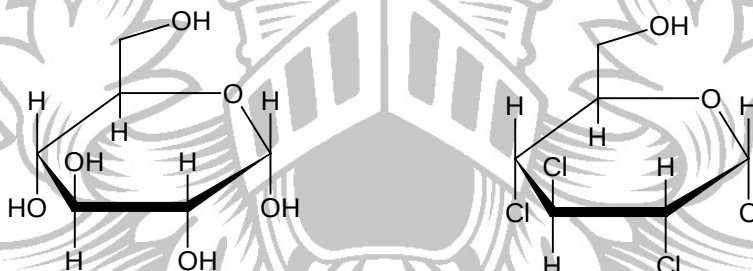


## Suggested Solutions to N2012 H2 Chemistry Paper 1 (9647/01)

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| C  | C  | D  | B  | C  | A  | D  | C  | A  | D  | D  | C  | B  | A  | C  | D  | D  | C  | C  | C  |
| 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| D  | B  | B  | D  | C  | A  | C  | B  | B  | A  | B  | D  | A  | B  | B  | B  | D  | A  | B  | B  |

## Working for Suggested Solutions to N2012 H2 Chemistry Paper 1 (9647/01)

1.



Molecular formula when all OH directly bonded to ring replaced with Cl is  $C_6H_8O_2Cl_4$ , empirical formula is  $C_3H_4OCl_2$

Answer: C

2.

[O]:  $Fe \rightarrow Fe^{2+} + 2e^-$ ; [R]:  $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Overall eqn:  $2Fe^{3+} + Fe \rightarrow 3Fe^{2+}$

To have equal no. of moles of  $Fe^{2+}$  and  $Fe^{3+}$  at the end, must have excess  $Fe^{3+}$ , Fe must be limiting, hence A is out since A is in stoichiometric ratio.

|              | $Fe^{3+}$ | Fe | $Fe^{2+}$ |
|--------------|-----------|----|-----------|
| Initial /mol | 5         | 1  | 0         |
| Change /mol  | -2        | -1 | +3        |
| Final /mol   | 3         | 0  | 3         |

Answer: C

3.

No unpaired s or unpaired p electron :  $s^2, s^2p^6$  or  $[Ar]3d^x4s^2$  or  $[Ar]3d^x$  configuration. Look out for species with noble gas configuration or transition metal atoms (exception of Cr and Cu which are  $[Ar]3d^54s^1$  and  $[Ar]3d^{10}4s^1$ ) or transition metal ions with at least +2 charge cos all 4s electrons removed.  
Sc:  $[Ar]3d^14s^2$

Answer: D.

4. There are at least 13 electrons, hence this cannot be a period 2 element. Neither is this a group 13 element as the biggest jump is not between the 3<sup>rd</sup> and 4<sup>th</sup> electron but between the 2<sup>nd</sup> and 3<sup>rd</sup> electron from the first 2 IE. It may be a group 2 element since the big jump is between 2<sup>nd</sup> and 3<sup>rd</sup> electron. After the big jump from the 2<sup>nd</sup> to 3<sup>rd</sup> electron, the IE of the next 8 electrons removed increases gradually, thus they must be in the same electronic shell. There is a large jump between the 10<sup>th</sup> and 11<sup>th</sup>, thus, the 11<sup>th</sup> to 13<sup>th</sup> electron must be from the inner electronic shell.  
Possible configuration: \_\_\_\_\_ ns<sup>2</sup>np<sup>6</sup>(n+1)s<sup>2</sup>  
It cannot be a d-block element. For a d-block element, a possible configuration is: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>x</sup> 4s<sup>2</sup>. If so, there will not be such a big jump between the 2<sup>nd</sup> and 3<sup>rd</sup> electron to be removed as the 3d and 4s orbitals are close in energy.  
Answer: B
5. Water has 2 lone pairs on O and 2 protonic H. Hence can form 2 H-bonds per molecule. HF has 3 lone pairs on F and 1 protonic H. Hence can only form 1 H-bond per molecule.  
Water can form more H-bonds on average than HF.  
This reason is more important than A, where water forms stronger H-bonds than HF as one could also argue that F is more electronegative hence H attached to F is more protonic and HF can form stronger H-bonds than water.  
Answer: C
6. According to the equation, there is decrease in no. of moles of gas in the forward equation, thus  $\Delta S < 0$ . Since H-bonds are formed between CO<sub>2</sub> and H<sub>2</sub>O,  $\Delta H < 0$ .  
Answer: A
7. Cell 1:  $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$   
Cell 2:  $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$   
 $Q = I \times t$  and  $Q = n_e F$   
Hence,  $n_e F = I \times t$ . Since  $t$  and  $F$  are constant,  $n_e \propto I$ .  
Equating electrons from both eqns:  
Cell 1:  $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$  X 2  
Cell 1:  $4 \text{Cl}^- \rightarrow 2 \text{Cl}_2 + 4 \text{e}^-$   
Cell 2:  $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$   
For the same current, Vol of Cl<sub>2</sub> will be twice of O<sub>2</sub>. Hence, for equal vol of Cl<sub>2</sub> and O<sub>2</sub>, current for cell 2 must be 2 I. If O<sub>2</sub> must be twice of Cl<sub>2</sub> then Cell 2 current must be 4 I.  
Answer: D
- 8.
- |              | 2 H <sub>2</sub> | CO        | CH <sub>3</sub> OH |
|--------------|------------------|-----------|--------------------|
| Initial /mol | 2                | 1         | 0                  |
| Change /mol  | -x               | - 1/2 x   | + 1/2 x            |
| Final /mol   | 2 - x            | 1 - 1/2 x | 1/2 x              |
- Answer: C
9. Pyruvic acid is a weak acid, hence upon titration with NaOH, at equivalence point, pH > 7 due to anion hydrolysis.  
 $\text{CH}_3\text{COCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COCOOH} + \text{OH}^-$   
Answer: A

10. Aspirin:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ .  
At pH = 1, there is a high  $[\text{H}^+]$ , thus, the above equilibrium position is shifted to the left.  
 $[\text{H}^+] \neq [\text{A}^-]$  since at pH 1,  $\text{H}^+$  does not come from HA alone but also comes from the stomach acid.  
Since equilibrium position is shifted to the left,  $[\text{HA}] > [\text{A}^-]$ .  
 $[\text{H}^+] > [\text{HA}] > [\text{A}^-]$   
Answer: D

11. HCl and NaOH are mixed:  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ . HCl used is in excess. Since there is excess strong acid, the resulting mixture is NOT a buffer. The pH would be due to the excess  $\text{H}^+$  from the strong acid present.

$$\begin{aligned}\text{No. of moles of excess HCl} &= 0.004 - 0.0025 \\ &= 0.0015 \text{ mol}\end{aligned}$$

There are 0.0015 mol of  $\text{H}^+$  in  $1 \text{ dm}^3$ , thus,  $[\text{H}^+] = 0.0015 \text{ mol dm}^{-3}$

$$\text{pH} = -\lg(0.0015) = 2.82$$

Answer: D

12.

| No. of half lives | Uranium-238   | Lead          |
|-------------------|---------------|---------------|
| 0                 | 1             | 0             |
| 1                 | $\frac{1}{2}$ | $\frac{1}{2}$ |
| 2                 | $\frac{1}{4}$ | $\frac{3}{4}$ |

After 2 half lives, ratio of uranium-238: Lead is  $\frac{1}{4} : \frac{3}{4}$  which is 1:3. Hence after 2 half lives, time taken is  $2 \times 4.5 \times 10^9 \text{ years} = 9.0 \times 10^9 \text{ years}$ .

Answer: C

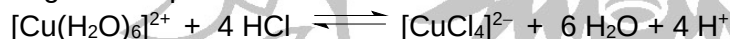
13. For first order reactions, half life is independent of  $[\text{H}_2\text{O}_2]$ , hence, doubling the concentration from  $0.1 \text{ mol dm}^{-3}$  to  $0.2 \text{ mol dm}^{-3}$  has no effect.  $t_{1/2} = \ln 2/k$ . Since  $\ln 2$  and  $k$  are constants,  $t_{1/2}$  is constant and likewise, time taken to decompose by 10 % will also be constant at 5 minutes.

Answer: B

14. Uncatalysed is 1 step, catalyzed reaction will be 2 steps. Catalysed reaction will also have lower  $E_a$ . However, enthalpy  $\Delta H$  remains the same since the reactants  $\text{SO}_2 + \text{O}_2$  and the product  $\text{SO}_3$  is the same.

Answer: A

15. When conc HCl reacts with  $\text{Cu}^{2+}$ , the water ligands are replaced with  $\text{Cl}^-$ . No change in oxidation state of  $\text{Cu}^{2+}$ , hence no. of d-electrons remain the same. However, since there is a change in ligands, the energy gap between the split d-orbitals will change since water ligands and  $\text{Cl}^-$  will cause different degree of repulsion with the electrons in the d-orbitals.



Answer: C

16. Reactivity of Group 2 elements with water increases from Mg to Ba (down the group) as the valence electrons become further from nucleus, hence more easily lost to reduce water to  $\text{H}_2$  gas. CaO also readily forms  $\text{Ca}(\text{OH})_2$  with water. Hence, reaction of Mg with  $\text{H}_2\text{O}$  (l) will occur least readily. However, with steam, Mg will react more readily as temperature is higher.

NOTE: the product of Mg with steam is MgO as temperature is higher, hence, the  $\text{Mg}(\text{OH})_2$  would have decomposed to MgO. Thus, MgO is formed instead of  $\text{Mg}(\text{OH})_2$ .

Answer: D

17. The element has a high density and melting point, hence it must be a transition element. The slightly larger increase from the first to second electron could be due to the fact that the first electron is removed from 4s while second electron is from 3d subshell.

Answer: D

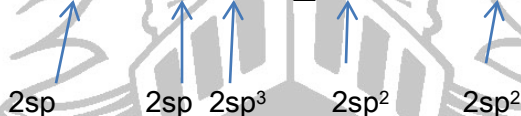
18. **Not in syllabus**

With hot sodium hydroxide, chlorine forms sodium chlorate(V),  $\text{NaClO}_3$ .



Answer: C

19.

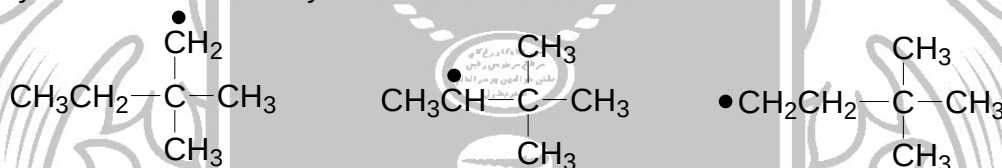


There is no  $2sp - 2sp^2$  overlap since the  $sp$  and  $sp^2$  C are not next to each other.

At the  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  bonds, the pi bonds are formed by the side on overlap between the 2p orbitals of C. The 1s and 2sp overlap occur between the triple bonded C and the H atom which uses its 1s orbitals for sigma bond with the 2sp hybrid orbital of C.

Answer: C

20. X is an alkyl radical. Possible alkyl radicals are:



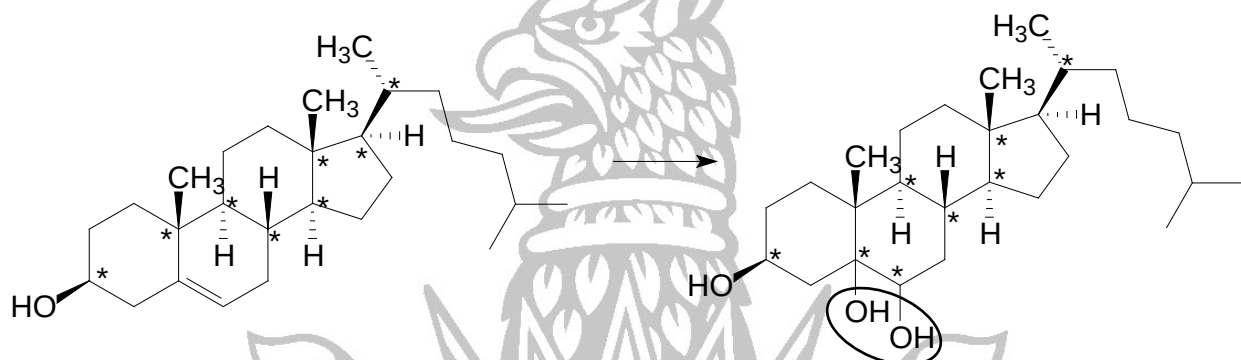
There are 3 possible  $\text{X}\cdot$ . (NOTE: the 3  $\text{CH}_3$  groups are identical as they are bonded to the same C, thus form the same radical when the H is removed from any of them).

Answer: C

21. Reduction only occur at the  $\text{C}=\text{O}$ , hence must use  $\text{NaBH}_4$ .  $\text{H}_2$  with Ni or Pt will reduce both  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  of the ketone group. (NOTE:  $\text{LiAlH}_4$  will reduce both  $\text{COOH}$  and  $\text{C}=\text{O}$  of aldehydes and ketones).  $\text{H}_2\text{O}$  and  $\text{H}^+$  is used for hydrolysis of CN group to  $\text{COOH}$ .

Answer: D

22.



Cold potassium manganate(VII) reacts with the C=C to form a diol. The 2 Carbons will hence become chiral thus there is an increase of 2 chiral carbons and all C=C becomes saturated.

Answer: B

23. The leaving group and attacking nucleophile for a nucleophilic reaction must be  $\delta^-$ . The C bonded to the leaving group has to be  $\delta^+$  to be able to attract the electron rich nucleophile. For the C to be  $\delta^+$ , the leaving group has to be more electronegative than C, so leaving group is  $\delta^-$ . Nucleophile is electron rich, thus is  $\delta^-$ .

Answer: B

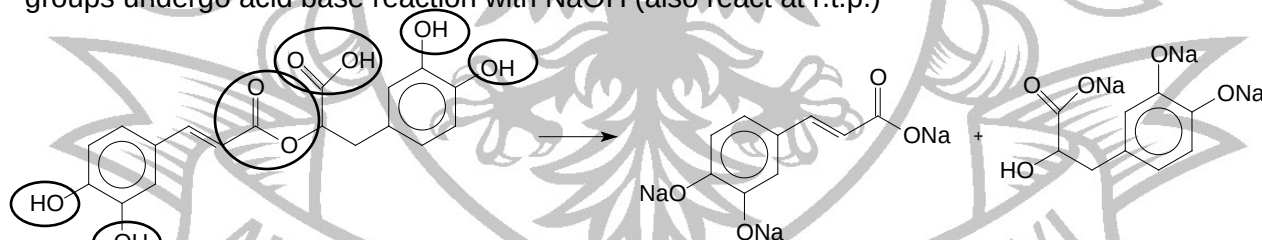
24. In CFCs, there are C-H, C-F and C-Cl bonds. The C-Cl bonds are the weakest as Cl is bigger than H and F, thus the orbitals of Cl is the most diffused leading to the poorest overlap of orbitals of C and Cl. Thus, in the stratosphere, the UV light would preferentially break the C-Cl bond. A replacement for the CFCs would be to have a molecule whereby there are no C-Cl bonds or any atoms bigger than Cl bonded to C as such atoms would have even more diffused orbitals and form weaker bonds with C (e.g. C-Br bonds).

A and B have C-Br bonds which can break more easily to give  $\text{Br}\cdot$  that will deplete the ozone layer. C has C-Cl bonds which will break and form  $\text{Cl}\cdot$ .

D has only C-H bonds which are stronger than C-Cl bonds and less likely to break and give free radicals. Thus, this is the best replacement for CFCs.

Answer: D

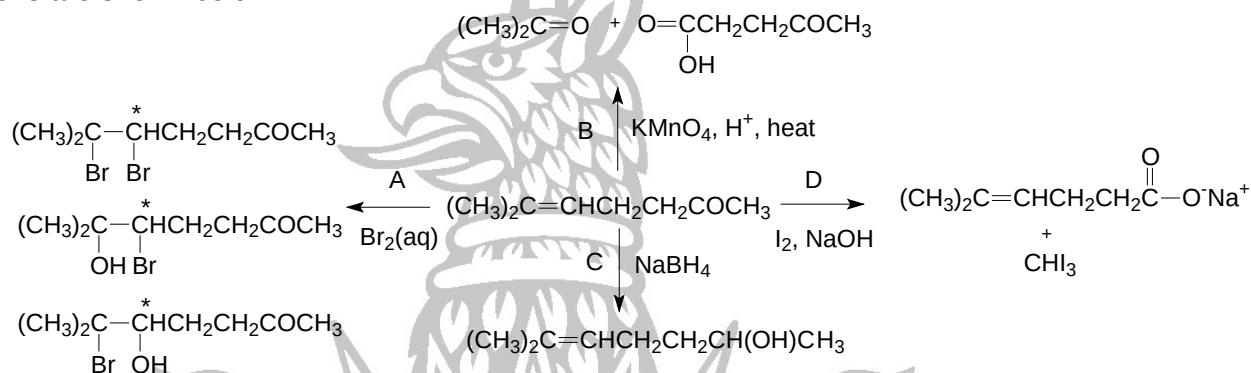
25. When heated with NaOH (aq), the ester groups will be hydrolysed and the phenol and carboxylic acid groups undergo acid base reaction with NaOH (also react at r.t.p.)



Hence, 6 moles of NaOH required.

Answer: C

26. Reactions are shown below:



(NaBH<sub>4</sub> in C only reduces C=O of aldehydes and ketones)

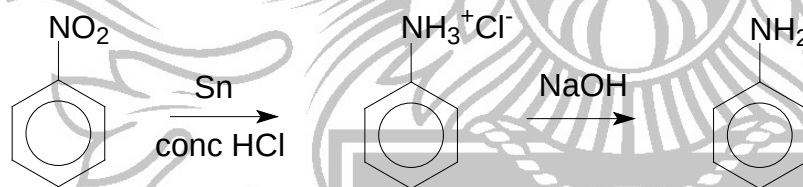
Answer: A

27. **Not in syllabus**

α-helix is secondary structure, stabilized only by hydrogen bonds.  
Disulfide and van der Waals found only in tertiary structures of proteins.

Answer: C

28. Phenylamine is basic and would form the salt when it is formed from reduction of nitrobenzene in acidic medium due to conc HCl. NaOH has to be added to displace out the weak base, phenylamine from its salt as shown below.



Answer: B

29. A: Amides, RCONH<sub>2</sub> does not have an acidic COOH and basic amine group on the same molecule thus cannot form zwitterions. It is amino acids that form zwitterions as shown below



B: Lone pair on N of amides can delocalize into the adjacent C=O group as shown below, thus are less available for donation to a H<sup>+</sup> ion. Hence, amides are not basic. (true)

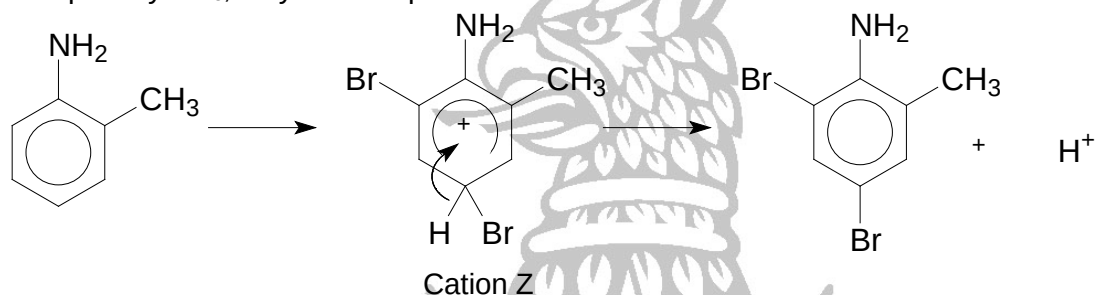


C: Even if this statement is true (see above), the C-N bond having double bond character simply means the bond is stronger and more difficult to break. It does not explain why amides are not basic.

D: Amides are not acidic. The N-H bonds are not broken to give H<sup>+</sup> ions as a negative charge located on N is not stable as N is less electronegative than atoms like O.

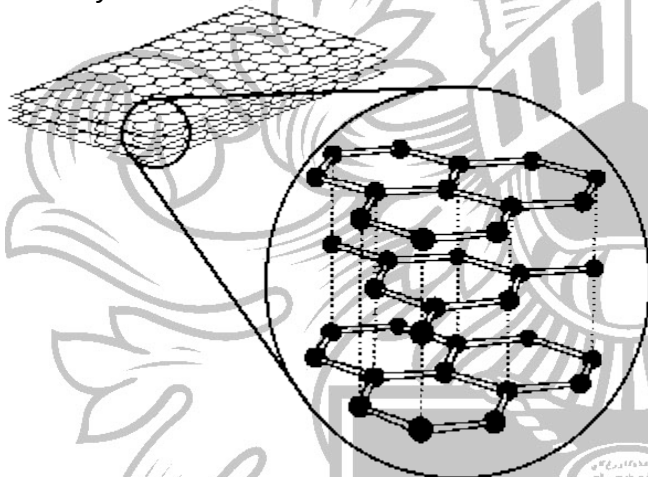
Answer: B

30.  $\text{NH}_2$  group strongly activating and would direct the Br to 2,4 and 6 positions but since the 2<sup>nd</sup> position is occupied by  $\text{CH}_3$ , only 4 and 6 position react.  $\text{H}^+$  is lost from cation Z as shown below.



Answer: A.

31. The lattice contains delocalized electrons between the layers. Each C atom is bonded to three other C atoms in a hexagon. Valency of C however is still 4 as C has 4 valence electrons. Hence, (3) is false.



Answer: B

32.  $Q = I \times t$ , where  $Q = n_e \times F$ .  
Hence,  $n_e = \frac{I \times t}{F}$  where  $n_e$  is no. of moles of electrons which would result in no. of moles of Cu formed according to the following equation:  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ .  
Hence, mass of Cu only depends on I which is current and t which is time.

2. Increasing conc of  $\text{Cu}^{2+}$  will not affect the mass of Cu.  $\text{Cu}^{2+}$  reduction potential is +0.34 V which is greater than that of water which is -0.83 V. Thus,  $\text{Cu}^{2+}$  will always be selectively reduced at the cathode as compared to water.

NOTE: Concentration will only affect WHAT is selectively discharged at the anode or cathode, not HOW MUCH is discharged.

E.g. For NaCl, if  $[\text{Cl}^-]$  is high, the oxidation potential -1.36V will increase until it is above that of water which is -1.23 V, thus,  $\text{Cl}^-$  would be selectively oxidized to  $\text{Cl}_2$  at high concentrations. If  $[\text{Cl}^-]$  is low, then the oxidation electrode potential will be below water and water will be oxidized to  $\text{O}_2$  instead.

3: Anion does not matter as it will be attracted to the anode and whether it will be oxidized or not depends on the oxidation electrode potential as compared to water.

Answer: D

33. When [1-bromobutane] is increased from 0.1 to 0.2 mol dm<sup>-3</sup>, the rate is doubled from 1.5 x 10<sup>-5</sup> to 3.0 x 10<sup>-5</sup> mol dm<sup>-3</sup> s<sup>-1</sup>. Hence, R ∝ [1-bromobutane], first order wrt 1-bromobutane. (1<sup>st</sup> and 2<sup>nd</sup> expt). When [HS<sup>-</sup>] is increased from 0.1 to 0.3 mol dm<sup>-3</sup>, the rate is doubled from 1.5 x 10<sup>-5</sup> to 4.5 x 10<sup>-5</sup> mol dm<sup>-3</sup> s<sup>-1</sup>. Hence, R ∝ [HS<sup>-</sup>], first order wrt HS<sup>-</sup>. (1<sup>st</sup> and last expt).

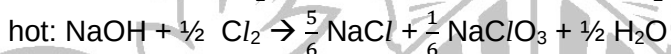
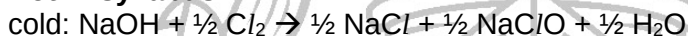
$$R = k[1\text{-bromobutane}][\text{HS}^-]$$

$$\text{Using expt 1 data, } k = \frac{1.5 \times 10^{-5}}{0.1 \times 0.1} = 1.5 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

Answer: A

34. 1.  $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$ ;  $\text{Na} + \frac{1}{2} \text{Cl}_2 \rightarrow \text{NaCl}$ ;  
1 mole of Mg requires twice the amt of Cl<sub>2</sub> as compared to 1 mole of Na. => True  
2.  $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$ ;  $\text{KBr} + \frac{1}{2} \text{Cl}_2 \rightarrow \text{KCl} + \frac{1}{2} \text{Br}_2$   
1 mole of H<sub>2</sub> require twice the amt of Cl<sub>2</sub> as compared to 1 mole of KBr. => True

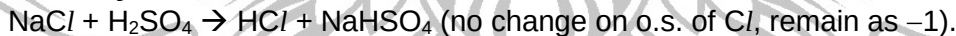
3. **Not in syllabus**



Mole ratio of Cl<sub>2</sub> to NaOH the same in both cases. => False

Answer: B

35. 1. Anode:  $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$  (o.s. of Cl increase from -1 to zero, hence by one unit)  
2.  $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$  (o.s. of Cl decrease from zero to -1, hence by one unit)  
3. **Not in syllabus**



NOTE: HCl is not further oxidized by H<sub>2</sub>SO<sub>4</sub> )

Answer: B

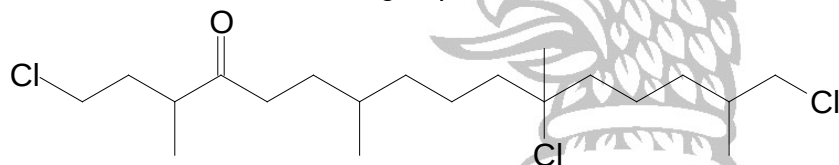
36. 1. Ca only has oxidation state of +2 as the next electron to be removed is from an inner 3p orbital which is in a inner principal quantum shell nearer the nucleus, thus require a lot of energy  
2. Ca<sup>2+</sup> cannot act as an oxidizing agent in aqueous solutions. To be an oxidizing agent, it has to be reduced to Ca. The reduction potential of Ca<sup>2+</sup> to Ca is very negative, -2.87 V, much lower than the reduction potential of water, which is -0.83V, thus in all cases, water will be selectively reduced.  
3. All metal loses electrons to form cations, since electrons are lost, the remaining electrons would experience greater attraction to the nucleus which contains the same number of protons as the original atom. Thus, all cations will be smaller than their corresponding atoms.

Answer: B

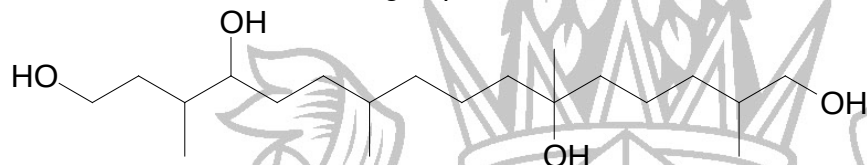
37. 1. CH<sub>3</sub>CH=CH<sub>2</sub> could also be a by-product. Even though alkenes are generally formed when NaOH is in ethanol instead of aqueous medium, NaOH is still a base in aqueous medium and can eliminate the acidic HBr from 1-bromopropane to form a small amount of the alkene.  
2. The alcohol product is neutral and will NOT react with NaOH to form CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>ONa  
3. It is impossible for the OH group to be formed on the 2<sup>nd</sup> carbon as the original Br is on the first carbon, hence upon substitution, the resulting OH must be on the 1<sup>st</sup> carbon.

Answer: D

38. 1.  $\text{Cl}_2$  (g) and UV light can form  $\text{Cl}\cdot$ , which can attack ANY C–H bonds and substitute the H with Cl in a free radical substitution mechanism.  
2.  $\text{SOCl}_2$  substitutes all –OH groups with Cl.

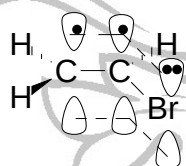


3.  $\text{H}_2/\text{Pt}$  can reduce the  $\text{C}=\text{O}$  group of the ketone.

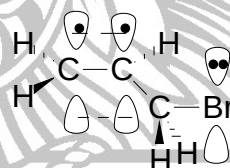


Answer: A

39. 1. The electrons on Br can delocalize into the  $\text{C}=\text{C}$  due to a continuous p-orbital overlap between the Br and  $\text{C}=\text{C}$ . This increases the electron density of the C–Br bond, resulting in some double bond character, thus the C–Br bond is stronger and more difficult to break, thus Br is less likely to be substituted by nucleophiles.



Br can overlap with  $\text{C}=\text{C}$



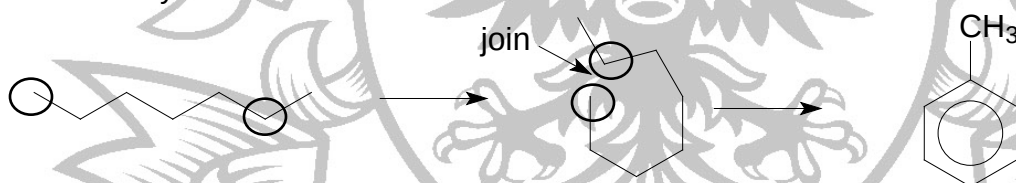
Br cannot overlap with  $\text{C}=\text{C}$

$\text{CH}_2=\text{CHCH}_2\text{Br}$  is reactive as the p-orbitals of Br is not able to form a continuous overlap with the p-orbitals of the  $\text{C}=\text{C}$ , thus the lone pair on Br cannot delocalize into the  $\text{C}=\text{C}$ . There is no double bond character in the C–Br bond.

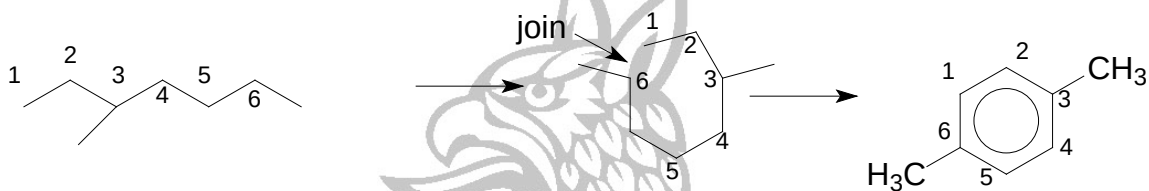
2. The pi electrons makes the  $\text{C}=\text{C}$  electron rich, thus would also repel the electron rich nucleophiles.  
3. Even though the C–Br bond has some double bond character, it is not a full  $\text{C}=\text{Br}$  double bond thus will not have restricted free rotation. Anyway, restricted free rotation results in cis-trans isomers, not unreactivity.

Answer: B

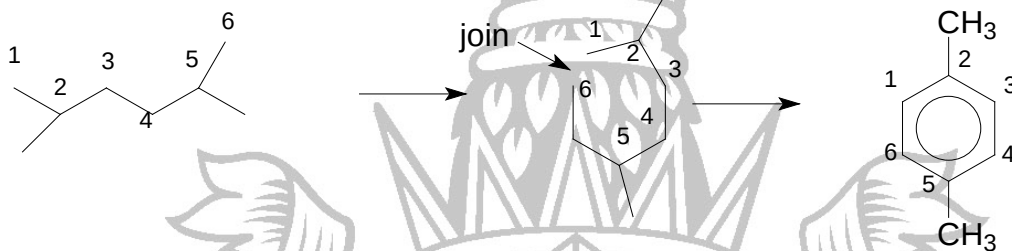
40. How methylbenzene is formed:



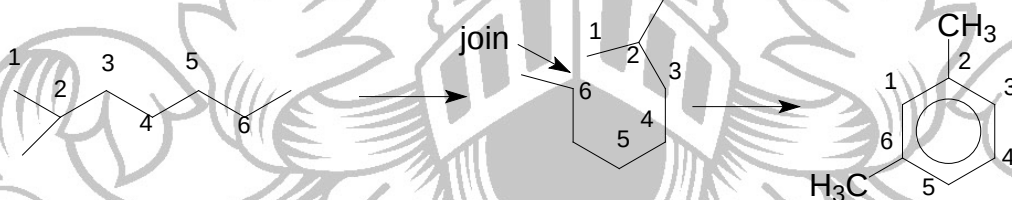
1. Form 1,4-dimethylbenzene as shown:



2. Form 1,4-dimethylbenzene as shown:



3. Form 1,3-dimethylbenzene as shown:



Answer: B

### Suggested Solutions for N2012 H2 Chemistry Paper 2 (9647/02)

- 1 (a)  $\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})$
- (b) A mixture of ethanoic acid and sodium ethanoate forms an acidic buffer that provides a constant acidic pH that is required for the reaction to occur.
- (c) **Part 1: Preparation of 250 cm<sup>3</sup> of solution H<sub>2</sub>O<sub>2</sub> of concentration 3.0 mol dm<sup>-3</sup>:**

Let volume of 7.5 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> to be used be V cm<sup>3</sup>

$$\frac{V \times 10^{-3} \times 7.5}{250} \times 1000 = 3.0 \Rightarrow V = 100.00 \text{ cm}^3$$

**Part 2: Experiment to determine order of reaction with respect to H<sub>2</sub>O<sub>2</sub>:**

- Using a burette, add 100.00 cm<sup>3</sup> of 7.5 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> to a 250 cm<sup>3</sup> volumetric flask.
- Top up to the mark with deionized water and stopper the flask and shake well to produce a homogeneous solution. Label this solution **C**. Solution **C** contains 3.0 mol dm<sup>-3</sup> of H<sub>2</sub>O<sub>2</sub>.
- Using a 50 cm<sup>3</sup> measuring cylinder, measure out 25 cm<sup>3</sup> of solution **C** into a 250 cm<sup>3</sup> conical flask.
- Using a 25 cm<sup>3</sup> measuring cylinder, measure out 25 cm<sup>3</sup> of ethanoic acid and add it to solution **C** in the conical flask.

- Using another 50 cm<sup>3</sup> measuring cylinder, measure out 50 cm<sup>3</sup> of solution **A** and add it to the mixture in the 250 cm<sup>3</sup> conical flask. At the moment immediately after all of **A** is added, start the stop watch.
- Swirl the mixture once and place it on a white tile. Record the time taken for the blue black colour to appear to the nearest second.
- Repeat steps 3 to 6 with the following volumes of solutions according to the following table.

| Expt no. | Volume of <b>A</b> / cm <sup>3</sup> | Volume of CH <sub>3</sub> COOH / cm <sup>3</sup> | Volume of H <sub>2</sub> O <sub>2</sub> , <b>C</b> / cm <sup>3</sup> | Volume of H <sub>2</sub> O / cm <sup>3</sup> | Total volume/ cm <sup>3</sup> | t/s | $\frac{1}{t}/s^{-1}$ |
|----------|--------------------------------------|--------------------------------------------------|----------------------------------------------------------------------|----------------------------------------------|-------------------------------|-----|----------------------|
| 1        | 50                                   | 25                                               | 25                                                                   | 0                                            | 100                           |     |                      |
| 2        | 50                                   | 25                                               | 20                                                                   | 5                                            | 100                           |     |                      |
| 3        | 50                                   | 25                                               | 15                                                                   | 10                                           | 100                           |     |                      |
| 4        | 50                                   | 25                                               | 10                                                                   | 15                                           | 100                           |     |                      |
| 5        | 50                                   | 25                                               | 5                                                                    | 20                                           | 100                           |     |                      |

**Part 3: Proposed graph to be plotted:**

Plot a graph of  $\frac{1}{t}$  against volume of **C** used.

- If a horizontal line is obtained, the reaction is zero order wrt H<sub>2</sub>O<sub>2</sub>
- If a straight line through the origin is obtained, the reaction is first order wrt H<sub>2</sub>O<sub>2</sub>

**Alternative method of derivation of suitable graph to be plotted:**

$$\text{rate} = k[\text{H}_2\text{O}_2]^n$$

When total volume of all experiments to be 100 cm<sup>3</sup> since [H<sub>2</sub>O<sub>2</sub>] is directly proportional to volume of H<sub>2</sub>O<sub>2</sub> used. Also, a fixed amount of product I<sub>2</sub> must be produced when colour change is observed and to ensure that rate  $\propto \frac{1}{\text{time}}$ . Hence the same amount of sodium thiosulfate must be used for all experiments.

$$\Rightarrow \frac{1}{\text{time}} = k(\text{V}_{\text{H}_2\text{O}_2})^n$$

$$\ln\left(\frac{1}{\text{time}}\right) = n \ln(\text{V}_{\text{H}_2\text{O}_2}) + \ln k$$

Plot a graph of  $\ln(1/\text{time})$  against  $\ln[\text{H}_2\text{O}_2]$  used to determine order of reaction wrt to H<sub>2</sub>O<sub>2</sub>. The graph obtained is a straight line passing through a positive y-intercept ( $\ln k$ ) and its gradient corresponds to the order of reaction wrt H<sub>2</sub>O<sub>2</sub>.

**Teachers Comments**

- A** containing CH<sub>3</sub>COO<sup>-</sup>Na<sup>+</sup> must be mixed in same proportion with CH<sub>3</sub>COOH to as that stated in question (A: CH<sub>3</sub>COOH = 50cm<sup>3</sup>: 25cm<sup>3</sup>) to ensure that the reaction mixture is adequately buffered.
- The amount of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> used must be fixed so that the same amount of I<sub>2</sub> is produced to ensure rate  $\propto \frac{1}{t}$  where  $t$  is time taken to produce the blue black colour of I<sub>2</sub>. Hence, the same volume of **A** must be used in all experiments since **A** contains S<sub>2</sub>O<sub>3</sub><sup>2-</sup>.
- You need to prepare sufficient 3.0 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> for all experiments. Note that during dilution of H<sub>2</sub>O<sub>2</sub>, you must use apparatus like volumetric flask, pipette and/or burette. During dilution of H<sub>2</sub>O<sub>2</sub>, volume measurement with the use of measuring cylinders, beakers or conical flasks is not acceptable.

4. If 50 cm<sup>3</sup> of **B** containing 25 cm<sup>3</sup> of 1.5 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> in a total volume of 100 cm<sup>3</sup> gives a time of 20 s, to ensure that at least one experiment is faster than 20 s, we need to use higher concentration of H<sub>2</sub>O<sub>2</sub> (i.e. 1.5 mol dm<sup>-3</sup>) in 25 cm<sup>3</sup> of solution **C**.
5. Total volume for ALL experiments should be 100 cm<sup>3</sup> since the teacher used a total of 100 cm<sup>3</sup> in her experiment. In addition, when total volume of reaction mixture is kept constant, concentration of reagent used is directly proportional to its volume used.

(d) Hydrogen peroxide is strongly oxidizing and corrosive, hence gloves should be worn during the experiment to prevent the direct contact of hydrogen peroxide with the skin.

2 (a) (i) Alkane/hydrocarbons

(ii) The high temperature at the internal combustion engine causes the nitrogen and oxygen in the air to react and form NO.

(iii) Sulfur containing amino acids such as methionine and cysteine present in proteins found in living matter.

(b) (i)  $\Delta H^{\circ}_{\text{reaction}} = -396 - (-297) = \underline{-99.0 \text{ kJ mol}^{-1}}$

(ii)  $\Delta G^{\circ}_{\text{reaction}} = -99 - [(298)(-93.5 \times 10^{-3})] = \underline{-71.1 \text{ kJ mol}^{-1}}$

(c) (i)  $-71.1 \times 1000 = -2.303(8.31)(298)\log K_c$   
 $K_c = 2.93 \times 10^{12}$

$\Delta G$  must be converted to Joules since the unit for R is Joules as well.

(ii)  $K_c$  value is extremely large implying that the forward reaction is effectively complete.

\*Note: N≡N bond is very strong and that is one reason why a high temperature is required, so that energy for bond breaking is available.

(iii) The reaction to form SO<sub>3</sub> could have a high activation energy, hence not kinetically feasible. This is why a V<sub>2</sub>O<sub>5</sub> catalyst is required in the Contact process.

\*Note: 1)  $\Delta G$  for this reaction is calculated to be <0, so the reaction is thermodynamically feasible. 2) A catalyst does not affect equilibrium position and yield. The reason a catalyst is used is always to speed up reaction. Thus, kinetics is the relevant concern in this question.

(iv) A catalyst provides an alternative pathway with lower activation energy. For example the SO<sub>2</sub> and O<sub>2</sub> molecules are absorbed onto the surface of the catalyst; they are brought into close proximity at the correct orientation, as well as weakening the bonds within SO<sub>2</sub> and O<sub>2</sub> molecules. Thus, more reactants have energy higher than activation energy can participate in the reaction. This speeds up the reaction.

Comments: the overall theme of this question is to integrate the factors that drive or allow a chemical reaction to take place

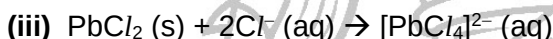
- 1)  $\Delta H$ , chem bonding (a)(ii)
- 2)  $\Delta H$ , thermodynamics,  $\Delta G$ , equilibrium position (b), (c)(i)-(ii)
- 3) Kinetics. (c)(iii)-(iv)

3 (a) (i)  $K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 \text{ mol}^3 \text{ dm}^{-9}$

(ii) Solubility of  $\text{PbCl}_2 = \frac{4.7}{207.2 + 71.0} = 0.01691 \text{ mol dm}^{-3}$   
 $[\text{Pb}^{2+}] = 0.01691 \text{ mol dm}^{-3}$   
 $[\text{Cl}^-] = 2 \times 0.0169 = 0.03381 \text{ mol dm}^{-3}$   
 $K_{sp} = (0.01691)(0.03381)^2 = \underline{1.9 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9} (2.s.f)}$

(b) (i) immediately: white ppt formed  
 after one hour in daylight: White ppt turns black/grey as  $\text{Ag}^+$  is reduced to  $\text{Ag}$ .

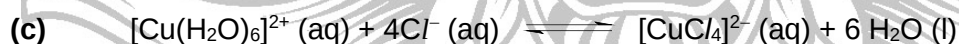
(ii) Add aqueous  $\text{NH}_3$  to the white ppt. If the white ppt is soluble in aqueous ammonia to give a colourless solution, it is  $\text{AgCl}$ .



In the presence of concentrated  $\text{HCl}$ ,  $[\text{Cl}^-]$  is high and a soluble complex  $\text{PbCl}_4^{2-}$  is formed, thus  $[\text{Pb}^{2+}]$  is lowered and the ionic product falls below the  $K_{sp}$  of  $\text{PbCl}_2$  thus the ppt of  $\text{PbCl}_2$  dissolves.

OR

In the presence of concentrated  $\text{HCl}$ ,  $[\text{Cl}^-]$  increase and the equilibrium above shifts to the right, resulting in the formation of a soluble complex  $\text{PbCl}_4^{2-}$ , while  $\text{PbCl}_2(s)$  is consumed, and thus dissolves.



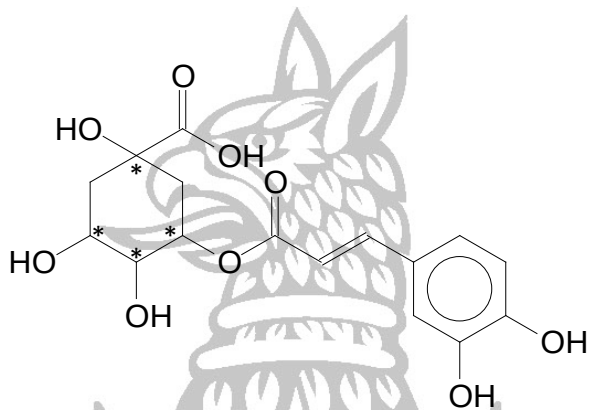
When concentrated  $\text{HCl}$  is added, the above equilibrium position shifts to the right by Le Chatelier's Principle to form the yellow  $\text{CuCl}_4^{2-}$ . When water is added, the equilibrium position shifts to the left to reform the blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ .

(d) (i) In acidic solution,  $[\text{H}^+]$  is highest, the equilibrium position  $\text{H}_2\text{S} (g) + aq \rightleftharpoons \text{H}^+ (aq) + \text{HS}^-$  and  $\text{HS}^- (g) + aq \rightleftharpoons \text{H}^+ (aq) + \text{S}^{2-}$  lies to the left thus the  $[\text{S}^{2-}]$  is very low. Since the  $K_{sp}$  of  $\text{CuS}$  is the smallest, only the ionic product of  $\text{CuS}$  exceeds its  $K_{sp}$  while the ionic product of  $\text{NiS}$  and  $\text{ZnS}$  remains below their  $K_{sp}$ , hence only  $\text{CuS}$  is precipitated.

(ii)  $K_{sp}$  of  $\text{NiS}$  is the largest. In alkaline solution,  $[\text{H}^+]$  is the lowest, thus the equilibrium positions  $\text{H}_2\text{S} (g) + aq \rightleftharpoons \text{H}^+ (aq) + \text{HS}^-$  and  $\text{HS}^- (g) + aq \rightleftharpoons \text{H}^+ (aq) + \text{S}^{2-}$  lies to the right and  $[\text{S}^{2-}]$  is increased significantly, thus the ionic product of  $\text{NiS}$  increases above its  $K_{sp}$  and hence it is precipitated. In neutral or acidic solutions, the  $[\text{S}^{2-}]$  is low enough such that  $\text{IP} < K_{sp}$  and hence no precipitation is observed.

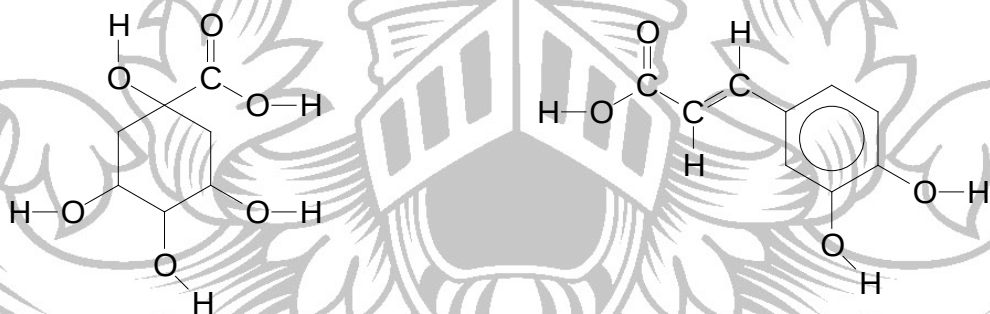
(iii) In neutral solution,  $[\text{H}^+]$  is  $10^{-7} \text{ mol dm}^{-3}$  and is higher than in (ii), thus  $[\text{S}^{2-}]$  is higher than in (ii). At this  $[\text{S}^{2-}]$ , the ionic product of  $\text{ZnS}$  will already exceed its  $K_{sp}$  hence, in neutral and alkaline solution,  $\text{ZnS}$  will be precipitated.

4 (a) (i) Carboxylic acid, tertiary alcohol, secondary alcohol, ester, phenol.

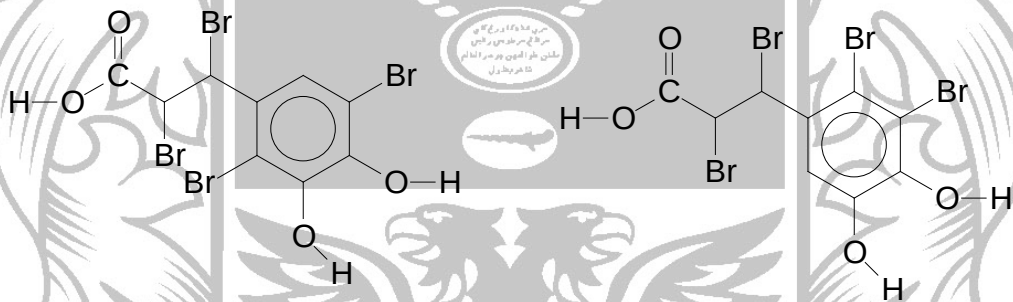


(ii) 4 chiral centres

(b) (i) Since two products are obtained, a hydrolysis reaction of the ester group must have occurred.



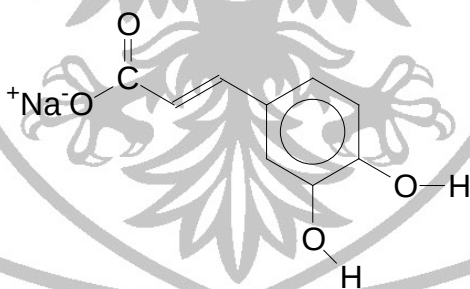
(c) Any one of the following structures.



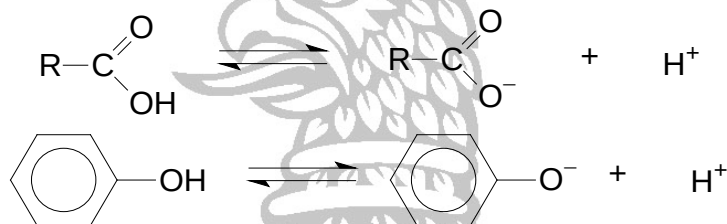
\*note:  $\text{Br}_2$  in organic solvent is used, so tri-bromination at the arene does not take place.

(d) (i)

Structural formula of S



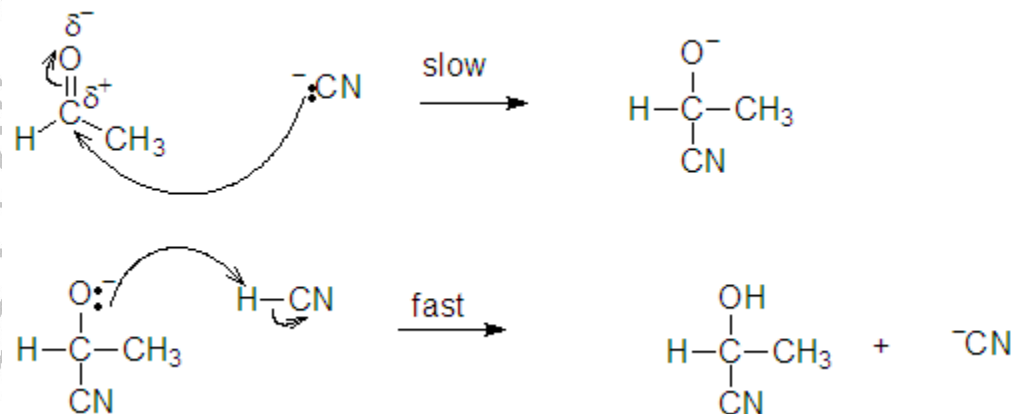
- (ii) Only the carboxylic acid is acidic enough to react with  $\text{NaHCO}_3$  which is a weak base. The two phenol groups are weaker acids than the carboxylic acid, thus is less likely to donate  $\text{H}^+$  to the weak base  $\text{NaHCO}_3$ .



Phenol is a weaker acid than carboxylic acid since in the carboxylate ion, the negative charge is delocalized between two electronegative oxygen atoms which is more effective in dispersing the negative charge on the anion as compared to the phenoxide, where the negative charge is partially delocalized into the benzene ring.

- 5 (a) (i) **Reagent:**  $\text{HCN}$  **Condition:** trace amount of  $\text{NaCN}$  as catalyst  
**Type of reaction:** Nucleophilic addition

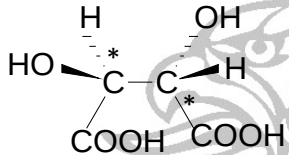
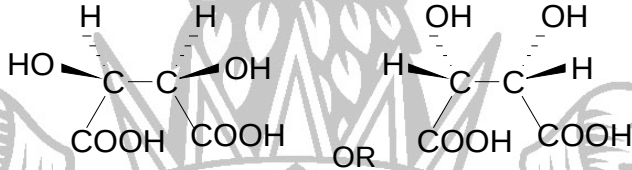
- (ii) **Mechanism:** Nucleophilic addition



- (b) (i) Lactic acid has a chiral carbon and no plane of symmetry through the molecule. Only 1 enantiomer is present in lactic acid.
- (ii) In the slow step, the  $\text{CN}^-$  can attack the planar carbonyl carbon of ethanal from either side with equal probability, resulting in the formation of a racemic mixture of enantiomers, thus optical activity cancel out.

(c)

| Molecule | Explanation                                                                                                            |
|----------|------------------------------------------------------------------------------------------------------------------------|
| A (or B) | <p>Since A rotates plane polarized light, it has two chiral centres with no plane of symmetry through the molecule</p> |
| B (or A) | B must be a mirror image of A since it rotates plane polarized light                                                   |

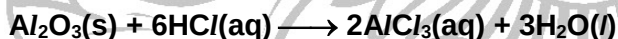
|   |                                                                                                                                                                                                                |
|---|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|   | in the opposite direction<br>                                                                                                 |
| C | C does not rotate plane polarized light, hence must have a plane of symmetry through the molecule. C is a meso compound.<br> |

### Suggested Solutions for N2012 H2 Chemistry Paper 3 (9647/03)

- 1 (a) MgO, is an ionic oxide, therefore it is basic and react with acids while P<sub>4</sub>O<sub>10</sub>, a covalent oxide, hence it is acidic and reacts with bases as shown in the equations below.

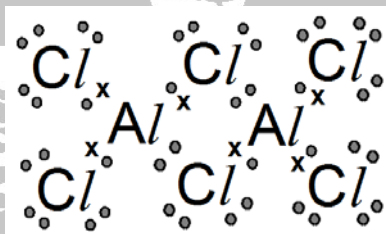


Al<sub>2</sub>O<sub>3</sub> is an amphoteric oxide that reacts with both acids and bases.



Across the period, the oxides become less basic and more acidic. Al<sub>2</sub>O<sub>3</sub> is amphoteric as it is an ionic oxide with covalent character. The covalent character is due to the high charge density of Al<sup>3+</sup> that polarize and distort the electron cloud of O<sup>2-</sup>.

(b) (i)



(ii) Trigonal planar (3 bond pairs, zero lone pairs)

(iii) When temperature increases, by Le Chatelier's Principle, the equilibrium position will shift to the right to favour the forward endothermic reaction to absorb some of the added heat in the system.

Note that the forward reaction is endothermic as it involves breaking of dative bonds to form AlCl<sub>3</sub>.

(iv)  $pV = \frac{m}{M} RT$

$$1.16 \times 10^5 \times 250 \times 10^{-6} = \frac{1.5}{M} \times 8.31 \times 500$$

$$M = 214.9 \text{ g mol}^{-1}$$

$$M_r = \underline{214.9}$$

(v)  $y = 1 - x$

$$267x + 133.5(1-x) = 214.9$$

$$133.5x = 81.4$$

$$x = \underline{0.610}$$

$$y = \underline{0.390}$$

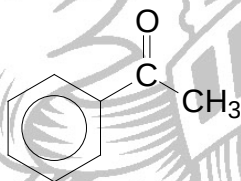
$$\text{Partial pressure of Al}_2\text{Cl}_6 = 0.610 \times 1.16 \times 10^5 = \underline{7.08 \times 10^4 \text{ Pa}}$$

$$\text{Partial pressure of AlCl}_3 = 0.390 \times 1.16 \times 10^5 = \underline{4.53 \times 10^4 \text{ Pa}}$$

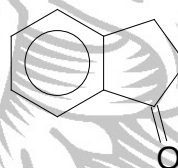
$$(vi) K_p = \frac{P_{\text{AlCl}_3}^2}{P_{\text{Al}_2\text{Cl}_6}} = \frac{(4.53 \times 10^4)^2}{(7.08 \times 10^4)} = \underline{2.90 \times 10^4 \text{ Pa}}$$

Note the difference between  $K_p$  and  $K_c$  expressions. Do not use square brackets for partial pressures (i.e.  $[P_{\text{AlCl}_3}]$  is not acceptable) as  $[\ ]$  are used for concentrations, not partial pressures.

(c)(i)



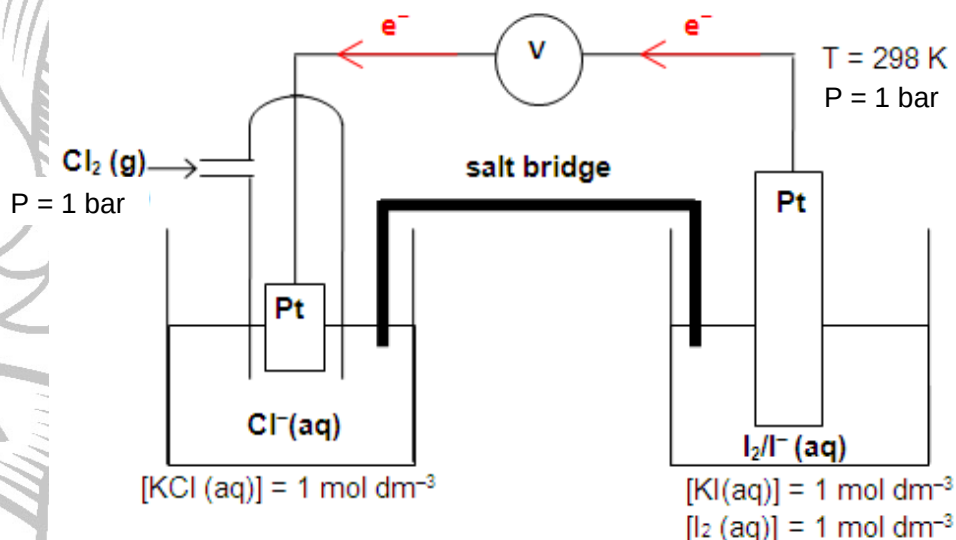
**A**



**B**

- (ii) Add both compounds separately to aqueous iodine in NaOH and warm. **A yellow ppt of CHI<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>COO<sup>-</sup>Na<sup>+</sup> are formed for compound A as it undergoes oxidation but not compound B.** Note that hot acidified KMnO<sub>4</sub> is not acceptable as both A and B will decolourise the purple solution with effervescence of CO<sub>2</sub>.

2 (a)(i)

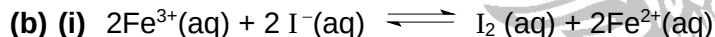
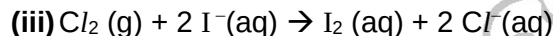


- (ii) Set up the electrochemical cell as shown above.

Read off the  $E_{\text{cell}}^0$  value on the voltmeter. The greater the  $E_{\text{cell}}^0$  value, the greater the difference in electrode potentials of the two half cells.

Monitor the direction of the flow of electrons to identify the electrode that is positively charged. The

electrode that is more positively charged will contain the stronger oxidizing agent in its half-cell and is preferentially reduced.



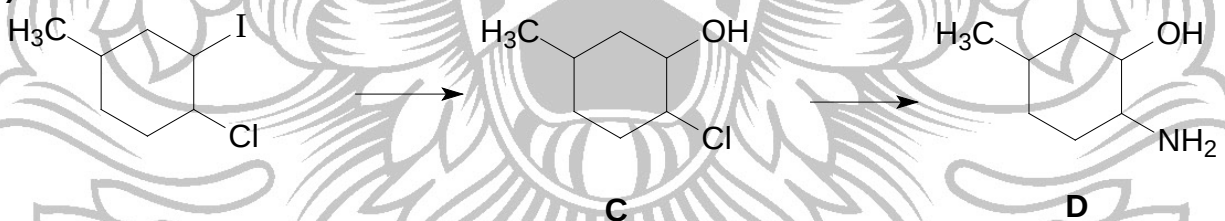
(ii) Addition of  $\text{CN}^-$  causes formation of  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  complexes.

$E^\ominus([\text{Fe}(\text{CN})_6]^{3-} | [\text{Fe}(\text{CN})_6]^{4-})$  is +0.36V which is less positive than  $E^\ominus(\text{Fe}^{3+} | \text{Fe}^{2+})$  that is + 0.77V.

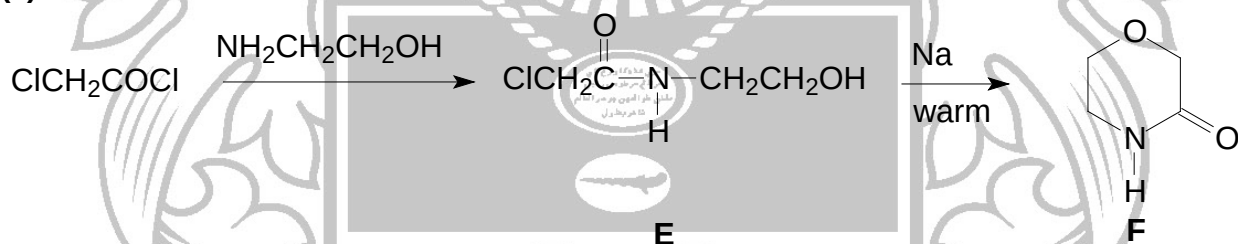
Hence,  **$[\text{Fe}(\text{CN})_6]^{3-}$  has weaker oxidizing power than  $\text{Fe}^{3+}$**  under standard conditions. In addition,  $E^\ominus([\text{Fe}(\text{CN})_6]^{3-} | [\text{Fe}(\text{CN})_6]^{4-})$  is less positive than  $E^\ominus(\text{I}_2 | \text{I}^-)$  that is +0.54V. Hence, **position of equilibrium in (b)(i) shifts to the left due to the decrease in the oxidizing power of  $[\text{Fe}(\text{CN})_6]^{3-}$ .**

(c) Ease of hydrolysis increases from chloro to bromo to iodoethane as **the size of the halogen atom, X increases in size from chlorine to bromine to iodine.** Thus, the **valence orbitals become more diffused and the effectiveness of the overlap between the orbitals of carbon and X atom decreases.** **The C–X bond strength decreases and becomes more easily broken.**

(d) (i)

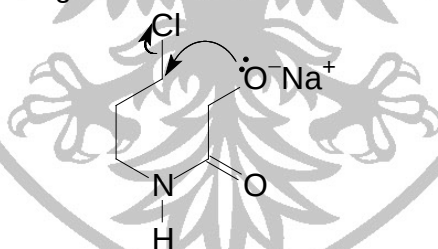


(ii)



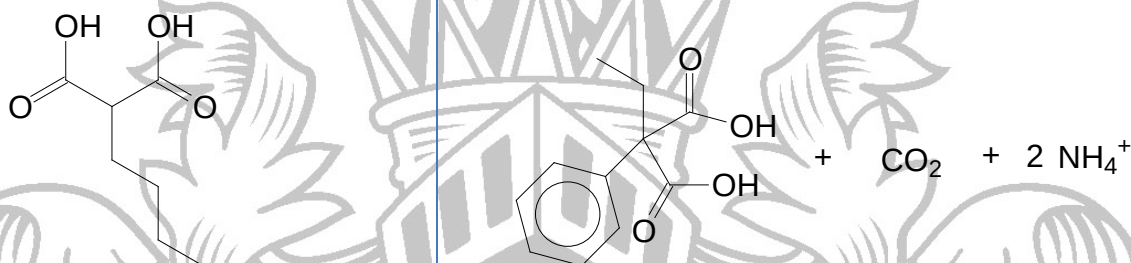
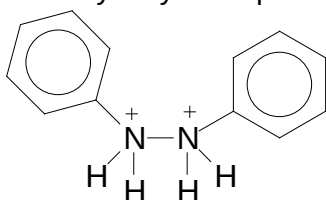
The acid chloride is more reactive than the chloroalkane as the electron-withdrawing O in the  $\text{C}=\text{O}$  group draws electrons away from the carbon bonded to Cl, thus makes the C more  $\delta^+$  and susceptible to nucleophilic attack. The lone pair of electrons on N is more available than O in the  $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$  as N is less electronegative than O. Hence, in the first step, the lone pair on N attacks the acid chloride to form E.

When Na is added, the following reaction occurs to form F

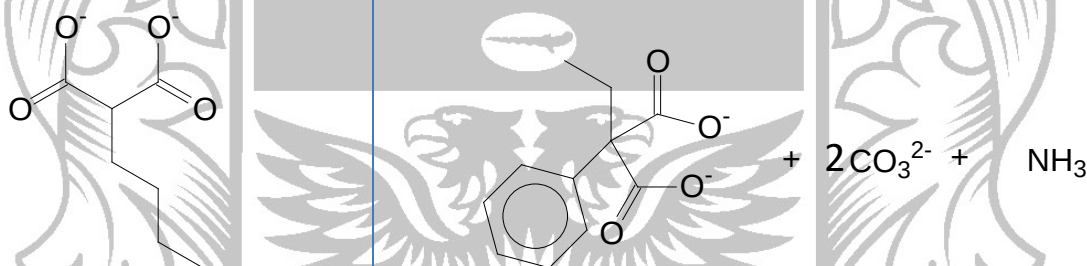
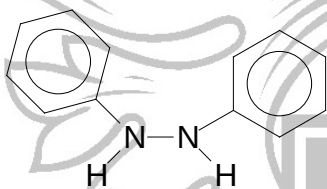


(e) (i) Aqueous  $\text{H}_2\text{SO}_4$ , heat for acidic hydrolysis OR Aqueous  $\text{NaOH}$ , heat for alkaline hydrolysis

(ii) Acid hydrolysis: Aqueous  $\text{H}_2\text{SO}_4$ , heat



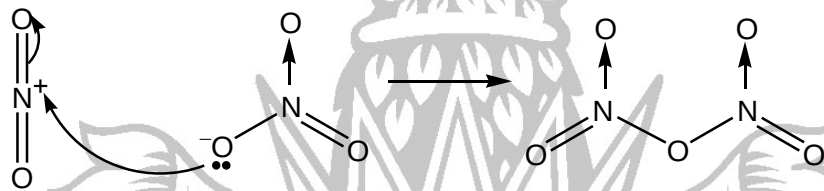
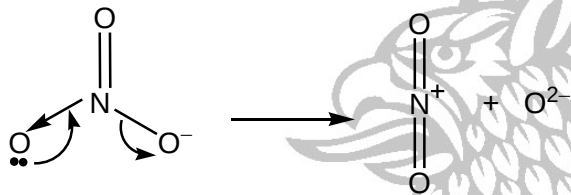
OR  
Base hydrolysis: Aqueous  $\text{NaOH}$ , heat



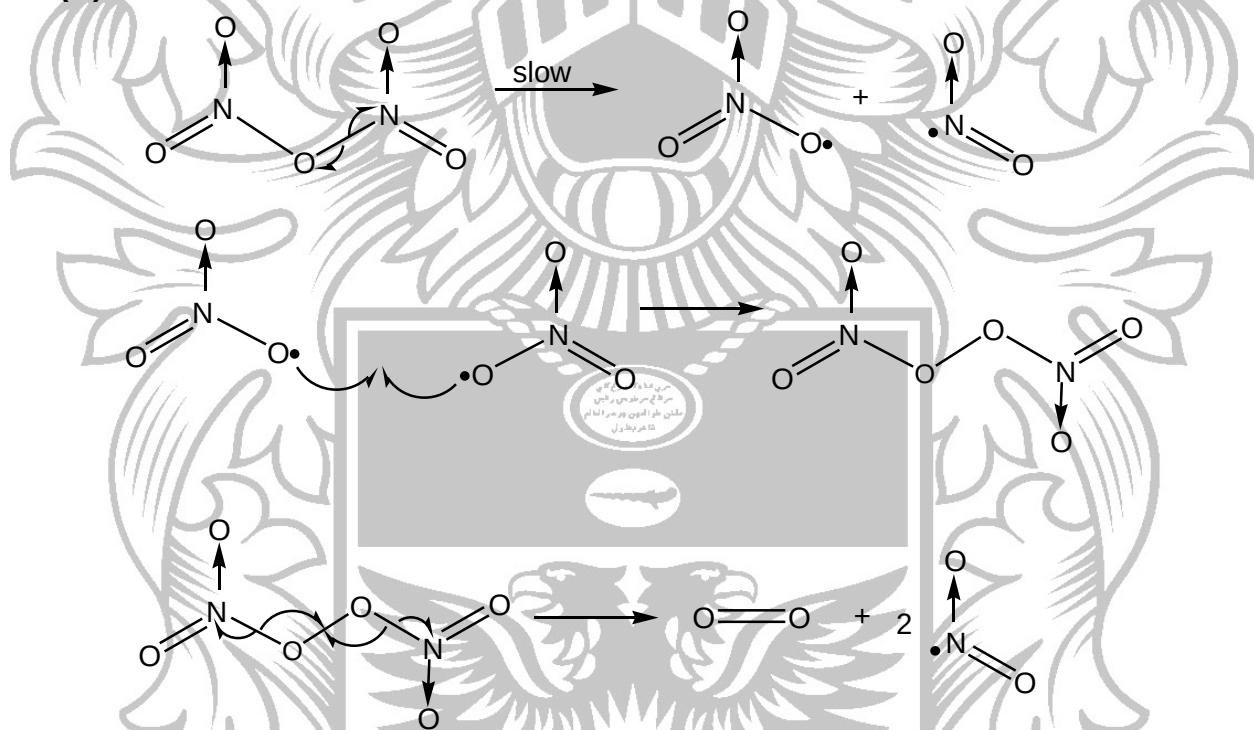
3 (a) (i)  $2 \text{Mg}(\text{NO}_3)_2 (\text{s}) \rightarrow 2 \text{MgO} (\text{s}) + 4 \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$ : Equation will be given

(ii) Down the group, **cationic size of  $\text{M}^{2+}$  increases**, thus the **charge density of the group 2 cations decreases**. **Polarising power of the cations decreases**, thus the **electron cloud of the  $\text{NO}_3^-$  is polarized to a lesser extent and the N-O bonds are weakened less**. **Down the group, more energy required to break the N-O bonds in the group 2 nitrates, thus thermal stability increases**.

3(b) (i)



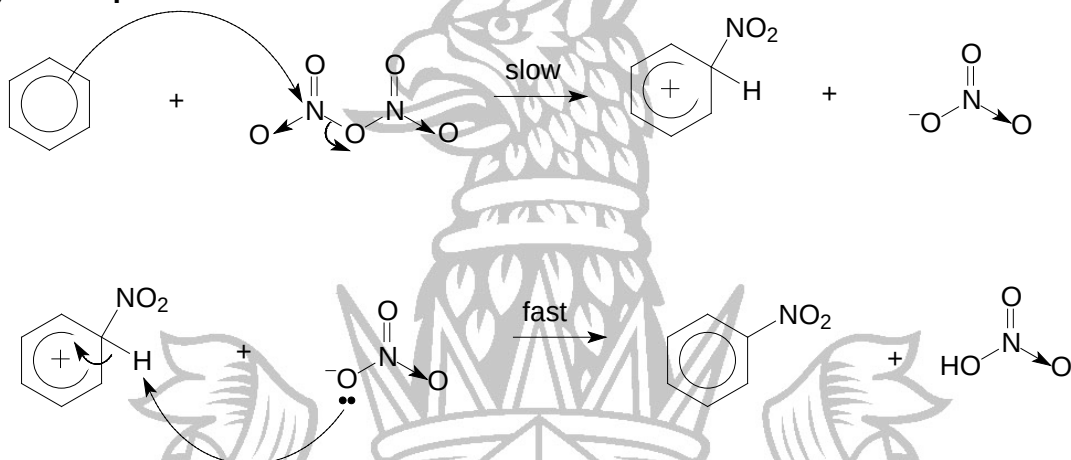
(iii)



(iv) The reaction is first-order wrt  $\text{N}_2\text{O}_5$  and hence step 1 which involves only 1 molecule of  $\text{N}_2\text{O}_5$  is the slowest step.

(c) (i) Since  $\text{N}_2\text{O}_5$  exists as  $\text{NO}_2^+$  and  $\text{NO}_3^-$  and nitrobenzene is the product,  $\text{NO}_2^+$  is the electrophile. Thus, the other product is  $\text{HNO}_3$  which is formed when  $\text{NO}_3^-$  acts as a base to remove  $\text{H}^+$  from the carbocation intermediate in the electrophilic substitution reaction.

### 3(c)(ii) Electrophilic substitution



(d) (i)  $\Delta H^\circ_{\text{reaction}} = \Delta H^\circ_{\text{f}}(\text{NO}_3) + \Delta H^\circ_{\text{f}}(\text{NO}_2) - \Delta H^\circ_{\text{f}}(\text{N}_2\text{O}_5)$   
 $+ 92.5 = \Delta H^\circ_{\text{f}}(\text{NO}_3) + 33.2 - 5$   
 $\Delta H^\circ_{\text{f}}(\text{NO}_3) = \underline{+ 64.3 \text{ kJ mol}^{-1}}$

(ii)  $\Delta H^\circ_{\text{reaction}} = 2 \Delta H^\circ_{\text{f}}(\text{NO}_2) - 2 \Delta H^\circ_{\text{f}}(\text{NO}_3)$   
 $= 2(33.2) - 2(+64.3)$   
 $= \underline{- 62.2 \text{ kJ mol}^{-1}}$

- (e) Reaction 1 and 2 have **positive entropy due to increase in no. of moles of gases formed**, but **reaction 2 is exothermic as well, hence,  $\Delta G$  will be negative at all temperatures and would be more spontaneous than reaction 1 which is endothermic.  $\Delta G$  of reaction 1 will only be negative at higher temperatures.**

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

- 4 (a) If  $\text{H}^+$  where  $\frac{e}{m} = 1$  gives an angle of deflection,  $\theta$  of  $+15^\circ$ , since  $\theta = k \left(\frac{e}{m}\right)$ ,  $k = 15$   
 $\text{D}^-: \frac{e}{m} = \frac{1}{2}$ , hence  $\theta = 15 \times \frac{1}{2} = \underline{-7.5^\circ}$   
 $\text{T}^+: \frac{e}{m} = \frac{1}{3}$ , hence,  $\theta = 15 \times \frac{1}{3} = \underline{+5.0^\circ}$   
 $\text{He}^{2+}: \frac{e}{m} = \frac{1}{2}$ , hence  $\theta = 15 \times \frac{1}{2} = \underline{+7.5^\circ}$

- (b) (i) From (a),  $\theta = k \left(\frac{e}{m}\right)$  where  $k = 15$   
 $5 = 15 \left(\frac{e}{12}\right) \Rightarrow e = \underline{+4}$

- (ii) mass number = 12, hence, no. of neutrons =  $12 - 6 = \underline{6}$ .  
 Since charge of R is +4, No. of electrons =  $6 - 4 = \underline{2}$

4(c) (i) Ionic radii from data booklet:

| $\text{Na}^+$ | $\text{Si}^{4+}$ | $\text{P}^{3-}$ | $\text{Cl}^-$ |
|---------------|------------------|-----------------|---------------|
| 0.095 nm      | 0.041 nm         | 0.212 nm        | 0.181 nm      |

$\text{Na}^+$  and  $\text{Si}^{4+}$  are smaller than  $\text{P}^{3-}$  and  $\text{Cl}^-$  as  $\text{P}^{3-}$  and  $\text{Cl}^-$  have **one more electronic shell** as compared to  $\text{Na}^+$  and  $\text{Si}^{4+}$ , thus, **the valence electrons are further away from the nucleus.**

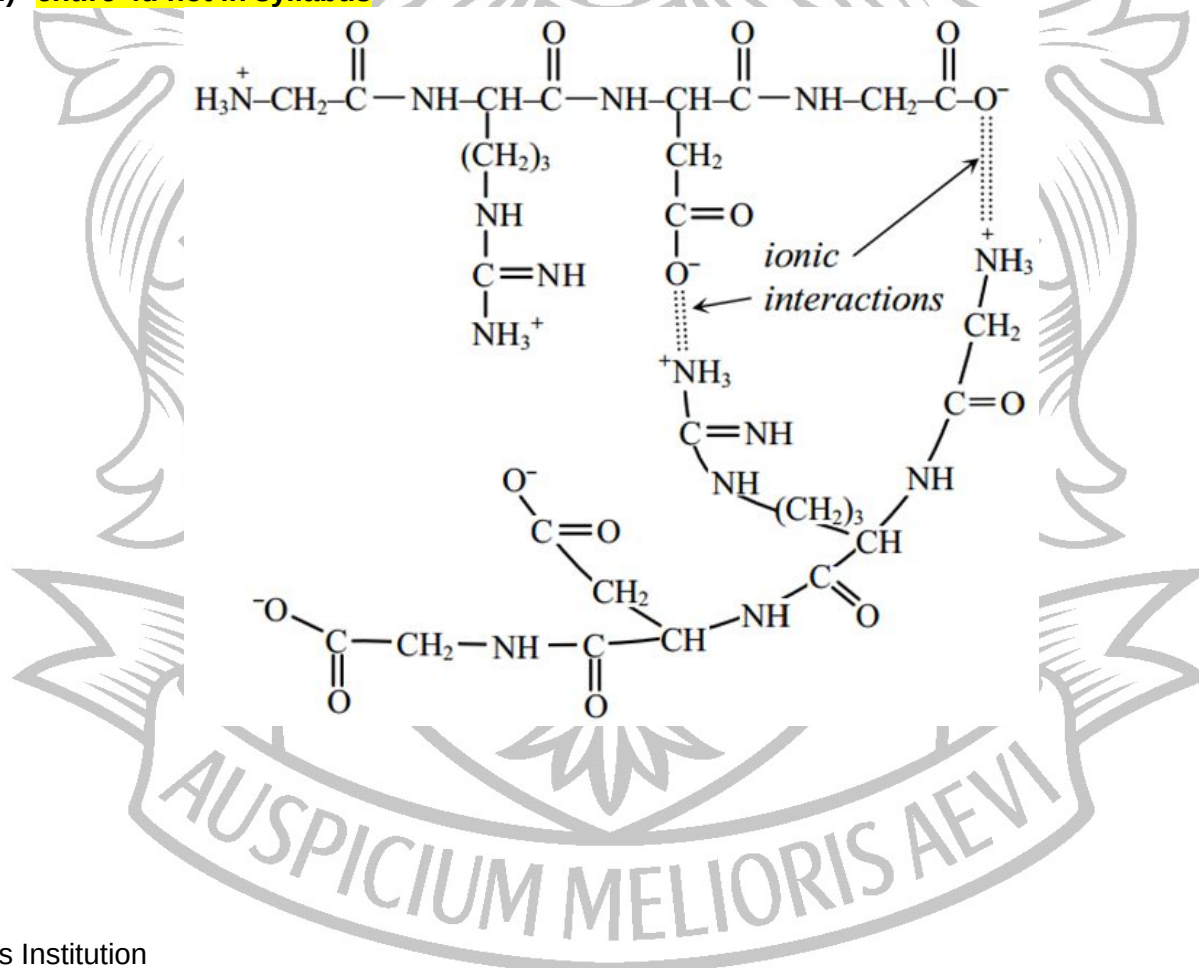
$\text{Si}^{4+}$  is smaller than  $\text{Na}^+$ . **Both ions are isoelectronic, hence both have similar shielding effect, but  $\text{Si}^{4+}$  has more protons, hence greater nuclear charge. Effective nuclear charge of  $\text{Si}^{4+}$  is greater than  $\text{Na}^+$  thus the valence electrons of  $\text{Si}^{4+}$  experience greater attraction to the nucleus and is smaller.  $\text{Cl}^-$  is smaller than  $\text{P}^{3-}$  for the same reason.**

(ii) Na and Si have **giant metallic lattice** and **giant covalent lattice** respectively while P and Cl have **simple molecular structure and exists as  $\text{P}_4$  and  $\text{Cl}_2$  molecules.** More energy is required to break the metallic bonds between  $\text{Na}^+$  and its delocalized sea of electrons and the covalent bonds between Si atoms as compared to the weak instantaneous dipole-induced dipole forces between  $\text{P}_4$  or  $\text{Cl}_2$  molecules. Thus, melting points of Na and Si is more than  $\text{P}_4$  and  $\text{Cl}_2$ .

For Si and Na, **more energy is required to break the stronger covalent in Si as compared to the metallic bonds in Na, thus Si has higher melting point than Na.**

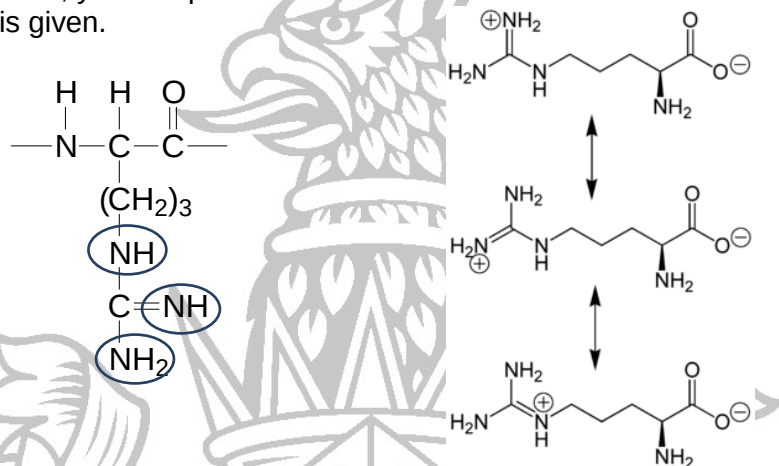
**$\text{P}_4$  has a larger electron cloud which is more polarizable than  $\text{Cl}_2$ , thus the instantaneous dipole-induced dipole forces between  $\text{P}_4$  molecules is stronger, thus require more energy to break.  $\text{P}_4$  has a higher melting point than  $\text{Cl}_2$ .**

(d) (i) **entire 4d not in syllabus**



4(d) (i)

NOTE: For the arginine residue, you can protonate at ANY of the 3 N atoms circled below in the side chain since no  $pK_b$  value is given.



However, in reality, the proton would attach itself to the  $=NH$  group to produce the symmetrical  $R-NH-C(NH_2)_2^+$  cation. This cation is stabilized by resonance as shown above.

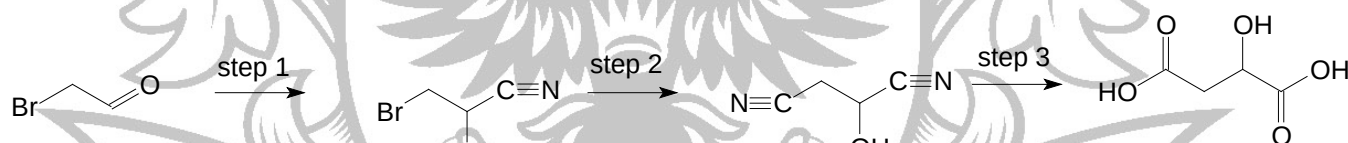
- (ii) Ionic interactions between  $NH_2$  groups of arginine or  $COOH$  groups of aspartic acid  
van der Waals' (not hydrophobic) attractions between nonpolar hydrocarbon groups of the side chains of the amino acids.  
 (Also, disulfide (not disulfite) linkages between the  $SH$  groups of the side chains)

(e) (i) Ester

(ii)



5(a)

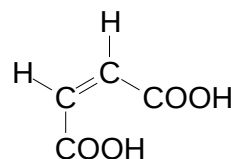
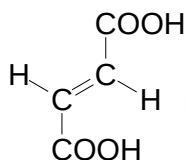


Step 1:  $KCN$ , dilute  $HCl$ , trace of  $KCN$  as catalyst

Step 2:  $KCN$ , aqueous ethanol, heat (or heat under reflux)

Step 3: dilute  $HCl$ , heat (or heat under reflux)

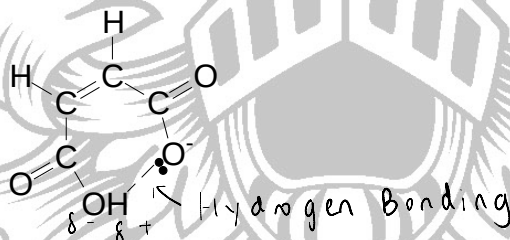
(b) (i) cis-trans isomerism



(ii) excess concentrated sulfuric acid, 170 °C

5(b)(iii) **K** produce the more stable monoanion as the  $pK_a(1)$  is smaller implying it is **more difficult for the mono anion of K to accept  $H^+$** . Likewise  $pK_a(2)$  is larger, implying it is **more difficult for the monoanion to lose a 2<sup>nd</sup> proton, thus monoanion of K more stable.**

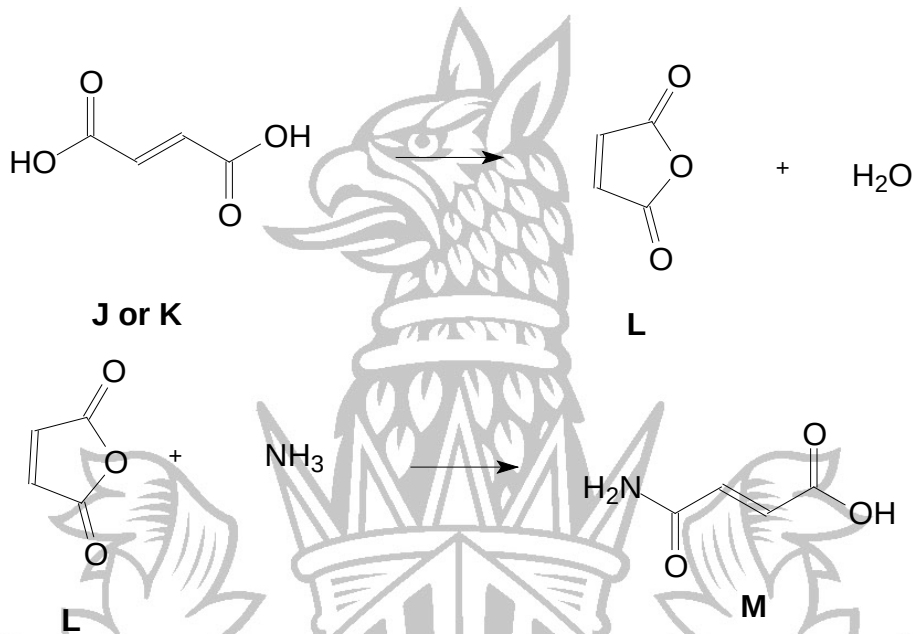
(iv) The more stable anion is produced from the **cis isomer** as **intramolecular hydrogen bonding can exist** as shown below as the oxygen with the negative charge is in close proximity to the protonic H of the adjacent COOH group.



Note:  $pK_a(1)$  of the cis isomer should be smaller since the monoanion is more stable and less likely to accept back  $H^+$  as compared to the trans isomer. The cis isomer is **K** and trans isomer is **J**. ( $pK_a(2)$  of the cis isomer is larger as it is now more difficult to lose the 2<sup>nd</sup> proton as it is involved in intramolecular hydrogen bonding.)

(c)

| Evidence                                                                                       | Deductions                                                                                                                                                                                                                                                                   |
|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>L</b> , $C_4H_2O_3$ is neutral, no reaction with sodium metal or 2,4-dinitrophenylhydrazine | Loss of 1 mole of water since <b>J/K</b> is $C_4H_4O_4$ but <b>L</b> is $C_4H_2O_3$ .<br>Condensation reaction between two $-OH$ of the COOH groups, losing one mole of water.<br>Absence of carboxylic acid since it is neutral<br>No alcohol group or aldehyde and ketone. |
| <b>L</b> reacts with ammonia to give <b>M</b> , $C_4H_5NO_3$ .                                 | <b>M</b> could be an amide and this could be a <i>nucleophilic substitution</i> reaction between <b>L</b> and $NH_3$ .<br><b>L</b> is an acid derivative.                                                                                                                    |
| Evidence                                                                                       | Deductions                                                                                                                                                                                                                                                                   |
| <b>M</b> gives a salt with NaOH but not HCl                                                    | <b>M</b> is acidic as it undergoes acid base reaction with NaOH.<br>Hence, COOH group present in <b>M</b> .<br>Since <b>M</b> does not react with HCl, there is no basic amine group.                                                                                        |
| <b>M</b> decolourise $Br_2$                                                                    | $C=C$ present, electrophilic addition reaction between <b>M</b> and $Br_2$                                                                                                                                                                                                   |



(d)

| Evidence                                                           | Deductions                                                                                        |
|--------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| Malic acid heated with $\text{K}_2\text{Cr}_2\text{O}_7$ to form N | [O] reaction of secondary alcohol to ketone                                                       |
| Heating N produce P, $\text{C}_3\text{H}_4\text{O}_3$ and gas Q    | <b>Gas Q could be <math>\text{CO}_2</math></b> due to loss of one C since N has 4 C and P has 3 C |
| N and P react with 2,4 dinitrophenylhydrazine                      | N and P contain the carbonyl group, condensation reaction with 2,4 dinitrophenylhydrazine         |
| P give yellow ppt with aqueous alkaline iodine                     | Methyl ketone present, $\text{CHI}_3$ is the yellow ppt.                                          |

