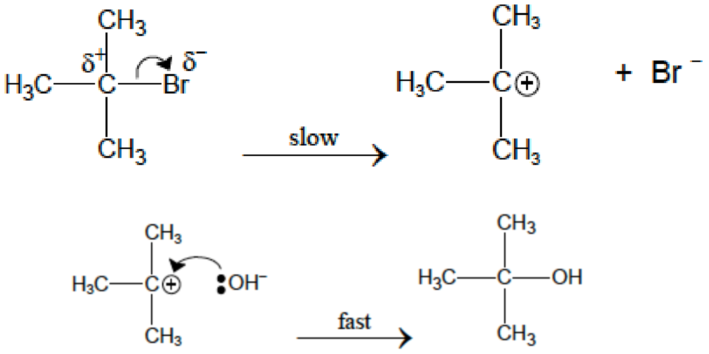
(c)

$CH_3CH_2CH{=}CHCH_3$ is more stable than $CH_3CH_2CH_2CH{=}CH_2$ due to greater number of alkyl groups.
Higher E_a for pathway leading to production of less $CH_3CH_2CH{=}CHCH_3$.

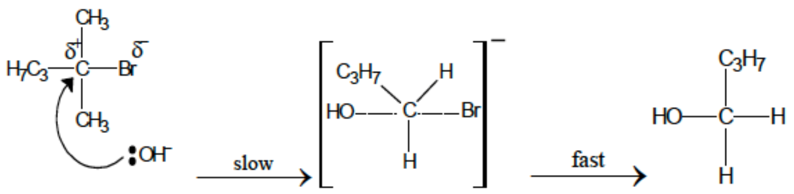
19 YJC/2010/P3/Q2(a) Level of Difficulty: [☆☆]

ai For $(CH_3)_3Br$, concentration of halogen doubles, while concentration of OH^- remains constant, rate doubles. First order with respect to $(CH_3)_3Br$. By inspection, concentration of OH^- doubles while $[(CH_3)_3Br]$ remains constant, rate remains unchanged, hence zero order with respect to OH^-.Rate = $k[(CH_3)_3Br]$
For $CH_3CH_2CH_2CH_2Br$, Rate = $k\,[CH_3CH_2CH_2CH_2Br][OH^-]$

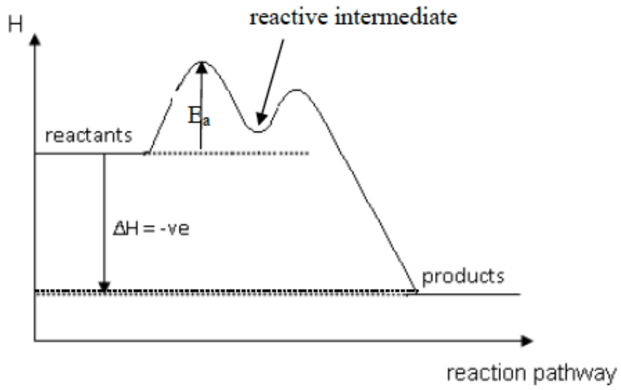
aii SN1 for $(CH_3)_3Br$

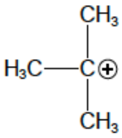


SN2 for $CH_3CH_2CH_2CH_2Br$,



aiii Energy profile for $(CH_3)_3Br$

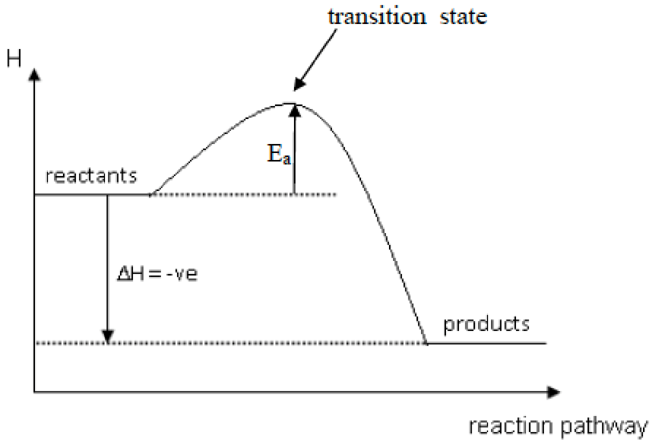




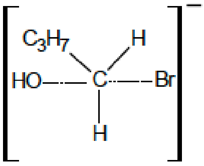
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}{}^{\oplus}$

reactive intermediate

Energy profile for $CH_3CH_2CH_2CH_2Br$



where transition state is



20 NJC/2010/P2/Q5(c) Level of Difficulty: [✯✯✯]

5 (c) (i) Iodine – oxidizing agent
H_2SO_4 – catalyst

5 (c) (ii) $NaHCO_3$ – quench reaction by reacting with the catalyst, H_2SO_4: conc of iodine present at diff time intervals can then be found.

NaOH – cannot be used as it can react with iodine producing sodium iodide and sodium iodate.

5 (c) (iii) Zero order wrt iodine
First order wrt sulphuric acid
(support answers with relevant explanation or working)

5 (c) (iv) Extrapolate curve to y-axis to find volume of thiosulfate required to react with the iodine present initially or at t = 0 min in a **10.0 cm^3 reaction mixture**.
Vol of thiosulfate reqd = 20.0 cm^3
Use the equation $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ to find amount of thiosulfate required to react with iodine present in **10.0 cm^3 reaction mixture** and hence conc of thiosulfate used. Conc. of thiosulfate used = 1.00×10^{-4} mol dm^{-3}

5 (c) (v) Overall order of reaction is 2.
Since reaction is 1st order wrt sulphuric acid, zero order wrt iodine, hence it is 1st order wrt propanone

TOPIC 9.1: THE PERIODIC TABLE: CHEMICAL PERIODICITY

1 ACJC/2010/P3/Q2(a) & (b) Level of Difficulty: [✭]

(a) Describe the reactions between water and **(i)** magnesium chloride and
(ii) silicon tetrachloride separately.
Write balanced equations where appropriate.

[4]

(b) The oxide of an element in Period 3 of the Periodic Table dissolves readily in water to give a colourless solution, **Y**. When **Y** is added to an aqueous solution of an aluminium salt, a white precipitate is observed, which dissolves in excess of **Y** to give a colourless solution, **Z**. When hydrochloric acid is added to **Z**, a white precipitate is obtained which then dissolves in excess of hydrochloric acid.

(i) Identify **Y** and write balanced equations for its reactions with the aluminium salt.

(ii) Explain the reaction of hydrochloric acid with **Z** .

[4]

2 HCI/2010/P3/Q1(a) Level of Difficulty: [✭]

Phosphorus is a non-metal which was discovered by the German physician Hennig Brand in 1669. In his experiments, Brand found that the white material (white phosphorus) glowed in the dark and spontaneously burst into a bright white flame when burned in air.

(i) Write equations, including state symbols, for the reactions that occur when a sample of phosphorus is burned in excess oxygen, and water is added to the resulting oxide.

(ii) Suggest the pH of the aqueous solution formed.

[3]

3 HCI/2010/P3/Q3(a) Level of Difficulty: [✭]

The chlorides of magnesium and silicon differ in their reactions with water. Describe and explain these differences in terms of their structure and bonding, writing equations for any reactions that occur.

[4]

4 MI/2010/P2/Q2(c) & (d) Level of Difficulty: [✭]

(c) Sketch a graph to show the variations of melting points of the oxides of Period 3 elements. [1]

Suggested Answers

1 ACJC/2010/P3/Q2(a) & (b) Level of Difficulty: [☆]

$MgCl_2$ readily dissolves in water through ion-dipole interactions. The aq. solution is slightly hydrolysed to give a very weakly acidic solution. (Mg^{2+} has a reasonably high charge density and hence is capable of polarizing the water molecules.-optional no mark allocated)

$$Mg(H_2O)_6^{2+}(aq) \rightleftharpoons Mg(H_2O)_5(OH)^+ + H^+(aq)$$

Silicon tetrachloride dissolves readily in water and is completely hydrolysed to give an acidic solution. Copious white fumes are liberated.
(This happens because Si has low-lying vacant 3d-orbitals to accommodate the lone pairs of electrons from water.- no marks, refer question)

$$SiCl_4(l) + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

($SiO_2.2H_2O$ or H_4SiO_4 are also acceptable)

Y is sodium hydroxide.

$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s) \quad +OH^-(aq) \rightarrow Al(OH)_4^-(aq)$$

The white ppt is $Al(OH)_3$ formed when HCl(aq) reacts with the complex ion and with excess of HCl(aq) the $Al(OH)_3$ dissolves to give Al^{3+}(aq), a clear colourless solution

2 HCI/2010/P3/Q1(a) Level of Difficulty: [☆]

(i) $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$

OR $4P(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$

OR $2P(s) + \frac{5}{2}O_2(g) \rightarrow P_2O_5(s)$

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

OR $P_2O_5(s) + 3H_2O(l) \rightarrow 2H_3PO_4(aq)$

(ii) pH = 2

3 HCI/2010/P3/Q3(a) Level of Difficulty: [☆]

Magnesium chloride has a giant ionic lattice structure.
It dissolves in water to form a slightly acidic solution as Mg^{2+} has a high charge density and undergoes hydrolysis in water.

$$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$$

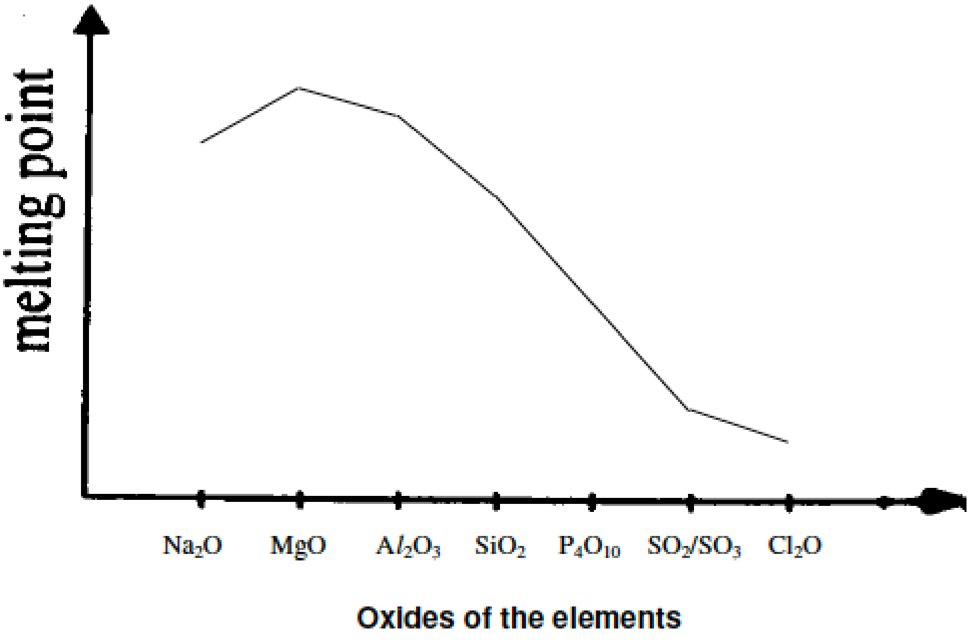
$$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$$

Silicon chloride is a simple covalent molecule with dispersion forces between molecules. It undergoes complete hydrolysis in water to give a highly acidic solution of pH 1-2.

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$$

OR $$SiCl_4(l) + 4H_2O(l) \rightarrow SiO_2.2H_2O(s) + 4HCl(aq)$$

4 MI/2010/P2/Q2(c) & (d) Level of Difficulty: [☆]



Compound	Sodium oxide	Aluminium oxide	Phosphorus(V) oxide
pH of the resultant solution formed when the oxide is added to water	13 – 14	7	1 – 2
Equations to show reaction with water, if any	$Na_2O + H_2O \rightarrow 2NaOH$; $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$;		

5 MJC/2010/P2/Q2(a) Level of Difficulty: [☆]

(i) $MgCl_2$ has a giant ionic lattice structure held by strong electrostatic forces of attraction between the oppositely charged Mg^{2+} and Cl^- ions. A large amount of energy is required to overcome the strong electrostatic forces of attraction, hence the melting point is high.

Aluminium chloride has a simple molecular structure.

The molecules are non-polar and held by which can be easily broken during melting weak induced dipole-induced dipole attractions/ Van der Waal's forces of attraction. A small amount of energy is required to overcome the weaker forces of attraction between the molecules, hence the melting point is low.

(ii) Al_2Cl_6 undergoes both hydration and hydrolysis when dissolved in water. The high charge density of hydrated Al^{3+} ion enables it to attract electrons away from one of its surrounding water molecules, thereby polarising and weakening the O-H bond to a greater extent which results in the release of a proton pH = 3.0

$$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$$

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$$

PCl_5 undergoes complete hydrolysis to form a strongly acidic solution with pH=1.0/2.0

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

6 NYJC/2010/P3/Q4(a) & (b) Level of Difficulty: [✩]

(i) Silicon has numerous known isotopes of which ^{28}Si, ^{29}Si and ^{30}Si are stable. Given that 3.1% of naturally occurring silicon is ^{30}Si, calculate the natural abundance of ^{28}Si.

Let the abundance of ^{28}Si be x %

❶ $$\frac{x}{100}(28) + \frac{100-3.1-x}{100}(29) + \frac{3.1}{100}(30) = 28.1$$

$$x = 93.1\%$$

❶ for correct answer

(ii) Solid silicon melts at 1414 °C and is used widely industrially to manufacture computer chips. Describe the structure and bonding in solid silicon.

❶ Silicon has a giant covalent structure with strong covalent bonds between Si atoms.

(iii) Account for its use in computer chips.

[4]

❶ Silicon has low electrical conductivity hence is used as a semi-conductor.

(i) Show by writing appropriate equations the acid-base nature of SiO_2.

SiO_2 is an acidic oxide

❶ $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

(ii) Suggest a property of SiO_2 that accounts for its use in *Simethicone* to treat stomach disorders.

❶ No reaction with aqueous acid.
❶ SiO_2 has a strong lattice structure with strong covalent bonds between Si and O atoms that makes it insoluble in water.

7 PJC/2010/P2/Q3(a) Level of Difficulty: [☆]

(i) **Across period 3,**

- **increase in nuclear charge due to increase in number of protons.**
- **screening effect is approximately constant as the number of inner filled quantum shells remains the same.**
- **effective nuclear charge increases / stronger electrostatic attraction between the nucleus and valence electrons.**
- **more energy required to remove outermost / valence electron**

(ii) **Chlorides hydrolyse in water to form acidic solutions of HC*l*.**
$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

(iii) **$AlCl_3$ first dissolves to form $[Al(H_2O)_6]^{3+}$ ion.**
$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

Al^{3+} has high charge density / polarising power. Al^{3+} polarises surrounding coordinated H_2O molecules and weakens the O-H bonds, causing them to release H^+ ions.

$[Al(H_2O)_6]^{3+}(aq) \rightarrow [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

8 RVHS/2010/P3/Q1(g) Level of Difficulty: [☆]

$MgCl_2$ forms a weakly acidic (or neutral solution) with pH = 6.5 (or 7).

$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$ (for neutral solution)

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) = [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$ (both equations for weakly acidic solution)

PCl_5 forms a strongly acidic solution with pH = 2.

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

9 SRJC/2010/P2/Q1 Level of Difficulty: [☆]

Removing the 4th valence electron **requires a vast amount of energy**./ There is a **large jump** from the **3rd to 4th IE.**

The **4th electron** is removed from an **inner shell** / There are **3 valence electrons.**

Therefore, element **X** is from **group III**.

X is **aluminium**.

$4\ Al\ (s) + 3\ O_2\ (g) \rightarrow 2\ Al_2O_3\ (s)$

It undergoes **neutralisation with both acids and bases** to form salt and water.

$Al_2O_3\ (s) + 6\ HCl\ (aq) \rightarrow 2\ AlCl_3(aq) + 3\ H_2O\ (l)$

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

$2\ Al\ (s) + 3\ Cl_2\ (g) \rightarrow Al_2Cl_6\ (s)$ or $Al\ (s) + 3/2\ Cl_2 \rightarrow AlCl_3$

$AlCl_3$ undergoes **hydrolysis to give an acidic solution (pH ≈ 3).**

The high charge density of Al^{3+} ion **polarises** one of its surrounding **water molecules** hence weakening the O-H bond which results in the **release of a proton**:

$AlCl_3\ (s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}\ (aq) + 3Cl^-\ (aq)$

$[Al(H_2O)_6]^{3+}\ (aq) \rightarrow [Al(H_2O)_5(OH)]^{2+}\ (aq) + H^+\ (aq)$

Electrons are added to the **next valence shell**.

The **distance** between the nucleus and the valence electrons **increases**.

Decrease in electrostatic forces of attraction between the nucleus and valence electrons.

Less energy needed to remove the valence electron, thus 1st I.E. decreases.

Element X will have a higher first ionization energy.

10 TJC/2010/P3/Q5(a) Level of Difficulty: [☆]

(i)

- Na_2O has a giant ionic structure and consists of strong ionic bonds. The O^{2-} ion reacts with water to give a strongly alkaline solution. pH = 13
- $Na_2O + H_2O \rightarrow 2NaOH$
- SiO_2 is a covalent oxide with a giant molecular structure. Strong covalent bonds are present between its atoms. It is insoluble in water. Hence pH remains as 7.
- P_4O_{10} (or P_4O_6) is a covalent oxide with a simple molecular structure. Weak van der Waals' forces are present between the molecules. There are energetically accessible vacant d orbitals for dative bonding with water molecules. P_4O_{10} (or P_4O_6) dissolves readily in water to give an acidic solution of pH 2.
- $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ OR $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$
- All pH correct

(ii)

- Silicon dioxide has a giant molecular structure while P_4O_{10} (or P_4O_6) has a simple molecular structure.
- Melting of silicon dioxide involves breaking of strong covalent bonds, while melting of P_4O_{10} (or P_4O_6) involves breaking of weak van der Waals' forces. Since van der Waals' forces are weaker than covalent bonds and require less energy to overcome. Hence the melting point of P_4O_{10} (or P_4O_6) is lower.

(iii)

- $BeO + 2H^+ \rightarrow Be^{2+} + H_2O$
- $BeO + 2OH^- + H_2O \rightarrow Be(OH)_4^{2-}$

11 VJC/2010/P2/Q2(a) Level of Difficulty: [☆]

2(a)(i)

$MgCl_2$ has ionic bonding between Mg^{2+} and Cl^- ions.
$AlCl_3$ has dispersion forces between the molecules.
More energy is needed
to break the stronger ionic bonding in $MgCl_2$ leading to its higher melting point.

(ii)

When $MgCl_2$ reacts with water, pH of solution formed is 6.5.

$MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$
When $AlCl_3$ reacts with water, pH of solution formed is 3.

$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$

(iii)

MgO reacts slowly with water
to form a solution of pH 8 (accept 8–9).

$MgO + H_2O \rightleftharpoons Mg(OH)_2$
BaO reacts readily with water
to form a solution of pH 12.
$BaO + H_2O \rightarrow Ba(OH)_2$

(iv)(I)

$Ga_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Ga(OH)_4]$
$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$

(II)

$Ga_2O_3 + 6HCl \rightarrow 2GaCl_3 + 3H_2O$

12 YJC/2010/P2/Q4 Level of Difficulty: [☆]

	P	O
% by mass	43.7	56.3
No of moles	1.410	3.519
Ratio	1.00	2.50
	2	5

$(31 \times 2 + 16 \times 5)n = 288$
$n = 2$

molecular formula P_4O_{10}

T which is P_4O_{10} has molecular structure with molecules held by weak Van der Waals forces easily overcomed by small amount of energy.
Al_2O_3 has giant ionic structure with oppositely charged ions held by strong ionic bonds which require large amount of energy to overcome.
Hence T has a low melting point.

$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$
$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$
$P_4O_{10} + 12OH^- \rightarrow 4PO_4^{3-} + 6H_2O$

Na_2O dissolves in water readily to form a strong alkaline solution with pH=13.

$Na_2O + H_2O \rightarrow 2NaOH$

T, P_4O_{10} dissolves in water to form a strong acid solution with pH = 2.

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

[4]

13 YJC/2010/P3/Q3(d) Level of Difficulty: [☆]

NaCl (s) +aq → Na+ (aq) + Cl- (aq) ; pH = 7

$MgCl_2 (s) + aq \rightarrow [Mg(H_2O)_6]^{2+} (aq) + 2Cl^- (aq)$
$[Mg(H_2O)_6]^{2+}(aq) \leftrightarrows [Mg(H_2O)_6(OH)]^+(aq) + H^+(aq)$; pH= 6.5

$Al_2Cl_6(s) + 12H_2O(l) \rightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$
$[Al(H_2O)_6]^{3+}(aq) \leftrightarrows [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$; pH = 3

14 CJC/2010/P3/Q1(b) Level of Difficulty: [☆☆]

- protective coating is Al_2O_3

  which is amphoteric and so, is removed by dilute HCl or NaOH(aq).

  $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
  $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$

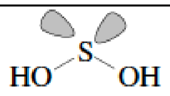
- pure Al would then react with dilute HCl or NaOH(aq) to give effervescence of $H_2(g)$, a colourless gas.

  $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$
  $2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2$

[or $2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$ or $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$]

- The formation of $H_2(g)$ leads to a bubbling effect which provides an additional mechanical cleaning mechanism.

15 NJC/2010/P2/Q6 Level of Difficulty: [✮✮]

6 (a)	On going across Period 3, the hydroxides go from basic to acidic. This systematic variation is the result of (i) the trend in the electronegativity of the elements, which leads to (ii) the difference in the bonding between the elements and the hydroxide. Explanation: ➢ Going across Period 3, there is an increase in the effective nuclear charge of the elements, resulting in the increase in their electronegative values. ➢ This means that the *difference in electronegativity* between the elements and the hydroxide becomes smaller on going across the Period 3 hydroxides, resulting in the bonding between them changing from ionic to covalent. ➢ Ionic oxides/hydroxides are basic because of the presence of OH^- ions, and the covalent oxides/hydroxides are acidic due to the interactions of the partially positive elements with water, releasing H^+ ion.
(b)	Aqueous aluminium nitrate has Al^{3+}(aq) ions. These small and highly charged ions can polarize water molecules and undergo cation hydrolysis: $[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$ The H_3O^+ ions produced in this hydrolysis decompose Na_2CO_3 to give CO_2 gas and this acid-carbonate reaction causes the equilibrium above to go to completion. $[Al(H_2O)_5(OH)]^{2+}$ undergoes further hydrolyses as follows until $Al(OH)_3$(s) results. $[Al(H_2O)_5(OH)]^{2+} + H_2O \rightleftharpoons [Al(H_2O)_4(OH)_2]^+ + H_3O^+$ $[Al(H_2O)_4(OH)_2]^+ + H_2O \rightleftharpoons [Al(H_2O)_3(OH)_3] + H_3O^+$
(c)	 has two lone pairs of electrons around S, which force the HŐŠOH bond angle to be much smaller than the tetrahedral angle. This result in the two O atoms brought very close together. Both of these O atoms carry considerable partial negative charge and each also possesses two lone pairs of electrons. The very strong repulsion between them makes the molecule highly unstable. Thus $S(OH)_2$ is unable to exist.
(d)	Cl(OH)

16 NJC/2010/P3/Q4(a) Level of Difficulty: [☆☆]

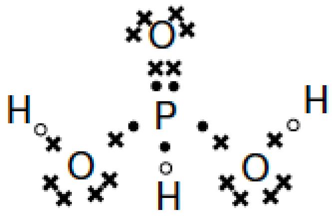
(i) P is less electronegative than Cl, hence H_2O attacks the partial positively charged P and displace Cl to form H_3PO_3 and HCl.

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

N is more electronegative than Cl, hence H_2O attacks the partial positively charged Cl to form HOCl and NH_3.

$NCl_3 + 3H_2O \rightarrow 3HOCl + NH_3$

(ii)



17 NYJC/2010/P2/Q7 Level of Difficulty: [☆☆]

Similar electronegativities OR similar charge density [1]

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

$[Al(H_2O)_6]^{3+} + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$ [1]

$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$ [1]

$BeCl_2$ and BCl_3 are covalent chlorides with a simple molecular structure. They undergo hydrolysis in water to form acidic solution, similar to $AlCl_3$ and $SiCl_4$. [1]

$BeCl_2 + 4H_2O \rightarrow [Be(H_2O)_4]^{2+} + 2Cl^-$

$[Be(H_2O)_4]^{2+}(aq) + H_2O(l) \rightleftharpoons [Be(H_2O)_3OH]^+(aq) + H_3O^+(aq)$ [1]

pH of aqueous $BeCl_2 = 3$ [1]

$BCl_3\ (l) + 3H_2O(l) \rightarrow B(OH)_3(s) + 3HCl\ (aq)$ [1]

pH of aqueous $BCl_3 = 2$ [1]

TOPIC 9.2: GROUP II ELEMENTS

1 ACJC/2010/P2/Q2(a) Level of Difficulty: [✯]

The use of the Data Booklet is relevant to this question.

The nitrates, carbonates and hydroxides of Group II elements can undergo thermal decomposition.

(i) Write a balanced equation, with state symbols, for the decomposition of calcium nitrate.

(ii) The nitrates of lead and zinc can undergo thermal decomposition similar to calcium nitrate. The decomposition temperatures of the three nitrates are given in the following table.

Compound	**decomposition temperature / °C**
Lead(II) nitrate, $Pb(NO_3)_2$	290
Zinc nitrate, $Zn(NO_3)_2$	105
Calcium nitrate, $Ca(NO_3)_2$	132

Explain the data in the table by quoting relevant values from the *Data Booklet* and using your understanding of the trend in the decomposition temperatures of the Group II nitrates.

2 CJC/2010/P2/Q6(b) Level of Difficulty: [✯]

(b) The carbonates of Group II elements, similar to their nitrates, can be decomposed by heat.

(i) Write a balanced equation for the thermal decomposition of $MgCO_3$.

(ii) Describe and explain the trend in thermal stabilities of the carbonates of Group II elements from Mg to Ba.

3 HCI/2010/P3/Q5(a) Level of Difficulty: [✯]

(a) Norsethite, $Ba_xMg_y(CO_3)_z$, is a mineral consisting of barium carbonate and magnesium carbonate. The decomposition temperatures of barium carbonate and magnesium carbonate are 1350 °C and 540 °C respectively.

(i) Account for the difference in decomposition temperatures of barium carbonate and magnesium carbonate.

Write equation(s) for any reaction(s) that occur on heating norsethite to 800 °C.

(d) **(i)** All water or acid soluble barium compounds are poisonous. At low doses, barium acts as a muscle stimulant, while higher doses affect the nervous system, causing cardiac irregularities.

Barium sulfate is frequently used clinically as a radiocontrast agent for X-ray imaging and is known as a 'barium meal'. It is usually administered orally as a suspension of fine particles in an aqueous solution.

Anhydrous magnesium sulfate is commonly used as a dehydrating agent in organic synthesis. Magnesium sulfate paste has also been used as an agent for dehydrating boils and is an effective aid against acne.

Briefly explain the contrasting characteristic of barium sulfate and magnesium sulfate as described above.

(ii) Barium carbonate is more toxic than barium sulfate when ingested. With an aid of an equation, explain this fact.

[3]

Suggested Answers

1 ACJC/2010/P2/Q2(a) Level of Difficulty: [☆]

$2Ca(NO_3)_2\ (s) \rightarrow 2CaO\ (s) + 4NO_2\ (g) + O_2\ (g)$ or

$Ca(NO_3)_2\ (s) \rightarrow CaO\ (s) + 2NO_2\ (g) + \frac{1}{2}O_2\ (g)$

The decomposition temperature increases in the order from in the order from zinc nitrate to calcium nitrate to lead nitrate. This is because the ionic radius of Zn^{2+} is smaller than Ca^{2+} which in turn is smaller than Pb^{2+}.

The smaller the ionic radius, the higher the charge density (all have the same charge) and, hence the greater the polarising power of the ion which can therefore distort the electron cloud of the nitrate anion more and weaken the N-O bond to a greater extent. Hence zinc nitrate has the lowest thermal stability and can decompose at the lowest temperature.

2 CJC/2010/P2/Q6(b) Level of Difficulty: [☆]

$MgCO_3(s) \rightarrow MgO(s) + CO_2\ (g)$

Ionic charge remains constant at +2, but the ionic radius increases down the group. Hence the **charge density decreases down the group.**
Thus, the **anions is less polarised** by the cation and the electron clouds are distorted to a lesser extent.
Therefore, **thermal stability increases down the group.**

3 HCI/2010/P3/Q5 Level of Difficulty: [☆]

(i) Mg^{2+} cation has a higher charge density and distorts the carbonate electron cloud more. Hence, $MgCO_3$ decomposes at a lower temperature than $BaCO_3$.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

OR

$$Ba_xMg_y(CO_3)_z \rightarrow xBaCO_3 + yMgO + yCO_2$$

(ii) $$Ba_xMg_y(CO_3)_z(s) \rightarrow xBaO(s) + yMgO(s) + zCO_2(g)$$

$$n_{CO2} = \frac{72}{24000} = 0.003 \text{ mol}$$

$$BaO(s) + 2HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + H_2O(l)$$

Similarly, $Mg(NO_3)_2$ is also formed.

$$Ba(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HNO_3(aq)$$

$$nBaSO_4 = nBaO = \frac{0.35}{(137+32.1+64)} = 0.001502 \text{ mol}$$

$x : z$
$= 1 : 2$

By balancing O atoms,
$3z = x + y + 2z$
$\Rightarrow z = x + y$
$\Rightarrow x = y$

$\therefore$ **$x = y = 1; z = 2$**

(iii) CO forms strong dative bond with Fe^{2+} of haemoglobin OR undergo ligand exchange and this is an irreversible process.
Thus haemoglobin is unable to transport oxygen , causing death as the body is deprived of oxygen.

4 MI/2010/P3/Q1(a) Level of Difficulty: [☆]

cation/M^{2+} radius/size increases down the group / M^{2+} charge density decreases ;

anion/carbonate ion/CO_3^{2-} suffers less polarisation/distortion ;

carbonates become more stable down the Group/higher decomposition temperature ;

ionic radii quoted: ***;***

Ca^{2+}: 0.099 nm

Zn^{2+}: 0.074 nm

Pb^{2+}: 0.120 nm

thus we expect $ZnCO_3$ to be less stable, but $PbCO_3$ to be more stable;

5 MJC/2010/P2/Q6(a) & (b) Level of Difficulty: [☆]

6(a) **(i)** Unlike all other Group II elements, beryllium oxide is amphoteric and it reacts with an acid and base in the same way as aluminium.

Reaction with HCl: $BeO + 2\ H^+ \rightarrow Be^{2+} + H_2O$

Reaction with NaOH: $BeO + 2\ OH^- + H_2O \rightarrow [Be(OH)_4]^{2-}$

(ii) $Al_4C_3 + 6\ H_2O \rightarrow 2\ Al_2O_3 + 3\ CH_4$

(b) **(i)** Down the group,

- ionic size of cation increases
- charge density of cation decreases
- polarising power of cation decreases
- polarising effect on CO_3^{2-} anion decreases *or* the ability of the cation to distort the anion charge cloud of CO_3^{2-} decreases
- thermal stability increases hence decomposition temperature increases

(ii) Be^{2+} behaves like Al^{3+} where it has a very high charge density that polarises CO_3^{2-} very easily compared to the rest of the Group II metal ions.

6 NJC/2010/P2/Q4(c) & (d) Level of Difficulty: [☆]

Decomposition temp of magnesium nitrate is lower than that of strontium nitrate.

Both magnesium and strontium ions have the same charge of +2.

Size of Mg^{2+} is smaller than Sr^{2+}

$\Rightarrow$ charge/size ratio of Mg^{2+} is larger than Sr^{2+}

$\Rightarrow$ Mg^{2+} is a better polarizer than Sr^{2+}

⇒ electron cloud of nitrate in magnesium nitrate will be distorted to a larger extent than that of strontium nitrate making the breaking of N-O bond easier

⇒decomposition temp of magnesium nitrate is lower than that of strontium nitrate.

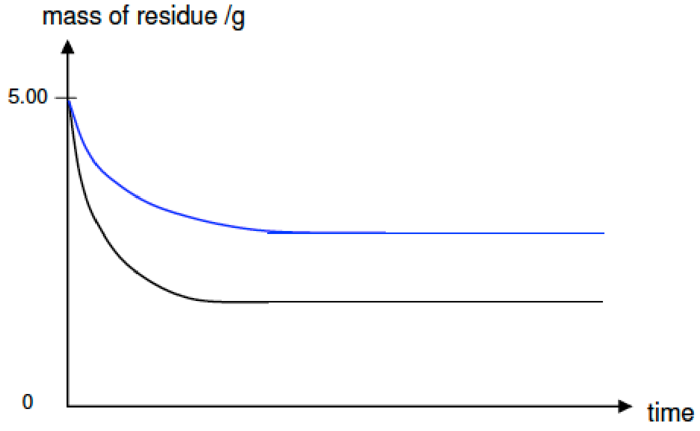
Solids obtained on heating strontium nitrate and magnesium nitrate are strontium oxide and magnesium oxides respectively.

SrO dissolves readily in water forming a colourless alkaline solution of $Sr(OH)_2$.

MgO is insoluble in water.

7 NYJC/2010/P2/Q5 Level of Difficulty: [☆]

$Ca(NO_3)_2(s) \rightarrow CaO(s) + 2NO_2(g) + \frac{1}{2} O_2(g)$



- Ba^{2+} has a larger ionic radius, hence charge density (thus polarising power) of Ba^{2+} is smaller than Mg^{2+}.
- The electron cloud of nitrate (for $Ba(NO_3)_2$) becomes less distorted or less polarised and hence breaks up less readily, and hence decomposition/thermal stability increases.

8 PJC/2010/P2/Q3(b) & (c) Level of Difficulty: [☆]

(b) (i) $Ca(NO_3)_2(s) \rightarrow CaO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

(ii) 1. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$

2. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$ **OR** $Ca^{2+}(aq) + 2OH^-(aq)$
$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$
A white precipitate of $CaCO_3$ is observed on bubbling in carbon dioxide.

(c) **$XCO_3(s) \rightarrow XO(s) + CO_2(g)$**

Amount of CO_2 = 1.25/44.0 = 0.0284 mol
Amount of XCO_3 = 0.0284 = 4.19/M_r of XCO_3
M_r of XCO_3 = 147.5

147.5 = A_r of X + 12.0 + 3(16.0)
A_r of X = 87.5
X is strontium.

9 RVHS/2010/P2/Q3 Level of Difficulty: [☆]

(a) $Ba(NO_3)_2(s) \rightarrow BaO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

(b) Mg^{2+} is smaller and has a higher charge density than Ba^{2+}, hence Mg^{2+} has a greater polarising power and weakens the N–O bonds in the NO_3^- anion to a greater extent. Consequently, $Mg(NO_3)_2$ decomposes at a lower temperature than $Ba(NO_3)_2$.

(c) $BaCO_3$ reacts with the acid in the stomach to form soluble Ba^{2+}.

10 SAJC/2010/P3/Q4(c)(iv) Level of Difficulty: [☆]

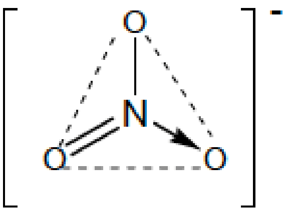
$MgCO_3$ decomposes at a lower temperature or more easily than $BaCO_3$.

This is because Mg^{2+} ion, being smaller and higher charged than Ba^{2+}, is able to polarise the large electron cloud of the carbonate ion more effectively, resulting in lower thermal stability in $MgCO_3$.

11 TJC/2010/P3/Q5(b) Level of Difficulty: [☆]

(i)
- $M(NO_3)_2\ (s) \rightarrow MO\ (s) + 2NO_2\ (g) + ½O_2\ (g)$

(ii)



-
- Trigonal planar

(iii)
- Ionic radii of Mg^{2+} 0.065nm, Ca^{2+} 0.099nm, Sr^{2+} 0.113nm
- Ionic radius increases down the group. The charge density and hence polarising power of M^{2+} decreases and nitrate is polarised to smaller extent.
- Thermal stability increases from magnesium nitrate to strontium nitrate.

(iv) pV = nRT

- number of moles of O_2 = $\dfrac{PV}{RT} = \dfrac{101\times10^3\times95\times10^{-6}}{8.31\times(30+273)}$ = 3.81×10^{-3} mol

(v) number of moles of $M(NO_3)_2.xH_2O$ = 0.00762 mol

number of moles of H_2O = $\dfrac{0.55}{18.0}$ = 0.0306 mol

- x = $\dfrac{0.0306}{0.00762}$ = 4
- M_r of $M(NO_3)_2$ = $\dfrac{1.80-0.55}{0.00762}$ = 164.0

  A_r of M = 164.0 – 2[14.0 + 3(16.0)] = 40.0
- *M* is calcium

  [the hydrate is $Ca(NO_3)_2.4H_2O$]

13 YJC/2010/P3/Q1(c) Level of Difficulty: [☆]

ci $2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$

cii Down the group, thermal decomposition temperature of nitrates increases. Down the group, charge density of metal cation decreases, polarizing ability decreases. Distortion of the electron cloud of nitrate decreases, hence weakening of N-O bond decreases. Thermal stability of nitrates increases, therefore temperature for decomposition increases.

14 SRJC/2010/P3/Q5(a) – (d) Level of Difficulty: [☆☆]

$Mg^{2+}|Mg$, $E^{\ominus}$ = -2.38V

$Ba^{2+}|Ba$, $E^{\ominus}$ = -2.92V

Reduction potential for Ba^{2+} is more negative than Mg^{2+}. Ba undergoes oxidation more readily than Mg, thus has to be kept in oil to avoid direct contact with atmospheric O_2.

Ba^{2+} has a low charge density (or low polarising power), thus its CO_3^{2-} ions is less polarised/distorted. Bunsen burner cannot reach a temperature high enough to decompose $BaCO_3$.

High charge density of Be^{2+} ions polarise CO_3^{2-} ions, distorting the electron cloud, thus $BeCO_3$ decomposes at room temperature.

$BeCO_3\ (s) \rightleftharpoons BeO\ (s) + CO_2\ (g)$

Presence of CO_2 shifts the eqm to the left, preventing $BeCO_3$ from decomposing.

Analysis: $Mg + NH_3 \rightarrow$ **P** $+ H_2$
P $+ H_2O \rightarrow$ **Q**(white solid) + **NH_3**
Element present in P is Mg and N

Amount of H^+ ion to neutralize ammonia $= 2 \times \frac{20.00}{1000} \times 0.1 = 0.00400$mol

Amount of **P** reacted with water $= \frac{0.198}{100.9} = 0.00196$ mol
Ratio P : NH_3
0.00196 : 0.00400
1: 2 (Since 1 mol of **P** forms 2 mol of NH_3)
Since there are 2 N, using $M_r = 100.9$, there will be 3 Mg
$P = Mg_3N_2$
$Q = MgO$
$3Mg + 2NH_3 \rightarrow Mg_3N_2 + 3H_2$
$Mg_3N_2 + 3H_2O \rightarrow 2MgO + 2NH_3$

$BaSO_4$ is **less soluble** than $MgSO_4$ as the **$\Delta H_{sol}(BaSO_4)$ is less exothermic**. Thus it can be administer as barium meal.

Mg^{2+} has high charge density and as such it can **attract the water molecules** in the treatment of boils.

Barium carbonate can react with the HC*l* in our stomach to form soluble barium salt which is highly toxic.

$BaCO_3 + HCl \rightarrow BaCl_2 + CO_2 + H_2O$

TOPIC 9.3: GROUP VII ELEMENTS

1 ACJC/2010/P2/Q4 Level of Difficulty: [☆]

(a) Aqueous bromine is decolourised when added to aqueous sodium thiosulfate. When excess of aqueous barium chloride is added to the resulting solution, a white precipitate is observed. This precipitate is filtered off, leaving a colourless filtrate.

(i) Write a balanced ionic equation for the reaction between bromine and sodium thiosulfate.

(ii) Identify the white precipitate.

(iii) To the colourless filtrate in **(a)** above, aqueous silver nitrate is added, followed by dilute aqueous ammonia solution.

Describe what is observed and give the formula of the **complex ion** formed after the addition of dilute aqueous ammonia solution.

(b) Aqueous bromine is added **separately** to aqueous potassium iodide and aqueous potassium chloride. To the each of the resulting mixtures, an equal volume of an organic solvent is added.

What will be the colour of the organic layer for each of the two mixtures? Write equations, if any, for the reactions in the two mixtures.

Aqueous bromine + aqueous potassium iodide

Aqueous bromine + aqueous potassium chloride

2 AJC/2010/P3/Q1(a) Level of Difficulty: [☆]

(i) Write an equation for the reaction between chlorine and hydrogen.

(ii) Describe and explain the trend observed in the reactions of the elements chlorine, bromine and iodine with hydrogen.

[3]

3 HCI/2010/P3/Q3(b), (c) & (d) Level of Difficulty: [☆]

Describe what you would see when a red-hot rod is plunged into separate jars containing HC*l* gas and HI gas. Account for the observations using appropriate data from the *Data Booklet*.

[2]

16 YJC/2010/P3/Q4(c) Level of Difficulty: [☆]

Describe and explain the difference seen when a hot glass rod is placed in two separate cylinders, one containing hydrogen chloride and the other containing hydrogen iodide.

[2]

Suggested Answers

1 ACJC/2010/P2/Q4 Level of Difficulty: [☆]

$4Br_2 + S_2O_3^{2-} + 5H_2O \longrightarrow 8Br^- + 2SO_4^{2-} + 10H^+$

Off white/ beige ppt formed,
with aq ammonia, the amount of ppt became less, leaving a cream ppt.

$Ag(NH_3)_2^+$

Aqueous bromine + aqueous potassium iodide

Colour: **Purple**

Equation: $Br_2(aq) + 2KI(aq) \longrightarrow 2KBr(aq) + I_2(aq)$

(or ionic equation)

Aqueous bromine + aqueous potassium chloride

Colour: **Orange**
No oxidation, colour is due to B

2 AJC/2010/P3/Q1(a) Level of Difficulty: [☆]

(a)(i) $Cl_2 + H_2 \rightarrow 2HCl$

(a)(ii) Cl_2 and H_2 explodes in the presence of light.
Br_2 and H_2 needs heating and a catalyst.
I_2 and H_2 needs heating and react only partially/ reaction is reversible.

Reactivity with H_2: $Cl_2 > Br_2 > I_2$
as H–X bond becomes weaker down the group.

3 HCI/2010/P3/Q3(b), (c) & (d) Level of Difficulty: [☆]

(b) HCl: no visible reaction
HI: violet fumes of I_2 observed.

H-X bond energy / kJ mol^{-1} : H-Cl (431); H-I (299).
The bond strength of H-Cl is greater than H-I.
OR Thermal stability of HCl is greater than HI.

(c) **(i)** Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e$
Cathode: $2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

(ii) $Q = I \times t = 5 \times 7 \times 60 \times 60 = 1.26 \times 10^5$ C
$Q = n_e \times F$

No. of moles of electrons passed = $\frac{1.26 \times 10^5}{96500}$ = 1.306 mol

No. of moles of chlorine = $\frac{1.306}{2}$ = 0.6529 mol

Mass of chlorine produced = 0.6529 x 2 x 35.5 = 46.4 g

(iii) $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36V$ -----(1)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.23V$

When dilute sodium chloride is used, the $E^\ominus(O_2/H_2O)$ is less positive than $E^\ominus(Cl_2/Cl^-)$ and H_2O is preferentially oxidised at the anode to give O_2 gas.

(d) **(i)** Disproportionation

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

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

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

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

4 MI/2010/P2/Q5 Level of Difficulty: [☆]

$F_2 + 2e \rightleftharpoons 2F^-$ $E^\ominus = +2.87V$
$Cl_2 + 2e \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36V$;

Cl_2 is a weaker oxidising agent compared to F_2 and hence has a lesser tendency to oxidize water to produce osygen gas. ;

Does not have available orbitals of suitably low energy for expansion of octet configuration

Large amount of energy required to overcome the strong hydrogen bonds to separate the molecules ;

Large amount of energy required to break the H – F bond. ;

$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$

$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$

5 MJC/2010/P2/Q3(c) Level of Difficulty: [✮]

(i) $4Br_2 + S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Br^-$

(ii) No. of moles of $S_2O_3^{2-}$ = 30/1000 x 0.100

= 0.00300 mol

$S_2O_3^{2-} \equiv 4Br_2 \equiv 6\ SiF_4$

No. of moles of SiF_4 = 6 x 0.003

= 0.018

Mass of SiF_4 = 0.018 x (28.1 +19.0 x 4)

= 1.9 g

(iii) Disproportionation

$3\ Br_2 + 6\ OH^- \rightarrow 5Br^- + BrO_3^- + 3\ H_2O$

6 NJC/2010/P3/Q4(b) Level of Difficulty: [✮]

(i) Thermal stability of hydrogen halide (HX) decreases down the Group. As size of the halogen atom increases down the Group, degree of orbital overlapping between the H and halogen atom decreases. Therefore, strength of H-X bond decreases and hence, less heat energy is required to break the H-X bond. This is evidenced from that fact that HCl shows little tendency to decompose to strong heating. HBr can be decomposed on strong heating, while HI will decompose and produce copious violet fumes of iodine vapour by introducing a red hot needle into a jar of HI.

(ii) $2\ ICl_3 + 3H_2O \rightarrow ICl$

7 NYJC/2010/P2/Q6 Level of Difficulty: [✯]

(i) From the reactions above, identify the halide in **X**.

Bromide or Br^- ❶

(ii) What is the colour of the precipitate formed with $AgNO_3(aq)$?

Cream ❶

(iii) Write balanced equations for the reaction of **X** with concentrated sulfuric acid.

$H_2SO_4 + NaBr \rightarrow HBr + NaHSO_4$ ❶

$H_2SO_4 + 2HBr \rightarrow SO_2 + 2H_2O + Br_2$ ❶

(iv) Identify the anion in **Y** and state the type of reaction that **Y** undergoes to produce the brown solution.

Anion in Y is iodide ❶

Type of reaction is redox or displacement reaction ❶

8 NYJC/2010/P3/Q1(a) Level of Difficulty: [✯]

$I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$

Cl_2 reacts explosively with hydrogen.
An equilibrium is established when I_2 reacts with hydrogen

H–Cl bond formed is the strongest hence HCl formed is very stable and readily formed. H–I bond formed is the weakest, thus when HI is formed, it readily decomposed. Hence the reaction between H_2 and I_2 is the slowest and reaches equilibrium.

9 PJC/2010/P3/Q2(b) Level of Difficulty: [✯]

(i) **$Br_2(aq) + 2NaAt(aq) \rightarrow 2NaBr(aq) + At_2(s)$**
Black solid astatine deposited

(ii) **$AgNO_3(aq) + NaAt(aq) \rightarrow AgAt(s) + NaNO_3(aq)$**
(Yellow) Solid AgAt would precipitate out and it is insoluble in excess aqueous ammonia

(iii) $\mathbf{NaAt(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HAt(g)}$

$\mathbf{2HAt(g) + H_2SO_4(l) \rightarrow At_2(s) + 2H_2O(l) + SO_2(g)}$

$\mathbf{8HAt(g) + H_2SO_4(l) \rightarrow 4At_2(s) + H_2S(g) + 4H_2O(l)}$

White fumes of HAt, black solid of At_2 and pungent gas of H_2S formed

10 RVHS/2010/P3/Q1(a) – (e) Level of Difficulty: [✯]

(a) Amount of $MnO_2 = \dfrac{1.00}{54.9 + 2 \times 16.0}$

$= 0.0115$ mol

Amount of $Cl_2 = \dfrac{276}{24000}$

$= 0.0115$ mol

Therefore $MnO_2 \equiv Cl_2 \equiv 2e^-$ $(2Cl^- \rightarrow Cl_2 + 2e^-)$

Oxidation number of Mn in Mn-containing product = +4 – 2 = +2

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

$MnO_2(s) + 2HCl(aq) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$

(b) **(i)** $I^-(s) + H_2SO_4(l) \rightarrow HSO_4^-(s) + HI(g)$

$8HI(g) + H_2SO_4(l) \rightarrow H_2S(g) + 4I_2(g) + 4H_2O(l)$

(ii) $Cl_2 + 2e^- = 2Cl^-$ $E^\ominus = +1.36$ V

$I_2 + 2e^- = 2I^-$ $E^\ominus = +0.54$ V

$E^\ominus(Cl_2/Cl^-)$ is more positive than $E^\ominus(I_2/I^-)$, hence Cl^- is less easily oxidised than I^-.

(c) $2Br^-(aq) + Cl_2(g) \rightarrow Br_2(aq) + 2Cl^-(aq)$

(d) $F_2 + 2e^- = 2F^-$ $E^\ominus(F_2/F^-) = +2.87$ V

Fluorine is the strongest oxidising agent (and is the most reactive halogen).

Electrolysis (of molten sodium fluoride).

(e) Cl_2: Reacts explosively in sunlight but slowly in the dark

Br_2: Reacts at above 200 °C over Pt catalyst

I_2: Reacts at 400 °C over Pt catalyst (to form an equilibrium mixture)

The reaction of H_2 with Cl_2 is more exothermic than with Br_2 which is in turn more exothermic than with I_2 as the H—Cl bond is stronger than the H—Br bond which is stronger than the H—I bond. Hence the reaction with Cl_2 requires the mildest conditions and the reaction with I_2 requires the harshest conditions.

11 SAJC/2010/P2/Q6(c) Level of Difficulty: [☆]

$AgX\ (s) \rightleftharpoons Ag^+\ (aq) + X^-\ (aq)$ ----- eqm 1 where X is Cl or I.

$Ag^+(aq) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)$

The formation of $[Ag(NH_3)_2]^+$ decreases $[Ag^+]$, causing equilibrium 1 to shift to the right.

For $AgCl$, ionic product decreases below its K_{sp} value and hence the white ppt dissolves.

For AgI, the K_{sp} is lower and ionic product remains above its K_{sp} value. Hence yellow ppt does not dissolve.

12 SRJC/2010/P3/Q4(c)(i) & (ii) & (d) Level of Difficulty: [☆]

Order of boiling point : HI > HBr > HCl

Down the group,

- Number of electrons of HX **increases**
- Intermolecular VDW forces of attraction becomes **more extensive**
- **Larger amount of energy** required to separate the molecules

Order of thermal stability : HCl > HBr > HI

Down the group,

- Covalent bond length of H-X **increases OR** Covalent bond strength **decreases**
- Bond dissociation energy **decreases**

From data booklet:

$Cl_2 + 2e \rightleftharpoons 2Cl^-$ +1.36 V
$Br_2 + 2e \rightleftharpoons 2Br^-$ +1.07 V
$I_2 + 2e \rightleftharpoons 2I^-$ +0.54 V

From $E^\ominus$ values, the values become less positive down the group for the oxidation of **halides**

Tendency for oxidation to occur: $I^- > Br^- > Cl^-$

Reducing power: KI > KBr > KCl

$KI\ (s) + H_2SO_4\ (l) \rightarrow KHSO_4\ (s) + HI\ (g)$

$2\ HI\ (g) + H_2SO_4(l) \rightarrow I_2\ (g) + 2H_2O\ (l) + SO_2\ (g)$

$6HI\ (g) + H_2SO_4\ (l) \rightarrow 3I_2\ (g) + 4H_2O\ (l) + S\ (s)$

$8HI\ (g) + H_2SO_4\ (l) \rightarrow 4I_2\ (g) + H_2S\ (g) + 4H_2O$

$2OH^- (aq) + Cl_2 (aq) \rightarrow Cl^- (aq) + ClO^- (aq) + H_2O (l)$
Or
$2 NaOH (aq) + Cl_2 (aq) \rightarrow NaCl (aq) + NaClO (aq) + H_2O (l)$

Disproportionation reaction

$6 OH^- (aq) + 3 Cl_2 (aq) \rightarrow 5 Cl^- (aq) + ClO_3^- (aq) + 3 H_2O (l)$
Or
$6NaOH (aq) + 3Cl_2 (g) \rightarrow 5NaCl (aq) + NaClO_3 (aq) + 3H_2O (l)$

13 TJC/2010/P2/Q3(a) & (b) Level of Difficulty: [☆]

- **Solubility of AgCl = $\sqrt{1.6 \times 10^{-10}}$ = 1.26×10^{-5} mol dm^{-3}**

- $$\begin{cases} AgCl \rightleftharpoons Ag^+ + Cl^- & \text{------ (1)} \quad K_{sp} = [Ag^+][Cl^-] \\ Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ & \text{------ (2)} \end{cases}$$

- **When NH_3(aq) is added, it react with Ag^+ to form a complex ion as shown in equilibrium (2), hence lowering the concentration of Ag^+ in solution.**

- **By LCP, the position of equilibrium (1) shifts right when the concentration of Ag^+ decrease, hence the solubility of AgCl increases.**

OR

The ionic product of AgCl, $[Ag^+][Cl^-]$, decreases to a value lower than its K_{sp} hence AgCl will dissolve.

- **Bond energy of H-Cl, H-Br and H-I are 431, 366 and 299 kJ mol^{-1} respectively.**
- **As seen from the data, the H-X bond energy decreases down the group resulting in a decrease in the strength of the H-X bond. Hence thermal stability of the hydrogen halides decreases down the group.**

14 VJC/2010/P3/Q4(a) & (b) Level of Difficulty: [☆]

4(a)(i)

	$S_2O_3^{2-}$	$\mathbf{X}^-$	SO_4^{2-}
No. of moles	0.0125	0.0500 x 2 = 0.100	0.0125 x 2 = 0.0250
Mole ratio	1	8	2

$4\mathbf{X}_2 + S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 8\mathbf{X}^- + 10H^+$

(ii)

$\mathbf{Y}_2 + 2S_2O_3^{2-} \rightarrow 2\mathbf{Y}^- + S_4O_6^{2-}$

(iii)

Change in oxidation number of S in **(a)(i)** (from +2 to +6) is greater than in **(a)(ii)** (from +2 to +2½).
$\mathbf{X}_2$ is a stronger oxidising agent than $\mathbf{Y}_2$.

(b)(i)

Add hot aqueous sodium hydroxide to aqueous chlorine

(ii)

Ethanedioic acid is a reducing agent in the reaction.
Oxidation state of chlorine decreased from +5 in ClO_3^- to +4 in ClO_2.

15 YJC/2010/P3/Q2(b) Level of Difficulty: [☆]

Reducing strength of the HCl < HBr < HI.
Hence HCl cannot reduce H_2SO_4. HBr and HI reduce H_2SO_4 , hence brown $Br_2(g)$ and violet $I_2(g)$ form respectively. HBr being weaker reducing agent than HI reduces H_2SO_4 to SO_2 while HI reduces H_2SO_4 to H_2S.
$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$
$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$
$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$

16 YJC/2010/P3/Q5(c) Level of Difficulty: [☆]

Cl has a smaller atomic radius than I. Bond energy of HI is smaller than HCl, thermal stability of HCl is greater than HI. Therefore with same amount of heat from hot glass rod, HI dissociates readily to form violet fumes but HCl remains unchanged.

TOPIC 9.4: AN INTRODUCTION TO THE CHEMISTRY OF TRANSITION ELEMENTS

1 ACJC/2010/P3/Q5(b) – (d) Level of Difficulty: [✯]

(b) Iron(III) chloride is a dark brown solid which dissolves in water to give an acidic solution. This solution is often used, in the electronics industry, to dissolve the copper used in printed circuit boards.

(i) Explain, with the aid of a chemical equation, why aqueous iron(III) chloride is acidic.

(ii) Use the *Data Booklet* to explain why aqueous iron(III) chloride etches (dissolves) copper. Give relevant chemical equations.

(iii) If aqueous iron(III) chloride is treated with zinc followed by aqueous ammonia, what product would you expect to be formed?

[5]

(c) **(i)** A student suggested that aqueous iron(III) iodide could be prepared by the reaction between aqueous iron(III) sulfate and aqueous barium iodide.

Use relevant $E^{\ominus}$ data from the *Data Booklet* to explain why no iron(III) iodide is formed when these two solutions are mixed, and predict what reaction is likely to occur.

(ii) Iron(III) iodide has been successfully made under non-aqueous conditions by following method.

Iron pentacarbonyl, $Fe(CO)_5$, is reacted with iodine in hexane solution. This forms a solution of compound **X**, whose molecular formula is $FeC_4O_4I_2$.

A further calculated amount of iodine is added, and the solution exposed to uv light. A black precipitate of iron(III) iodide results, and a colourless gas is evolved.

State the co-ordination number of iron in the complex, $Fe(CO)_5$ and hence predict the shape of the complex, $Fe(CO)_5$. Describe the bonding between iodine and iron in compound **X** and write a balanced equation for the reaction between compound **X** and iodine.

[6]

(d) When a solution of $NaOCl$ is added to a strongly alkaline suspension of Fe_2O_3, a purple solution results. When $BaCl_2(aq)$ is added, a red solid is precipitated with the composition: Ba, 53.4%; Fe, 21.7%; O,24.9% by mass.

(i) Calculate the empirical formula of the red solid, and hence determine the oxidation number of iron in the red solid.

(ii) Construct a balanced ionic equation for the reaction between Fe_2O_3, OCl^- and OH^-.
[3]

2 AJC/2010/P2/Q2(a) Level of Difficulty: [✯]

The Al_2O_3–Cr_2O_3 ceramic is a solid solution of oxides of aluminium and chromium used in incinerators as refractory materials due to the ability to withstand high temperatures.

(a) Both Al_2O_3 and Cr_2O_3 are amphoteric.

(i) Write an equation for the reaction of Cr_2O_3 with aqueous sodium hydroxide.

(i) Using the given expression and relevant information from the *Data Booklet*, determine the value of *E* when $[Fe^{2+}]$ and $[Fe^{3+}]$ are equal.

(ii) Estimate the volume of $KMnO_4$ added which corresponds to your value of *E* in (c)(i).

(iii) Explain why there is a rapid increase in the value of *E* between 80.0 cm^3 and 120 cm^3 of $KMnO_4$.

(iv) Suggest why it was necessary to maintain a constant $[H^+]$ in this experiment.
[4]

Suggested Answers

1 ACJC/2010/P3/Q5(b) – (d) Level of Difficulty: [☆]

$Fe^{3+}(aq)$ has high charge density and can undergo hydrolysis with water

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+} + H_3O^+$$

$Cu^{2+} + 2e \rightleftharpoons Cu$ $E^\theta = +0.34V$
$2Fe^{3+} + 2e \rightleftharpoons 2Fe^{2+}$ $E^\theta = +0.77V$

$2Fe^{3+} + Cu \longrightarrow Cu^{2+} + 2Fe^{2+}$ $E^\theta = +0.43V > 0$, reaction is Feasible

Green ppt of $Fe(OH)_2$

$I_2 + 2e \rightleftharpoons 2I^-$ $E^\theta = +0.0.54V$
$2Fe^{3+} + 2e \rightleftharpoons 2Fe^{2+}$ $E^\theta = +0.77V$

$2Fe^{3+} + 2I^- \longrightarrow I_2 + 2Fe^{2+}$ $E^\theta = +0.23V > 0$, reaction is feasible.

Fe^{3+} will oxidize I^- to I_2 while itself is reduced to Fe^{2+}

co-ordination number =5

shape –trigonal bipyramidal

bonding between iodine and iron-dative covalent bond/co-ordinate bond /dative bond

$$2FeC_4O_4I_2 + I_2 \longrightarrow 2FeI_3 + 8CO$$

	Ba	**Fe**	**O**
Mass/g	**53.4**	**21.7**	**24.9**
No of mol	**53.4/137**	**21.7/55.8**	**24.9/16**
	= 0.390	**=0.390**	**= 1.56**
simplest ratio	**1**	**1**	**4**

Empirical formula = $BaFeO_4$
oxidation number = +6

$Fe_2O_3 + 10OH^- \longrightarrow 2FeO_4^{2-} + 5H_2O + 6e$ oxidation
$OCl^- + H_2O + 2e \longrightarrow Cl^- + 2OH^-$ reduction

$$\mathbf{Fe_2O_3 + 3OCl^- + 4OH^- \longrightarrow 2FeO_4^{2-} + 3Cl^- + 2H_2O}$$

2 AJC/2010/P2/Q2(a) & (b) Level of Difficulty: [☆]

(a)(i) $Cr_2O_3 + 2OH^- + 3H_2O \rightarrow 2Cr(OH)_4^-$

(a)(ii)
- In the presence of ligands, the partially–filled 3d orbitals of Cr^{3+} are split into two levels.
- The energy gap is small and corresponds to the visible light region.
- Energy is absorbed from the visible region when an electron promotes from a lower energy d–orbital to a vacant higher energy d–orbital, i.e. d–d transition.
- Colour of Cr^{3+}(aq) is complement to the colour absorbed.
- Al^{3+}(aq) is colourless as the energy required for electronic transition from 2p to 3s is large and falls outside the visible light region.

(a)(iii)
$Cr^{3+} + 3e \rightleftharpoons Cr$ $E^\ominus = -0.74$ V
$Mn^{2+} + 2e \rightleftharpoons Mn$ $E^\ominus = -1.18$ V
$Al^{3+} + 3e \rightleftharpoons Al$ $E^\ominus = -1.66$ V

Mn can reduce Cr^{3+} as its $E^\ominus$ is more negative than –0.74V

Mn cannot reduce Al^{3+} as its $E^\ominus$ is less negative than –1.66V

(b) ΔH_{hyd} of Cr^{3+} is less exothermic / smaller in magnitude than that of Al^{3+}.

Cr^{3+} is larger / has a smaller charge density than Al^{3+},
thus forms weaker ion–dipole interaction with water molecules.

3 AJC/2010/P3/Q1(c) Level of Difficulty: [☆]

(c)(i) The halogen is bromine.

	Cr	H_2O	Br
% mass	13.0	27.0	60.0
Moles	0.25	1.5	0.75
Ratio	**1**	**6**	**3**

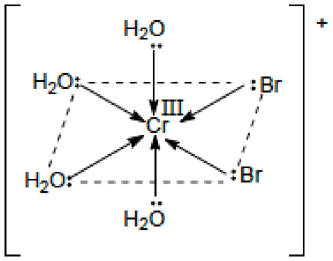
Empirical formula is **$Cr(H_2O)_6Br_3$**

(c)(ii) n(**A**) = 0.400 ÷ 399.7 = 0.001 mol
n(AgBr) = 0.188 ÷ 187.9 = 0.001 mol
1 mol of **A** contains 1 mol of free Br^- ion.

A is $[Cr(H_2O)_4Br_2]Br{\cdot}2H_2O$

(c)(iii) +3

(c)(iv)



4 AJC/2010/P3/Q3 Level of Difficulty: [☆]

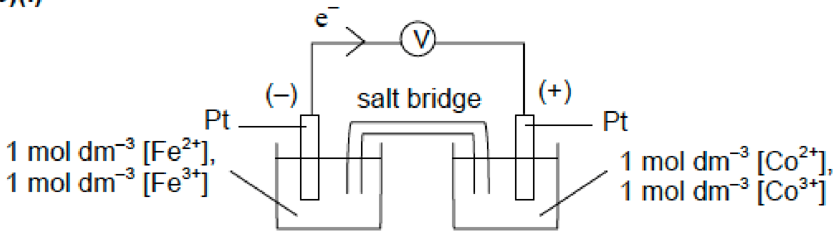
(a)(i) A transition element is a d–block element which forms one or more stable ions with incomplete d orbitals.

(a)(ii) $1s^22s^22p^63s^23p^63d^6$

(a)(iii) Pink solution turns purple, then blue.

Pink $[Co(H_2O)_6]^{2+}$ undergoes ligand exchange to form blue $[CoCl_4]^{2-}$.

(b)(i)



e.m.f. = (+1.82) – (+0.77) = **+1.05V**

(b)(ii) $E^\ominus(Fe^{3+}/Fe^{2+}) = +0.77V$
$E^\ominus(Fe(OH)_3/Fe(OH)_2) = -0.56V$

Addition of OH^- forms $Fe(OH)_2$ and $Fe(OH)_3$.
$E^\ominus$ value becomes more negative. Fe(II) is more easily oxidized.

(b)(iii) e.m.f. increases/ more positive than +1.05V.

(b)(iv) $4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + O_2 + 4H^+$

(b)(v) The reduction of Co(III) by water has a high activation energy / is slow.

(c) n(Co) plated = $\frac{8.00}{58.9}$

$Q = \frac{8.00}{58.9} \times 2 \times 96500 = 26214$ C

Time needed = $\frac{26214}{5}$ = **5240 s** (= 87.3 min)

(d)(i) Bidentate

(d)(ii) Six

(d)(iii) Excess NH_3 in ethanol, heat in sealed tube

(e)(i) Transition metals are able to exist in variable oxidation states.

(e)(ii) Step 1: $2Co^{3+} + 2I^- \rightarrow 2Co^{2+} + I_2$

Step 2: $2Co^{2+} + S_2O_8^{2-} \rightarrow 2Co^{3+} + 2SO_4^{2-}$

5 CJC/2010/P2/Q4(a) Level of Difficulty: [☆]

Ag $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ $4d^{10}\ 5s^1$.

A : AgI..............................

B : Cu........................

C : $CuSO_4$ or $[Cu(H_2O)_6]\ SO_4$

D : CuI ....

E : I_2 / KI_3........................

6 CJC/2010/P3/Q3 Level of Difficulty: [☆]

When ligands are attached to the centre metal ion, they will cause the degenerate d-orbitals to **split into 2 energy levels**.
The d orbitals are **partially filled**. When electron from the lower d-orbitals **absorbs energy in the visible light** region, it will be **excited** to the higher d* orbital. Such transition is **d-d* electronic transition**.
Complementary colours which are not absorbed will the reflected as the colour of the compound.

(I) 'red water'

$E_{Fe^{3+}/Fe^{2+}}$ will increase / more positive
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
Addition of red water will increase $[Fe^{3+}]$.
By LCP, position of equilibrium will shift to the right or more $[Fe^{2+}]$ is produced.

(II) pure water

$E_{Fe^{3+}/Fe^{2+}}$ will not change

Addition of pure water will decrease $[Fe^{3+}]$ and $[Fe^{2+}]$ to the same extent

(I) When 'red water' is added to aqueous KI, the solution turns brown.

$E^\ominus_{I_2/I^-} = +0.54$ V

$E^\ominus = 0.77 - 0.54 > 0$ or $E^\ominus_{Fe^{3+}/Fe^{2+}}$ is more positive than $E^\ominus_{I_2/I^-}$ or I^- is oxidized by Fe^{3+} to I_2

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

(II) When 'red water' is first added to aqueous KCN, a ligand replacement reaction takes place and an orange solution is formed. Upon the addition of aqueous KI, the orange solution remains.

$$[Fe(H_2O)_6]^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-} + 6H_2O$$

$E^\ominus = 0.36 - 0.54 < 0$

or $E^\ominus_{[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}}$ is less positive than $E^\ominus_{I_2/I^-}$

or I^- is a weaker ligand than CN^-, ligand replacement cannot occur

$E^\ominus = 0.77 - (-0.49) = 1.26 > 0$ Reaction is spontaneous/feasible

$2Fe^{3+} + C_2O_4^{2-} \rightarrow 2CO_2 + 2Fe^{2+}$

Ethanedioic acid is a weak acid; partial dissociation of ethanedioic acid provides less $[C_2O_4^{2-}]$.

$E^\ominus_{O_2/H_2O_2} = +0.68$ V

$E^\ominus = 0.77 - (0.68) = 0.09$

$E^\ominus$ value is small; reaction will not go to completion, not effective

Amt of AgCl = 4.30 / (108 + 35.5) = 0.0300 mol

Structural formula: $[Fe(H_2O)_6]Cl_3$

Amt of AgCl = 1.44 / (108 + 35.5) = 0.0100 mol

Structural formula: $[Fe(H_2O)_4Cl_2]Cl$

7 HCI/2010/P2/Q4 Level of Difficulty: [☆]

4(a) $Cr(s) + 3H^+(aq) \rightarrow Cr^{3+}(aq) + 3/2H_2(g)$
OR Combustion: $2Cr(s) + 3/2O_2(g) \rightarrow Cr_2O_3(s)$

4(b)(i) $[CrCl(H_2O)_5]Cl_2.H_2O$
$[Cr(H_2O)_6]Cl_3$
$[CrCl_3(H_2O)_3].3H_2O$

4(b)(ii) A solution of Cr^{3+} is acidic in nature due to the high charge density of the cation.
$[Cr(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Cr(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

4(b)(iii) chromium(III) hydroxide OR $Cr(OH)_3$ OR $[Cr(OH)_3(H_2O)_3]$

4(b)(iv) $[Cr(NH_3)_6]^{3+}$

4(b)(v) Ligand exchange has occurred. Different ligands cause different energy gaps, which correspond to different wavelengths of visible light being absorbed. Hence different colours are observed.

4(c)

1st colour change: $Cr_2O_7^{2-}$ (orange) → Cr^{3+} (green) $E^\ominus = +1.33 - (-0.76) = +2.09$ V
2nd colour change: Cr^{3+} (green) → Cr^{2+} (blue) $E^\ominus = -0.41 - (-0.76) = +0.35$ V
3rd colour change: Cr^{2+} (blue) → Cr^{3+} (green) (oxidation by air in acidic medium)
$E^\ominus = +1.23 - (-0.41) = +1.64$ V
OR Cr^{2+} (blue) → Cr^{3+} (green) (oxidation by H^+ in absence of air)
$E^\ominus = +0.00 - (-0.41) = +0.41$ V

8 MI/2010/P3/Q1(b) Level of Difficulty: [☆]

$Cu_2O_5CH_2$ / $CuCO_3 \bullet Cu(OH)_2$

D is CuO / copper(II) oxide ;

$Cu_2O_5CH_2 \rightarrow 2CuO + CO_2 + H_2O$

$$Amount\ of\ malachite = \frac{10}{2 \times 63.5 + 5 \times 16.0 + 12.0 + 2 \times 1.0} = 0.04525\ mol$$

$$Amount\ of\ D = 2 \times 0.04525 = 0.09050\ mol$$

$$Mass\ of\ D = 0.09050 \times (63.5 + 16.0) = 7.19\ g$$

E is copper; F is Fe^{2+} / $FeSO_4$

$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

blue ppt./solid formed

dissolves in excess NH_3 to give dark blue colour

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

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

9 MI/2010/P3/Q5(a) – (f) Level of Difficulty: [☆]

$x = +4$, $y = +5$

∵ of the similarity in energy level between 3d and 4s.
Hence a variable number of electrons can be removed.

$V^{2+} + Fe^{3+} \rightarrow V^{3+} + Fe^{2+}$

Reduction:	$Fe^{3+} + e \rightarrow Fe^{2+}$	+0.77	
Oxidation:	$V^{2+} + 2H_2O \rightarrow VO^{2+} + 2H^+ + 2e$	–0.08	;
Overall:	$2Fe^{3+} + V^{2+} + 2H_2O \rightarrow VO^{2+} + 2H^+ + 2Fe^{2+}$	+0.69V	;

Since $E^{\theta}_{cell} > 0$, V^{2+} should be oxidised to deep blue VO^{2+}.

However,
due to the low pH, i.e. high concentration of $[H^+]$, resulting in the shifting of the eqm position of the oxidation process to the left, i.e. the
$E^{\theta}\left(\frac{V^{2+}}{VO^{2+}}\right)$ becomes less positive ;
∴ E^{θ}_{cell} becomes less positive and oxidation process stops at the formation of V^{3+}.

Reduction:	$O_2 + 2H_2O + 4e \rightarrow 4OH^-$	+0.40
Oxidation:	$V^{2+} \rightarrow V^{3+} + e$	+0.26
Overall:	$O_2 + 2H_2O + 4V^{2+} \rightarrow 4V^{3+} + 4OH^-$	+0.66V

∴ V^{2+} is oxidised to V^{3+} by oxygen in air.

Fe^{3+} has a partially filled d subshell. ;
When SCN– ligand approaches Fe^{3+}, the d subshell splits into 2 sets of orbitals of different energy level. ;
When light is shone on it, energy is absorbed to promote an electron from the d orbitals of lower energy to those of higher energy. Part of the electromagnetic spectrum that is not absorbed is then reflected as the colour of the compound. ;

Due to mutual repulsion between V^{2+} and H^+, since both are positively charged

10 MJC/2010/P3/Q3(d) & (e) Level of Difficulty: [☆]

(d) **(i)** For $Fe^{3+}(aq)$, in the presence of the H_2O ligands, the d orbitals are split into two groups. This effect is known as d orbital splitting. The d electrons undergoes d-d transition and are promoted to the higher d orbital.

During the d-d transition, the d electron absorbs a certain wavelength of light from the visible region of the electromagnetic spectrum and emits the remaining wavelength which appears as the colour of the complex observed.

For $Sc^{3+}(aq)$, there are no d electrons hence there is no d-d transition.

(ii) The brown solution is (aqueous) I_2

For solution of pH = 1, reaction between Fe^{3+} and I_2

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\theta = +0.77V$ (reduction)

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\theta = +0.54V$ (oxidation)

$E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid}$

$E^\theta_{cell} = +0.77 - (+0.54) = +0.23$ V (> 0 feasible)

For solution of pH = 10, reaction between $Fe(OH)_3$ and I_2

$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2$ $E^\theta = -0.56V$ (reduction)

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\theta = +0.54V$ (oxidation)

$E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid}$

$E^\theta_{cell} = -0.56 - (+0.54) = -1.10$ V (< 0 not feasible)

Brown solution of I_2 is not formed.

(e) When dilute ammonia is added gradually,

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

A pale blue precipitate of $Cu(OH)_2$ is formed.

In excess ammonia,

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

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

As $[Cu(H_2O)_6]^{2+}$ is decreased, equilibrium position for Eqn (1) shifts to the left. Hence, ionic product $Cu(OH)_2$ will decrease to the extent that it is less than K_{sp} of $Cu(OH)_2$. Pale-blue precipitate of $Cu(OH)_2$ dissolves.

11 NJC/2010/P2/Q2 Level of Difficulty: [☆]

2 (a)	Cr [Ar] ↑ ↑ ↑ ↑ ↑ ↑ Cr in $[Cr(NH_3)_6]^{3+}$ [Ar] ↑ ↑ ↑
(b) (i)	Chromium had more number of protons which contribute to a greater actual nuclear charge. D-electrons are poor screeners and thus the shielding effect of chromium and potassium are similar. Therefore, chromium will have a higher effective nuclear charge which make the removal of the electron harder and it will require a higher first IE.
(b) (ii)	Chromium contribute more valence electron per atom (3d + 4s electrons) as compared to potassium which contribute only 4s electrons. Cr ion has higher charge density due to its high charge and smaller cationic radius Therefore, stronger electrostatic forces of attraction between Cr ions and the sea of electrons.

(c) (i)	$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$
(c) (ii)	74.4 tons
(d) (i)	$E^o_{cell} = +0.65V$ Orange solution turns green with effervescence
(d) (ii)	$E^o_{cell} = +1.37V$ Grey green solution turns yellow

12 NJC/2010/P3/Q2(c) Level of Difficulty: [☆]

2 (c) (i) **B** = $Mg(OH)_2$

D = $CuCl_4^{2-}$

2 (c) (ii) Aqueous Cu^{2+} has 5 degenerate d-orbitals.
H_2O ligands approach Cu^{2+} along the axis and split it up into 2 different energy levels..
Since Cu^{2+} have partially filled d-orbitals, electrons in the lower energy d-orbital will absorb light of a certain wavelength and get promoted to a higher energy d-orbital.
Blue colour is complementary of the wavelength absorbed.

2 (c) (iii) In **A** the ligands present is H_2O; In **C** the ligands present is NH_3
Different ligands split the d-orbitals to different extent, i.e. ΔE is different. Hence different wavelength is absorbed and therefore different colour is seen.

13 NYJC/2010/P2/Q8(a) Level of Difficulty: [☆]

		$E^\ominus$/V
$Cr^{3+}(aq) + e^-$ □	$Cr^{2+}(aq)$	-0.41
$Cr^{2+}(aq) + 2e^-$ □	$Cr(s)$	-0.91

[1]

Using the correct half equations:
Overall reaction equation: $Cr(s) + 2Cr^{3+}(aq) \rightarrow 3Cr^{2+}(aq)$
$E^\ominus_{cell} = -0.41 - (-0.91) = +0.50\ V > 0$; reaction is feasible. [1]

Green solution of Cr^{3+} turns blue due to the formation of Cr^{2+}. (Effervescence is also observed.) [1]

Any of the following: Fe^{2+}, Cr^{2+}, V^{2+}, VO^{2+} [1]

14 NYJC/2010/P3/Q3(b) Level of Difficulty: [☆]

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77\ V$
$I_2 + 2e \rightleftharpoons 2I^-$ $E^\ominus = +0.54\ V$
$E^\ominus_{cell} = +0.77 - (+0.54) = 0.23\ V$ [1]

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

Hence the solution turns brown due to the formation of aqueous iodine. [1]

Ligand exchange occurs. [1] **for stating.**

CN^- ligands displace water ligands from, Fe^{3+} to form the more stable complex $[Fe(CN)_6]^{3-}$ which is orange-red in solution.

- $[Fe(H_2O)_6]^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-} + 6H_2O$
  Brown orange-red

- $I_2 + 2e \rightleftharpoons 2I^-$ $E^\ominus = +0.54\ V$
  $[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^\ominus = +0.36\ V$

  $E^\ominus_{cell} = +0.36 - (+0.54) < 0$ [1]

- Since the $E^\ominus_{cell} < 0$, $[Fe(CN)_6]^{3-}$ will not be able to oxidise I^-. Hence the solution remains orange-red.

15 PJC/2010/P3/Q4(a) – (c) Level of Difficulty: [☆]

(a) **(i)** Melting points of transition metals are higher than that of calcium. (This is due to stronger metallic bond formed between the transition metal cations and the 'sea of delocalised electrons' compared to calcium metal.)

Transition metals have higher density than *s*-block elements (because transition metals have close-packed structures and relatively smaller atomic radii.)

(ii)

sub-atomic particles	number	relative charge	location
protons	27	+1	in nucleus
neutrons	32	0	in nucleus
electrons	27	-1	in orbitals / outside the nucleus

(iii) Calcium can only form a +2 oxidation state because there is a huge energy difference from the 2nd ionisation energy of calcium to the 3rd ionisation energy of Ca or any subsequent removal from the inner shell 3p electrons, which is closer to nucleus, would require more energy to remove. Co can form variable oxidations due to small energy difference between 3d and 4s orbital.

(b) **(i)** Let mass be 100 g.

Element:	Co	N	H	C*l*
Mass / g	25.2	24.0	5.1	45.7
Amt / mol	0.428	1.71	5.1	1.29
Mole ratio	1	4	12	3

Empirical formula is $CoN_4H_{12}Cl_3$.

6

(ii) Amount of AgC*l* precipitated = 9.97×10^{-3} mol

(iii) No. of free Cl^- ion from X that reacted with Ag^+ ions = $9.97 \times 10^{-3} / 0.01$
= 0.997 ≈ 1

There are 4 NH_3 and 2 Cl^- ligands surrounding the cobalt ion.

Structural formula is $[Co(NH_3)_4Cl_2]^+ Cl^-$. (reject $[Co(NH_3)_4Cl_2]^+$)

(iv) Oxidation state of Co = +3

(c)
- Blue ppt formed is $Co(OH)_2$.
  $Co^{2+}(aq) + 2OH^-(aq) \quad Co(OH)_2(s)$
- On adding excess $NH_3(aq)$, pink $[Co(H_2O)_6]^{2+}$ undergoes ligand exchange to form a soluble complex $[Co(NH_3)_6]^{2+}$, which accounts for the pale brown solution.

- **$[Co(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_6]^{3+} + e^-$ $E^{\ominus} = -0.11$ V**
  $\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$ $E^{\ominus} = +0.40$ V

  $2[Co(NH_3)_6]^{2+} + \frac{1}{2}O_2 + H_2O \rightarrow 2[Co(NH_3)_6]^{3+} + 2OH^-$
  $E^{\ominus}_{cell} = +0.40 - 0.11 = +0.29$ V > 0, reaction is energetically feasible

16 RVHS/2010/P2/Q2(c) & (d) Level of Difficulty: [✩]

(c) $E^{\ominus}(Fe^{2+}(aq)/Fe(s)) = -0.44$ V

$E^{\ominus}(Cu^{2+}(aq)/Cu(s)) = +0.34$ V

$E^{\ominus}(Cu^{2+}(aq)/Cu(s))$ is more positive than $E^{\ominus}(Fe^{2+}(aq)/Fe(s))$, hence Cu^{2+} is preferentially reduced over Fe^{2+}.

(d) **(i)** Al^{3+}, Pb^{2+}

(ii) Any one of the following:

- Add any soluble chloride or sulfate (e.g. HC*l*, H_2SO_4) to the filtrate. The formation of a white ppt indicates presence of Pb^{2+}(aq), while Al^{3+}(aq) does not give any ppt.
- Add any soluble carbonate (e.g. Na_2CO_3) to the filtrate. The formation of a white ppt with effervescence (of colourless odourless gas which gives a white ppt with limewater) indicates presence of Al^{3+}(aq), while Pb^{2+}(aq) gives a white ppt only. (Recall that a solution of Al^{3+} is acidic due to hydrolysis.)
- Add any soluble chromate(VI) (e.g. K_2CrO_4) to the filtrate. The formation of a yellow ppt indicates presence of Pb^{2+}(aq), while Al^{3+}(aq) turns the yellow solution of chromate(VI) to orange.
- Add any soluble iodide (e.g. KI) to the filtrate. The formation of a yellow ppt indicates presence of Pb^{2+}(aq), while Al^{3+}(aq) does not give any ppt.

17 RVHS/2010/P3/Q5 Level of Difficulty: [✩]

(a) A transition element is a *d*-block element which forms at least one stable (simple) ion with a partially-filled *d*-subshell.

(b) Cu^{2+} contains partially filled 3*d* orbitals (electronic configuration $1s^22s^22p^63s^23p^63d^9$). In the presence of ligands in the hydrated ion, the 3*d* orbitals are split into 2 sets of non-degenerate orbitals (or orbitals with different energies). The difference in energy (ΔE) between the 2 sets of 3*d* orbitals is small and radiation from the visible region of the electromagnetic spectrum is absorbed when an electron moves from a lower energy *d*-orbital to a partially-filled *d* orbital of higher energy. The colour observed corresponds to the complement of the absorbed colours. Hence, the hydrated copper(II) ion is coloured.

Cu^+ contains completely filled 3*d* orbitals (electronic configuration $1s^22s^22p^63s^23p^63d^{10}$) and *d-d* electronic transition cannot occur. Hence, Cu_2SO_4 is colourless.

(c) White solid dissolves to give a blue solution and a pink/reddish brown solid.

Cu$^+$ undergoes disproportionation to give Cu^{2+} and Cu.

$Cu^+ + e^- = Cu$ $E^{\ominus} = +0.52$ V

$Cu^{2+} + e^- = Cu^+$ $E^{\ominus} = +0.15$ V

$2Cu^+ \rightarrow Cu^{2+} + Cu$ *or* $Cu_2SO_4 \rightarrow CuSO_4 + Cu$

$E^{\ominus}_{cell} = +0.52 - (+0.15) = +0.37$ V > 0 V (energetically feasible)

(d) $Cu^{2+} + 2e^- = Cu$ $E^{\ominus} = +0.34$ V

$VO_3^- + 4H^+ + e^- = VO^{2+} + 2H_2O$ $E^{\ominus} = +1.00$ V

$Cu(s) + 2VO_3^-(aq) + 8H^+(aq) \rightarrow Cu^{2+}(aq) + 2VO^{2+}(aq) + 4H_2O(l)$

$E^{\ominus}_{cell} = +1.00 - (+0.34) = +0.66$ V > 0 V (energetically feasible)

$VO^{2+} + 2H^+ + e^- = V^{3+} + H_2O$ $E^{\ominus} = +0.34$ V

$Cu(s) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$

$E^{\ominus}_{cell} = +0.34 - (+0.34) = 0$ V (in equilibrium)

A blue-green solution (of blue VO^{2+} and green V^{3+} in equilibrium) will be obtained.

(e) **(i)** Repulsion between the two negatively charged reactants causes the reaction to have a high activation energy.

(ii) $Cu^{2+}(aq)$ acts as a homogeneous catalyst.

(iii) The *EDTA* ligand forms a stable complex with Cu^{2+} and therefore removing the Cu^{2+} catalyst.

(f) **(i)** aliphatic aldehyde

(ii) $2Cu^{2+}(aq) + 2OH^-(aq) + 2e^- \rightarrow Cu_2O(s) + H_2O(l)$

(g) **(i)** Blue solution turns brown (with black ppt) and cream ppt formed.

$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(s/aq)$

(ii) Amount of $S_2O_3^{2-}$ needed $= 0.100 \times \dfrac{15.8}{1000}$

$= 0.00158$ mol

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ $(2S_2O_3^{2-} \equiv I_2)$

$$\text{Amount of } I_2 \text{ produced} = \frac{0.00158}{2}$$
$$= 0.000790 \text{ mol}$$

$2Cu^{2+} \equiv I_2$

$$\text{Amount of Cu in sample} = 2 \times 0.000790$$
$$= 0.00158 \text{ mol}$$

$$\text{Mass of Cu in sample} = 0.00158 \times 63.5$$
$$= 0.100 \text{ g}$$

$$\text{\% by mass of Cu in sample} = \frac{0.100}{2.0} \times 100\%$$
$$= 5.00\%$$

18 SAJC/2010/P2/Q2(b) Level of Difficulty: [☆]

(i) Transition metals have degenerate partially filled 3d orbitals which split into two groups with a small energy gap. When electrons promote from lower to higher energy level, radiation from visible light spectrum is absorbed.

Light not absorbed is reflected and seen as the colour.

Tin compounds have fully occupied 4d orbitals, so no d-d transition can occur.

(ii) $E^o(Co^{3+}/Co^{2+}) = +1.82$ V; $E^o(I_2/I^-) = +0.54$ V ;

$E^o(S_2O_8^{2-}/SO_4^{2-}) = +2.01$ V

$2Co^{3+} + 2I^- \rightarrow 2Co^{2+} + I_2$ $E^o = +1.28$V

$2Co^{2+} + S_2O_8^{2-} \rightarrow 2Co^{3+} + 2SO_4^{2-}$ $E^o = +0.19$V

Co^{3+} can exist in variable oxidation states and act as homogenous catalyst by lowering the activation energy in a reaction involving two negatively charged ions.

19 SAJC/2010/P3/Q5(c) & (d) Level of Difficulty: [☆]

(c) Any 2:

- More dense due to larger atomic mass and/or smaller radius.
- Hard and strong or higher melting point due to more delocalised electrons contributed from 3d and 4s subshells, resulting in stronger metallic bonding.
- 1st & 2nd I.E. relatively constant / increases minimally as electrons are added into the inner 3d subshell, resulting in increase in shielding effect canceling the increase in nuclear charge and hence insignificant increase in effective nuclear charge.

(c) Any 2:

- More dense due to larger atomic mass and/or smaller radius.
- Hard and strong or higher melting point due to more delocalised electrons contributed from 3d and 4s subshells, resulting in stronger metallic bonding.
- 1st & 2nd I.E. relatively constant / increases minimally as electrons are added into the inner 3d subshell, resulting in increase in shielding effect canceling the increase in nuclear charge and hence insignificant increase in effective nuclear charge.

(d) (i) $2MnO_2(s) + 4OH^-(aq) + O_2(g) \rightarrow 2MnO_4^{2-}(aq) + 2H_2O(l)$

(ii) $3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(l)$

Disproportionation reaction has taken place.

Mn(VI) is oxidised to Mn(VII) and reduced to Mn(IV) at the same time.

(iii) Because of the close similarity in energy of the 4s and 3d electron in Mn, it is able to lose all of the electrons in the 3d and 4s subshells, hence it can exhibit variable oxidation states.

(iv) $MnO_2(s)$ is a heterogeneous catalyst.

It works by providing a surface onto which H_2O_2 molecules are adsorbed and from which oxygen and water are desorbed.

The availability of 3d and 4s electrons allows the ready exchange of electrons between the MnO_2 catalyst and the H_2O_2 to form weak bonds, weakening the bonds in H_2O_2 and hence lowering the activation energy for the decomposition process.

20 SRJC/2010/P3/Q1(d) & (e) Level of Difficulty: [☆]

2 **negatively charged ions** ($S_2O_8^{2-}$ and $[CH(OH)(CO_2^-)]_2$) are involved which is highly unfavourable due to electrostatic **repulsion**.

Co^{3+} serve as a homogeneous catalyst due to Co ability to exist in variable oxidation state. Sc can only exists in Sc^{3+} thus it is unable to function as a catalyst.

Step 1: $[CH(OH)(CO_2^-)]_2$ reacts with Co^{3+}

$[CH(OH)(CO_2^-)]_2$ is oxidised to CO_2 and $2HCO_2^-$
Co^{3+} is reduced to Co^{2+}
$6Co^{3+} + [CH(OH)(CO_2^-)]_2 + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6\,Co^{2+}$
E^θ_{cell} of above reaction = +1.82– (+ 1.02) = + 0.8 V
E^θ_{cell} >0, reaction is **feasible**.

Step 2: Regenerate the Co^{3+} catalyst
Co^{2+} is oxidised to Co^{3+}
$S_2O_8^{2-}$ is reduced to $2SO_4^{2-}$
$2\,Co^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + 2\,Co^{3+}(aq)$
E^θ_{cell} = +2.01 – (+ 1.82) = + 0.19 V
E^θ_{cell} >0, reaction is **feasible**.

❶When NH_3 is first added to Cu^{2+} (aq):
($NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$) optional to write
$Cu^{2+}(aq) + 2\,OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ --- (1)
blue ppt

- Ionic product, $[Cu^{2+}][OH^-]^2 > K_{sp}$ of $Cu(OH)_2$
- Blue ppt of $Cu(OH)_2$ is formed.

❷When excess NH_3 is added to Cu^{2+} (aq):
$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+}(aq) + 4H_2O(l)$ --- (2)

☑ NH_3 ligands replaces the H_2O ligands, forming a more stable deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex with Cu^{2+}(aq).
☑ $[Cu^{2+}]$ decreases as it is being used to form the complex
☑ equilibrium position in (1) shifts left to increase $[Cu^{2+}]$
☑ Pale blue ppt ,$Cu(OH)_2$, dissolves.

The **d orbitals are split into two groups** due to the ability of the ligands to split them into 2 different energy levels.

The **d electron** undergoes **d-d transition** and is **promoted to a higher energy d orbital**

The d electron **absorbs certain wavelength of light energy** from the visible region of the electromagnetic spectrum and **transmits the remaining wavelength** which appears as the **colour observed**.

22 TJC/2010/P2/Q5(a)(iv) & (v) Level of Difficulty: [☆]

- **Firstly, it is due to the high charge density and hence high polarizing power of the cation which produces a strong tendency towards dative bond (covalent bond) formation with ligands.**

- **Secondly, it is due to the availability of low lying vacant 3d orbitals in the cation to accommodate the lone pair of electron from the ligands resulting in dative bond formation.**

- $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77\ V$
  $[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^\ominus = +0.36\ V$
- **In the presence of cyanide ions, the electrode potential becomes less positive implying that the Fe(III) oxidation state is less likely to be reduced to the Fe(II) oxidation state hence the +3 oxidation state is more stable.**

23 TJC/2010/P3/Q3 Level of Difficulty: [☆]

(a) **(i)**
- Transition elements are d-block elements which form at least one ion with a partially filled d subshell.

(ii)
- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

(iii)
- +2, +3 & +6

(b) **(i)**
- The N and O atom can each donate a lone pair of electrons to Cr^{3+} ion.
- Dative /coordinate bond

(ii)
- 6 & Octahedral

(c) **(i)**
- Red /Orange

(ii)
- For chromium complex, the chromium ion has **partially filled 3d orbitals**.
- In the presence of ligands, **the five 3d orbitals are no longer degenerate and split into two energy levels** due to the repulsion of the metal ion and the ligands.

  When an **electron is promoted from lower energy d orbital to higher energy (d-d transition)**, an amount of energy has to be absorbed in the visible region of the electromagnetic spectrum. The colour observed is complement to the light absorbed.

(d)
- It is produced in the body/so it should not be toxic/stable

(e) **(i)**
- $6CrO_2 + 10H^+ \rightarrow 4Cr^{3+} + Cr_2O_7^{2-} + 5H_2O$
- $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

(ii)

No of moles of Fe^{2+} = 10.0 x 0.02/1000 = 2.00 x 10^{-4}

$Cr_2O_7^{2-} \equiv 6Fe^{2+} \equiv 6CrO_2$

No of moles of CrO_2 = 2.00 x 10^{-4}

Mass of CrO_2 = 2.00 x 10^{-4} x 84 = 1.68 x 10^{-2} g.

[working:1 mark, answer:1 mark, ECF if correct calculations is done based on wrong equations written in (e)(i)]

(f) (i)
- $N_2(g)$ and $H_2O(g)$
- $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$

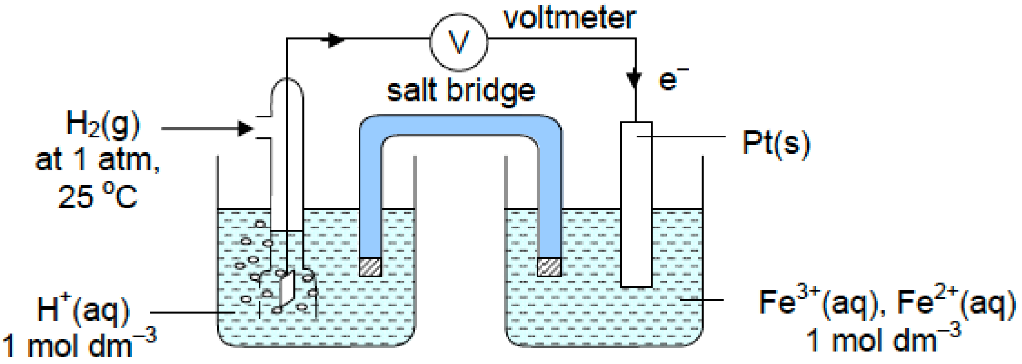
[Oxid no: N(-3) Cr(+6) Cr(+3) N(0)]

(Gases formed are colourless and odourless, so they cannot be NH_3 or NO_2. Since oxidation state of Cr decreased from +6 to +3, oxidation state of the other element must have increased. In the reactant, H has O.S. of +1 and cannot be oxidised further. Hence, N could have been oxidised from -3 to 0 oxidation state, forming N_2. The other gas formed is H_2O.)

(ii)
- NH_3 gas evolved turns moist red litmus blue and orange dichromate(VI), $Cr_2O_7^{2-}$, solution turns yellow as chromate(VI), CrO_4^{2-} is formed.
- $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$
- $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

24 VJC/2010/P3/Q1(a) & (c) Level of Difficulty: [☆]

1(a)(i)



(ii)

$E^\ominus_{cell} = E^\ominus(Ag^+|Ag) - E^\ominus(Fe^{3+}|Fe^{2+}) = +0.80 - (+0.77) = +0.03\text{ V} > 0$

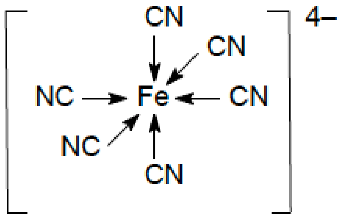
Since $E^\ominus_{cell} > 0$, reaction is thermodynamically feasible.

Ag^+ will oxidise Fe^{2+} to Fe^{3+}, itself reduced to Ag.

OR $Ag^+(aq) + Fe^{2+}(aq) \rightarrow Ag(s) + Fe^{3+}(aq)$

The solution changes from pale green to yellow with deposits of silver metal.

(iii)



Coordination number of iron is 6.

(iv)

$2[Fe(CN)_6]^{4-} + Cl_2 \rightarrow 2[Fe(CN)_6]^{3-} + 2Cl^-$

(c)(i)

Cobalt(II) salt is behaving as a catalyst.

(ii)

Any three of the following.
The rate of reaction between sodium tartrate and hydrogen peroxide in the absence of a catalyst is slow. Hence, only a slow stream of carbon dioxide is produced.
When cobalt(II) salt is added as catalyst, rate of reaction increases rapidly. Hence a vigorous effervescence of carbon dioxide occurs.
Cobalt(II) salt changes from pink to green colour which is the intermediate formed in the catalysed reaction.
When the reaction stops, pink colour is restored. Cobalt(II) salt is regenerated. Hence cobalt (II) serves as a catalyst.

25 YJC/2010/P3/Q1(d) Level of Difficulty: [☆]

di The close proximity in energy of 3d and 4s electrons allows iron to absorb similar amount of energy to form ions of roughly same stability by losing different number of electrons.

dii Fe^{2+} provides an alternative route with a lower activation energy as Fe^{2+} overcome the repulsion between the two negatively charged $S_2O_8^{2-}$ and I^-.

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ $E_{cell} = 2.01 - 0.77 = 1.24V$
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ $E_{cell} = 0.77 - 0.54 = 0.23V$

26 HCI/2010/P3/Q4(a) - (c) Level of Difficulty: [☆☆]

(a) **(i)** +3

(ii) Orange / red / yellow

(iii) In the presence of an octahedral ligand field, the degenerate <u>d-orbitals will split into two energy levels</u>.
In the partially filled d-orbitals (d^4) , <u>electrons are able to promote from the lower to the higher level</u> by absorbing energy in the visible spectrum (blue-green).
The colour shown is the complementary colour (orange-red or yellow).

(b) **(i)** SO_4^{2-}

[R] $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ $E^\ominus$ +1.52 V
[O] $SO_4^{2-} + 2H^+ + 2e \rightarrow SO_3^{2-} + H_2O$ $E^\ominus$ < +1.52 V

(ii) From the titration results,

$$\frac{n_{MnO_4^-}}{n_{SO_3^{2-}}} = \frac{25.0 \times 0.020}{12.5 \times 0.10} = 0.4 \text{ or } \frac{2}{5}$$

Each mol of MnO_4^- accepts 5 mol of electrons when reduced to Mn^{2+}.

This means 2 mol of MnO_4^- accepts 10 mol of e^- from 5 mol of SO_3^{2-};

or each SO_3^{2-} ion loses $\frac{10}{5} = 2$ electrons.

Hence oxidation state of S increases by 2 units from +4 (in SO_3^{2-}) to + 6 (in SO_4^{2-})

(c) **(i)** When $[Fe^{2+}] = [Fe^{3+}]$, $ln\frac{[Fe^{3+}]}{[Fe^{2+}]} = 0$.

Hence, $E = E^{\ominus}(Fe^{3+}/Fe^{2+}) = +0.77$ V.

(ii) Vol of $KMnO_4$ = 50.0 cm^3

(iii) The equivalence point is reached between 80 and 120 cm^3 (precisely at 100 cm^3). This means that the E value switches from a calculation based on Fe^{3+}/Fe^{2+} to one based on MnO_4^-/Mn^{2+}.

(iv) The *E* value of MnO_4^-/Mn^{2+} (and hence, the oxidizing power of MnO_4^-) is dependent on $[H^+]$;
or changes in $[H^+]$ affects the value of the measured *E*, because of
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$.

TOPIC 10.3: MECHANISMS AND REACTIONS

10.3.1 Hydrocarbons

1 ACJC/2010/P3/Q1(a),(d) Level of Difficulty: [☆]

Octane is commonly used as a fuel or a precursor in the production of other chemicals. The standard enthalpy change of combustion of octane produces 5470kJ of energy per mole of octane, hence it produces a large amount of energy for a small molecular mass hydrocarbon. Having a small molecular mass results in octane to have a lower boiling point as compared to the other fractions of crude oil, making it easier to be removed by fractional distillation as compared to hydrocarbons which have a larger number of carbon atoms. Hence, octane is a useful source of fuel for motor vehicles. One of the isomers of octane, 2,2,4-trimethylpentane (also known as isooctane), is a substance used for the octane-ratings of fuel.

(a) **(i)** State and explain briefly an ill-effect of the use of fossil fuel has on the environment.

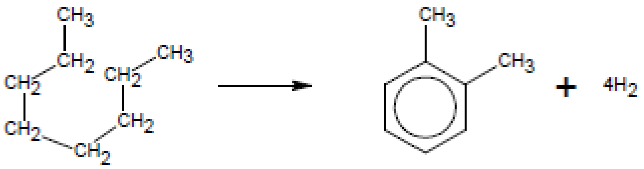
(ii) Suggest and explain briefly a specific alternative to using fossil fuel as fuel for motor vehicles.

[3]

Reforming takes straight chain hydrocarbons in the C_6 to C_8 range from the gasoline or naphtha fractions and rearranges them into compounds containing benzene rings.

Hydrogen is produced as a by-product of the reactions. A catalytic mixture of Pt and Al_2O_3 at a temperature of 500°C and pressure of 20 atm is used.

Reforming of octane produces 1,2-xylene as shown by the equation below.



1,2-xylene

(d) 3,4-dimethylphenylamine is a raw material for the production of vitamin B2 and it can be produced from 1,2-xylene using a 2-steps reaction scheme.

(i) Suggest the 2-steps reaction scheme, stating the reagents and conditions required and drawing the appropriate intermediate(s).

(ii) Describe the mechanism of the first step in **(d)(i)**.

[6]

2 CJC/2010/P3/Q1(c) Level of Difficulty: [☆]

(c) One of the products formed in **(b)** is used in the chlorination of methylbenzene. Identify this compound. Outline the mechanism for the chlorination of methylbenzene, showing clearly the role of this compound in the mechanism. [5]

(the product formed in (b) is $AlCl_3$)

3 MJC/2010/P2/Q3(b) Level of Difficulty: [☆]

2-chloropropane can be made by the chlorination of propane.

(i) Outline the reaction mechanism of its formation, labelling each step in the mechanism appropriately.

(ii) Explain why the reaction requires only a flash of ultraviolet light rather than prolonged radiation.

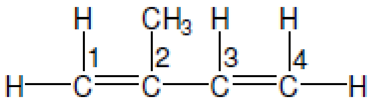
18 NYJC/2010/P2/Q9(a)(i),(ii) Level of Difficulty: [☆☆☆]

9(a) The following table shows the enthalpy change of hydrogenation of two dienes: 2-methylbuta-1,3-diene and penta-1,4-diene.

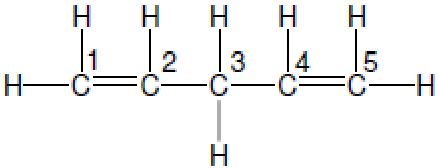
Diene	*Product*	*Enthalpy change of hydrogenation/ kJ mol^{-1}*		
		Expected, a	*Observed, b*	*Difference (a – b)*
$CH_2{=}CHC(CH_3){=}CH_2$ 2-methylbuta-1,3-diene	$CH_3CH_2CH(CH_3)_2$	– 244	– 229	– 15
$CH_2{=}CHCH_2CH{=}CH_2$ penta-1,4-diene	$CH_3CH_2CH_2CH_2CH_3$	– 252	– 253	1

(i) The enthalpy change of hydrogenation data shows that 2-methylbuta-1,3-diene is more stable than expected. Explain by making reference to the p orbitals in the molecule.

(ii) Deduce whether the bond length between C2 and C3 in 2-methylbuta-1,3-diene is shorter or longer than that between C2 and C3 in penta-1,4-diene.



2-methylbuta-1,3-diene



penta-1,4-diene

Suggested Answers

1 ACJC/2010/P3/Q1(a),(d) Level of Difficulty: [☆]

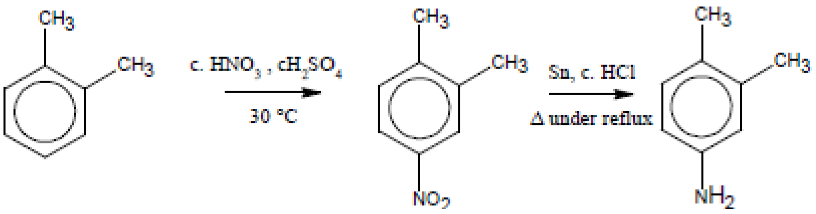
(a) **(i)** State and briefly explain an ill-effect the use of fossil fuel has on the environment.

- **Green house effect – Due to CO_2 emission which traps UV rays resulting in global warming.**

(and any other logic answers)

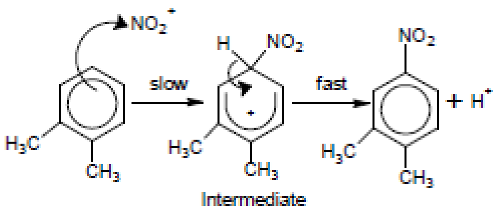
(ii) Suggest and explain a specific alternative to using fossil fuel as fuel for motor vehicles.

- **Hydrogen fuel cells.**
- **Indirect combustion of hydrogen gas which produces electric power to run vehicles without emission of CO_2. Product is H_2O which is non-toxic.**



Electrophilic substitution

$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$



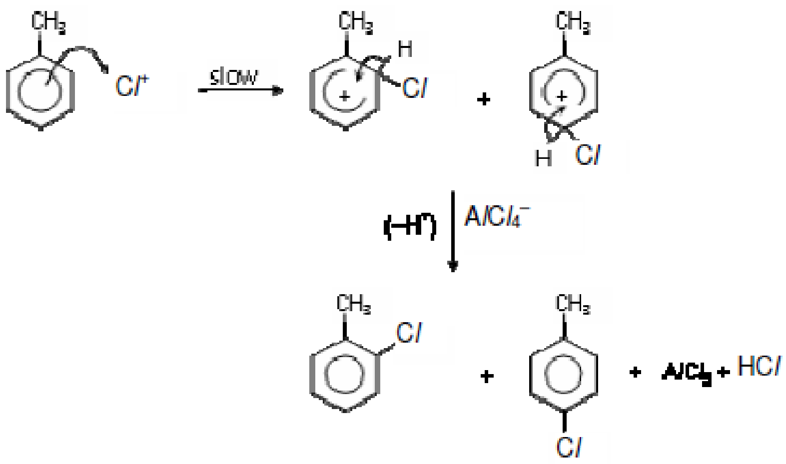
Generating the electrophile
Arrows + fast/slow
Intermediates

[5]

2 CJC/2010/P3/Q1(c) Level of Difficulty: [☆]

- $AlCl_3$ – functions as catalyst / halogen-carrier.
- electrophilic substitution

$Cl_2 + AlCl_3 \rightarrow Cl^+ + AlCl_4^-$



3 MJC/2010/P2/Q3(b) Level of Difficulty: [☆]

(i) ***Initiation stage***

$$Cl_2 \xrightarrow{\text{Ultraviolet light}} 2\,Cl\bullet$$

Propagation stage

$$CH_3CH_2CH_3 + Cl\bullet \longrightarrow CH_3\dot{C}HCH_3 + HCl$$

$$^{\bullet}CH_3CHCH_3 + Cl_2 \longrightarrow CH_3CH(Cl)CH_3 + Cl\bullet$$

Termination stage

$2\ Cl\bullet \longrightarrow Cl_2$

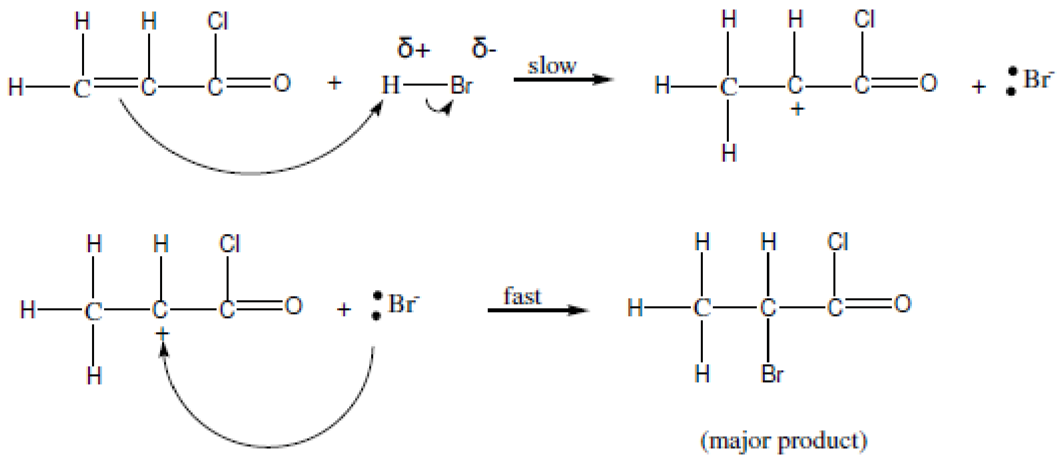
$CH_3\dot{C}HCH_3 + Cl\bullet \longrightarrow CH_3CH(Cl)CH_3$

$CH_3\dot{C}HCH_3 + CH_3\dot{C}HCH_3 \longrightarrow CH_3CH(CH_3)CH(CH_3)CH_3$ or C_6H_{14}

(ii) Condition of heat or uv light applies only in initiation step as chlorine free radicals are regenerated in propagation stage to keep reaction going.

4 NJC/2010/P2/Q5(a)(i) Level of Difficulty: [☆]

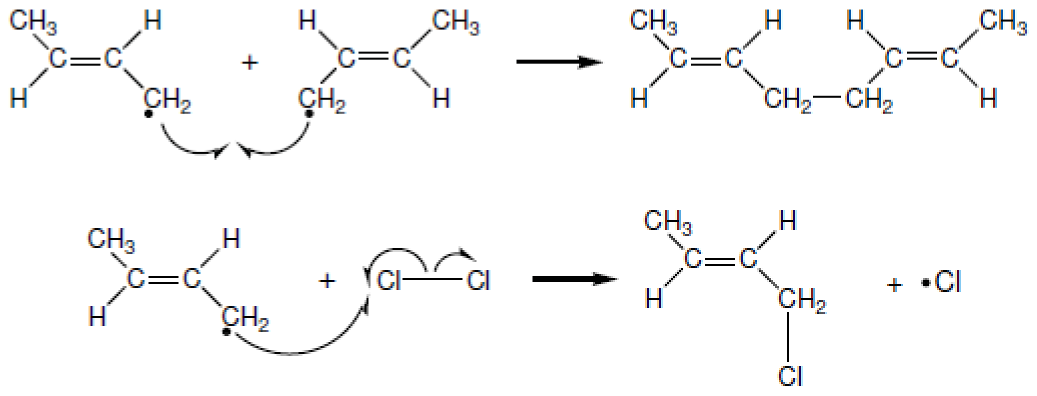
Electrophilic Addition

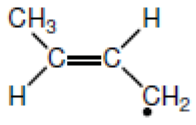


5 NJC/2010/P3/Q4(c) Level of Difficulty: [☆]

(c) (i) Only a few Cl· radicals are required to initiate/kick-start the propagation reaction, hence short duration of radiation will be sufficient.

4 (c) (ii)



When  radical reacts with Cl_2, 1-chlorobut-2-ene is formed.

6 PJC/2010/P3/Q1(b)(ii)-(iv) Level of Difficulty: [☆]

(ii) The N of NO_2^+ is electron-deficient species which attacks electron-rich benzene ring and accepts a pair of electrons from benzene.

(iii) $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$

(iv) lone electron pair on O of OH group is delocalised into the benzene ring, which strongly activates the benzene ring / increases electron density of benzene

7 PJC/2010/P3/Q4(d) Level of Difficulty: [☆]

(i) NaOH(aq), heat
C-F bond is stronger than C-Cl bond.

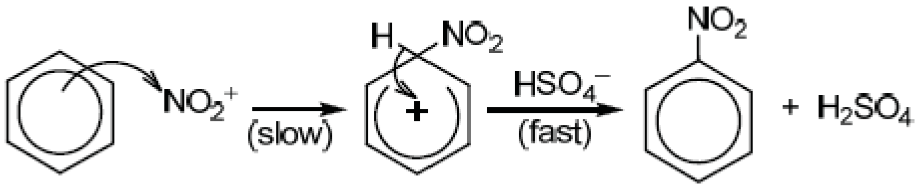
(ii) CFCs will cause ozone depletion by undergoing photochemical / free radical substitution reactions with O_3.

Substitute CFC with HCFC OR Liquid Petroleum Gas as propellant in aerosol sprays OR replace aerosol sprays with manual pump sprays.

8 RVHS/2010/P2/Q4(b)(i) Level of Difficulty: [☆]

(i) Electrophilic substitution

(Generation of electrophile) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$



9 SRJC/2010/P3/Q4(a)(i) Level of Difficulty: [☆]

Propagation:

$Br^\bullet + CH_3CH_2CH_3 \rightarrow CH_3\dot{C}HCH_3 + HBr$

$CH_3\dot{C}HCH_3 + Br_2 \rightarrow CH_3CH(Br)CH_3 + Br^\bullet$

$Br^\bullet + CH_3CH(Br)CH_3 \rightarrow HBr + CH_3CH(Br)CH_2^\bullet$

$CH_3CH(Br)CH_2^\bullet + Br_2 \rightarrow CH_3CH(Br)CH_2Br + Br^\bullet$

10 TJC/2010/P2/Q4(d)(ii) Level of Difficulty: [☆]

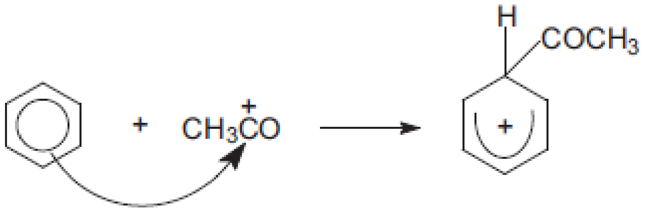
- There is planar arrangement about the carbonyl carbon.
- The carbonyl carbon can be attacked by CN^- either from the top of the plane or the bottom of the plane, each direction of attack with equal probability. This leads to the formation of two mirror images which are non-superimposable (as there is a chiral centre).

11 VJC/2010/P3/Q4(d)(i) Level of Difficulty: [☆]

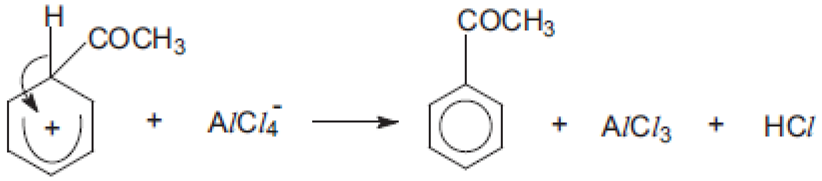
(d)(i)

Mechanism: electrophilic substitution

$$CH_3COCl + AlCl_3 \rightarrow \underset{\text{electrophile}}{CH_3CO^+} + AlCl_4^-$$



resonance–stabilised
carbocation intermediate



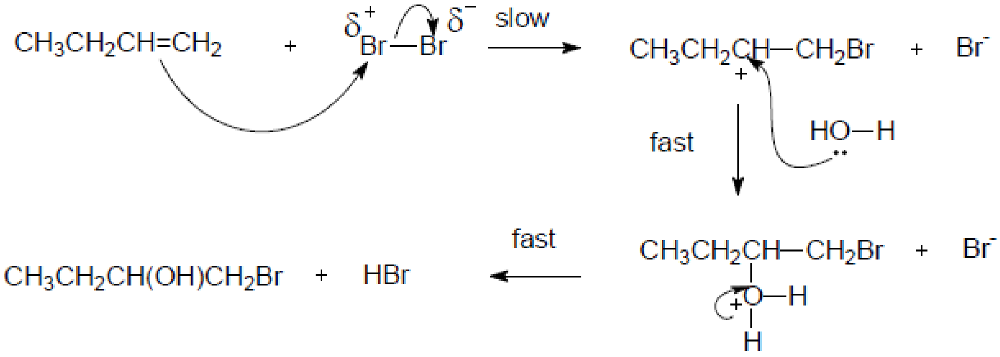
$AlCl_3$ catalyst is regenerated.

12 AJC/2010/P3/Q2(b) Level of Difficulty: [☆☆]

(b)(i) Step I: excess concentrated H_2SO_4, 180 °C

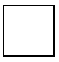
(b)(ii) $CH_3CH_2CH(OH)CH_2Br$

(b)(iii) Electrophilic addition

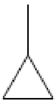


The water nucleophile can attack the trigonal planar carbocation from top and bottom with equal probability, giving rise to a racemic mixture.

(b)(iv)

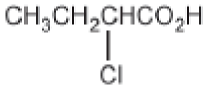


or

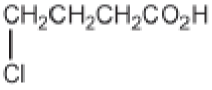


13 NYJC/2010/P3/Q5(a) Level of Difficulty: [☆☆]

(i)


$CH_3CH_2CH(Cl)CO_2H$


$CH_3CH(Cl)CH_2CO_2H$

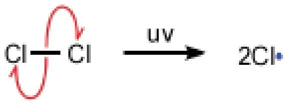

$CH_2(Cl)CH_2CH_2CO_2H$

3 correct [2], 2 correct [1], 3:2:2; statistical ratio [1]

(ii)

Free radical substitution

Initiation [1]


$Cl{-}Cl \xrightarrow{uv} 2Cl\bullet$

Propagation [1]

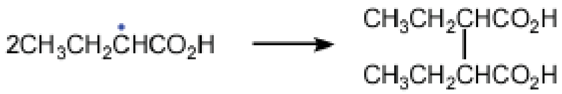
$CH_3CH_2CH_2CO_2H + Cl\bullet \longrightarrow CH_3CH_2\dot{C}HCO_2H + HCl$

$CH_3CH_2\dot{C}HCO_2H + Cl_2 \longrightarrow CH_3CH_2CHClCO_2H + Cl\bullet$

Termination [1]

$Cl\bullet + Cl\bullet \longrightarrow Cl_2$

$CH_3CH_2\dot{C}HCO_2H + Cl\bullet \longrightarrow CH_3CH_2CHClCO_2H$

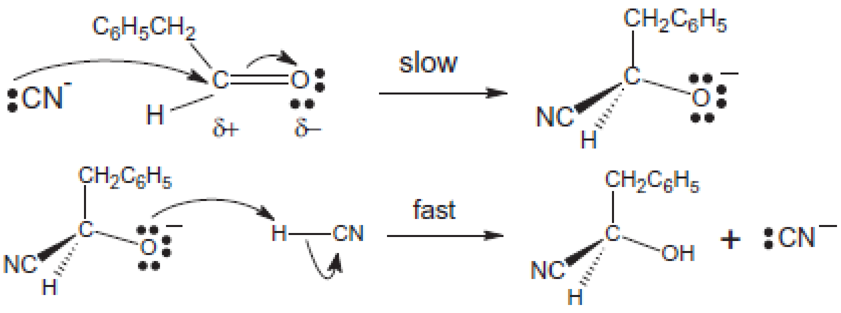

$2CH_3CH_2\dot{C}HCO_2H \longrightarrow CH_3CH_2CH(CO_2H){-}CH(CO_2H)CH_2CH_3$

14 PJC/2010/P2/Q4(d)(iii)-(v) Level of Difficulty: [☆☆]

(iii) **optical isomerism**

(iv) **nucleophilic addition**

$\mathbf{HCN + NaOH \rightarrow NaCN + H_2O}$



(v) **As the reaction involves a carbocation intermediate which has a <u>trigonal planar</u> geometry about the C with the positive charge. CN^- has <u>equal likelihood of attacking on either side</u> of the planar, resulting in the formation of a <u>racemic mixture</u> which has equimolar quantities of the two enantiomers. Thus, the <u>optical activity is cancelled out</u>.**

15 YJC/2010/P3/Q4(b) Level of Difficulty: [☆☆]

bi In propagation step, two alkyl radicals are formed. They are the more stable tertiary $(CH_3)C^{\circ}$ and less stable primary $(CH_3)_2CCH_2^{\circ}$. More stable alkyl radical results in the formation of major product while the less stable radical results in the formation of minor product.

bii Bond energy of F_2 = 158 kJ mol^{-1} , while bond energy of Br_2 = 193 $kJmol^{-1}$. Fluorine will react more vigorously because the F-F bond is weaker than Br-Br bond according to bond energies.

biii Bond between C-I and I-I are so weak , they break and form readily. Hence reaction becomes reversible.

16 AJC/2010/P3/Q5(b),(c),(d) Level of Difficulty: [☆☆☆]

(b)(i)

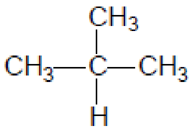
$$M_r \text{ of } \mathbf{R} = \frac{0.10 \times 8.31 \times (127+273)}{101 \times 10^3 \times 58.8 \times 10^{-6}} = \underline{56.0}$$

(b)(ii)

Q: $CH_2{=}CHCH_3$

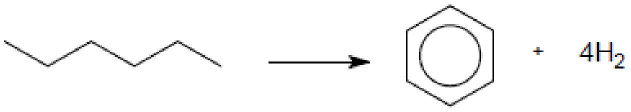
R: $CH_3CH{=}CHCH_3$

S: $CH_3CH_2CH_2CH_3$ or



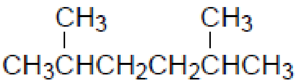
$CH_3CH(CH_3)CH_3$

(c)(i)



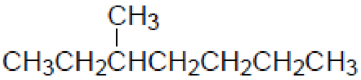
(c)(ii) Oxidation / aromatization / cyclisation / elimination

(c)(iii)



$CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$

or



$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_3$

(d)(i) Oxidation number of C in glucose = 0
Oxidation number of C in methane = – 4
Oxidation number of C in ethanol = – 2

(d)(ii) Bubble gaseous products through sodium hydroxide to remove the acidic CO_2.

(d)(iii) More heat is produced during production of methane / reaction is more exothermic.

Advantage:
The heat could be recycled and used in other industrial processes.

Disadvantage:
The combustion of methane produces less heat than the combustion of ethanol.
or
The production of methane has a higher maintenance cost.

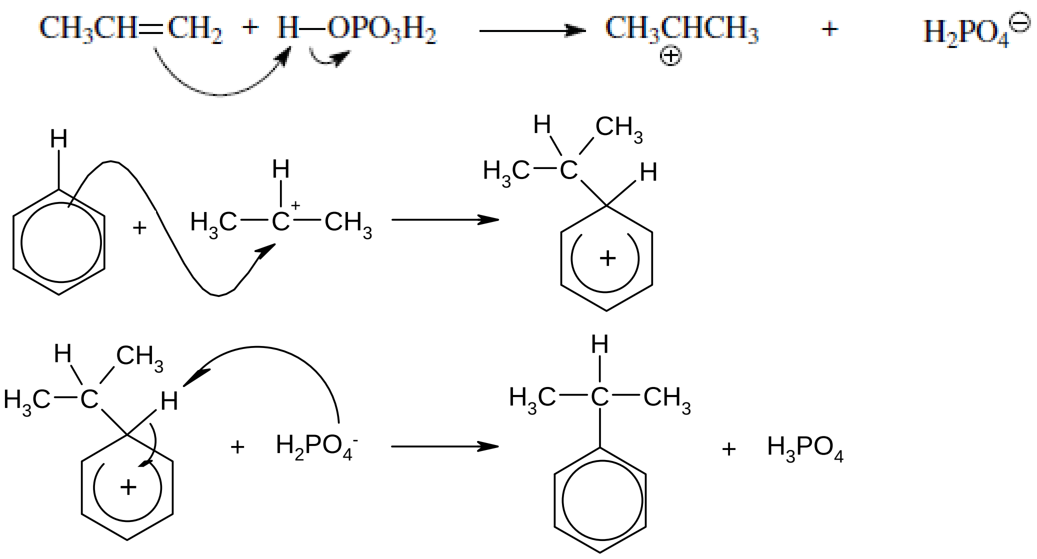
(d)(iv) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

<u>One mole of glucose</u> will burn to give <u>6 moles of CO_2</u>, regardless of whether it is used to form methane or ethanol.

17 <u>NJC/2010/P3/Q5(a)(i)</u> Level of Difficulty: [☆ ☆ ☆]

(i) Electrophilic Substitution
<u>Mechanism</u>

- Generation of electrophile



18 <u>NYJC/2010/P2/Q9(a)(i),(ii)</u> Level of Difficulty: [☆ ☆ ☆]

(i)

2-methyl-buta-1,3-diene is a conjugated diene. The extent of **overlap of the unhybridized p orbitals** of the 4 sp^2 C can overlap with each other causing the **π electrons to spread out, or delocalize** over the entire π framework (or over the 4 carbon atoms). Electron delocalization leads to a lower energy and hence leads to stability.

(ii)

The bond length will be **shorter** due to **sp^2-sp^2 overlap** that strengthens the bond between C2 and C3.

10.3.2 Halogen Derivatives

1 CJC/2010/P3/Q2(c)(iii) Level of Difficulty: [☆]

The reaction between 2-bromobutane and aqueous sodium hydroxide when heated under reflux is represented by the equation below.

$$CH_3CHBrCH_2CH_3 + OH^- \rightarrow CH_3CH(OH)CH_2CH_3 + Br^-$$

(iii) Describe the type of mechanism involved.
(given that in part (i) and (ii) it was determined that: rate = k [$CH_3CHBrCH_2CH_3$])

2 HCI/2010/P2/Q3(c) Level of Difficulty: [☆]

(i) Ammonia acts as a nucleophile in its reaction with bromoethane to form ethylamine $CH_3CH_2NH_2$.

Ethylamine reacts with aqueous ethanoic acid and ethanoyl chloride to give **K** and **L** respectively.

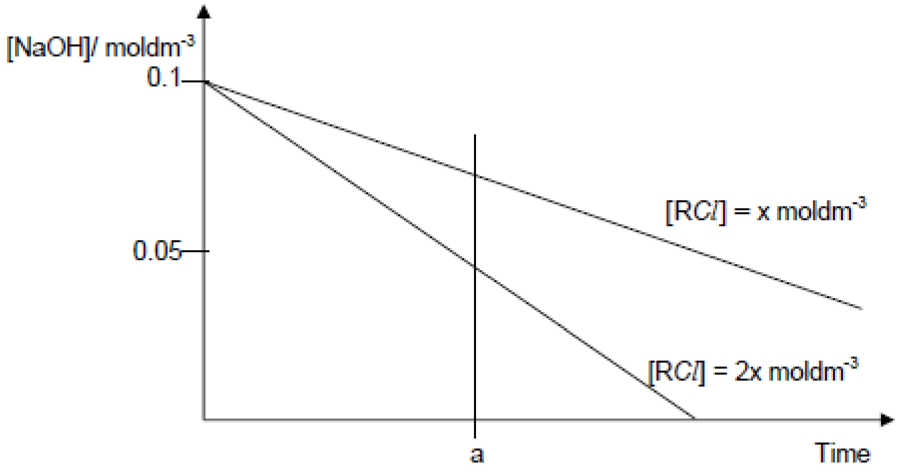
Draw the structural formula of **K** and **L**

(ii) A by-product of the reaction of bromoethane with ammonia is compound **M**, which has the formula $C_8H_{20}NBr$ and gives an immediate precipitate with aqueous silver nitrate.

Suggest the structural formula of compound **M**.

3 ACJC/2010/P3/Q2(c) Level of Difficulty: [☆☆]

(c) The graph below shows the reaction between aqueous sodium hydroxide and a solution of a saturated alkyl chloride at temperature T°C.



(i) Referring to the graph above, deduce the order of reaction with respect to sodium hydroxide and RC*l* and hence write down the rate law.

(ii) Is RC*l* most likely to be a primary, secondary or tertiary alkyl halide?

(iii) Draw a labelled energy profile diagram for the reaction.

(iv) Briefly explain how one of the graphs above may be obtained experimentally.

The beaker is placed on a piece of white paper on which a black cross has been marked. The time taken for the contents of the test tube to mask the black cross is measured. The results on three separate test tubes are given below.

Tube 1: black cross always clear
Tube 2: 10 s
Tube 3: 1 s

(i) Match each of the letters **A**, **B** and **C** with the test tube which most closely corresponds to its behaviour.

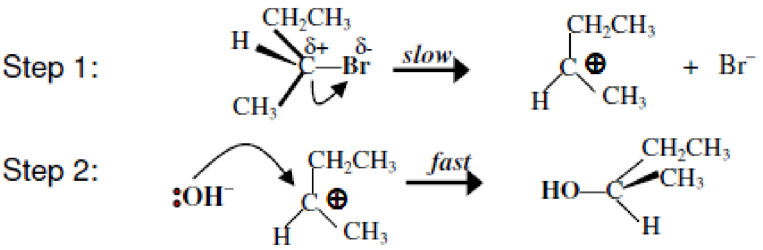
(ii) Briefly explain your answer.

(iii) Explain how the time taken to mask the black cross would be affected if compound **A** is replaced with $C_6H_5CH_2Cl$.

Suggested Answers

1 CJC/2010/P3/Q2(c)(iii) Level of Difficulty: [☆]

Nucleophilic substitution (S_N1)



2 HCI/2010/P2/Q3(c) Level of Difficulty: [☆]

3(c)(i) K: $CH_3CH_2NH_3^+CH_3CO_2^-$ **L:** $CH_3CH_2NHCOCH_3$

3(c)(ii) J: $(CH_3CH_2)_4N^+Br^-$

3 ACJC/2010/P3/Q2(c) Level of Difficulty: [☆☆]

(i) Referring to the graph above, deduce the order of reaction with respect to sodium hydroxide and RCl and hence write down the rate law.

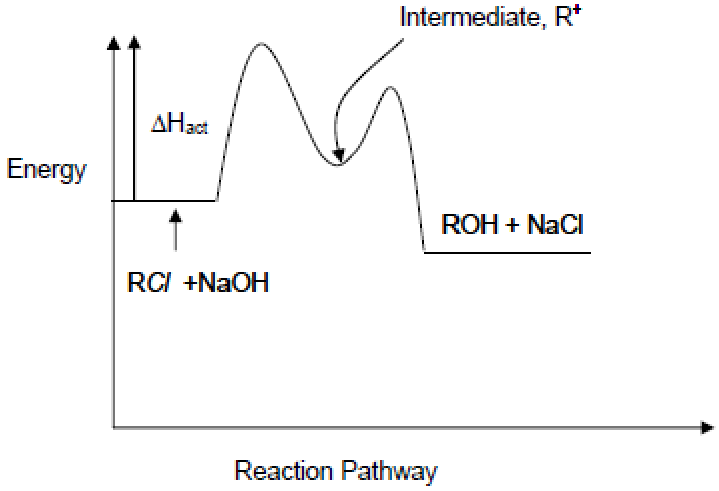
Gradient for [RCl] = x mol dm^{-3} is half that for [RCl] = 2x mol dm^{-3} . Hence first order wrt to RCl. Both graphs are straight lines with a negative gradient, hence zero order wrt to NaOH

Rate = k [RCl]

(ii) Is RCl most likely to be a primary, secondary or tertiary alkyl halide?

Tertiary alkyl halide.

(iii) Draw a labelled energy profile diagram for the reaction.



You may label the 2 humps as partial bond breaking and partial bond forming.

(iv) Briefly explain how one of the graphs above may be obtained experimentally.

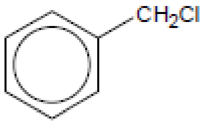
Pipette out 10 cm^3 (can accept 25 cm^3 even though it is wasteful and time consuming) of the reaction mixture at regular intervals, chill immediately and titrate with HCl(aq) or H_2SO_4(aq) of known concentration to calculate the [NaOH] remaining.

(v) Aqueous hydrochloric acid and $(CH_3)_2CCHCl$ are separately used in the place of the saturated alkyl chloride in the reaction in **(c)** above. How would the rate of reaction of these two compounds compare with the rate of reaction of RC*l*? Give your reasons

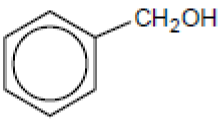
Aqueous hydrochloric acid is a strong acid and is completely ionized in water. The neutralization reaction is <u>immediate</u>. (1m)

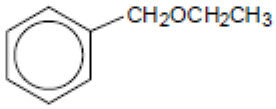
The rate of reaction of $(CH_3)_2CCHCl$ is much slower. (1/2m)$(CH_3)_2CCHCl$ contains a C=C.(1/2m) The C-Cl bond shows double bond characteristics(1m) and hence difficult to break it.

(v) Identify 2 possible products formed when ethanolic sodium hydroxide is heated under reflux with



[12]



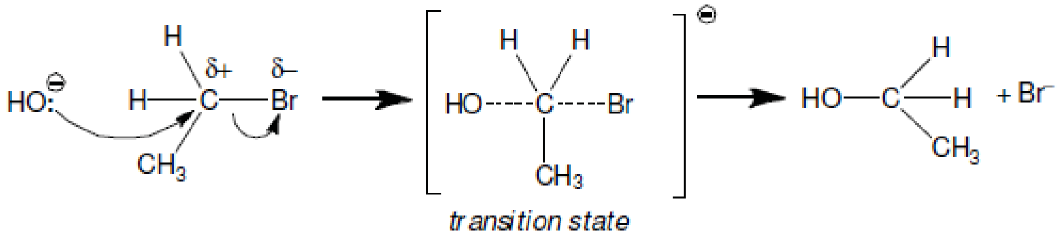


4 <u>CJC/2010/P2/Q3(d)</u> Level of Difficulty: [☆☆]

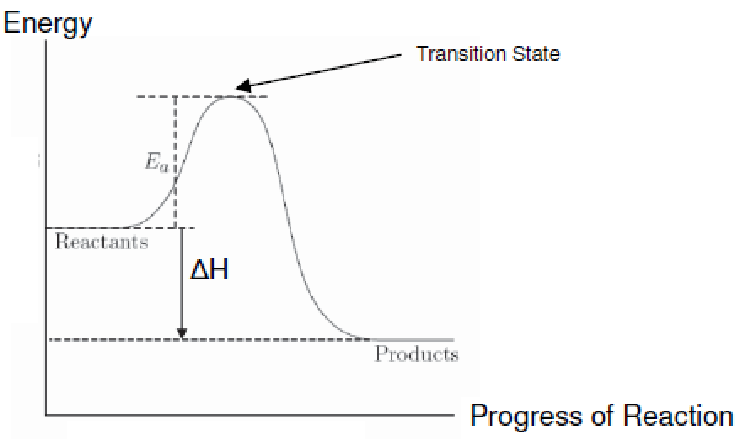
The <u>bond energy of C-C*l* is 340 kJ mol^{-1}</u> and C-F is 485 kJ mol^{-1}.
It will require <u>more energy</u> for homolytic fission to take place for C-F bond thus it is <u>harder to produce F•, as compared to C*l*• (or simply produce radicals)</u>

5 HCI/2010/P2/Q5(b) Level of Difficulty: [☆☆]

5(b)(i) Name: Nucleophilic substitution, S_N2



5(b)(ii)



5(b)(iii) Iodoethane has a faster rate of hydrolysis.
Iodine is bigger hence the C–I bond is longer and therefore weaker.

6 MJC/2010/P3/Q5(a),(b) Level of Difficulty: [☆☆]

(a) **(i)** Electron cloud size: 2-chlorobutane < 2-iodobutane
Extent of distortion of electron cloud:
2-chlorobutane < 2-iodobutane

Extent of intermolecular Van der Waal's forces of attraction:
2-chlorobutane < 2-iodobutane

Less energy required to break weaker intermolecular forces of attraction between 2-chlorobutane molecules compared to 2-iodobutane molecules, hence lower boiling point.

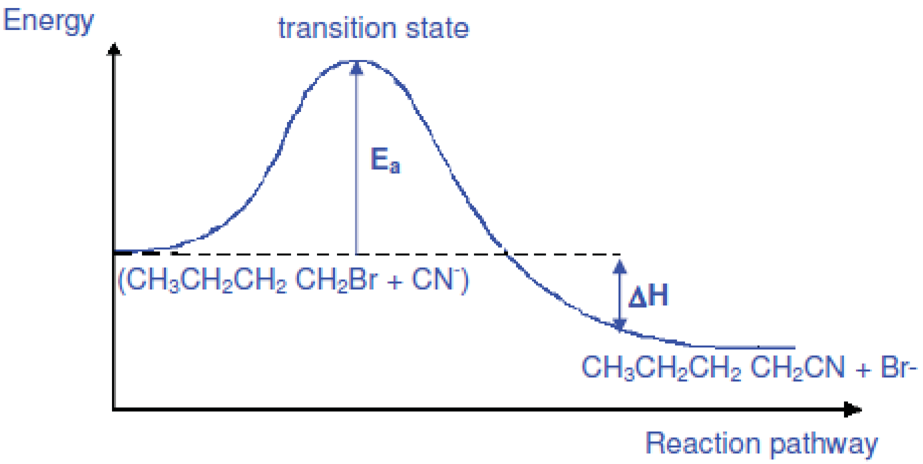
(ii) Bond length of C–X: $C{-}Cl < C - I$
Bond strength of C–X: $C{-}Cl > C - I$
Ease of breaking of C–X bond: $C{-}Cl < C - I$
Ease of nucleophilic substitution / formation of X^-:
2-chlorobutane < 2-iodobutane

Hence AgI (yellow) precipitate forms more quickly than $AgCl$ (white) precipitate

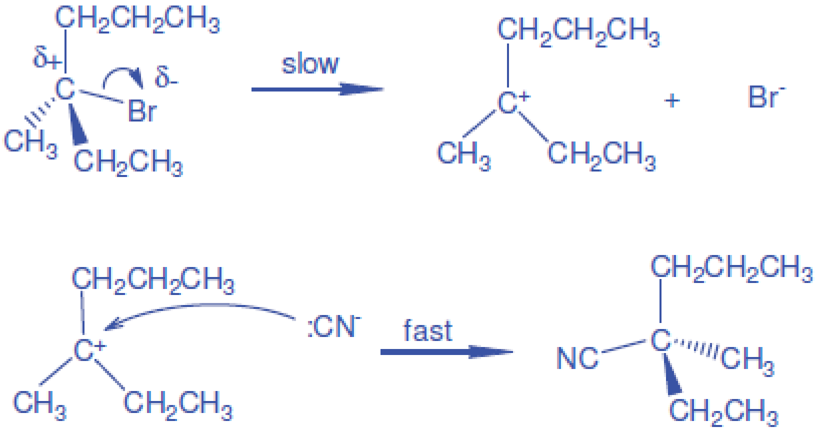
(iii) For butanoyl chloride, the carbonyl C atom has two electronegative atoms (O and C*l*) bonded to it compared to 2-chlorobutane with C*l* as the only electronegative atom.

Due to the electron-withdrawing effects of O and C*l*, the carbonyl C atom in butanoyl chloride is more electron deficient than the halogenoalkane C, hence it is more susceptible to nucleophilic substitution.

(b) **(i)**



(ii)



Compound **G**

(iii) Carbocation intermediate formed (sp^2 hybridised) is (trigonal) planar, hence CN^- nucleophile has equal probability of attacking from either plane of the carbocation intermediate, forming a racemic mixture. The racemic mixture contains equal proportions of each enantiomer, thus is optically inactive.

7 NJC/2010/P3/Q4(d) Level of Difficulty: [☆☆]

4 (d) 1-chlorobut-2-ene undergoes **nucleophilic substitution/hydrolysis** with NaOH(aq) to form **AgCl white ppt**.

2-chlorobut-2-ene does not undergo nucleophilc substitution. The C-Cl bond is harder to break due to overlap of Cl p orbital with the adjacent C=C bond. Hence no free Cl^- ions is formed to react with Ag^+ to form **AgCl white ppt**.

8 SAJC/2010/P2/Q5 Level of Difficulty: [☆☆]

(a) Rate = k[A]

Rate = k[B][NaOH]

(b) **(i)** Compound **A**: Graph 2

Compound **C**: Graph 1

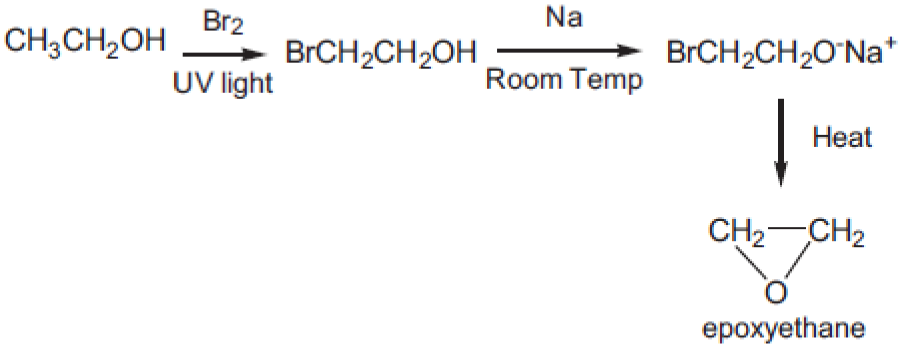
(ii) Since I atom is larger, there is less effective overlap between the atomic orbitals. C – I bond is longer. Hence C – I bond is weaker and rate of hydrolysis for compound **C** is faster.

9 TJC/2010/P3/Q1(c) Level of Difficulty: [☆☆]

(i) • $CH_3CH_2OCH_2CH_3$

(ii) • $CH_2{=}CH_2$

(iii) •• (1 mark for each step)

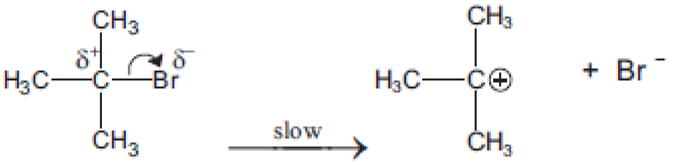


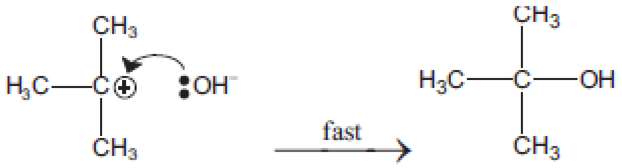
(iv) • Possible answers:

- – As the first step involves free radical substitution, a mixture of bromo-substituted products will be obtained and $BrCH_2CH_2OH$ may not be the major product.
- – $BrCH_2CH_2O^-$ can react with another $BrCH_2CH_2O^-$ to give $BrCH_2CH_2OCH_2CH_2O^-$ and other straight chain products.
- – Epoxyethane has a highly strained three-membered ring which makes it reactive/unstable.

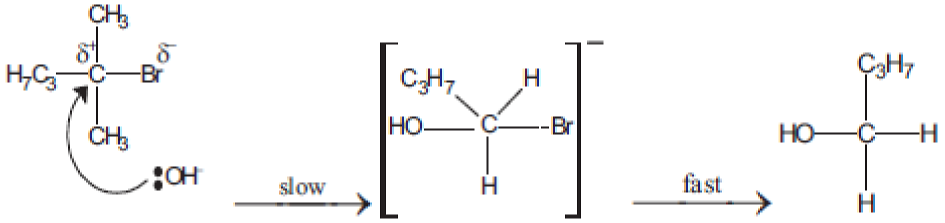
10 YJC/2010/P3/Q2(a)(ii),(iii) Level of Difficulty: [☆☆]

aii SN1 for $(CH_3)_3Br$

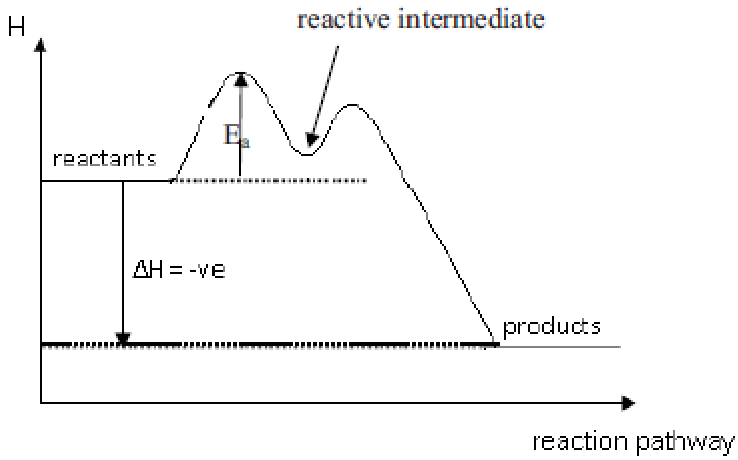


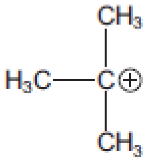


SN2 for $CH_3CH_2CH_2CH_2Br$,



aiii Energy profile for $(CH_3)_3Br$





reactive intermediate

Energy profile for $CH_3CH_2CH_2CH_2Br$

11 NYJC/2010/P3/Q2(a) Level of Difficulty: [☆ ☆ ☆]

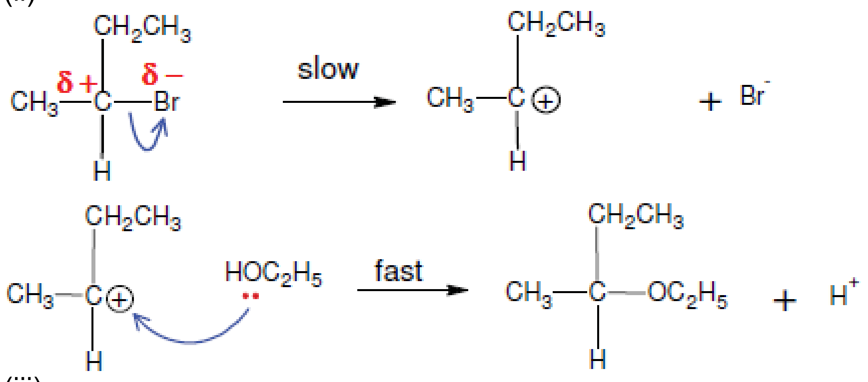
(i)

- 3° alkyl halide (2-bromo-2-methylpropane) reacted fastest in the $AgNO_3$ test while it hardly showed any reaction in NaI test.
- 1° alkyl halide (1-bromobutane) reacted slowest in $AgNO_3$ test while it reacted the fastest in NaI test.

1 mark for observation

- 3° alkyl halides form **stable carbocations** and tend to react via S_N1 mechanism, which can be seen from its fast reaction in the $AgNO_3$ test. **[1]**
- On the other hand, there is a great amount of **steric hindrance** caused by the 3 R groups in 3° alkyl halides, hence causing reaction via S_N2 mechanism to be very slow. **[1]**

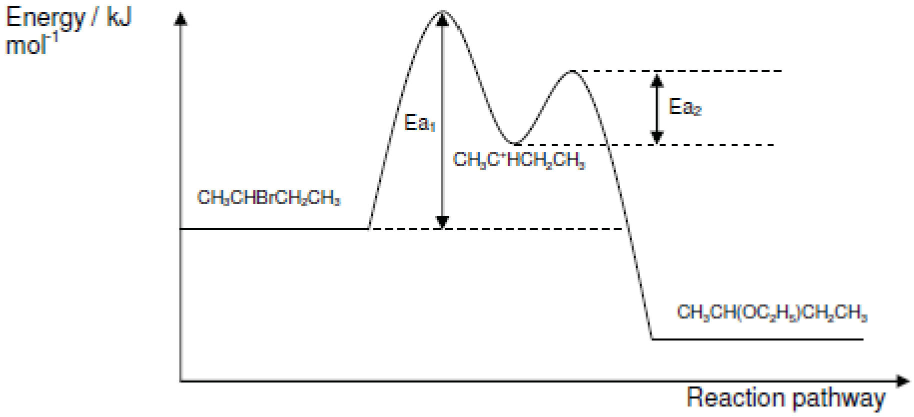
(ii)



(iii)

- Resulting compound does not rotate plane polarized light.
- Nucleophile attacks the planar carbocation from either sides, forming equimolar amounts of enantiomers. Hence a racemic mixture is formed.

(iv)



Marking points:

- **Axes are correctly labeled**
- **Reactant, intermediate and products are correct**
- **Shape of curve is correct (Ea1 > Ea2)**

(v)

For 1-chlorobutane:

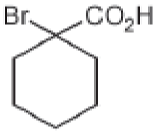
- Time take for ppt to appear > 1 min.
- C-Cl bond is shorter and stronger than C-Br bond, hence less easily hydrolysed

For ethanoyl bromide:

- Ppt formed immediately
- Positive dipole on C is increased due to the highly electron-withdrawing C=O group, hence more susceptible to nucleophilic attack.

12 NYJC/2010/P3/Q5(b),(c) Level of Difficulty: [☆☆☆]

(b)(i)

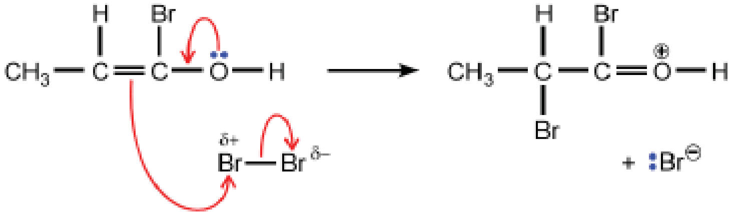


(ii)

A: CH_3CH_2COBr

B: $CH_3CHBrCOBr$

(c)(i)



arrow from lone pair on O to C-O bond [1]

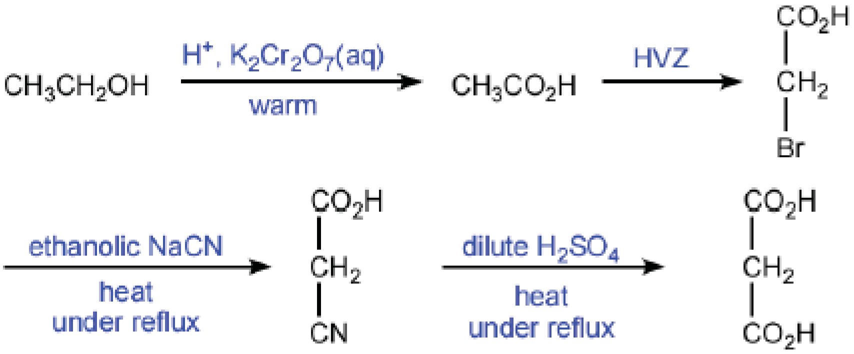
arrow from π bond to Br and arrow from Br-Br bond to Br [1]

(ii)

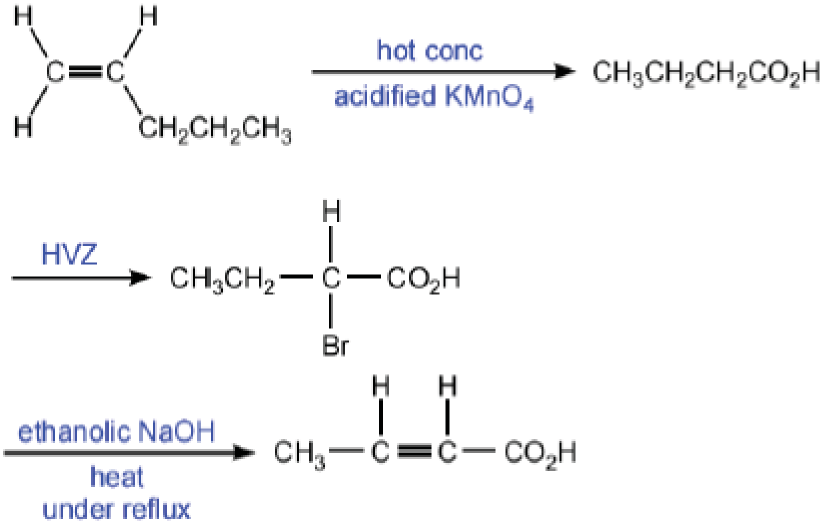
electrophile

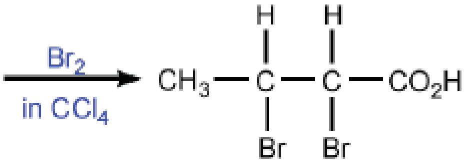
Award mark only if explanation shows understanding

(d)(i)



(ii)





$\xrightarrow[\text{in } CCl_4]{Br_2} CH_3CHBrCHBrCO_2H$

13 VJC/2010/P2/Q5(c) Level of Difficulty: [☆☆☆]

(c)(i)

	Tube 1	Tube 2	Tube 3
Compound	**C**	**A**	**B**

(ii)

C_6H_5COCl undergoes hydrolysis more readily than $C_6H_5CH_2Br$ as the carbonyl carbon atom is more electron deficient due to two electronegative atoms (O and C*l*).

C_6H_5I has no reaction because the C–I bond is strengthened (OR has partial double bond character) by the overlapping of the *p* orbital of I with the π orbitals of the benzene ring.

(iii)

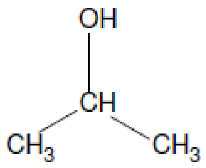
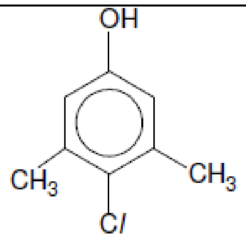
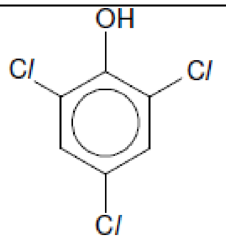
Time taken would be longer (than 10 seconds).

$C_6H_5CH_2Cl$ undergoes hydrolysis less readily than $C_6H_5CH_2Br$ as the C–C*l* bond is stronger (OR BE(C–C*l*) > BE(C–Br)).

10.3.3 Hydroxy Compounds

1 CJC/2010/P3/Q5(b),(c)(i) Level of Difficulty: [☆]

(b) IPA, Dettol and TCP are three hydroxy compounds often used as disinfectants and antiseptics.

			
Common Name	IPA	Dettol	TCP
K_a / mol dm^{-3}	7.94×10^{-18}	1.99×10^{-10}	6.46×10^{-7}

(i) Write a chemical equation to represent the acid dissociation of Dettol in water.

(ii) Calculate the pH of 0.20 mol dm^{-3} of Dettol.

(iii) Compare and explain the relative acidity of IPA and Dettol.

(iv) Explain why TCP is a stronger acid than Dettol.

[8]

(c) TCP can be made in the laboratory from phenol.

(i) State the reagents required, and give a balanced equation for this reaction.

2 AJC/2010/P2/Q4(c) Level of Difficulty: [☆☆☆]

(c) Tert–butanol reacts with hydrobromic acid in the following reaction to form 2–bromo–2–methylpropane.

$$(CH_3)_3COH + HBr \longrightarrow (CH_3)_3CBr + H_2O$$

(i) What *type of reaction* occurs here?

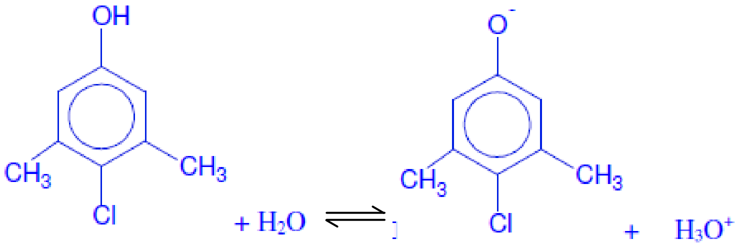
(ii) The conversion of tert–butanol into 2–bromo–2–methylpropane occurs in a three–step mechanism.
The first step is an acid–base reaction between tert–butanol and hydrobromic acid. Write an equation to represent this.

(iii) Hence, describe step two and three of the mechanism. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

Suggested Answers

1 CJC/2010/P3/Q5(b),(c)(i) Level of Difficulty: [☆]

(b)(i)



(ii)

Let Dettol be HA,

HA □ $H^+ + A^-$

Equilibrium $0.2 - x$ x x where $[H^+] = x$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.2 - x}$$

Assuming x is much smaller than 0.2,

$$1.99 \times 10^{-10} = \frac{x^2}{0.2}$$

$$x = [H^+] = \sqrt{3.98 \times 10^{-11}} = 6.31 \times 10^{-6} \text{ mol dm}^{-3}$$

$pH = -\log_{10}(6.31 \times 10^{-6}) = \underline{5.20}$

(iii)

Strength of acid: IPA < Dettol

IPA is less acidic than Dettol, as it has alkyl or methyl groups that are electron releasing and results in **less polarised and stronger** O-H bond. Hence the O-H bond is **less likely to dissociate** giving H^+ ions.

Dettol is a stronger acid than IPA, as the **lone pair of electrons on the oxygen atom can delocalize into the benzene ring**, which results in **more polarised and weaker** O-H bond. Hence the O-H bond is more likely to dissociate giving H^+ ions.

OR

the phenoxide formed is a more stable conjugate base due to the negative charge on the oxygen can be delocalised with in the ring.

Alkoxide formed is less stable as the negative charge is localised on the oxygen and intensified by the electron donating alkyl groups, thus more likely to susceptible to protons.

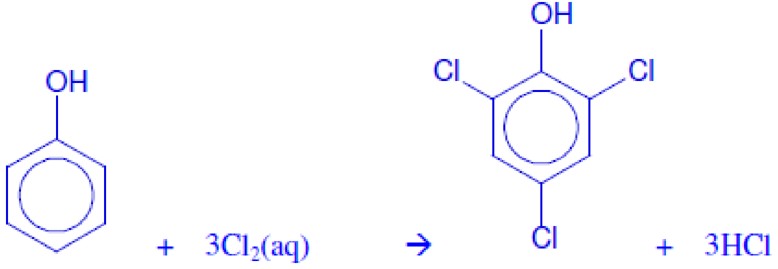
(iv)

TCP is a stronger acid than dettol, as it has **more electron-withdrawing chlorine atoms** substituent attached to the benzene ring, which results in a **stronger electron-withdrawing effect** and **more polarised and weaker O-H bond**

or **more stable conjugate base**, hence the H^+ ions will be formed more easily.

(c)(i)

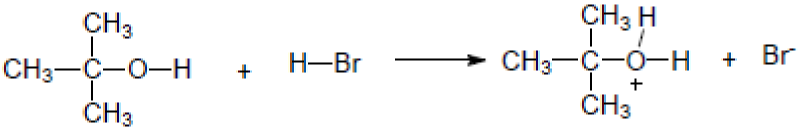
Reagents: Aqueous Chlorine



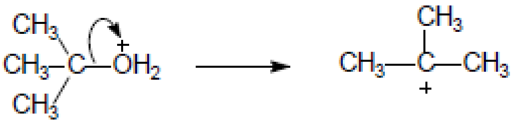
2 AJC/2010/P2/Q4(c) Level of Difficulty: [☆☆☆]

(c)(i) Nucleophilic substitution

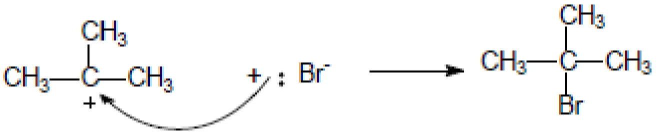
(c)(ii) Step 1:



(c)(iii) Step 2:



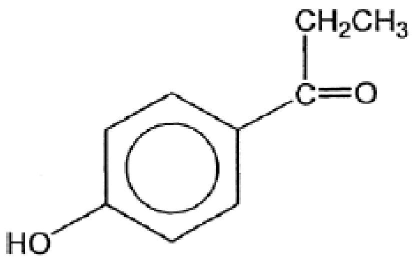
Step 3:



10.3.4 Carbonyl Compounds

1 MI/2010/P2/Q7 Level of Difficulty: [☆☆]

P reacts with hydrogen cyanide to form two stereoisomers.



P

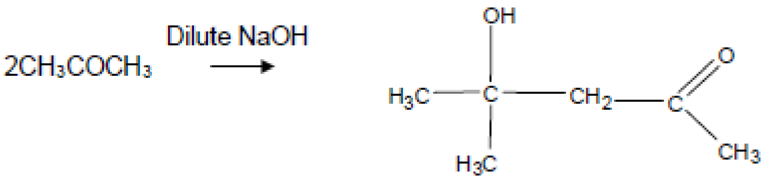
(a) Describe the mechanism for the reaction between **P** and hydrogen cyanide. [3]

(b) Using your answer in **(a)**, explain briefly why a pair of stereoisomers is formed. [2]

(c) Suggest how the pair of stereoisomers can be distinguished. [1]

2 ACJC/2010/P2/Q5(b) Level of Difficulty: [☆☆☆]

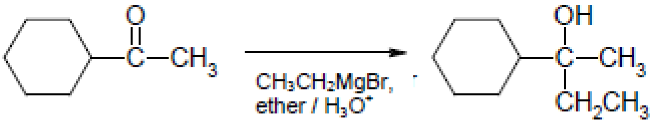
(b) Aldehydes and ketones which possess at least one hydrogen on the neighbouring carbon atom to the carbonyl group, (for example, C<u>H</u>CO), undergo the aldol addition in the presence of dilute solutions of bases.



Predict the other products that will be formed when a mixture of propanone and ethanal react with dilute aqueous sodium hydroxide.

3 YJC/2010/P3/Q1(b) Level of Difficulty: [☆☆☆]

Cyclohexylethanone also reacts with a Grignard reagent as follows.



The Grignard reagent CH_3CH_2MgBr is generated via the reaction of Mg with CH_3CH_2Br in ether solution.

(i) State the function of the Grignard reagent in this reaction.
(ii) Hence by means of equations, describe the mechanism in **(b)(i)**.

[5]

Suggested Answers

1 MI/2010/P2/Q7 Level of Difficulty: [☆☆]

(a)

1m for correct curly arrows showing the nucleophilic attack and lone pairs of electrons on CN^-

1m for correct structure of intermediate

1m for correct structure of product

(b)

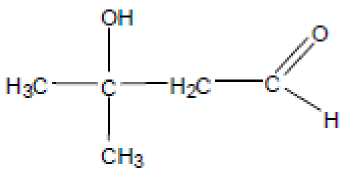
Shape about carbonyl carbon is trigonal planar. ;

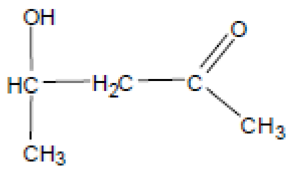
Allows equal chance of CN^- approaching the carbonyl carbon from both the top and bottom of the plane, resulting in the formation of a pair of stereoisomers. ;

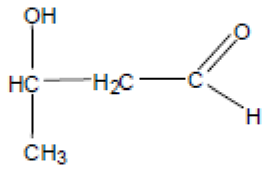
(c)

The pair of stereoisomers can be distinguished by their different response when plane – polarized light is shone on them, i.e. each of them will rotate plane – polarized light in opposite directions.

2 ACJC/2010/P2/Q5(b) Level of Difficulty: [☆☆☆]



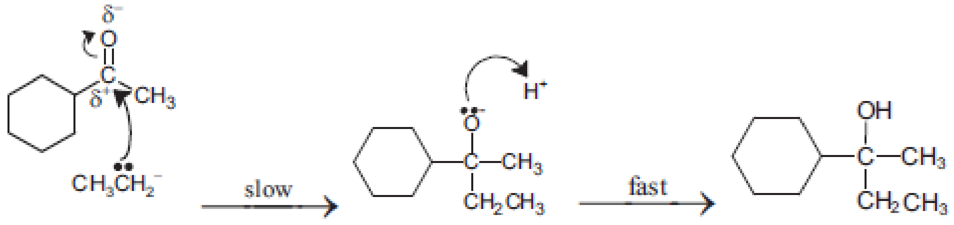




3 YJC/2010/P3/Q1(b) Level of Difficulty: [☆☆☆]

bi nucleophile

bii Nucleophilic addition mechanism



10.3.5 Carboxylic Acid and Derivatives

1 RVHS/2010/P2/Q1(f) Level of Difficulty: [✯]

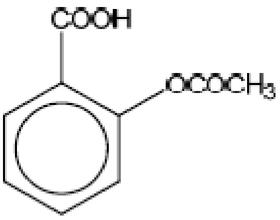
The pK_a values for three monocarboxylic acids are given below.

acid	pK_a
CH_3COOH	4.73
CCl_3COOH	0.63
C_6H_5COOH	4.20

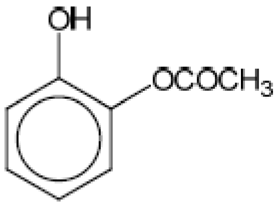
Explain the differences in the pK_a values.

2 SAJC/2010/P2/Q7(c)(iv) Level of Difficulty: [✯]

Explain how the acidity of aspirin will compare with the compound below.



Aspirin



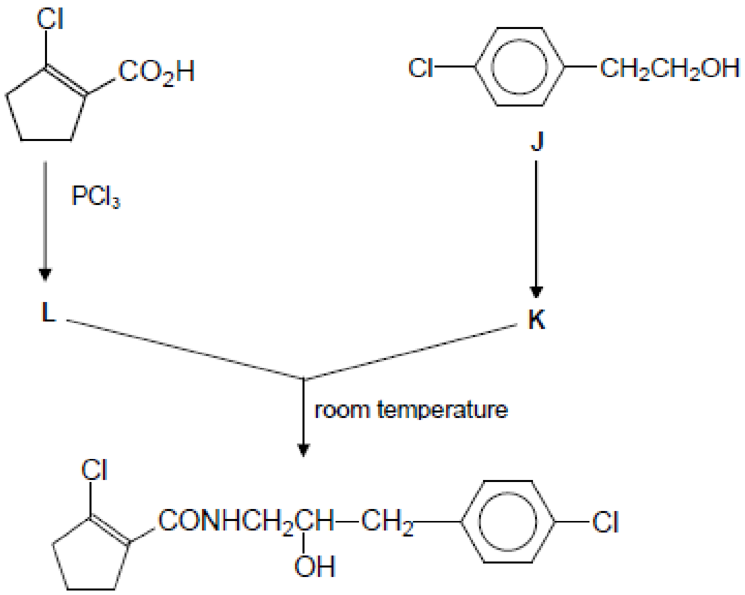
3 SRJC/2010/P3/Q2(c)(i) Level of Difficulty: [✯]

Ethanoyl chloride, CH_3COCl and chloroethanoic acid, $CH_2ClCOOH$ are halogen containing organic compound. When both are added to separate portions of water, two solutions with pH values 0.5 and 3.0 are obtained.

(i) Suggest, using relevant equations, which pH value is associated with ethanoyl chloride and chloroethanoic acid respectively.

4 ACJC/2010/P3/Q4(b) Level of Difficulty: [☆☆]

(b) The scheme below shows the final stages in the synthesis of compound **M**.



M

(i) Draw the structural formulae of compounds **L** and **K**.

(ii) Give the synthetic route, involving *not more than three steps*, from **J** to **K**. In your answer, suggest the reagent(s) and conditions involved in each step and draw the structural formulae of the intermediate organic products.

(iii) Identify the type(s) of stereoisomerism shown by compound **M**. State the total number of possible stereoisomers.

(iv) In the reaction of **L** and **K** to form **M**, another organic compound can also be formed. Draw the structural formula of the organic compound and explain how its formation may arise.

(v) State the type of reaction taking place when compound **M** reacts with each of the following reagents:

I sodium metal

II bromine water

[14]

5 VJC/2010/P2/Q5(b) Level of Difficulty: [☆☆]

(b) The acidities of CH_3CO_2H, C_6H_5OH and CH_3CH_2OH are different.

(i) Explain the relative acidities of CH_3CO_2H, C_6H_5OH and CH_3CH_2OH in terms of their structures.

(ii) Hence or otherwise, arrange in decreasing order of pK_b values of their conjugate bases.

(iii) Given that a saturated aqueous solution of C_6H_5OH has a pH of 5.0 and a pK_a of 9.95. What is the solubility of C_6H_5OH in mol dm^{-3}?

Suggested Answers

1 RVHS/2010/P2/Q1(f) Level of Difficulty: [☆]

CH_3COOH has the highest pK_a and is the weakest acid as the methyl group is electron donating and intensifies the negative charge of the COO^- group, making the ethanoate anion the least stable.

C_6H_5COOH has a lower pK_a than CH_3COOH as the negative charge of the COO^- group is delocalised into the benzene ring, making the benzoate anion more stable than the ethanoate anion.

CCl_3COOH has the lowest pK_a and is the strongest acid as the electron-withdrawing Cl atoms disperses the negative charge of the COO^- group, making the CCl_3COO^- anion the most stable.

2 SAJC/2010/P2/Q7(c)(iv) Level of Difficulty: [☆]

Aspirin more acidic.

Carboxylate anion is more stable than the phenoxide ion due to the delocalisation of negative charge over 2 oxygen and 1 carbon.

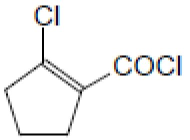
3 SRJC/2010/P3/Q2(c)(i) Level of Difficulty: [☆]

$CH_3COCl + H_2O \rightarrow HCl + CH_3COOH$
Ethanoyl chloride undergoes **hydrolysis**, resulting in the formation of a **strong acid** HCl. **pH = 0.5**

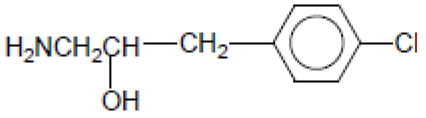
$CH_2ClCOOH + H_2O \rightleftharpoons H_3O^+ + CH_2ClCOO^-$
Chloroethanoic acid is a **weak acid** that undergoes **partial dissociation**. **pH = 3**

4 ACJC/2010/P3/Q4(b) Level of Difficulty: [☆☆]

(b) (i) • L

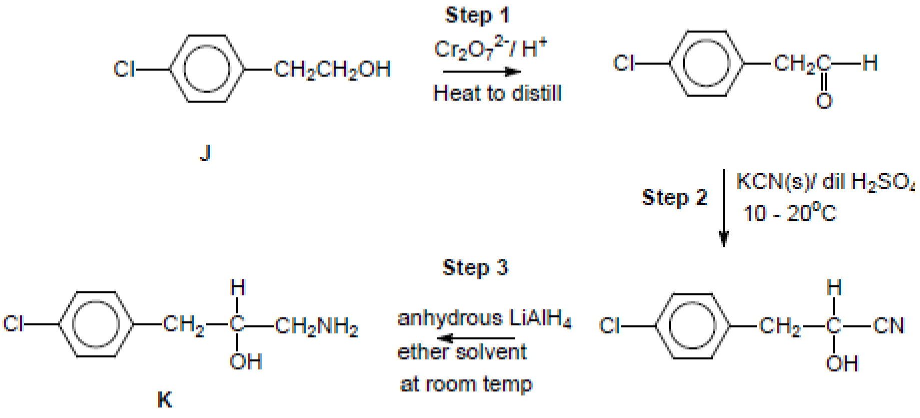


• K



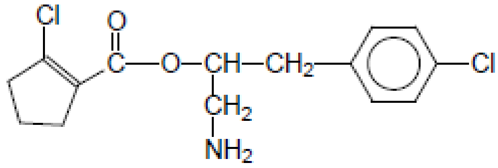
[2]

(ii)



[6]

(iii)
- **optical isomerism**
- **2** [2]

(iv)
- 

- **Esterification takes place in the reaction between –COCl and –OH functional groups**

(v)
- **I : Redox / reduction**
- **II : electrophilic addition**

5 VJC/2010/P2/Q5(b) Level of Difficulty: [☆☆]

(b)(i)

Acidity decreases in the order: $CH_3CO_2H > C_6H_5OH > CH_3CH_2OH$.
Stability of ion decreases in the order: $CH_3CO_2^- > C_6H_5O^- > CH_3CH_2O^-$.
CH_3CO_2H is the strongest acid as the $CH_3CO_2^-$ ion is resonance–stabilised (OR stabilised to a greater extent by delocalisation of the negative charge over the C and 2 O atoms).
C_6H_5OH is a stronger acid than CH_3CH_2OH as the $C_6H_5O^-$ ion is more stabilised due to the delocalisation of the negative charge into the benzene ring.
The $CH_3CH_2O^-$ ion is destabilised as the negative charge is intensified by the electron–donating inductive effect of the ethyl group.

(ii)

pK_b decreases in the order: $CH_3CO_2^- > C_6H_5O^- > CH_3CH_2O^-$.

(iii)

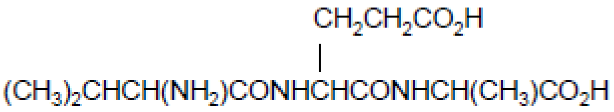
$-\lg [H^+] = 5.0$
$[H^+] = 1.0 \times 10^{-5}$ mol dm^{-3}
$$K_a = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]}$$
$10^{-9.95} = (1.0 \times 10^{-5})^2 / [C_6H_5OH]$
$[C_6H_5OH] = 0.891$ mol dm^{-3}

Solubility of $C_6H_5OH = 0.891$ mol dm^{-3}

10.3.5 Nitrogen Compounds

1 ACJC/2010/P2/Q6(a) Level of Difficulty: [☆]

Insulin is the hormone essential for carbohydrate metabolism. Partial hydrolysis of insulin gives the following tripeptide



$$(CH_3)_2CHCH(NH_2)CONH\overset{\overset{CH_2CH_2CO_2H}{|}}{C}HCONHCH(CH_3)CO_2H$$

(a) (i) Draw the structural formulae of the constituent amino acids which could be obtained by further hydrolysis of this tripeptide.

(ii) In solution, amino acids exist as *zwitterions*. Use one of the constituent amino acid produced by hydrolysis to illustrate what is meant by this term.

(iii) How would you expect the melting point and the solubility in water, of an unionized covalent form of the amino acid to compare with the actual properties of the zwitterionic form?

(iv) In aqueous solution, amino acids can act as buffers. By means of an equation, show how the given constituent amino acid can act as buffer when small amount of dilute HC*l* is added to its solution.

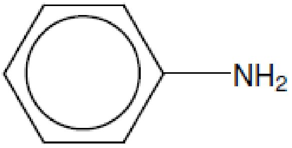
2 CJC/2010/P3/Q4(b) Level of Difficulty: [☆]

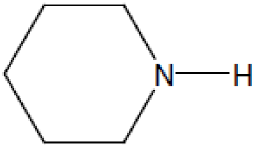
Explain the difference in basicity between ethylamine, $CH_3CH_2NH_2$ and phenylamine, $C_6H_5NH_2$. [3]

3 HCI/2010/P2/Q3(d) Level of Difficulty: [☆]

Arrange the following compounds in order of increasing pK_b value. Explain your answer.

$CH_3CH_2NH_2$





4 MI/2010/P3/Q1(c) Level of Difficulty: [☆]

Ammonia is a base. Arrange the following nitrogen compounds in order of increasing pK_b. Explain your answer. [4]

ammonia, ethylamine, 2-chloroethylamine, phenylamine

5 MI/2010/P3/Q2(f)-(h) Level of Difficulty: [☆]

(f) Polymerisation also occurs in nature, e.g. formation of proteins.

Describe how peptide bonds are formed between amino acids during the formation of a tripeptide. Include diagrams and displayed formulae in your answer. You may use the general formula of amino acid, $H_2NCHRCO_2H$, in your

Suggested Answers

1 ACJC/2010/P2/Q6(a) Level of Difficulty: [✩]

(i) Draw the structural formula of the constituent amino acids which could be obtained by further hydrolysis of this tripeptide.

$(CH_3)_2CHCH(NH_2)CO_2H$
$H_2NCH(CH_2CH_2CO_2H)CO_2H$
$H_2NCH(CH_3)CO_2H$

(ii) In solution, amino acids exist as *zwitterions*. Use one of the constituent amino acids produced by hydrolysis to illustrate what is meant by this term.

H_3N^+-$CH(CH_3)$-CO_2^- / $H_3N^+CH(CH_2CH_2CO_2H)CO_2^-$/ $(CH_3)_2CHCH(NH_3^+)CO_2^-$

(iii) How would you expect the melting point and the solubility in water, of an unionized covalent form of the amino acid to compare with the actual properties of the zwitterionic form? Explain.

Zwitterionic form would be **more soluble in water** with a **higher melting point** than the covalent form due to **ion-dipole interactions with water [1]** and **cation-anion attractions in the crystal lattice [1].** *Marks awarded only when explanation given*

(iv) Amino acids can acts as buffers in solution. By means of a balanced equation, show how the given constituent amino acid can act as buffer when dilute HC*l* is added to its solution.

H_3N^+-$CH(CH_3)$-CO_2^- + $HCl \rightarrow Cl^-H_3N^+$-$CH(CH_3)$-$CO_2H$
H_3N^+-$CH(CH_3)$-CO_2^- + $H^+ \rightarrow H_3N^+$-$CH(CH_3)$-CO_2H
H_2N-$CH(CH_3)$-CO_2H + $HCl \rightarrow Cl^-H_3N^+$-$CH(CH_3)$-$CO_2H$
H_2N-$CH(CH_3)$-CO_2H + $H^+ \rightarrow H_3N^+$-$CH(CH_3)$-CO_2H

Any one of the above equations
Must be balanced [1]

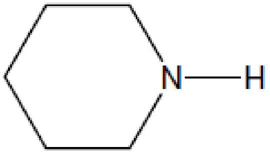
2 CJC/2010/P3/Q4(b) Level of Difficulty: [✩]

Phenylamine is a weaker base than ethylamine.

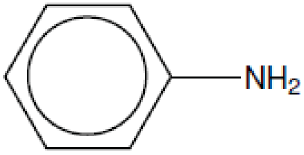
The p-orbital of N overlaps with the π-electron cloud of the benzene ring in phenylamine. The lone pair on N is less available to accept a proton and thus is a weak base.
In ethylamine, the electron donating –CH_3 group increases the availability of lone pair on N to accept proton. Thus ethylamine is a stronger base than phenylamine.

3 HCI/2010/P2/Q3(d) Level of Difficulty: [✩]

Correct ranking:



$CH_3CH_2NH_2$



$C_5H_{10}NH$ is more basic than $CH_3CH_2NH_2$ as it has more electron-donating alkyl groups, thus increasing the availability of lone pair of electrons on N for acid-base reaction.

Phenylamine is the least basic because the lone pair of electrons on N is delocalized into the benzene ring so less available for acid-base reaction.

4 MI/2010/P3/Q1(c) Level of Difficulty: [✭]

Sequence: ethylamine, 2-chloroethylamine, ammonia, phenylamine ;

Presence of electron – donating alkyl groups in ethylamine and 2-chloroethylamine increases the electron density on the N atom, making the lone pair of electrons on N atom more available for coordination to a proton.
∴Ammonia is a weaker base than both ethylamine and 2-chloroethylamine

Presence of electron-withdrawing Cl atom in 2-chloroethylamine attract electrons away from the nitrogen atom, i.e. decreases the electron density on N atom. When compared to ethylamine, the lone pair of electrons on N atom of 2-chloroethylamine is less available for coordination to a proton.
Lone pair of electrons on the N atom in phenylamine is partially delocalised by the interaction with the electron cloud of the benzene ring, making it less available for coordination to a proton. ;
∴Phenylamine is the weakest base.

5 MI/2010/P3/Q2(f)-(h) Level of Difficulty: [✭]

(f)

Condensation reaction with the elimination of water

at least one peptide bond drawn out in full

correct formula of the tripeptide

(g)

acid/H^+/HCl etc. or alkali/OH^-/NaOH

heat/boil/reflux if temp given >90 °C

(h)(i)

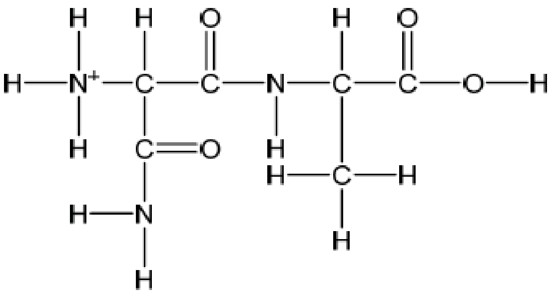
–S–H groups (allow sulfide/S/cysteine residue)

(ii)

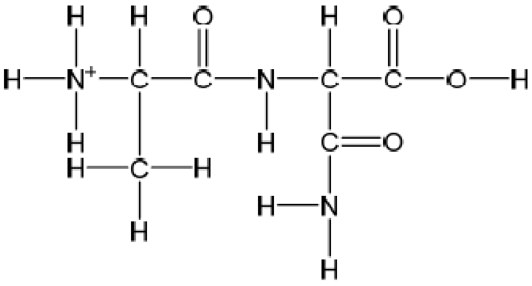
disrupts the 3-dimensional structure of the enzyme AND hence inhibits/reduces/decreases the enzyme activity/stops normal function ;

6 RVHS/2010/P2/Q4(c)(ii) Level of Difficulty: [☆]

(ii)



or

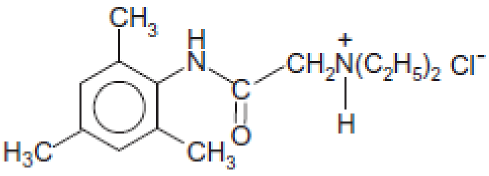


7 TJC/2010/P2/Q6(a)(i),(ii) Level of Difficulty: [☆]

(i)

- Circle the nitrogen that is attached to the two ethyl groups.
- Alkyl groups are electron donating, hence lone pair on nitrogen is more available for donation to acid/ dative bonding to a proton, thus rendering it to be basic.
- Electron withdrawing character of the carbonyl group reduces the electron density on the nitrogen atom, making the lone pair of electrons less available for dative bonding to a proton.

(ii)



8 AJC/2010/P2/Q6(c) Level of Difficulty: [☆☆]

(c)(i) The peptide bond is not formed using the α–acid group of the N–terminal amino acid.

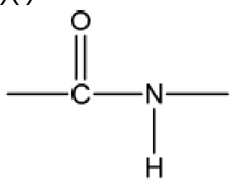
(c)(ii) $2\ G\text{–}SH + \frac{1}{2}\ O_2 \rightarrow G\text{–}S\text{–}S\text{–}G + H_2O$

(c)(iii) Heavy metal ions and reducing agents.

Observation: precipitation or coagulation

9 CJC/2010/P3/Q4(c),(d) Level of Difficulty: [☆☆]

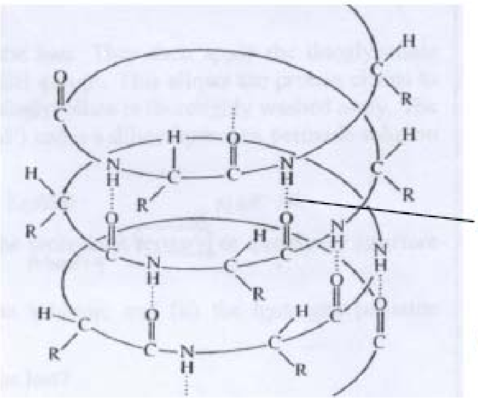
(c)(i)



Peptide or amide linkage

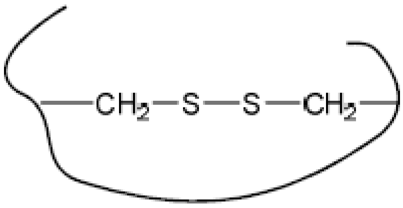
(ii)

The chain is held in a helix by hydrogen bonds formed between the C=O and N-H of the peptide bonds within the chain.



OR Draw and label hydrogen bond

(iii)

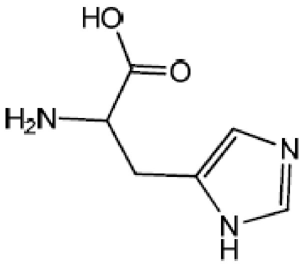


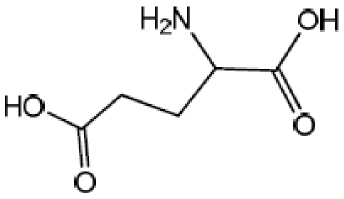
(iv)

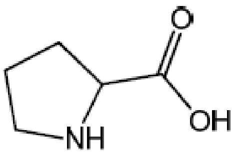
Heavy metal ions can react with the –SH group to form strong metal sulfide bonds, preventing the formation of disulfide linkages.

(c)

Dilute HCl or NaOH, heat



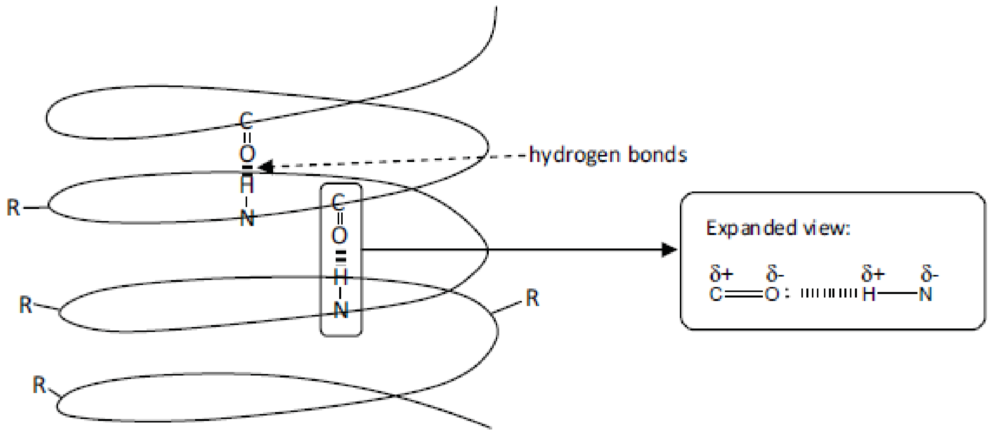




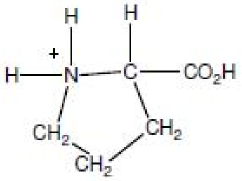
10 HCI/2010/P3/Q2(b) Level of Difficulty: [☆☆]

(i) The enzyme lowers the activation energy or providing an active site for reacting particles to come close together.

(ii)



(iii)



(iv) **F:** disulphide bridge -CH_2-S-S-CH_2-
G: hydrogen bonding (include diagram between –CH_2OH and any other suitable group)

11 MJC/2010/P2/Q5 Level of Difficulty: [✩✩]

(a) **(i)** Analysis:

Hydrolysis of peptide **Y** → gain in 1 H_2O for every peptide bond broken.

No. of peptide bonds broken = <u>6</u>

M_r of peptide **Y** = 2 x 181 + 3 x 165 + 174 x 2 - 6 x 18

= <u>1097</u>

(ii) At low concentration of peptide **Y**,

- Rate of reaction increases linearly as active sites of the enzyme are not fully occupied
- Reaction is approximately first order wrt the concentration of peptide **Y**.

However, at high concentration of peptide **Y**,

- Rate of reaction is constant
- Rate is independent of concentration of peptide **Y** as all active sites occupied
- Reaction is zero order wrt the concentration of peptide **Y**.

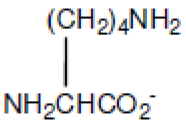
(b) **(i)** Any 2 of the following: Serine, Aspartic acid, Lysine, Histidine.

This is due to the formation of hydrogen bonding between the amino acids and water molecules.

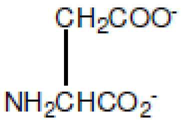
(ii) At low pH,

- Excess H^+ will react with basic amine group in histidine/lysine of the chymotrypsin.
- Hence, low pH will disrupt ionic bonds and hydrogen bonds formed between basic amine group in histidine/lysine and the acidic carboxylic group in aspartic acid which are critical to the tertiary and quaternary structure of the enzyme.
- This will thus lead to changes in enzyme shape and shape of active site and hence loss of enzyme activity and denaturation.

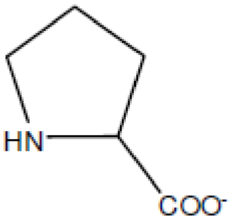
(c)



$NH_2CH(CO_2^-)(CH_2)_4NH_2$



$NH_2CH(CO_2^-)CH_2COO^-$



12 MJC/2010/P3/Q1(a)(i),(b) Level of Difficulty: [☆☆]

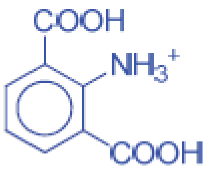
1(a) **(i)** For the amide, the electron-withdrawing effect of the carbonyl group reduces the electron density on the N atom, making the lone pair less available to accept a proton, hence it is a weaker base compared to the amine.

(b) **(i)** K_b value of *Procaine* > K_b value of *Lidocaine*. For the 2 samples of equal concentration, number of free mobile ions for *Procaine* is greater than that of *Lidocaine*.

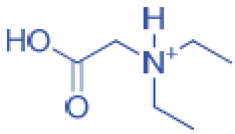
(ii) Add aqueous Br_2 at r.t.p separately to each of the unknown compounds.

Reddish brown Br_2 decolorizes in Procaine and a white ppt is formed while reddish brown Br_2 does not decolorize in Lidocaine.

(iii)



and



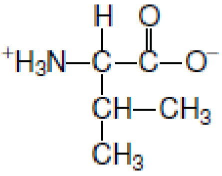
13 NJC/2010/P2/Q7 Level of Difficulty: [☆☆]

(a)(i)

At the alkaline pH of 10.76, the dissociation of the amino group of the side chain was suppressed. Hence, arginine exists as zwitterions at the pI value of 10.76.

$$\square\text{~}NH_2 + H_2O \rightleftharpoons \square\text{~}NH_3^+ + OH^-$$

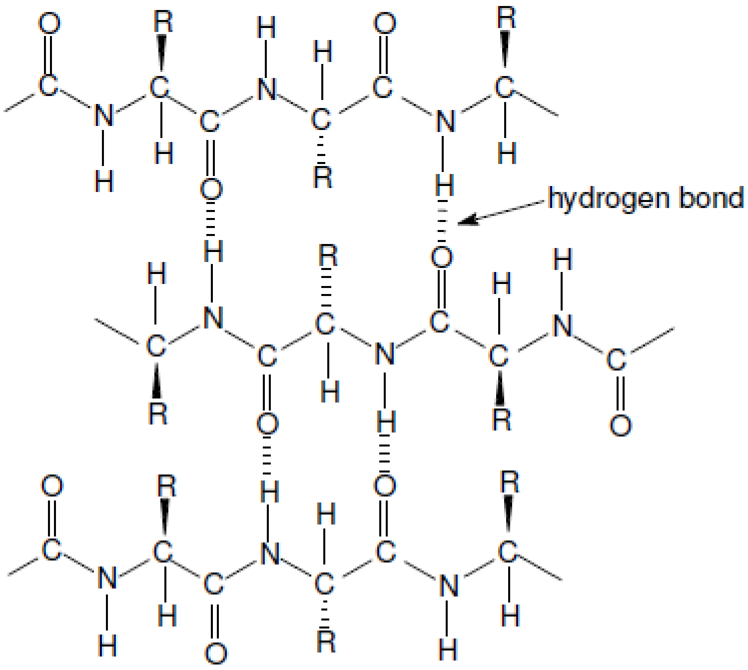
(ii)



$^+H_3N{-}CH(CH(CH_3)_2){-}COO^-$

(b)(i)

Beta pleated sheet



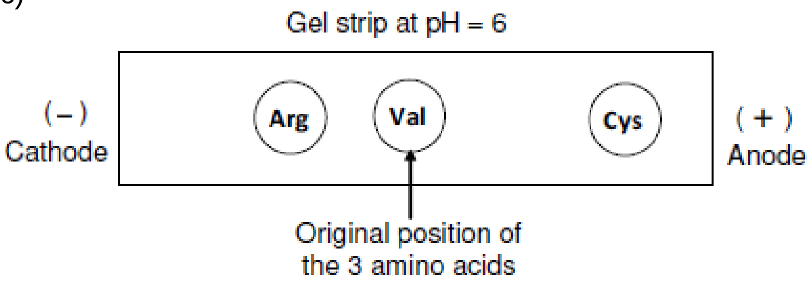
(ii)

1. Disulfide bridge: Cys and Cys
2. Hydrogen bond : (1) Arg and Tyr

   (2) Arg and Arg

   (3) Tyr and Tyr
3. Hydrophobic interaction: Val and Val

(c)



At pH of 6:

As pI of Arg is above pH 6 (acid medium), Arg is protonated to form a positively charged cation and migrates towards cathode.

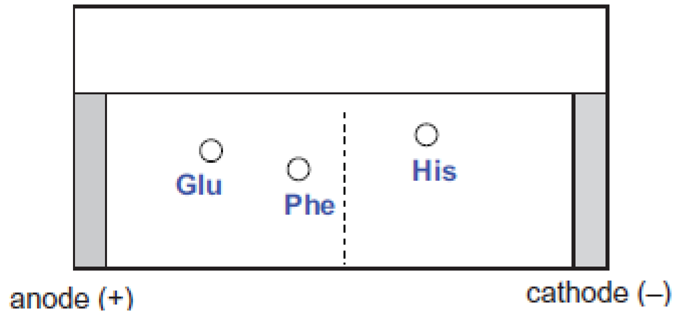
As pI of Cys is below pH 6 (alkaline medium) Cys is deprotonated in alkaline medium to form a negatively charged anion and migrates towards anode.

As pI of Val is close to pH 6, Valine exists mostly in the form of zwitterions and remains close to the original center position.

Since M_r of Cys is smaller than Arg, Cys migrates faster Arg.

14 PJC/2010/P2/Q4(b) Level of Difficulty: [☆☆]

(b)



(c) (i) **The tertiary structure of a protein is the three dimensional structure / conformation of the polypeptide where the secondary structure and the unstructured length of peptide devoid of secondary structure is held by interactions between the side chain groups.**

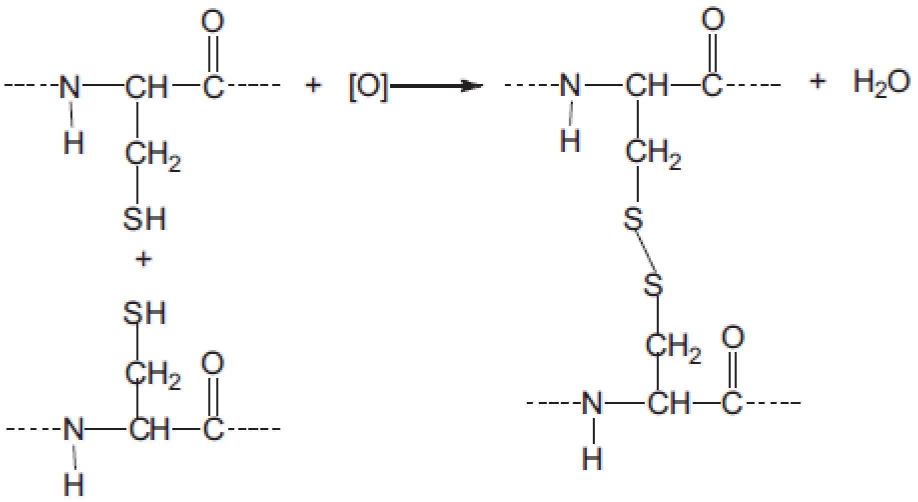
(ii) **phe contains a non-polar benzene group that will form van der Waals' forces of attraction while thr has a –OH group that can participates in hydrogen bonding.**

As the strength of hydrogen bonds is stronger than van der Waals' forces, the change in the side chain groups can cause the folding / conformation of the enzyme to differ.

15 RVHS/2010/P3/Q2(b) Level of Difficulty: [☆☆]

(i) The tertiary structure of a protein is the overall three-dimensional shape of a polypeptide, as stabilised by the side-chain interactions.

(ii)



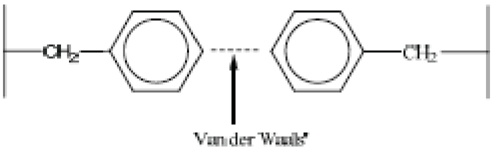
(iii) Ionic interactions, hydrogen bonding and van der Waals' forces.

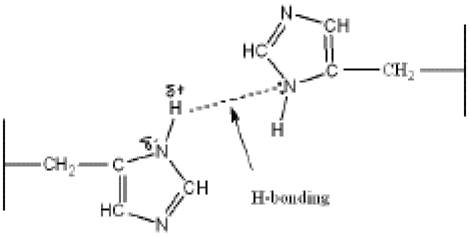
(iv) Heavy metal ions form ionic interactions with the $-COO^-$ groups on the side chains and disrupt the ionic interactions in the tertiary structure. This brings about the formation of insoluble protein salts (i.e. precipitation of protein) and leads to denaturation.

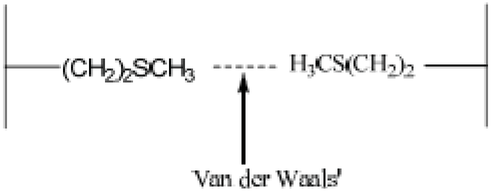
Heavy metal ions have a high affinity for sulfur and disrupt the disulfide bridges in the tertiary structure, leading to denaturation.

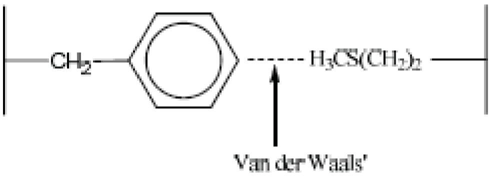
16 SAJC/2010/P2/Q8 Level of Difficulty: [☆☆]

(a) H-bond + any one of the VDW









Note: Disulfide bonds do not form

(b) Adding acidic vinegar causes disruption of hydrogen bonds between the His side chain.

Grilling or heating causes disruption of VDW or hydrogen bonds between the side chains.

Protein is denatured and loses its native conformation.

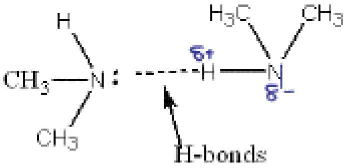
17 SAJC/2010/P3/Q2(a),(c) Level of Difficulty: [☆☆]

(a) (i) Phenylalanine exists as zwitterions and hence, forms strong ion-dipole interactions with H_2O which provides sufficient energy to overcome the electrostatic forces of attractions / ionic bonding between the zwitterions.

Phenylamine is insoluble in water as the presence of non-polar bulky benzene ring which limits the formation of H-bond.

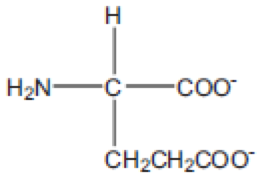
(ii) Trimethylamine has a lower boiling point as the main interaction is permanent dipole-permanent dipole interaction /VDW while for dimethylamine, H-bond exists which is a stronger interaction.

Hence, more energy is needed to break the H-bonds.

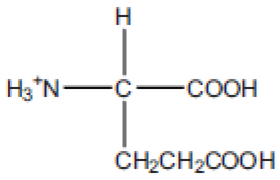


(iii) The lone pair of electrons on N in trimethyamine is more available for protonation due to the presence of 3 electron donating methyl groups.
The lone pair of electrons on N in phenylamine is delocalised into the benzene ring, making it less available for protonation.

(c) (i) I - NaOH II - HC*l*

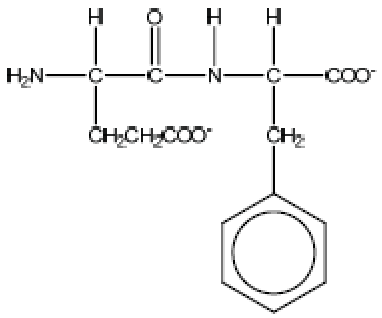


$H_2N-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_2COO^-}{C}}-COO^-$

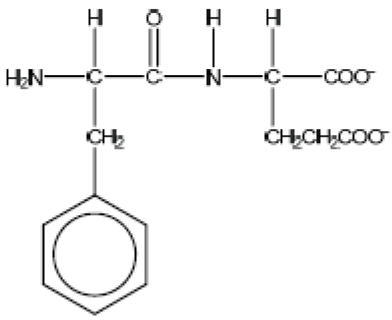


$H_3{}^+N-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_2COOH}{C}}-COOH$

(ii)



or

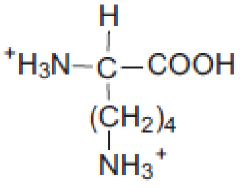
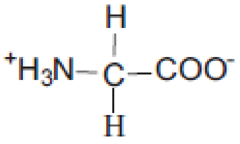
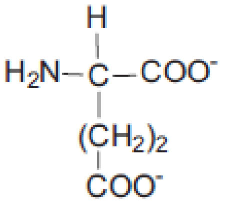


18 SRJC/2010/P2/Q4(b) Level of Difficulty: [☆☆]
(i)
Hydrogen bonds are formed between O atom of **(-C=O)** group and the H atom of **(-N-H)** group.

(ii)
There is **no H-atom on the N atom** *(of the cyclic amide)* **available for H-bonding with the O atom of C=O of the fourth peptide** on the backbone chain. Or the cyclic structure interfere with the hydrogen

19 SRJC/2010/P3/Q2(a) Level of Difficulty: [☆☆]
(i)

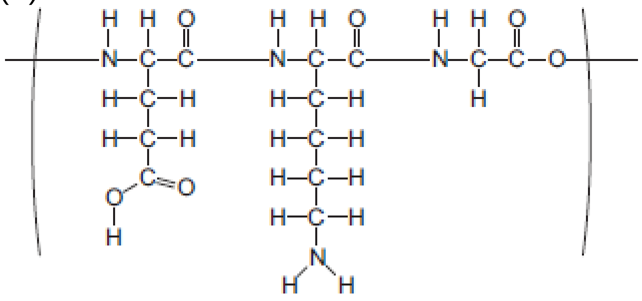
pH=6

Amino acid	Lys	Gly	Glu
Predominant Specie	 ${}^+H_3N-\overset{\displaystyle H}{\underset{\displaystyle (CH_2)_4NH_3^+}{C}}-COOH$	 ${}^+H_3N-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-COO^-$	 $H_2N-\overset{\displaystyle H}{\underset{\displaystyle (CH_2)_2COO^-}{C}}-COO^-$
Position on plate	Towards the cathode	Centre / Stationary	Towards the anode

(ii)

The student will **<u>not</u>** be **<u>successful.</u>**
<u>Large</u> amount of energy (>100°C) is required to break the **<u>strong ionic bonds</u>** in the tertiary structure between **<u>ionic R groups</u>** or the hydrogen bonding in the secondary structure.

(iii)



20 <u>TJC/2010/P3/Q4(b)</u> Level of Difficulty: [☆☆]

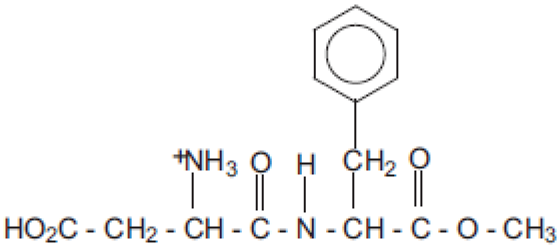
(i) • •Carboxylic acid, primary amine, substituted amide or amide and ester.

(ii) • Add $NaHCO_3$/Na_2CO_3
• Effervescence of CO_2 which gave a white ppt with limewater OR

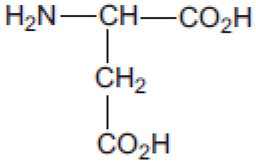
add PCl_5; white fumes of HC*l* evolved OR add Na metal; effervescence observed

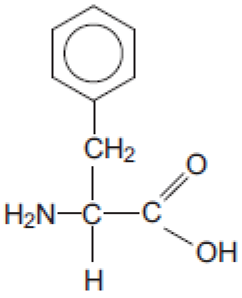
Note : There is no simple test for esters (acid hydrolysis and test for acid or alcohol is not acceptable)

(iii) •



(iv) ••





(v) • The R group which contains $-CO_2H$ group, can interact with other polar R groups (containing –OH / C=O or $-CH_2CO_2H$) via hydrogen bonding.
Or when ionized to $-CH_2CO_2^-$ in aqueous medium can form **ionic bonds / electrostatic attraction** with **cationic R groups** *e.g.* those with $-^+NH_3$

•The R group which is non-polar can interact with other non-polar R groups via induced dipole-induced dipole interaction/vdw forces.

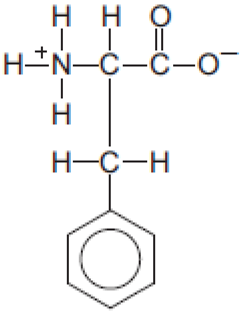
21 VJC/2010/P3/Q5(a)-(c) Level of Difficulty: [☆☆]

5(a)(i)

Isoelectric point refers to the pH at which **all** amino acids exist as **zwitterions**, hence there will be **no migration** of amino acids when placed in an electric field.

Zwitterion is a **dipolar ion** with **a positive charge** and **a negative charge**, hence it is **electrically neutral** such as amino acids, $^{+}NH_3$–CHR–COO^{-}.

(ii)



(iii)

$C_6H_5CH_2CH(NH_2)CO_2H + HCl \rightarrow C_6H_5CH_2CH(CO_2H)NH_3^{+}\ Cl^{-}$

$C_6H_5CH_2CH(NH_2)CO_2H + NaOH \rightarrow C_6H_5CH_2CH(NH_2)CO_2^{-}\ Na^{+} + H_2O$

[Can express in zwitterionic forms too.]

(iv)

Phenylalanine has a **giant ionic structure** consisting of **dipolar ions** held by **strong ionic bonds** which need **a lot of energy** to overcome. Hence, it has a high melting point and exists as a solid at room temperature.

Being ionic, phenylalanine can attract polar water molecules by forming **ion–dipole bonds**. The **energy liberated** from these interactions is sufficient to overcome the **ionic bonds** between phenylalanine and the **hydrogen bonds** between water molecules, enabling it to dissolve in water.

(b)

In fibrous proteins, the polypeptides are arranged in a **long and elongated structure** with **alkyl groups pointing towards the external surroundings**. The **hydrophobic alkyl groups** will **repel** water molecules causing the proteins to be insoluble in water.

In globular proteins, the polypeptides are folded into a compact rounded structure with **hydrophobic alkyl groups** located **inside** the structure, away from the aqueous surroundings. The **hydrophilic alkyl groups** are located on the **surface** of the protein structure, and they can attract water molecules enabling globular proteins to dissolve in water.

(c)(i)

–CONH– + $H_2O \rightarrow$ –CO_2H + –NH_2

(ii)

Pepsin undergoes **denaturation** when boiled.
Boiling provides **heat energy** that can **disrupt** the **bonds and forces of attractions between R groups** responsible for stabilising the **tertiary structure and the hydrogen bonds between the peptide linkages responsible for stabilizing the secondary structures** of pepsin,
causing the polypeptide chains to **unfold/uncoil/unravel**.
As a result, pepsin is unable to perform its catalytic function.

22 YJC/2010/P3/Q3(a) Level of Difficulty: [☆☆]

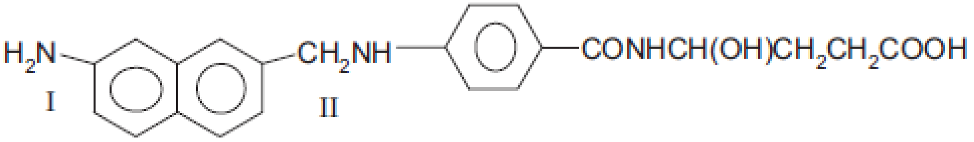
ai The quaternary structure of haemoglobin refers to the spatial arrangement of its four associated subunits each with its own haem group. The quaternary structure is stabilized by the four types of R-group interactions (hydrogen bonds, ionic bonds, disulfide linkages and van der Waals forces.

aii They all contain the **same sequence of amino acids (primary structure)**, hence the R-group interactions all occur in the same positions giving rise to the same tertiary structure.

aiii Extreme pH conditions will affect **charged R groups** containing NH_3^+ and COO^- , hence affecting the extent **of ionic interactions** leading to a change in tertiary structure and loss of function.

23 YJC/2010/P3/Q5(d)(i) Level of Difficulty: [☆☆]

di



I = pK_{b2} , II = pK_{b1} , lone pair of electrons on N of II is more available for dative bonding with H^+ due to the presence of electron donating R group.

24 ACJC/2010/P2/Q6(b) Level of Difficulty: [☆☆☆]

met-ala-gly **[1] for working**
gly-ala-gly
ala-gly-ala
ala-gly-arg
gly-arg-val
arg-val-lys

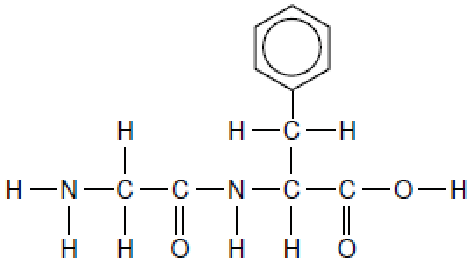
met-ala-gly-ala-gly-ala-gly-arg-val-lys **[1]**

25 NYJC/2010/P2/Q10 Level of Difficulty: [✫✫✫]

(a)

sequence of amino acid in the polypeptide

(b)(i)



(ii)

Gly – Phe – Phe – Tyr – Thr – Pro – Lys – Ala

(c)

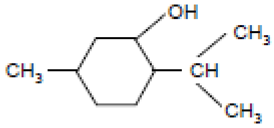
P: Cys.. **Q**: Cys (1) for both **P** and **Q** ....

Name of linkage: disulfide linkage (1)...

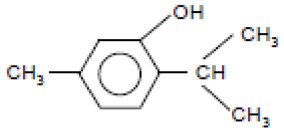
TOPIC 10.4: DISTINGUISHING TESTS

1 ACJC/2010/P3/Q3(d)(ii)

(d) Menthol is the main component in oil of peppermint, a plant extract obtained from the leaves and stems of *Menthe piperita*.



(ii) Synthetic menthol can be made from 3-hydroxymethylbenzene through Friedel-Crafts acylation using $(CH_3)_2CHCl$ and $AlCl_3$ giving the following intermediate:



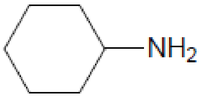
Describe simple chemical test which can be carried out to distinguish the intermediate from synthetic menthol.

2 AJC/2010/P2/Q6(a)

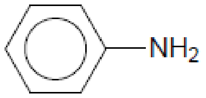
Organic compounds containing nitrogen are important to life and have wide applications in medicine and polymer science.

(a) Suggest methods by which the following organic nitrogen compounds could be distinguished from each other by a simple chemical test.

(i)



G



H

(ii) $HCONHCH_3$ CH_3CONH_2

J **K**

3 CJC/2010/P3/Q2(e)

Describe a chemical test to distinguish between 2-bromobutane and bromobenzene.

[2]

19 TJC/2010/P3/Q4(c)(i)

The HPLC chromatogram of the food additive mixture shows that it contains salicylic acid (2-hydroxybenzenecarboxylic acid) and benzenecarboxylic acid.

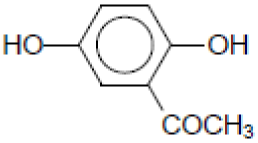
(i) You are given separate samples of these two acids, dissolved in a suitable solvent. State a chemical reagent that will distinguish between these two acids, giving the result of the test in each case.

20 VJC/2010/P2/Q4(a)

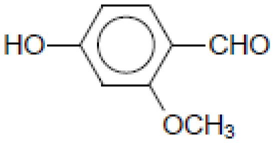
4(a) Suggest how the following compounds could be distinguished from each other by chemical tests. The distinguishing of some of these pairs may rely on a preliminary breaking–up of the compounds, and subsequent testing of the reaction products.

For each test, state the reagents and conditions you would use, and the observations you would make with **each** compound undergoing the test.

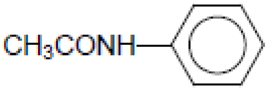
(i)



and

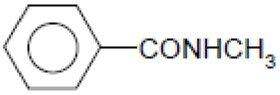


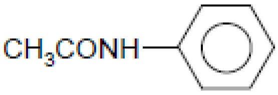
(ii) $CH_3CONHCH_3$ and



21 YJC/2010/P3/Q5(e)

(e) Suggest methods by which the following compounds can be distinguished from each other by chemical tests. The distinguishing of this pair of compounds may rely on a preliminary breaking up of the compounds, and subsequent testing of the reaction products.





Suggested Answers

1 ACJC/2010/P3/Q3(d)(ii)

Add **Br_2(aq)** to both compounds.
The intermediate would react with Br_2(aq) to form **white precipitate with decolourisation of Br_2(aq).**

(other possible answers: acidified $K_2Cr_2O_7$, and neutral $FeCl_3$)

2 AJC/2010/P2/Q6(a)

(a)(i) Add Br_2(aq) to each of the two compounds.

Compound **G**: No colour change
Compound **H**: Red–brown bromine turns colourless and white ppt formed

(a)(ii) Add $KMnO_4$ and dilute H_2SO_4 to each of the two compounds. Heat/ warm.

Compound **J**: Purple $KMnO_4$ decolourised and effervescence of CO_2
Compound **K**: No effervescence

3 CJC/2010/P3/Q2(e)

Reagents: Aq. / Ethanolic Silver nitrate, $AgNO_3$
Conditions: Heat
Observations: A cream precipitate will be observed for 2-bromobutane whereas no precipitate will be observed for bromobenzene.

4 CJC/2010/P3/Q5(c)(ii)

I. TCP and Dettol

Reagents: Acidified Potassium Manganate (VII)
Conditions: Heat
Observations:
Purple $KMnO_4$ turns colourless with dettol, no such observation with TCP.

OR
Reagents: Aqueous Bromine
Conditions: Room temperature
Observations:
Orange\brown solution turns colourless with dettol and white misty fumes of HBr is released, no such observation with TCP.

II. IPA and Dettol

Reagents: Iodine(aq) \ NaOH(aq)
Conditions: Warm
Observations:
Yellow ppt of triiodomethane, CHI_3 observed with IPA, no yellow ppt with dettol.

OR
Reagents: Acidified Potassium Dichromate
Conditions: Heat
Observations:
Orange $K_2Cr_2O_7$ turns green in colour with IPA, no such observation with dettol.

OR
Reagents: Aqueous Bromine
Conditions: Room temperature
Observations:
Orange\brown solution turns colourless with dettol and white misty fumes of HBr is released, no such observation with IPA.

OR
Reagents: **neutral** $FeCl_3$
Conditions: Room temperature
Observations:
Purple colouration formed with dettol but no such observation with IPA.

OR
Reagents: PCl_5
Conditions: Room temperature
Observations:
White misty fumes of HCl is formed with IPA but no such observation with dettol.

5 HCI/2010/P2/Q6(b)

6(b)(i) Secondary alcohol and ketone

6(b)(ii) E.g. use Br_2(aq), PCl_5 etc

6 MI/2010/P3/Q5(5)

(i)

alkaline aqueous iodine ($NaOH/I_2$)

J: yellow ppt seen

K: No yellow ppt observed.

(ii)

aqueous bromine

L: solution remains brown. No ppt formed.

M: brown bromine solution decolourises. white ppt seen.

(iii)

add $AgNO_3$(aq) (without heating)

N: white ppt observed

P: no white ppt observed

(iv)

$CuSO_4$ till excess

Q: solution remains pale blue

R: solution turn dark blue, then forms pale blue ppt with excess $CuSO_4$

7 NJC/2010/P3/Q2(b)

(b) (i) Brick red (reddish brown) precipitate.

(b) (ii) I_2; $NaOH$; warm
Progesterone gives a yellow ppt.

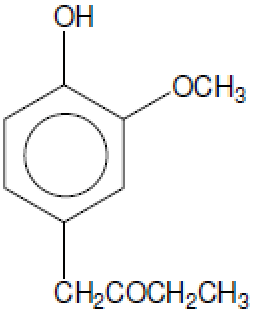
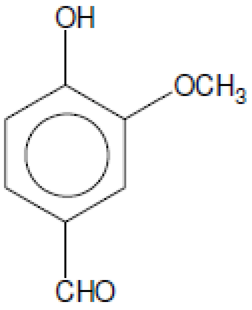
8 NJC/2010/P3/Q5(a)(ii)

5 (a) (ii) Add aqueous NaOH to a separating funnel containing the mixture of phenol and propanone. Shake thoroughly and drain off the aqueous layer. Acidify the aqueous layer with dilute HCl to recover the phenol.

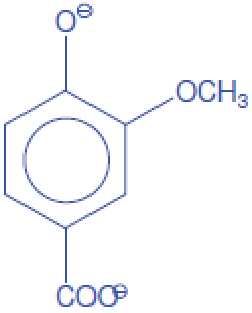
9 NYJC/2010/P3/Q9(b)(i)

(i)

Reagents and conditions: Tollen's reagent, warm

		
Observation	No Ag mirror is formed.	Ag mirror is formed.

(ii)



10 PJC/2010/P3/Q3(c)(i)

(i) 1) reagents and conditions: I_2, NaOH (aq), warm

Observation with lactic acid: Yellow ppt of CHI_3 formed

Observation with glycolic acid: No yellow ppt formed

OR

reagents and conditions: $KMnO_4$(aq), H_2SO_4(aq), heat

Observation with lactic acid: Purple $KMnO_4$ decolourises without effervescence of colourless gas

Observation with glycolic acid: Purple $KMnO_4$ decolourises with effervescence of colourless gas

2) reagents and conditions: neutral $FeCl_3$(aq)

Observation with glycolic acid: No violet complex formed

Observation with salicylic acid: violet complex formed

OR

reagents and conditions: Br_2(aq)

Observation with glycolic acid: Reddish brown Br_2(aq) remains

Observation with salicylic acid: Reddish brown Br_2(aq) decolourised

11 RVHS/2010/P2/Q4(d)(iii)

Any one of the following:

- Add neutral $FeCl_3$(aq). Purple colouration is formed with tyrosine, while no purple colouration is formed with alanine.
- Add Br_2(aq). Reddish brown Br_2 is decolourised with tyrosine, while no decolourisation with alanine.
- Add acidified $KMnO_4$(aq) and heat. Purple $KMnO_4$ is decolourised with tyrosine, while no decolourisation with alanine.

12 RVHS/2010/P2/Q5(a)

To distinguish jasmonic acid from the rest, use any one of the following tests:

- Add Na_2CO_3(aq). Effervescence (of a colourless odourless gas which gives a white ppt with limewater) occurs with jasmonic acid, but no gas is evolved with methyl jasmonate and jasmone.
- Add Na. Effervescence (of a colourless odourless gas which extinguishes a lighted splint with a 'pop' sound) occurs with jasmonic acid, but no gas is evolved with methyl jasmonate and jasmone.
- Add PCl_5 or $SOCl_2$. White fumes formed with jasmonic acid, but no white fumes with methyl jasmonate and jasmone.

To distinguish methyl jasmonate from the rest:

- Add acidified $K_2Cr_2O_7$(aq) and heat. Orange solution of $K_2Cr_2O_7$ turns green with methyl jasmonate, but $K_2Cr_2O_7$ remains orange for jasmonic acid and jasmone.

13 RVHS/2010/P3/Q1(f)

To distinguish 4-methylbenzyl bromide from **A**:

- Add NaOH(aq) and heat, then add excess dilute HNO_3 followed by $AgNO_3$(aq). Cream ppt formed with 4-methylbenzyl bromide but not with **A**.

To distinguish 4-methylbenzyl bromide from **B**:

- Add $AgNO_3$(aq). White fumes and cream ppt formed immediately with **B** but not for 4-methylbenzyl bromide.

14 RVHS/2010/P3/Q5(f)

(i) aliphatic aldehyde

(ii) $2Cu^{2+}(aq) + 2OH^{-}(aq) + 2e^{-} \rightarrow Cu_2O(s) + H_2O(l)$

15 SAJC/2010/P2/Q7(c)

Neutral $FeCl_3$ OR aq Br_2

16 SAJC/2010/P3/Q4(d)

(i) Reagents and conditions: Add $KMnO_4/H^+$, heat

Observation: Ethylbenzene - Purple manganate(VII) decolorised, colourless gas evolved formed white ppt with aqueous calcium hydroxide.

1,4-dimethylbenzene - Purple manganate(VII) decolourised but no gas evolved.

(ii) Reagents and conditions: aqueous bromine at room temperature

Observation: Phenylamine - Orange red solution decolourised, white ppt formed.

Benzylamide - Orange red solution remained and no white ppt formed.

(iii) Reagents and conditions: Heat with aqueous sodium hydroxide, followed by HNO_3 and finally aqueous silver nitrate.

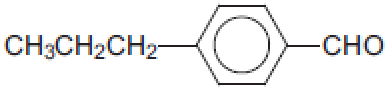
Observation: Chloroethylbenzene – White ppt formed.

Iodoethylbenzene – Yellow ppt formed.

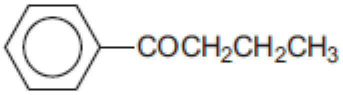
17 SRJC/2010/P2/Q3(d)

(i)

Test: Add Tollen's reagent and warm



: Silver mirror is observed.

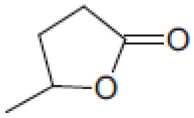


: No silver mirror is observed

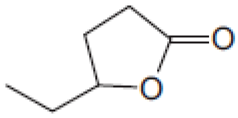
(ii)

Test: Add hot sodium hydroxide followed by aqueous iodine.

Or hot acid followed by alkaline aqueous iodine



: Brown iodine decolourises, yellow ppt observed



: No decolourisation, no yellow ppt observed

18 SRJC/2010/P2/Q5(a)

(i)

Reagent: **acidified potassium dichromate (VI)**, OR **$K_2Cr_2O_7/H^+$ (aq), heat/reflux**

Observation: **orange solution turns green**

(ii)

Reagent: **Br_2 (aq), r.t.p**

Observation: **decolourisation of reddish brown** bromine

19 TJC/2010/P3/Q4(c)(i)

(i)
- Add bromine water.
- White precipitate and decolourisation from reddish brown to colourless solution occurs for salicylic acid. There is no observable change for benzenecarboxylic acid.

Or

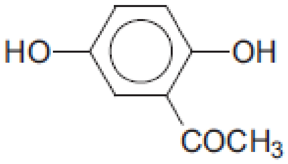
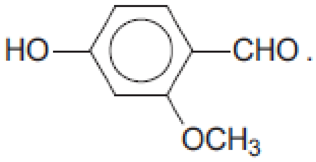
- Add neutral $FeCl_3$
- Violet colouration and buff ppt occurs for salicylic acid while only buff ppt for benzenecarboxylic acid.

20 VJC/2010/P2/Q4(a)

4(a)(i)

Reagent: alkaline aqueous I_2

Condition: warm (< 70 °C)

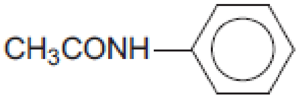
Observation: Yellow ppt (CHI_3) formed for  and no yellow ppt formed for  .

[OR Tollen's reagent, heat, Ag mirror formed for benzaldehyde only (no reaction with Fehling's solution)]

(ii)

Step 1:
Reagent: NaOH(aq)
Condition: heat

$CH_3CONHCH_3$ gives $CH_3CO_2^-Na^+$ and CH_3NH_2.


gives $CH_3CO_2^-Na^+$ and $C_6H_5NH_2$.

Step 2:
Reagent: Br_2(aq)
Condition: room temperature

$C_6H_5NH_2$ decolourises brown Br_2(aq) with formation of white ppt. No such observations for CH_3NH_2.

21 YJC/2010/P3/Q5(e)

e Step 1 – aqueous NaOH and heat
Step 2 – aqueous Br_2 , Br_2 decolourised by phenylamine

TOPIC 10.5: STRUCTURAL ELUCIDATION

1 MI/2010/P3/Q3(f) Level of Difficulty: [✩]

A is $C_8H_9NO_2$. On heating under reflux, with excess dilute hydrochloric acid, **A** yields two compounds **B**, C_6H_8NClO, and **C**, $C_2H_4O_2$.

After complete separation, **C** was found to react with sodium carbonate, liberating a colourless gas. **B** is soluble in aqueous sodium hydroxide, and gives a white precipitate with aqueous bromine.

Deduce the full structural formulae of compounds **A** to **C** and hence write balanced equations for all the reactions above. [8]

2 NJC/2010/P3/Q4(e) Level of Difficulty: [✩]

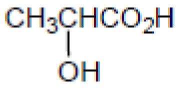
G, a compound having the same molecular formula as 1-chlorobut-2-ene, does not decolourise aqueous bromine. On treatment with alcoholic potassium hydroxide, it yields **H** which can be oxidised by hot acidified potassium manganate(VII) to give butanedioic acid.

Identify **G** and **H**, explaining the chemistry involved.

[4]

3 PJC/2010/P3/Q1(c) Level of Difficulty: [✩]

Lactic acid is the major acidic component of soured milk and it has the following structure.



$$CH_3CH(OH)CO_2H$$

On reduction, lactic acid is converted to **K**, $C_3H_8O_2$. **K**, on passing its vapour over hot Al_2O_3, gives compound **L**, C_3H_6O.

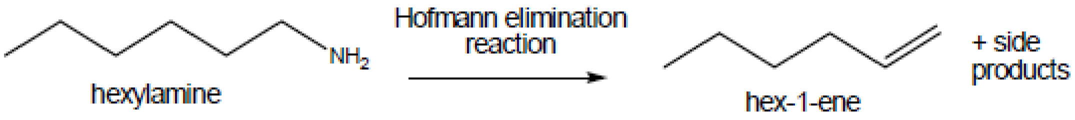
L gives no reaction with 2,4-dinitrophenylhydrazine but decolourises aqueous bromine. When **L** is treated with hot acidified $KMnO_4$, it gives carbon dioxide gas as the only carbon-containing product.

(i) Suggest a reducing agent to convert lactic acid to compound **K**.

(ii) Deduce the structures of compounds **K** and **L**, and explain the above reactions.

27 VJC/2010/P3/Q3(a) Level of Difficulty: [☆☆☆]

Like alcohols and halogenoalkanes, amines can be converted into alkenes by elimination reaction known as Hoffmann elimination reaction. For example, hexylamine is converted into hex–1–ene as shown.



An organic salt **A**, $C_7H_{14}NO_2$, contains a singly charged cation and a singly charged anion. On acidification with dilute hydrochloric acid, **A** forms two compounds, **B**, $C_2H_4O_2$ and **C**, $C_5H_{14}NCl$. **B** reacts with $LiAlH_4$ in dry ether to give **D**, C_2H_6O, which gives a yellow precipitate with alkaline aqueous iodine. **C** reacts with aqueous sodium hydroxide to form an amine which undergoes Hoffmann elimination reaction to give only one alkene **E**, C_5H_{10}. **E** reacts with hot acidified $KMnO_4$ to give **B** and propanoic acid as the only organic products.

Deduce the structures for each lettered compound, **A** to **E**, and give an account of the chemistry involved.

Write balanced equations for the reactions of

(I) **D** with alkaline aqueous iodine,

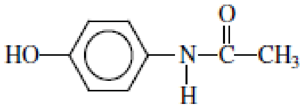
(II) **E** with hot acidified $KMnO_4$.

[10]

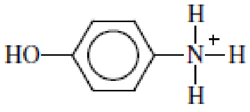
Suggested Answers

1 MI/2010/P3/Q3(f) Level of Difficulty: [☆]

1m for each structure (displayed formula)

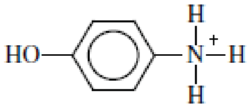


+ 2HCl →

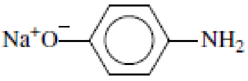


Cl^- + CH_3COOH ;;

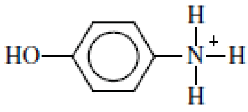
$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COO^-Na^+ + CO_2 + H_2O$;



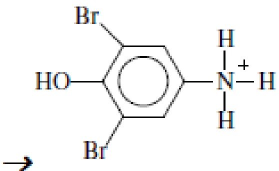
+ 2NaOH →



+ NaCl + $2H_2O$;

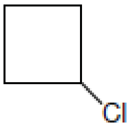


+ $2Br_2$ →

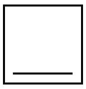


+ 2HBr ;

2 NJC/2010/P3/Q4(e) Level of Difficulty: [☆]



G



H

3 PJC/2010/P3/Q1(c) Level of Difficulty: [☆]

(i) **$LiAlH_4$ in dry ether**

(ii)

Info	**Deduction**	**Type of reaction**
K passes over hot Al_2O_3	**–**	**dehydration / elimination**
L does not react with 2,4-DNPH	**Q does not have carbonyl group**	**–**
L decolourises $Br_2(aq)$	**–**	**electrophilic addition**
L gives $CO_2(g)$ with $KMnO_4(aq)$	**Q has terminal alkene / $=CH_2$ group**	**oxidation**

K: $CH_3CH(OH)CH_2OH$
L: $CH_2=CHCH_2OH$

4 YJC/2010/P3/Q4(c) Level of Difficulty: [☆]

ci J = 2-bromopentane, K = 2-pentene, L = 1-pentene, M = butanoic acid, N = ethyl butanoate

$CH_3CH_2CH_2CHBrCH_3 + KOH \rightarrow CH_3CH_2CH=CHCH_3 + KBr + H_2O$
(or $CH_3CH_2CH_2CH=CH_2$)

$CH_3CH_2CH_2CH=CH_2 + 5[O] \rightarrow CH_3CH_2CH_2COOH + CO_2 + H_2O$

$CH_3CH_2CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2CH_2COOCH_2CH_3 + H_2O$

cii Cis-trans or geometric isomerism . Draw cis-2-pentene and trans-2-pentene

5 ACJC/2010/P3/Q3(e) Level of Difficulty: [☆☆]

Carvone reacts with 2,4-dinitrophenylhydrazine to yield an orange precipitate.
=> Carvone contains a ketone or aldehyde functional group.

Carvone does not rect with Tollen's reagent.
=> Carvone is not an aldehyde. Hence carvone contais a ketone functional group.

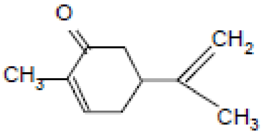
Carvone, $C_{10}H_{14}O$ reacts with H_2 to yield compound A $C_{10}H_{20}O$
=> 1 mol of carvone reacts with 3 mols of H_2.

(When carvone reacts with H_2 , the ketone group in carvone takes up 1 mol of H_2 to be reduced to a secondary alcohol in compound A. Hence carvone must contain two
C=C bonds which used up the other 2 mols of H_2)

(At this point, carvone can be deduced to have the same general carbon skeletal structure as compound A except that it contains a ketone group instead of an alcohol group and it has two C=C bonds)

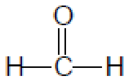
Carvone undergoes mild oxidation to produce methanal and a compound B
=> The two C=C bonds in carvone cleaves during the oxidation reaction. Since methanal is obtained, carvone contains a $=CH_2$ structural unit.

Structure of carvone



6 AJC/2010/P2/Q5 Level of Difficulty: [☆☆]

(a)

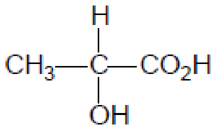


$H-\overset{\overset{O}{\|}}{C}-H$

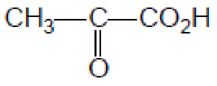
CH_3CO_2H

Compound **A** Compound **B**

(b)(i)



$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CO_2H$

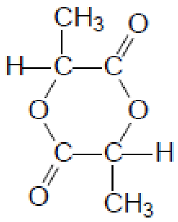


$CH_3-\underset{\underset{O}{\|}}{C}-CO_2H$

Compound **C** Compound **E**

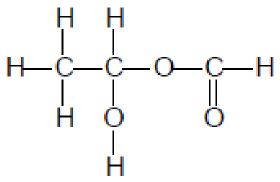
(b)(ii) $2CH_3CH(OH)CO_2H + Na_2CO_3 \rightarrow 2CH_3CH(OH)CO_2^-Na^+ + CO_2 + H_2O$

(b)(iii)



Type of reaction: esterification

(c)



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

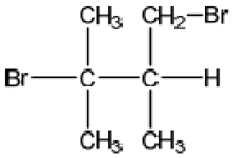
7 AJC/2010/P3/Q4(e) Level of Difficulty: [☆☆]

(e) **E** and **F** undergo nucleophilic substitution to give **G** and **H**.

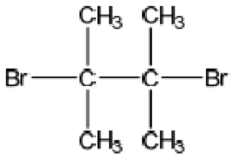
G undergoes oxidation to give **J**.

⇒ **G** contains 1 primary –OH group and 1 tertiary –OH group.

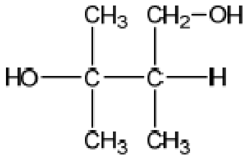
⇒ **H** contains 2 tertiary –OH groups.



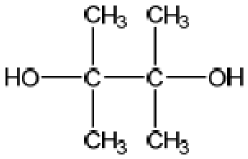
E



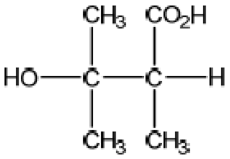
F



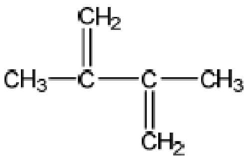
G



H



J



K

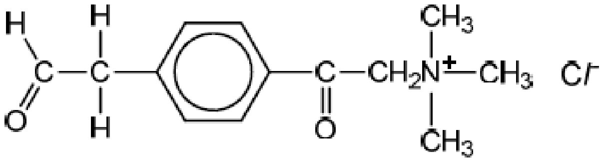
8 CJC/2010/P3/Q4(a) Level of Difficulty: [☆☆]

Both compounds react with Tollen's reagent → Both compounds contain an aldehyde

Gas turns red litmus paper blue: NH_3 (l) is released on heating with sodium hydroxide.

→ A primary amide (-$CONH_2$) is likely to be present.

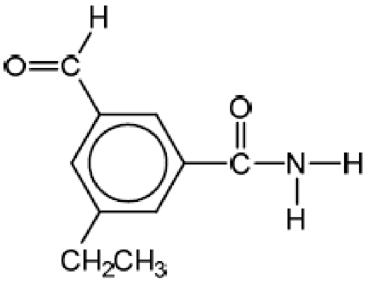
G can react with excess chloromethane to form a salt → G undergoes nucleophilic substitution with amine as the nucleophile to form a quarternary ammonium salt, J.



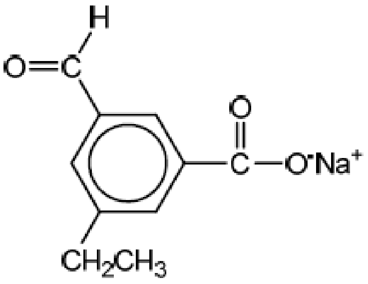
J:

A white ppt of AgC*l* is formed immediately upon adding $AgNO_3$ as the salt can dissolve in water to form Cl^- ions.

H undergoes side chain oxidation in acidified $KMnO_4$ to form L, indicating that F is a trisubstituted benzene.



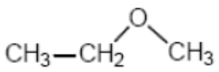
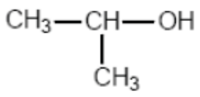
F:



H:

9 MI/2010/P2/Q1 Level of Difficulty: [✭✭]

(a)

X	Y	Z
	 $CH_3-CH(CH_3)-OH$	$CH_3-CH_2-CH_2-OH$

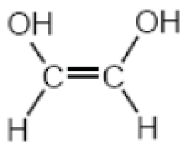
(b)

Compound Y and Z have stronger intermolecular forces of attraction between their respective molecules, i.e. hydrogen bonding, *;*

while compound X only has weaker temporary dipole – induced dipole forces of attraction between its molecules. *;*

The linear shape of compound Z, i.e. larger surface area, allow for stronger VDW forces than compound Y. Hence Y has a lower boiling point than Z.;

(c)

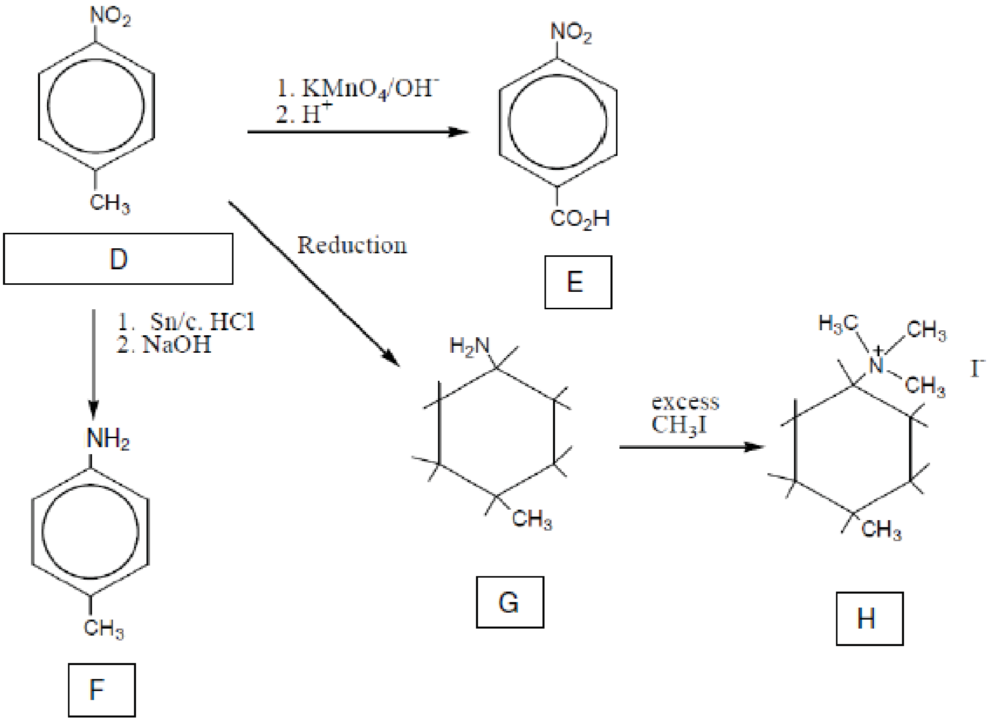


;

a greater number of hydrogen bonds formed due to the additional –OH group. *;*

10 MI/2010/P3/Q4(e) Level of Difficulty: [✭✭]

(i)



(ii)

acylation, both can act as nucleophile,

or acid-base reaction, both can act as base.

(iii)

x = 3.

1m for displayed structure

L is able to form ion-dipole interaction with water.

11 MJC/2010/P3/Q2(c)(iii) Level of Difficulty: [✮✮]

(1) C_2H_6.

(2) $PV = nRT = \frac{m}{M_r}RT$

$101000 \times 142 \times 10^{-6} = \frac{0.25}{M_r} \times 8.31 \times (127 + 273)$

$M_r = 57.9 \approx 58.0$

V is C_4H_{10}.

(3) $C_xH_y + (x+\frac{y}{4})\ O_2 \rightarrow xCO_2 + \frac{y}{2}\ H_2O$

Volume of excess $O_2 + CO_2 = 180\ cm^3$
Since NaOH absorbs acidic CO_2 gas.
➔ Volume of excess $O_2 = 60\ cm^3$
➔ Volume of $CO_2 = 180 - 60 = 120\ cm^3$
➔ Volume of O_2 used for combustion $= 250 - 60 = 190\ cm^3$

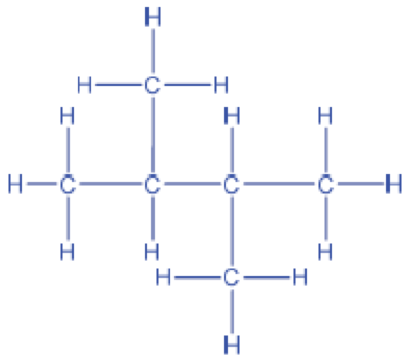
$\frac{120}{20} = x$

x = 6

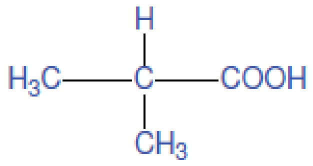
$\frac{190}{20} = (x+\frac{y}{4})$

y = 14

➔ W is C_6H_{14}.



(4) **S** is CH_3COOH, **T** is



$H_3C-C(H)(CH_3)-COOH$

12 MJC/2010/P3/Q5(c) Level of Difficulty: [☆☆]

(c) Empirical formula of H = $C_6H_{10}O$
Since M_r = 98.0, molecular formula of H = $C_6H_{10}O$

H does not undergo nucleophilic substitution with PCl_5 but undergoes oxidation with hot acidified $K_2Cr_2O_7$
⇒ **H** is an aldehyde

H undergoes oxidation with hot acidified $KMnO_4$ to form **I** (C_4H_8O) and 2 moles of CO_2
⇒ **H** is an alkene

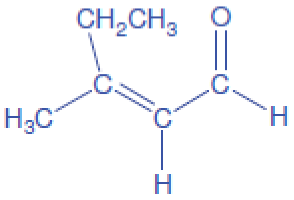
2 moles of CO_2 are formed from the oxidation forms ethanedioic acid of CO_2

I undergoes nucleophilic addition with HCN to form **J**
⇒ **I** is a ketone
⇒ **J** is a cyanohydrin / hydroxynitrile

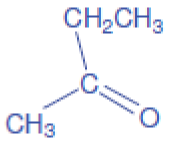
J undergoes reduction with $LiAlH_4$ in dry ether at r.t.p. to form **K** ($C_5H_{13}NO$)
⇒ **K** is an amine

H undergoes electrophilic addition with HBr to give **L** and **M**
⇒ **H** is an alkene
⇒ **L** and **M** are halogenoalkenes with chiral carbon / centres

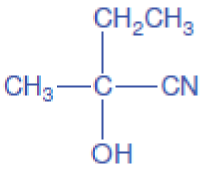
H



I

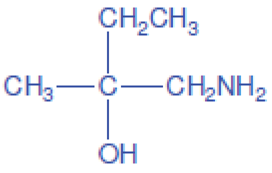


J



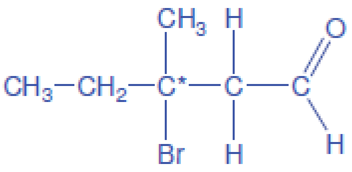
$CH_3-C(CH_2CH_3)(OH)-CN$

K



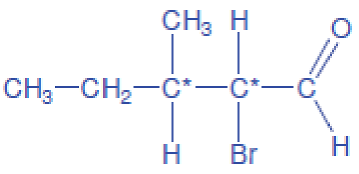
$CH_3-C(CH_2CH_3)(OH)-CH_2NH_2$

L



$CH_3-CH_2-C^*(CH_3)(Br)-C(H)(H)-CHO$

M



$CH_3-CH_2-C^*(CH_3)(H)-C^*(H)(Br)-CHO$

13 RVHS/2010/P2/Q1(a)-(e) Level of Difficulty: [☆☆]

(a)

$$n_{Ba(OH)_2} \text{ required} = 0.100 \times \frac{19.60}{1000}$$

$$= 0.00196 \text{ mol}$$

$Ba(OH)_2 \equiv 2RCOOH$

$$n_{RCOOH} \text{ used} = 0.00196 \times 2$$

$$= 0.00392 \text{ mol}$$

$$M_r \text{ of } \mathbf{A} = \frac{0.400}{0.00392}$$

$$= 102$$

(b) $pV = nRT$

$$(101 \times 10^3)(92.0 \times 10^{-6}) = n_C(8.31)(50 + 273)$$

$$n_C = 0.00346 \text{ mol}$$

$$M_r \text{ of } \mathbf{C} = \frac{0.300}{0.00346}$$

$$= 86.7$$

(c)

$$n_D = \frac{0.127}{22.4}$$

$$= 0.00567 \text{ mol}$$

$$n_{CO_2} = \frac{0.99}{12.0 + 2 \times 16.0}$$

$$= 0.0225 \text{ mol}$$

$$\text{Number of C atoms in 1 molecule of } \mathbf{D} = \frac{0.0225}{0.00567}$$

$$= 3.97$$

$$\approx 4$$

Hence molecular formula of **D** is C_4H_{10}.

(general formula of an alkane is C_nH_{2n+1})

(d)

A: $CH_3CH_2CH_2CH_2COOH$

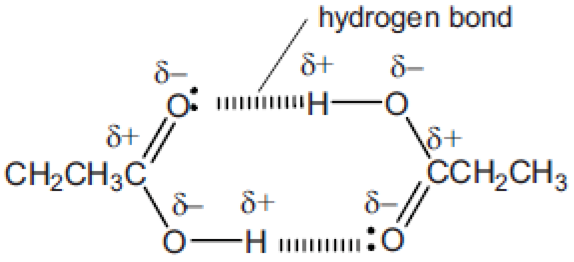
B: CH_3CH_2COOH

C: $CH_3CH_2CH_2CH_2CH_2CH_3$

D: $CH_3CH_2CH_2CH_3$

E: $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

(e)



When **B** is in its liquid state, dimerisation occurs whereby hydrogen bonds are formed between the two acid molecules as shown in the diagram. Hence, the molecular mass is almost twice the molecular mass of a single acid molecule.

However, when acid **B** is in its aqueous state, there is a much bigger proportion of water molecules compared to acid molecules and hydrogen bonds are formed between the acid molecules and water molecules instead, hence the molecular mass is that of a single acid molecule.

14 RVHS/2010/P3/Q3(b) Level of Difficulty: [☆☆]

(i) The reaction is autocatalytic as the Ag produced catalyses the reaction. The rate of reaction increases at first due to the formation of the Ag autocatalyst, then decreases as the reactants are used up.

(ii) **Z** undergoes condensation with 2,4-DNPH ⇒ **Z** is a carbonyl compound / contains ketone or aldehyde functional group

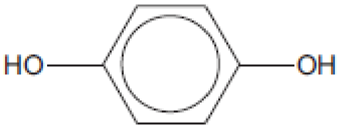
1 molar equivalent of **Z** undergoes electrophilic addition with 2 molar equivalents of Br_2 ⇒ **Z** contains two alkene functional groups

Z undergoes oxidation with hot acidified $KMnO_4$(aq) to give two identical compounds ⇒ **Z** contains a plane of symmetry

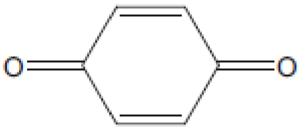
Y is insoluble in water (due to large hydrophobic benzene ring) but can undergo acid-base reaction with NaOH(aq) ⇒ **Y** contains phenol or carboxylic acid group

Y does not undergo acid-carbonate reaction with Na_2CO_3 ⇒ **Y** is not a carboxylic acid, so **Y** contains phenol group

Y undergoes acid-metal reaction with Na ⇒ **Y** contains phenol group



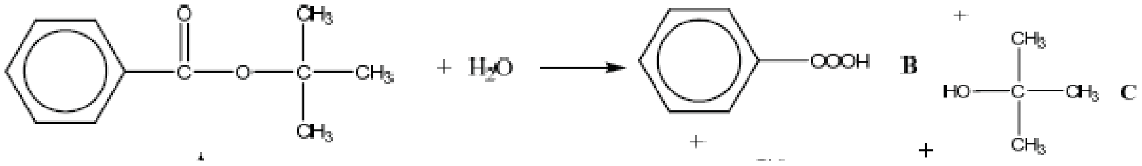
Y



Z

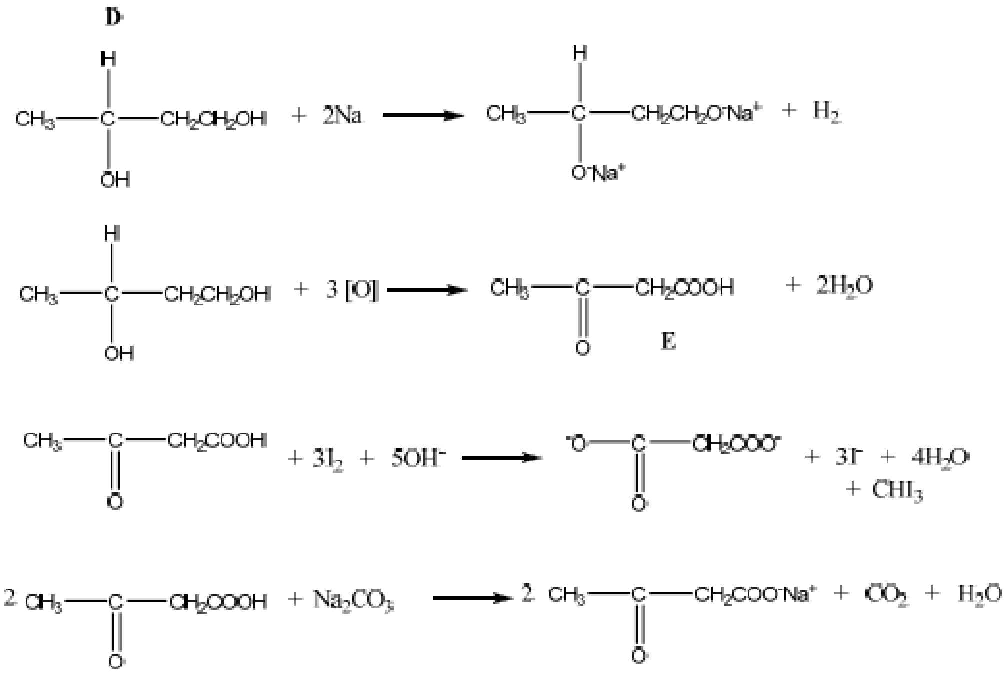
15 SAJC/2010/P3/Q1(b) Level of Difficulty: [☆☆]

(i)



A is neutral **A** undergoes hydrolysis to give **B** and **C**	**A** has no phenol and carboxylic acid **A** is an ester
C is cannot be oxidised	**C** is a tertiary alcohol
B is a white ppt	**B** is benzoic acid

(ii)

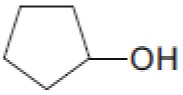


D reacts with 2 moles of Na	**D** contains 2 OH groups
D has no reaction with Na_2CO_3	**D** does not have COOH
E reacts with Na_2CO_3 to give CO_2	**E** contains COOH
D undergoes oxidation with $KMnO_4$.	**D** contains primary alcohol which oxidises to carboxylic acid
E reacts with iodoform test	**E** contains methyl ketone or CH_3CO- group. ($CH_3CH(OH)$- not acceptable as **E** is an oxidised product)

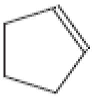
16 SRJC/2010/P2/Q5(c) Level of Difficulty: [☆☆]

(i)

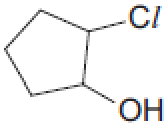
A:



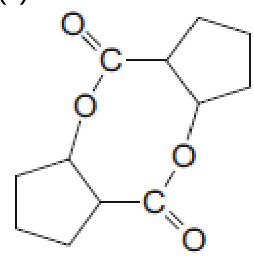
B:



C:

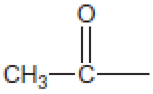
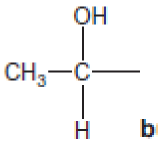


(ii)



17 TJC/2010/P2/Q4 Level of Difficulty: [✩✩]

(i)

A contains either  $CH_3-\overset{O}{\overset{\|}{C}}-$ **or**  $CH_3-\overset{OH}{\underset{H}{C}}-$ **but B does not.**

(ii)

Both A and B are carbonyl compounds.

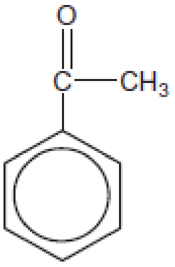
(iii)

- **No. of C atoms in one molecule of A =** $\frac{80}{10}$ **= 8**
- **No. of H atoms in one molecule of A =** $\frac{40}{10}\times 2$ **= 8**

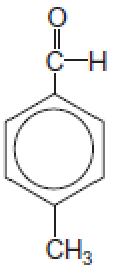
Let the molecular formula of compound A be $C_8H_8O_x$.
Since the M_r of A is 120.0, x = 1.

- **Molecular formula of A is C_8H_8O.**

(iv)

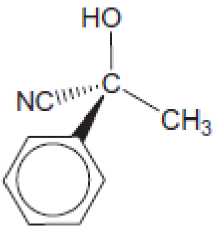


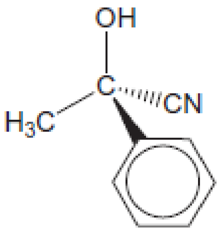
compound **A**



compound **B**

(v)

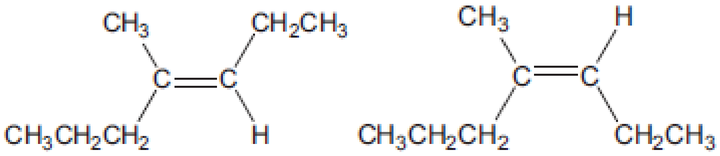




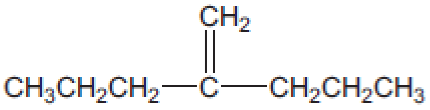
18 TJC/2010/P3/Q1(b) Level of Difficulty: [☆☆]

- As **B** is achiral, it does not contain a chiral centre or it has a plane of symmetry.
- **B** undergoes elimination with alcoholic potassium hydroxide to form alkenes **C**, **D** and **E**.
- Alkenes **C** and **D** undergo oxidation with hot concentrated acidic potassium manganate(VII).

C and **D** are geometrical isomers:

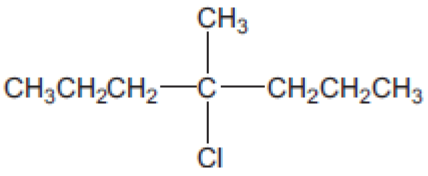


E:



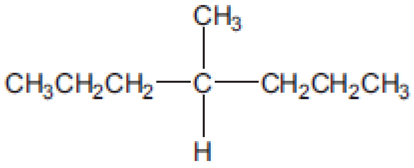
$CH_3CH_2CH_2-\overset{\overset{CH_2}{\|}}{C}-CH_2CH_2CH_3$

B:



$CH_3CH_2CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_2CH_3$

A:



$CH_3CH_2CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CH_2CH_3$

19 VJC/2010/P2/Q5(a) Level of Difficulty: [☆☆]

5(a)(i)

Element	C	H	O
% by mass	63.2	8.7	28.1
No. of moles	63.2 / 12.0 = 5.27	8.7 / 1.0 = 8.7	28.1 / 16.0 = 1.76
Mole ratio	3	5	1

Empirical formula of **X** is C_3H_5O.

(ii)

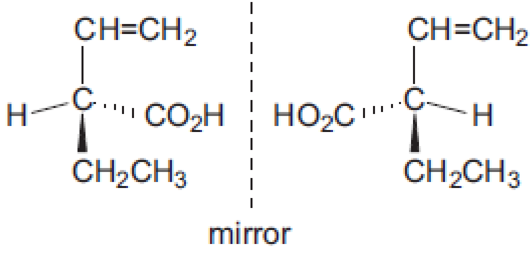
$$\text{No. of moles of } Br_2 = \frac{2.11}{2(79.9)} = 0.0132 \text{ mol}$$

$$M_r \text{ of } \mathbf{X} = \frac{1.50}{0.0132} = 113.6$$

(iii)

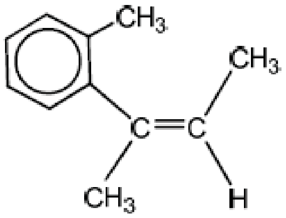
Let the molecular formula of **X** be $(C_3H_5O)_n$.
$(3 \times 12.0 + 5 \times 1.0 + 16.0)n = 113.6$
$n = 2$
Molecular formula of **X** is $C_6H_{10}O_2$.

(iv) $CH_2{=}CHCH(CH_2CH_3)CO_2H$

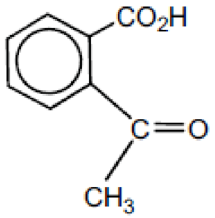


20 <u>HCI/2010/P3/Q4(d)</u> Level of Difficulty: [☆☆☆]

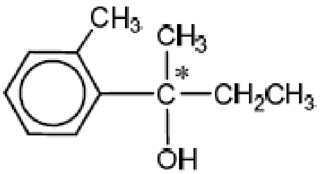
J



K



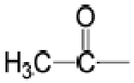
L



21 <u>HCI/2010/P3/Q5(d)</u> Level of Difficulty: [☆☆☆]

(i) **A** and **B** but not **C** react with Tollens' reagent ⇒ **A** and **B** are aldehydes, **C** is a ketone.

A and **C** react with alkaline aqueous iodine to give a yellow ppt ⇒ have



$H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}$ group.

∴ **A**: CH_3CHO; **B**: $HCHO$; **C**: $(CH_3)_2CO$

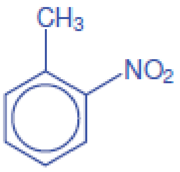
(ii) $$CH_3CO_2^- + CH_3CH_2Br \rightarrow \underset{\text{sweet-smelling liquid}}{CH_3CO_2CH_2CH_3} + Br^-$$

D: $CH_3CO_2^-$

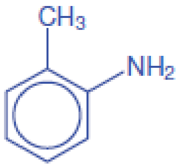
Nucleophilic substitution

(iii) HCHO will be oxidised to HCO_2H which is unstable and thus decomposes to <u>form CO_2 gas and H_2O.</u>

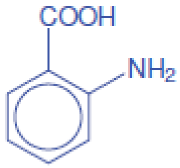
22 NYJC/2010/P3/Q4(c) Level of Difficulty: [☆☆☆]



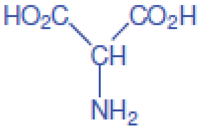
P



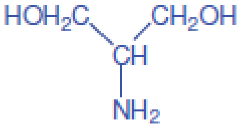
Q



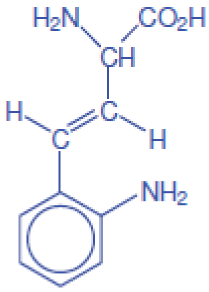
anthranilic acid



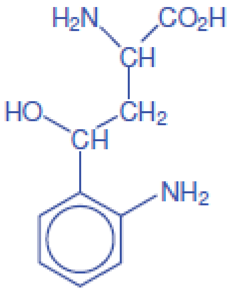
N



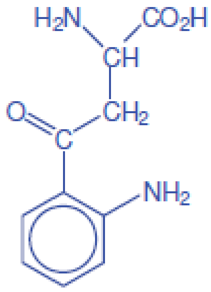
O



M

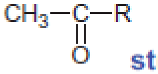


L



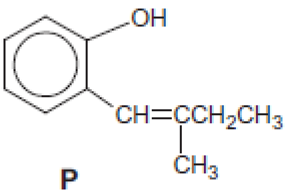
Kynurenine

23 PJC/2010/P3/Q5(d) Level of Difficulty: [☆☆☆]

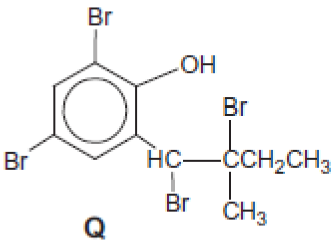
Question	Deductions	Type of reactions
Compound **Q**, $C_{11}H_{12}OBr_4$, is formed as a minor product when aqueous bromine is added to **P**.	–	**electrophilic addition**
P forms a white precipitate upon reaction with aqueous bromine.	**P has a phenol group.**	**electrophilic substitution**
When heated with acidified potassium manganate, **P** gives Compounds **R**, C_4H_8O, and **S**, $C_7H_6O_3$.	**P has alkene group.**	**oxidation**
Compound **R** produces an orange precipitate when reacted with 2,4-dinitrophenylhydrazine.	**R has ketone group.**	**condensation**
R also gives yellow precipitate when treated with aqueous alkaline iodine.	**R has**  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-R$ **structure (and the yellow ppt is CHI_3.)**	**(oxidation)**

2 moles of **S** reacts with 1 mole of sodium carbonate.	**One S has one carboxylic acid group.**	**(acid-carbonate)**
1 mole of **S** reacts with sodium metal to produce 1 mole of hydrogen gas.	**One S has one phenol and one carboxylic acid group.**	**(acid-metal)**
S reacts with phosphorous pentachloride to form Compound **T**.	–	**nucleophilic substitution**

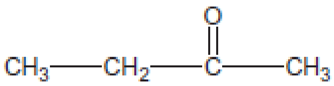
Structures:



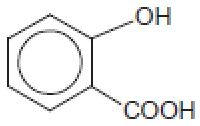
P



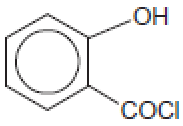
Q



R



S



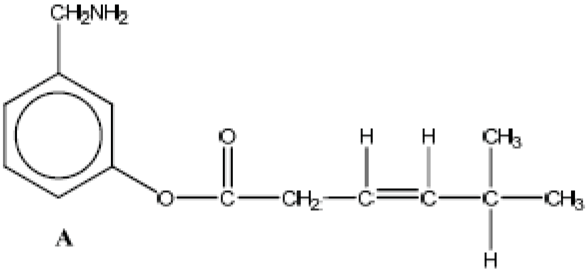
T

(either isomer of position 1,2 or 1,4 are acceptable)

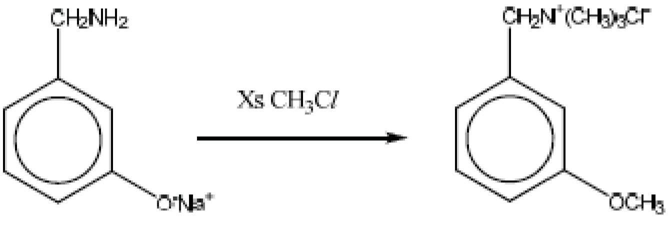
24 SAJC/2010/P3/Q3(c) Level of Difficulty: [☆☆☆]

A is basic	**A** contains amine group.
A reacts with NaOH to produce two cpds.	**A** is an ester undergoes hydrolysis, **A** is formed from a phenol and a carboxylic acid.

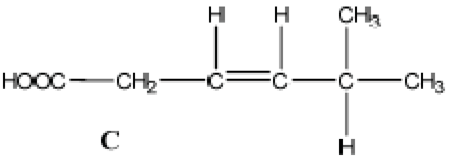
B reacts with excess CH_3Cl to form **D**	**B** is a primary amine, which undergoes nucleophilic substitution, to form a quarternary salt, **D**.
C liberates CO_2 with $NaHCO_3$	**C** contains carboxylic acid.
C, on hydrogenation, gives **G**, $C_7H_{14}O_2$,	**C** has contains 1 C=C bond.
C forms two different compounds with $KMnO_4$.	**C** undergoes vigorous oxidation.



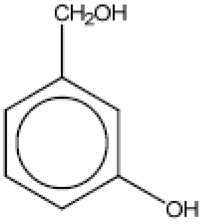
A



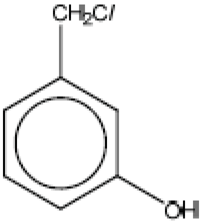
B **D**



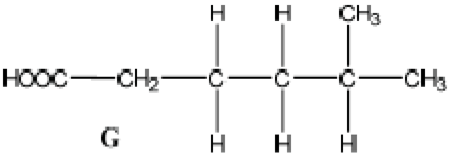
C



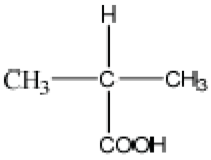
E



F

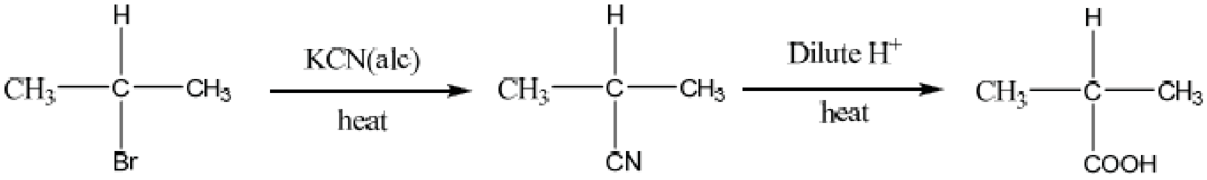


G



H

Synthesis of **H**



2 - bromopropane

H

25 SRJC/2010/P3/Q3(a) Level of Difficulty: [☆☆☆]

(i)

B undergoes reduction to form **C**. **B** contains 3 **alkene** groups.

After hydration, the triol cannot undergo further oxidation. The hydrated compound contains 3 **tertiary alcohol**.

Based on empirical formula calculation, D is **C_3H_6O**

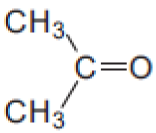
D contains a **carbonyl/ketone** group as it can undergo **condensation** with 2,4-DNPH. **E** **does not contain chiral carbon**..

E undergoes **oxidation** with alkaline aqueous iodine to form yellow ppt, CHI_3. E contains **methyl ketone**.

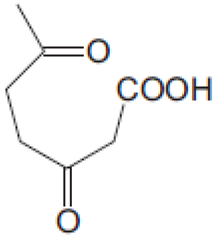
(Note: methyl alcohol is not acceptable as E is form from cleavage of C=C)

E undergoes **neutralisation** with aqueous sodium carbonate to form effervescence of **CO_2**. E contains a **carboxylic acid** group.

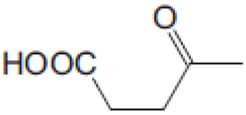
From the compound after reduction of F, it can be shown that F must contain **2 ketone** and **1 carboxylic acid group** as F is form from cleavage of C=C via **vigorous oxidation**.



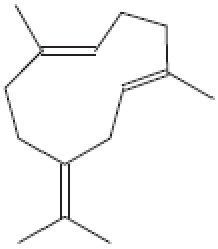
D



F



E



B

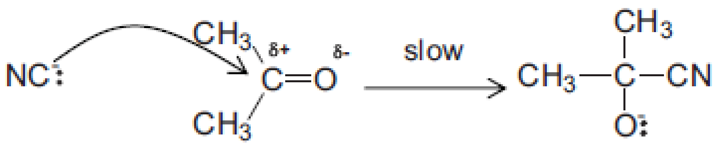
(ii)

Step 1:

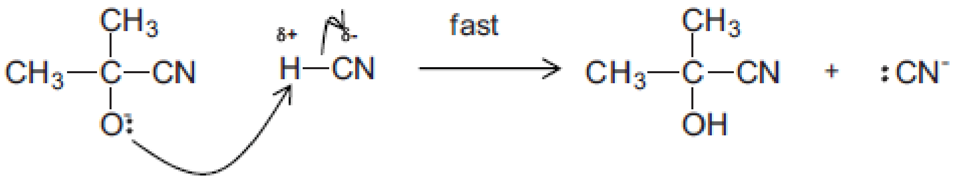
$HCN \rightleftharpoons H^+ + CN^-$

$NaCN \rightarrow Na^+ + CN^-$

Step 2:

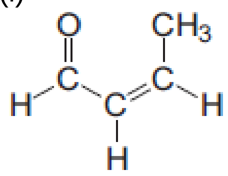


Step 3:



26 SRJC/2010/P3/Q3(b)(i),(iii)-(vi) Level of Difficulty: [✩✩✩]

(i)



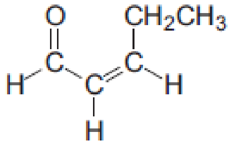
(iii)

The base acts as a **catalyst** so as to speed up the rate of the reaction

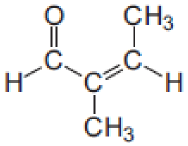
(iv)

CH_3CH_2CHO

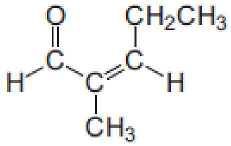
(v)



H:



J:



K:

(vi)

Both **H** and **J** are simple molecular structures with intermolecular van der Waals' forces of attraction.

Compound **H** has a **linear structure** while compound J has a **more spherical/ branched structure**.

Thus, **J** has a **smaller surface area**, and therefore **lesser energy** is required to overcome the intermolecular van der Waals' forces of attraction.

27 VJC/2010/P3/Q3(a) Level of Difficulty: [✩✩✩]

B is a carboxylic acid.
B is CH_3CO_2H.
B undergoes reduction with $LiAlH_4$ in dry ether
to give an alcohol, **D**.

D undergoes oxidation with alkaline $I_2(aq)$
to give a yellow ppt of CHI_3.
D contains $CH_3CH(OH)–$ group only.
D is CH_3CH_2OH.

E undergoes oxidative cleavage to give **B**, CH_3CO_2H, and propanic acid, $CH_3CH_2CO_2H$.
E is $CH_3CH{=}CHCH_2CH_3$.

C undergoes neutralisation with NaOH(aq) to form an amine.
Amine is $CH_3CH_2CH(NH_2)CH_2CH_3$.
An elimination in either way will yield the same alkene, **E**.
C is $CH_3CH_2CH(NH_3^+)CH_2CH_3\ Cl^-$.
A is $CH_3CH_2CH(NH_3^+)CH_2CH_3\ (CH_3CO_2^-)$.

(I)

$$CH_3CH_2OH + 4I_2 + 6OH^- \rightarrow HCO_2^- + CHI_3 + 5I^- + 5H_2O$$

(I)

$$CH_3CH{=}CHCH_2CH_3 + 4[O] \rightarrow CH_3CO_2H + CH_3CH_2CO_2H$$

[12.5, max 10]