2009 SAJC Prelim Paper 3 MARK SCHEME

1. (a) (i) $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

No. of moles of $C_2O_4^{2-}$ ions 0.025 x 0.1 = 0.0025

Given $C_2O_4^{2-} : MnO_4^-$ is 5:2,

No. of moles of MnO_4^- needed to oxidize $C_2O_4^{2-}$ = 0.0025 x 2/5 = 0.001

Thus,

Volume of MnO_4^- needed = (0.001 / 0.1) x 1000 = 10cm^3

(ii) Volume of MnO_4^- ions needed to oxidize X^{2+} ions = 15 – 10 = 5cm^3

No. of moles of MnO_4^- ions = [(15 – 10)/1000] x 0.1 = 0.0005

No of moles of electrons absorbed by MnO_4^- = 0.0005 x 5 = 0.0025

Mole ratio of **X**$^{2+}$: e = 1 : 1

Since 1 mole of X^{2+} loses 1 mole of electrons,

Oxidation state of **X** in the product = +3

(b) Compounds **A** and **B** and **C** all exist as simple covalent molecules.

Compound **A** is held by hydrogen bonding.

Compound **B** is held by weak induced dipole-induced dipole interactions (id-id)/weak VDW. Less energy is needed to overcome the weaker id-id interactions in **B**.

Although Compound **C** does not have H-bonding, having more electrons causes stronger id-id (or VDW, but not pd-pd) which compensates for the absence of H-bonding. Hence more energy is required to overcome the intermolecular forces of attraction in **C**.

(c) Since the oxide of **Y** can react with both NaOH and HCl, it is an amphoteric oxide. Among the possible elements, only the oxide of aluminium is amphoteric in nature: Compound **Y** is A*l*.

$$Al_2O_3\,(s) + 6HCl\,(aq) \rightarrow 2AlCl_3\,(aq) + 3H_2O\,(l)$$

$$Al_2O_3\,(s) + 2NaOH\,(aq) + 3H_2O\,(l) \rightarrow 2NaAl(OH)_4\,(aq)$$

In the presence of water, $AlCl_3$ undergoes hydrolysis to form an acidic solution, which reacts with the NaOH.

$$AlCl_3\,(s) + aq \rightarrow [Al(H_2O)_6]^{3+}\,(aq) + 3Cl^-\,(aq)$$

$$[Al(H_2O)_6]^{3+}\,(aq) + H_2O\,(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}\,(aq) + H_3O^+\,(aq)$$

Phosphorus chloride and phosphorus oxide will react with water but silicon oxide is insoluble in water.
Compound **Z** is P.

$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3\,(aq) + 3HCl\,(aq)$
or
$PCl_5\,(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 4HCl\,(aq)$

$P_4O_6\,(s) + 6H_2O\,(l) \rightarrow 4H_3PO_3\,(aq)$
or
$P_4O_{10}\,(s) + 6H_2O\,(l) \rightarrow 4H_3PO_4\,(aq)$

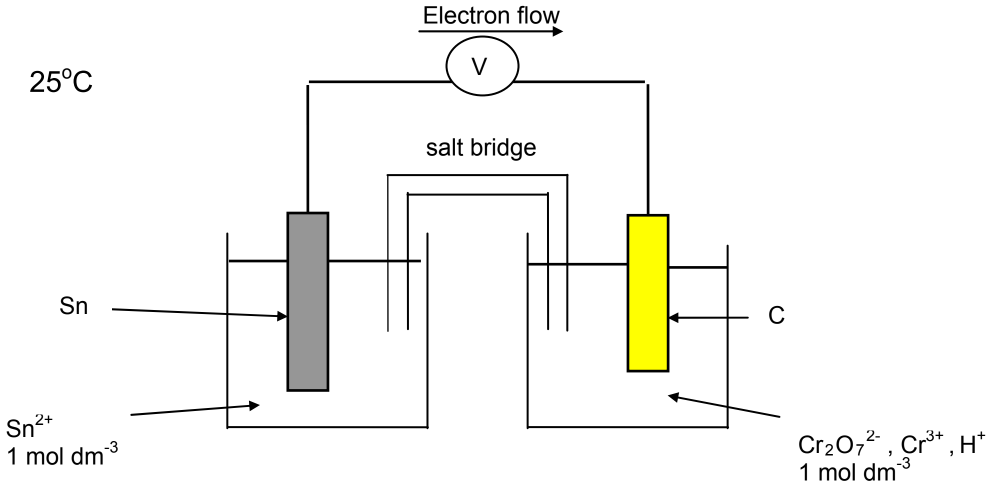
(d) **(i)** I_2, NaOH(aq), heat
No yellow ppt for **P**, yellow ppt for **Q**

(ii) H_2SO_4(aq) **[HCl(aq) not accepted]**, heat then add acidified $KMnO_4$ or heat with $KMnO_4 + H_2SO_4$(aq)
R will decolourise purple $KMnO_4$, **S** will not decolourise $KMnO_4$

(e)

$\longrightarrow \qquad \longrightarrow$

2. **(a)** **(i)**



(ii)

- **<u>Complete</u>** the circuit by allowing the **<u>ions</u>** to flow through
- maintain **<u>electrical neutrality</u>** by supplying ions to neutralize any built up of c solution;
- **<u>prevent</u>** mixing of the two solutions in the half-cells. [Any one]

(iii) $3Sn(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

$E^\theta = +1.33 + 0.14 = +1.47$ V

(iv) Q = It

= 0.2 x 9000 = **<u>1800</u>** C

Since 96500 x 2 C of electricity consumes 1 mole of Sn,

193000 C of electricity consumes 119 g of Sn

1800 C of electricity consumes **<u>1.11 g</u>** of Sn

(b) **(i)**

From data booklet,

$Co^{3+} + e \rightleftharpoons Co^{2+}$ $E^0 = +1.82$ V

$I_2 + 2e \rightleftharpoons 2I^-$ $E^0 = +0.54$ V

$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ $E^0 = +2.01$V

$2Co^{3+} + 2I^- \rightleftharpoons 2Co^{2+} + I_2$

$E^0 = +1.82 - 0.54 = +1.28 \text{ V} > 0$

$2Co^{2+} + S_2O_8^{2-} \rightleftharpoons 2Co^{3+} + 2SO_4^{2-}$

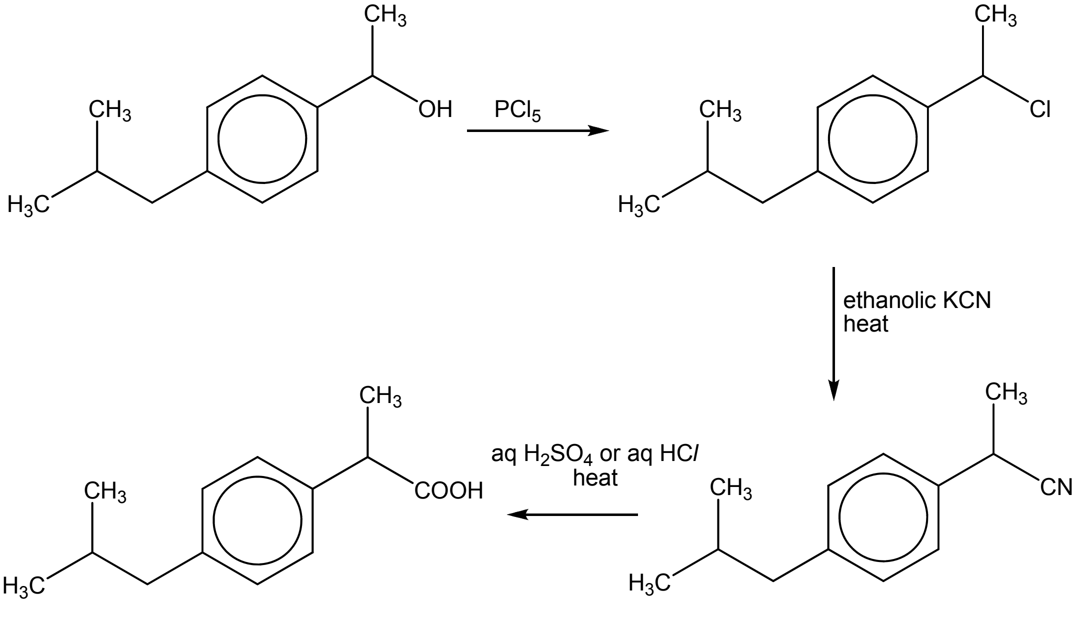
$E^0 = +2.01 - 1.82 = +0.19 \text{ V} > 0$

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

$[Cu(NH_3)_4(H_2O)_2]^{2+} + edta^{4-} \rightleftharpoons [Cuedta]^{2-} + 2\,H_2O + 4\,NH_3$

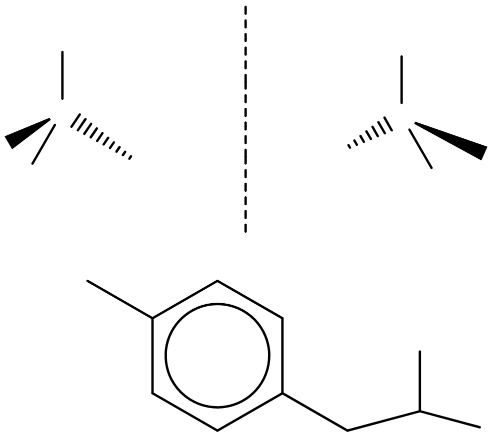
Strength of ligands : $H_2O < NH_3 < edta^{4-}$

(c) (i)



(ii) Optical isomerism due to the presence of a chiral carbon

Exists as a pair of non superimposable mirror images



(iii) **A** has a higher p*K*a as **A** is a weaker acid.

Ibuprofen contains a carboxylic acid. Carboxylate anion stabilized by delocalization of the electrons over the carbon atom and both oxygen atoms / distribution of negative charge over the C and 2O atoms

3. **(a)** **B** is NH_3 at 300K while **C** is CH_4 at 500K.

NH_3 at 300K deviates more than CH_4 at 200K.

This is because NH_3 molecules are held by stronger hydrogen bonding as compared to weaker induced dipole- induced dipole attraction between CH_4 molecules.

CH_4 at 500K deviates less than CH_4 at 300K. This is because at higher temperature, particles posses higher kinetic energy and is more able to overcome the forces of attractions between particles such that the collisions are more elastic.

(b) **(i)**

$$K_P = \frac{P_{CO}P_{H2}3}{P_{CH4}P_{H20}}$$

	CH_4	H_2O	CO	H_2
Initial pressure/atm	3.00	1.00	0	0
Change in pressure/atm	-0.66	-0.66	+0.66	+1.98
Partial pressure/atm	2.34	0.34	0.66	1.98

K_p = 6.44 atm^2

(ii) Equilibrium will shift to the left to lower the pressure of the system / to decrease the number of gaseous particles.

No effect on K_p as K_p is only dependent on temperature.

(iii) From graph, increase in temperature increases fraction of CO indicating forward reaction favoured.

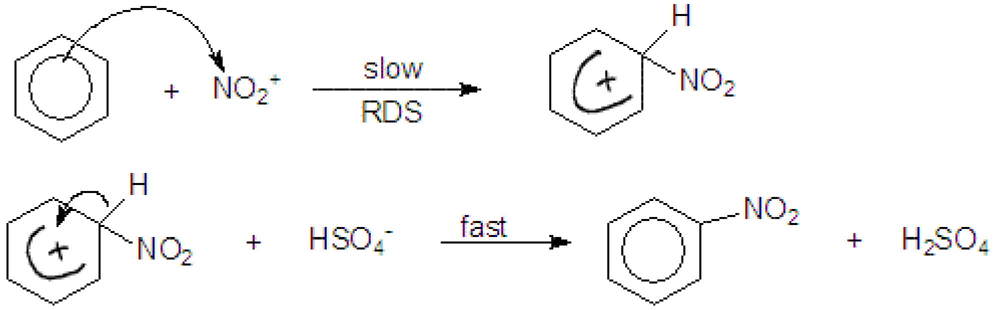
Reaction is endothermic to absorb the excess heat /to lower temperature.

(c) **(i)** Electrophilic substitution

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

Or

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2O + NO_2^+$



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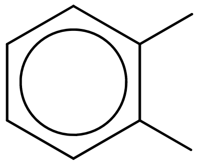
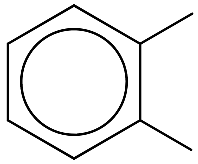
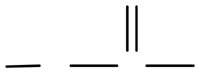
(ii) **II:** aq. HCl or aq H_2SO_4 heat followed by careful neutralization using aq. NaOH

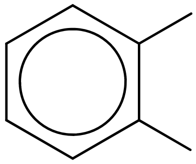
III: LiA/H_4 in dry ether (followed by aq NaOH if neutralization not mentioned in stage II)

(iii)









(iv) **R** has higher p*K*$_b$.

Br atom in **R** is electronegative/electron withdrawing

Lone pair of electrons on N less available for protonation.

R is less basic.

4. (a) (i) pH of lactic acid = 2.5

$[H^+] = 10^{-2.}$

Since lactic acid is a weak monobasic acid,

$K_a = [H^+]^2 / [CH_3CHOH(COOH)]$ OR $[H^+] = \sqrt{K_a[HA]}$

$= (10^{-2.5})^2 / 0.080$

$= 1.28 \times 10^{-4}$ mol dm^{-3}

(ii) Maximum buffer capacity occurs when [salt]=[acid]

$pH = pK_a$

$= -\log 1.25 \times 10^{-4}$

$=3.90$

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

$$CH_3CH(OH)COO^- (aq) + H^+ (aq) \rightleftharpoons CH_3CH(OH)COOH$$

The additional acid, H^+, is removed by large concentration of $CH_3CH(OH)COO^-$ from the salt.

Thus, H^+ changes very slightly and the pH remains almost constant.

(iv) At the equivalence point, only basic salt is present.

No. of moles of salt formed = $0.08 \times 10/1000 = 8 \times 10^{-4}$ mol

[salt] = $8 \times 10^{-4} / 26 \times 1000 = 0.031$ mol dm^{-3}

$[OH^-] = \sqrt{[(1 \times 10^{-14} / 1.25 \times 10^{-4}) \times 0.031]} = 1.55 \times 10^{-6}$ mol dm^{-3}

pOH = 5.8

pH = 8.2

A suitable indicator is phenolphthalein.

(b) (i) $2Ba(NO_3)_2 \longrightarrow 2BaO + 4NO_2 + O_2$

(ii) The temperature of the thermal decomposition **increases** down the group. This is because down the group,

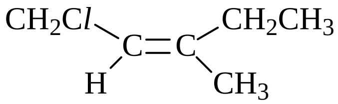
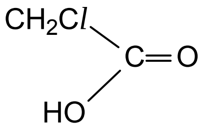
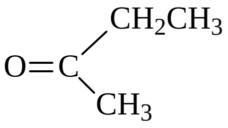
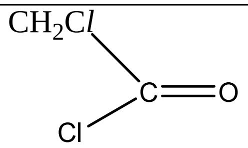
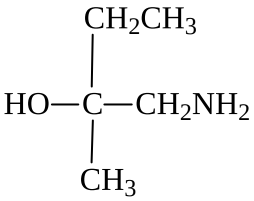
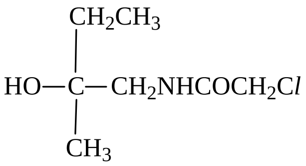
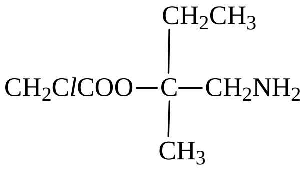
- the size of the cations increase
- hence polarizing power of cations decrease
- ability of cations to distort the large anion decrease
- nitrates are more stable to heat

(b) (iii) L.E is proportionate to ionic charge but inversely proportionate to ionic radius or L.E. $\alpha \dfrac{q^+q^-}{r^+ + r^-}$

- Ionic size of nitrate ion bigger than that of chloride
- Hence, LE for barium nitrate is <u>**SMALLER**</u> than barium chloride.

(c)

Information	**Deduction**
Stereoisomer **A**	- contains either an alkene with non-identical groups on the same carbon or chiral carbon
A reacts with hot acidified potassium manganate(VII) solution	- **A** undergoes oxidation - **A** contains C=C
B forms a yellow precipitate with hot alkaline iodine solution.	- **B** contains <u>CH_3CO-</u> (do not accept CH_3CHOH-)
Cold alkaline hydrogen cyanide was added to **B** and the mixture was reduced to form compound **C**	- **B** is a ketone which undergoes nucleophilic addition with HCN - **C** contains an amine functional group
Compound **D** formed white precipitate with ethanolic silver nitrate solution.	- **D** contains chloroalkane which forms AgCl
Compound **D** was reacted with phosphorous pentachloride to form compound **E**.	- **D** is an alcohol or carboxylic acid (do not accept D contains –OH group) which undergoes nucleophilic substitution / displacement reaction to form **E** which is a an acid chloride.
Compounds **C** and **E** were then reacted to form two compounds **F** and **G**, with identical molecular formula $C_7H_{14}O_2NCl$.	- condensation reaction took place
Compound **F** is neutral.	- **F** is an amide or **F** does not contain phenol/carboxylic acid/amine.

Compound	**Structure**	**Compound**	**Structure**
A		**D**	
B		**E**	
C	 $\mathrm{HO{-}\underset{CH_3}{\overset{CH_2CH_3}{C}}{-}CH_2NH_2}$	**F**	 $\mathrm{HO{-}\underset{CH_3}{\overset{CH_2CH_3}{C}}{-}CH_2NHCOCH_2Cl}$
		G	 $\mathrm{CH_2ClCOO{-}\underset{CH_3}{\overset{CH_2CH_3}{C}}{-}CH_2NH_2}$

5. **(a)** **(i)** It refers to the energy evolved when **1** mole of **gaseous** chloride ion is dissolved in an **infinite** amount of water.

(ii) Enthalpy change of solution of NaCl = Sum of hydration energies – LE

$-2 = [(\Delta H_{\text{Hydration}}(Na^+) + \Delta H_{\text{Hydration}}(Cl^-)] - (-722)$

$-2 = [-390 + \Delta H_{\text{Hydration}}(Cl^-)] + 722$

$\Delta H_{\text{Hydration}}(Cl^-) = -2 - 722 + 390$

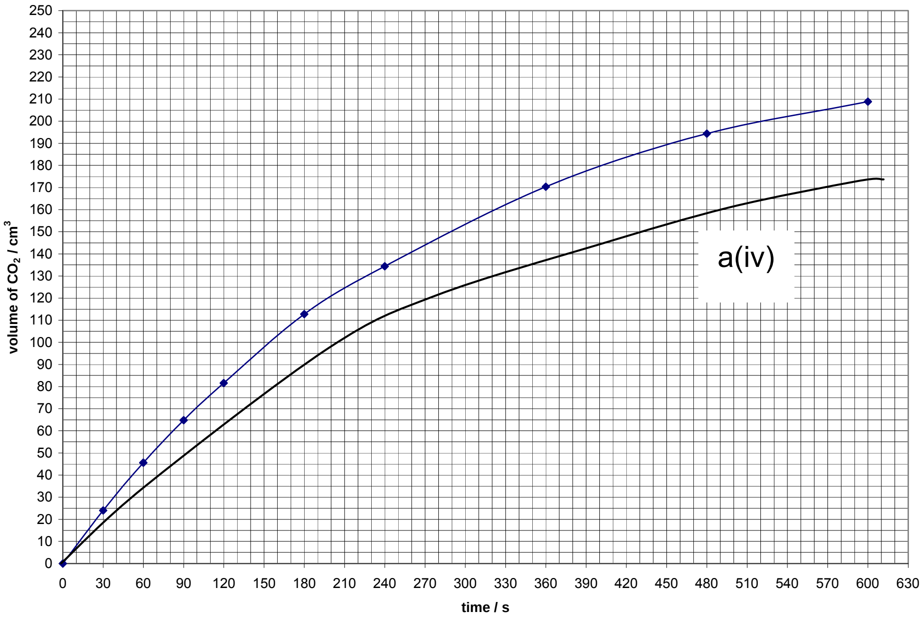
$= -334 \text{ kJ mol}^{-1}$

(iii) Enthalpy change of hydration is directly proportional to charge density of ion.
Ionic radius of chloride ion is smaller than iodide ion.
Hence the numerical value of enthalpy change of hydration of Iodide ion is smaller/hydration of iodide is less exothermic than that of chloride ion.

(b) **(i)** no. of mol of CO_2 = 0.01 mol

volume = 0.01 × 24 = 0.24 dm^3 = 240 cm^3

(ii)

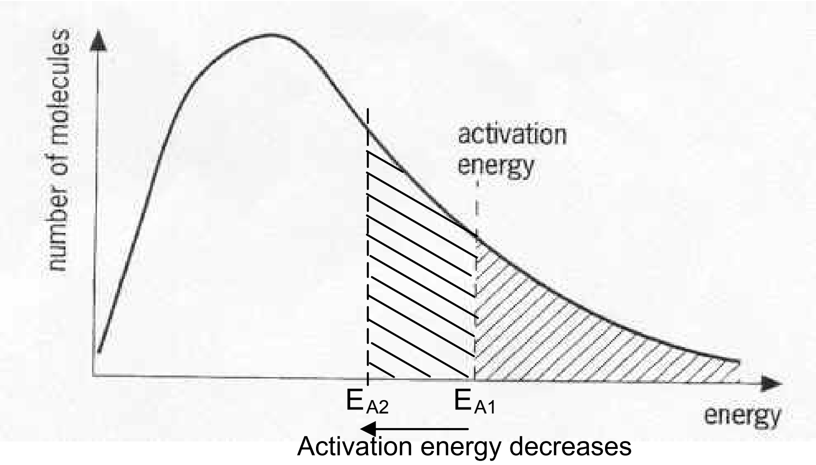


(iii) half-lives are constant at ≈ 200 s
1st order w.r.t. Br_2

Comparing expt 1 and 2, when [HCOOH] decreases by 4 times, rate decreases by 4 times
1st order w.r.t. HCOOH

(iv) Max vol = 192 cm^3 (graph should not exceed this value)
half-lives = 200 s
mark 2 co-ordinate points (200, 96) and (400, 144) on graph

(v)



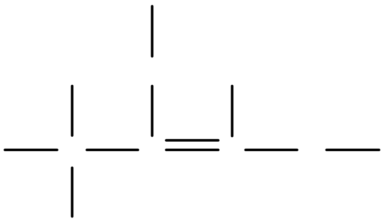
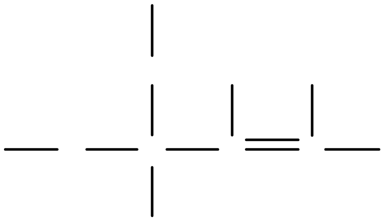
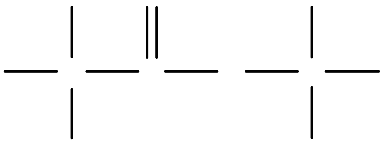
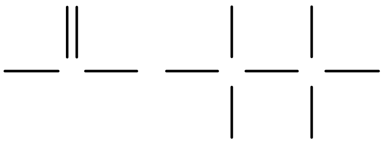
E_{A1} = activation energy of uncatalysed rxn
E_{A2} = activation energy of catalysed rxn

Catalyst lowers the activation energy by providing an alternative pathway. greater number of particles with energy <u>higher or equal</u> to activation energy. effective collision increases. Rate of reaction increases.

(c)

Information	**Deduction**
Both **A** and **B** do not react with Na_2CO_3	- **A** and **B** do not have –COOH
A and **B** do not give positive test	**A** and **B** do not contain any methyl ketone CH_3CO- or CH_3CHOH- group
0.370 g of **A** reacts with sodium to form a flammable gas that takes up 125.8 cm^3 of space at 32.5 °C and 101 kPa.	Flammable gas – H_2 No of moles of **A** = 0.370/74 = 0.005 mol $101000 \times 125.8 \times 10^{-6} = n \times 8.31 \times (273+32.5)$ No of moles of H_2 = 0.005 mol - mole ratio of **A** : H_2 = 1 :1 - **A** contains 2 alcohol groups
B does not react with Na	- **B** does not contain–OH group.

* Alternatively, students can give equations to illustrate the reactions undergone by **A** and **B**

	Structure		**Structure**
A	 or any structure with two OH groups (not CH_3CHOH-) and C=C. *  *[not stable]	**B**	 or 

H

H C

H