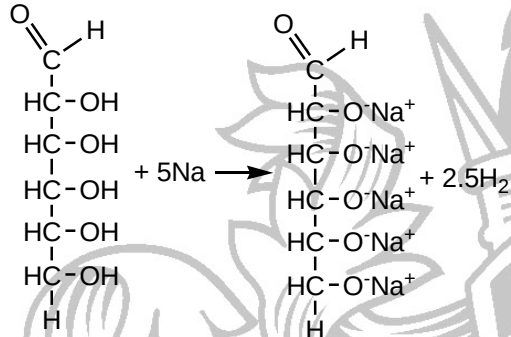


# Suggested Solutions to N2009 H2 Chemistry Paper 1 (9746/01)

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

## Detailed Working for Suggested Solutions to N2009 H2 Chemistry Paper 1 (9746/01)

Q1



Ans: A

Q2 Amt of  $\text{C}_2\text{O}_4^{2-} = 2 \times 10^{-3} \text{ mol}$   
since 1 mol of  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$  gives 2 mol of  $\text{C}_2\text{O}_4^{2-}$

$$\text{Amt of } \text{MnO}_4^- = \frac{2.0 \times 10^{-3}}{5} \times 2 = 8 \times 10^{-4} \text{ mol}$$

$$\text{Conc of } \text{MnO}_4^- = \frac{8.0 \times 10^{-4} \text{ mol}}{0.020 \text{ mol dm}^{-3}} \times 1000 \text{ cm}^3 / \text{dm}^3 = 40 \text{ cm}^3$$

Ans: B

Q3

|   | Proton No | Electronic Configur <u>n</u> | Ion/ Atom       |
|---|-----------|------------------------------|-----------------|
| A | 11        | 2.8                          | $\text{Na}^+$   |
| B | 16        | 2.8.8.                       | $\text{S}^{2-}$ |
| C | 17        | 2.8.8.                       | $\text{Cl}^-$   |
| D | 18        | 2.8.8.                       | Ar              |

Ans: A

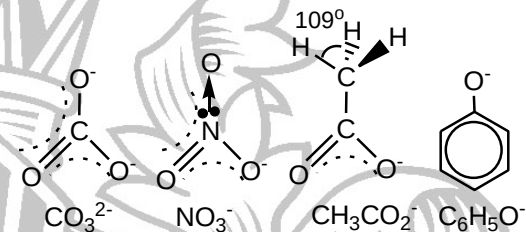
Q4 From Data Booklet,

|   | Metal | 1 <sup>st</sup> I.E. | 2 <sup>nd</sup> I.E. | 1 <sup>st</sup> +2 <sup>nd</sup> I.E. |
|---|-------|----------------------|----------------------|---------------------------------------|
| A | Co    | 757                  | 1640                 | 2397                                  |
| B | Cr    | 653                  | 1590                 | 2243                                  |
| C | Cu    | 745                  | 1960                 | 2705                                  |
| D | Ni    | 736                  | 1750                 | 2486                                  |

|  |    |     |      |      |
|--|----|-----|------|------|
|  | Al | 577 | 1820 | 2397 |
|--|----|-----|------|------|

Ans: A

Q5



All have delocalized electrons. Ans: C

Q6

In the absence of water,  $\text{HCl(g)}$  remained as an undissociated simple molecule, and not dissociated into  $\text{H}^+$  and  $\text{Cl}^-$  ions, thus it does not have acidic properties. Ans: B

Q7  $PV = nRT$

$$P = \frac{nRT}{V}$$

$$P = \frac{(1.6 \times 10^{-3} \text{ mol})(8.31 \text{ JK}^{-1} \text{ mol}^{-1})(273 + 273) \text{ K}}{(3.0 \times 10^{-3} \text{ m}^3)} \text{ Pa}$$

Ans: D

Q8 Ans: C

(A)  $\text{CaC}_2\text{O}_4$  should have lower solubility product than  $\text{MgC}_2\text{O}_4$  as it is less soluble and they are both similar salts.

(B)  $\text{CaC}_2\text{O}_4$  should have numerically lower lattice energy than  $\text{MgC}_2\text{O}_4$  as  $\text{Ca}^{2+}$  is larger than

$$\text{Mg}^{2+} \text{ \& } L.E. \propto \frac{q^+ q^-}{r^+ + r^-}$$

(C)  $\Delta H_{\text{soln}} = \Delta H_{\text{hyd}} - L.E.$  Generally, the more exothermic or more negative  $\Delta H_{\text{soln}}$  is, the more

soluble the salt.  $\Delta H_{\text{hyd}} \propto \frac{q^+}{r^+}$  and  $\text{Ca}^{2+}$  is larger

than  $\text{Mg}^{2+}$ , thus  $\text{Ca}^{2+}$  has lower  $\Delta H_{\text{hyd}}$  than  $\text{Mg}^{2+}$  considering that both ions have same charge.

(D) Electropositive values are not related to solubility.

**Q9**  $\Delta G = \Delta H - T\Delta S$   $\Delta H \approx 0 \Rightarrow \Delta G = -T\Delta S$   
 $\Rightarrow \Delta S$  &  $\Delta G$  have opposite signs  
 Since pure water is separated from that contaminated with ions (and molecules), with the increased ordering of state,  $\Delta S$  must be negative  
 $\Delta G$  is positive (non-spontaneous).  
 Ans: B

**Q10**

Freezing at melting is a reversible process as both solid and liquid co-exist at dynamic equilibrium,  
 $\Delta G = 0$ .  $\Delta H$  is negative since heat is evolved.  
 $\Delta G = \Delta H - T\Delta S = 0$

$$\Delta G = \left(\frac{54}{18.0} \text{ mol}\right)(-6.0 \times 10^3 \text{ J mol}^{-1}) - (273\text{K})(\Delta S) = 0$$

$$\Delta S = -66 \text{ J K}^{-1} \quad \text{Ans: A}$$

**Q11**

Cathode:  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (reduction)  
 Anode:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$  (oxidation)

Statement X is wrong as  $[\text{Zn}^{2+}] > 1 \text{ mol dm}^{-3}$  favours reduction at anode  $E_{\text{cell}} < E^{\ominus}_{\text{cell}}$ .

Statement Y is correct as  $[\text{H}^+] > 1 \text{ mol dm}^{-3}$  favours reduction at cathode,  $E_{\text{cell}} > E^{\ominus}_{\text{cell}}$ .

Ans: C

**Q12**  $PV = nRT$   $P = \frac{nR}{V} T$

Gradient of the graph is directly proportional to amount of gaseous particles. Amount of gaseous particles increases as dissociation of  $\text{X}_2$  is favoured at higher temperature since bond dissociation is endothermic. Gradient of graph should be doubled when  $\text{X}_2$  is dissociated into X at higher temperature.

Ans: B

**Q13**

At lower [ethanal], active sites of enzymes are not saturated and available, thus reaction is 1<sup>st</sup> order with respect to ethanal.

At higher [ethanal], active sites are saturated and reaction is zero order with respect to ethanal.

Ans: C

**Q14**

Water vapour would be produced on the decomposition of amphoteric aluminium hydroxide.

The heat absorbed by the decomposition reaction acts as a retardant by delaying ignition of the associated substance. The water released would also act as an extinguisher (dilutes any combustible gases and inhibits oxygen from aiding the combustion).

Ans: (B)

**Q15**

(A) Cu atom ( $Z=29$ ) has more electrons than Mg( $Z=12$ ) atom.

(B)  $\text{Cu}^{2+}: 1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^9$   
 $\text{Mg}^{2+}: 1\text{s}^2 2\text{s}^2 2\text{p}^6$

(C)  $\text{Cu}^{2+}: 1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^9$   
 Mg:  $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2$

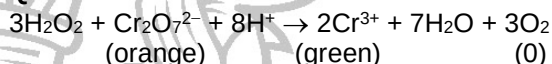
Same number of quantum shells

(D) Cu:  $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^{10} 4\text{s}^1$   
 $\text{Mg}^{2+}: 1\text{s}^2 2\text{s}^2 2\text{p}^6$

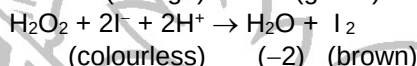
Cu has 2 more **electron shells** (quantum shells:  $n=3$  &  $4$ ) than  $\text{Mg}^{2+}$ .

Ans: D

**Q16**



(orange) (green) (0)



(colourless) (-2) (brown)

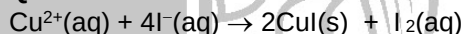
Ans: C

**Q17** From Data Booklet,

| (A)                                    | B   | C    | N    | O    |
|----------------------------------------|-----|------|------|------|
| 1 <sup>st</sup> IE/kJmol <sup>-1</sup> | 799 | 1090 | 1400 | 1310 |
| (B)                                    | Co  | Ni   | Cu   | Zn   |
| 1 <sup>st</sup> IE/kJmol <sup>-1</sup> | 757 | 736  | 745  | 908  |
| (C)                                    | Mg  | Ca   | Sr   | Ba   |
| 1 <sup>st</sup> IE/kJmol <sup>-1</sup> | 736 | 590  | 548  | 508  |
| (D)                                    | Si  | P    | S    | Cl   |
| 1 <sup>st</sup> IE/kJmol <sup>-1</sup> | 786 | 1060 | 1000 | 1260 |

Ans: B

**Q18**



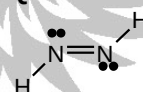
White ppt brown solution



$$E^{\ominus}_{\text{cell}} = +0.15\text{V} - (+0.54\text{V}) = -0.39\text{V}$$

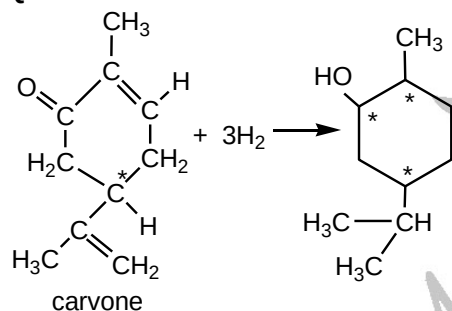
Ans: D

**Q19**



There is 1 lone pair and 2 bonding pairs about N atom. Bonding pair-lone pair repulsion is stronger than bonding pair-bonding pair repulsion, thus the bond angle is approximately 118°. Ans: B

Q20

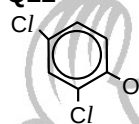


Ans: D

Q21

Bromine is an electrophile that is added onto the C=C bond. Ans: A

Q22



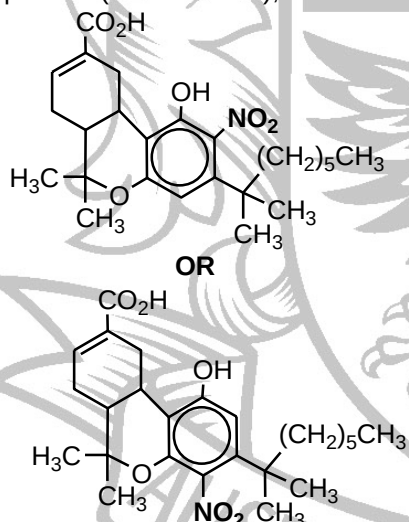
is the nucleophile that replaces  $\text{Cl}^-$  in  $\text{C}/\text{CH}_2\text{CO}_2\text{H}$ , thus reaction is nucleophilic substitution. Ans: D

Q23

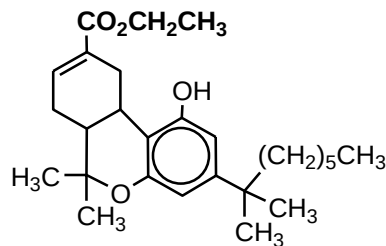
Halogen compound **S**, a halogenoarene, cannot undergo nucleophilic substitution with ethanol due to partial double bond character in C-Cl bond. Thus, it is unable to release free  $\text{Cl}^-$  ions that can be precipitated with free  $\text{Ag}^+$  ions. Ans: D

Q24

(A) It reacts with  $\text{HNO}_3(\text{aq})$  to form a substitution product (shown below), not an addition product.

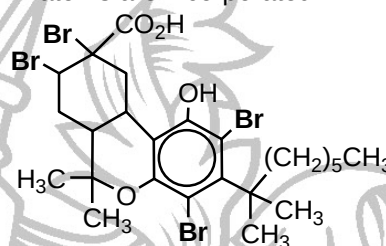


(B) It will only form a single ester (shown below), not a diester upon heating with ethanol with conc  $\text{H}_2\text{SO}_4$ .



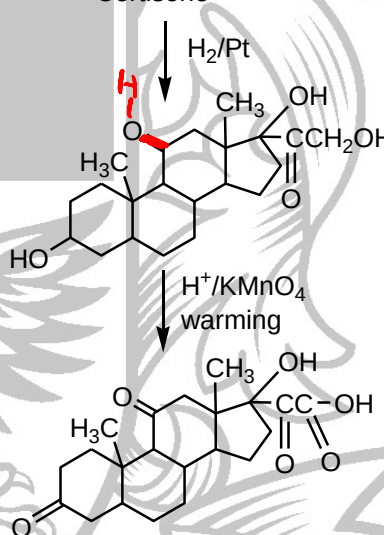
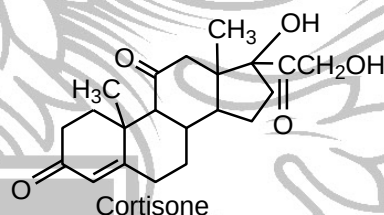
(C)  $\text{K}_2\text{Cr}_2\text{O}_7$  cannot oxidise the C=C bond or the alkyl side chain of the aromatic ring, thus no colour change is expected.

(D) The product formed is shown below. Note that 4 Br atoms are incorporated.



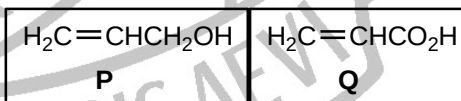
Ans: D

Q25



Ans : B

Q26  $\text{NaBH}_4$  can only reduce aldehydes and ketones.



Ans : A

**Q27**

Phenol is the least acidic of the 4 compound.

Carboxylic acids are stronger acid. The negative charge is delocalised between 2 oxygen atoms in the anions of the other 3 carboxylic acids.

Bromoethanoic acid and chloroethanoic acid are more acidic than propanoic acid due to presence of electron-withdrawing halogen atoms which further de-intensify the negative charge on the anions of the carboxylic acids.

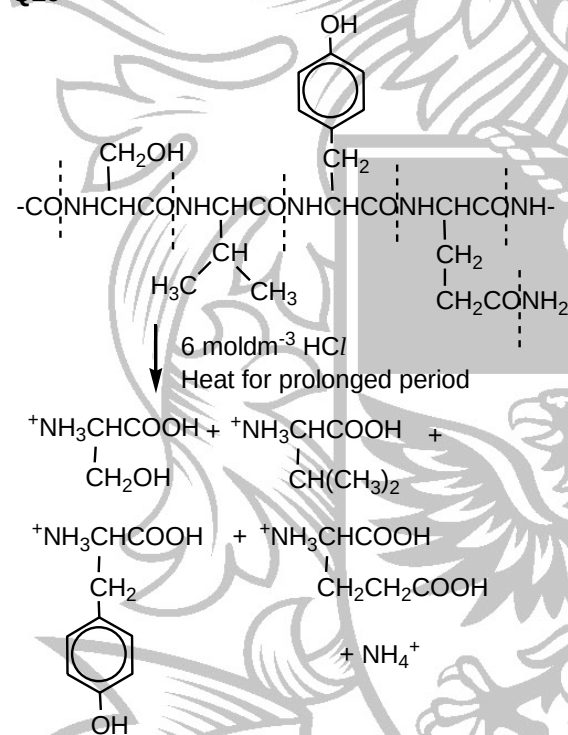
Chlorine is a stronger electron-withdrawing group than bromine as it is more electronegative, thus chloroethanoic acid is the most acidic of the 4 compounds.

Ans: C

**Q28**

Amine is basic and dissolves in acid to form an ionic salt that is soluble (miscible) in the aqueous layer. Benzene has no reaction with aqueous acids, thus remains immiscible with the aqueous layer.

Ans: C

**Q29**

Ans: C

**Q30**

Pentapeptide is formed where 4 peptide bonds are formed, thus 4 moles of water is removed.

Total  $M_r = 2(75) + 89 + 2(105) - 4(18) = 377$  Ans: B

**Q31 Deduce the possible empirical formula**

| C:                                               | H:  | O    | OR | C:                                   | H:  | S    |
|--------------------------------------------------|-----|------|----|--------------------------------------|-----|------|
| 54.5                                             | 9.1 | 36.4 |    | 54.5                                 | 9.1 | 36.4 |
| 12.0                                             | 1.0 | 16.0 |    | 12.0                                 | 1.0 | 32.1 |
| 4                                                | 8   | 2    |    | 4                                    | 8   | 1    |
| <b>(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)</b> |     |      |    | <b>(C<sub>4</sub>H<sub>8</sub>S)</b> |     |      |

Ans: A

**Q32**

1. C-C-C bond angle in diamond is 109.5° and C-C-C bond angle in graphite is 120°.
2. The shortest C-C bond is in graphite (sp<sup>2</sup> overlap), not in diamond (sp<sup>3</sup> overlap).
3. All covalent bonds are of the same strength in diamond as well as graphite (due to the delocalization of  $\pi$  electrons).

⇒ Ans: D

**Q33**

1. With increase in [ethanol], oxidation (to ethanoic acid) is favoured rather than reduction (acid to alcohol). So the **reduction** electrode potential of electrode 1 become more negative.
2. Oxygen (from 0 to -2), and not hydrogen, is reduced at Electrode 2.
3. Oxygen is NOT reduced at electrode 1.

⇒ Ans: D

**Q34**

1. Half-life is  $2.0 \times 10^{-4}$  s since this is duration when  $[\bullet\text{OH}]$  decreases from 10.0 to 5.0 as well as from 5.0 to 2.5.
2. Since  $\bullet\text{OH}$  has a constant half-life, thus reaction is 1<sup>st</sup>-order w.r.t.  $\bullet\text{OH}$ .
3. Overall reaction order cannot be deduced as the order of reaction w.r.t. methane cannot be deduced when its concentration did not change in this experiment.

⇒ Ans: B

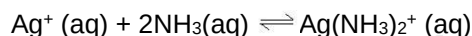
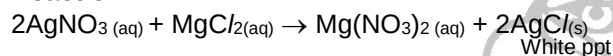
**Q35**

Statement 1 is correct but statement 3 is incorrect since there is no metallic bonding in hydroxyapatite and Statement 2 is incorrect as loss of Ca happens more readily since it forms a more soluble salt.

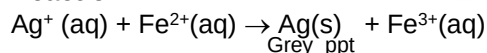
⇒ Ans: D

**Q36**

**Reaction 1**

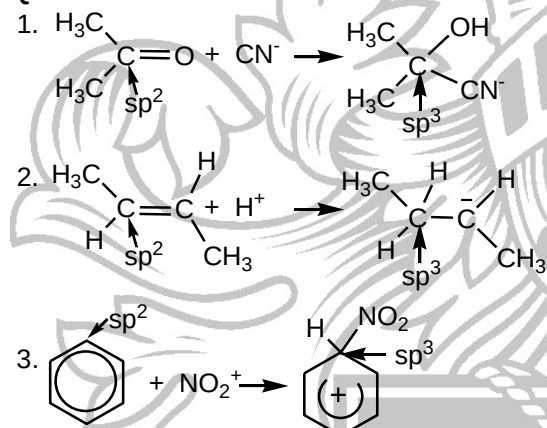


**Reaction 2**



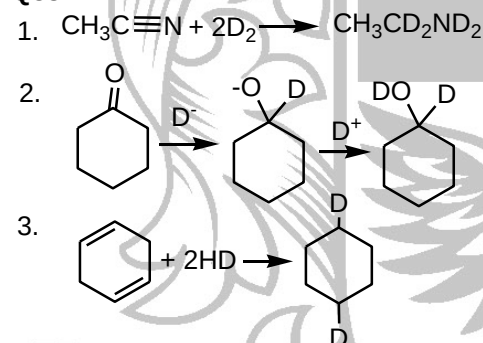
1.  $\text{Ag}^+$  acts as oxidising agent in reaction 2 as it is reduced from +1 to 0 oxidation state.
2. In reaction 1, the soluble complex formed is between  $\text{Ag}^+$  and  $\text{NH}_3$ , NOT between Ag metal and  $\text{NH}_3$ .
3. Iron(II) ions are reagents, not catalyst, in reaction 2.

**Q37**



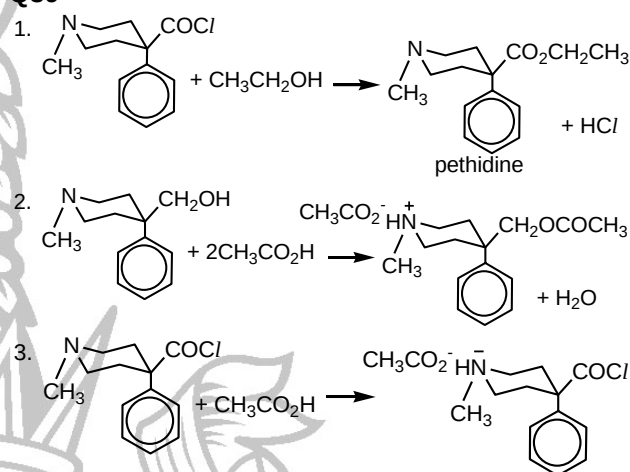
All 3 options are correct  $\Rightarrow$  Ans: A

**Q38**



Ans: B

**Q39**



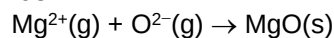
Ans: D

**Q40**

1.  $\text{H}_3\text{N}^+\text{CHR}\text{CO}_2^-$  is the zwitterionic form of protein that is formed at the equivalence point or its isoelectric point,  $\text{pI}$ , which may not be equal to 7.
2.  $\text{pH}=\text{pK}_1$  coincides with the maximum buffer capacity before the 1<sup>st</sup> equivalence point is reached. The species that are present when  $\text{pH}=\text{pK}_1$  are the cationic form,  $\text{H}_3\text{N}^+\text{CHR}\text{CO}_2\text{H}$  and the zwitterionic form,  $\text{H}_3\text{N}^+\text{CHR}\text{CO}_2^-$ .
3. There is no negative net charge on the zwitterionic form of the amino acid ( $\text{H}_3\text{N}^+\text{CHR}\text{CO}_2^-$ ) when the slope of the curve is at a maximum or its equivalence point.

**Suggested Solns for N2009 H2 Chemistry Paper**  
**2 (9746/02)**

**1(a)** Lattice energy of MgO is defined as the enthalpy change when one mole of MgO is formed from gaseous  $\text{Mg}^{2+}$  ions and  $\text{O}^{2-}$  ions at 1 bar and 298K.



**1(b)(i)**

| Ion              | $\text{Cl}^-$ | $\text{Br}^-$ | $\text{I}^-$ |
|------------------|---------------|---------------|--------------|
| Ionic radius /nm | 0.181         | 0.195         | 0.216        |

Since  $L.E. \propto \frac{q^+ q^-}{r^+ + r^-}$  and the same charges of ions

and the same cation, ionic radius increases from  $\text{Cl}^-$  to  $\text{Br}^-$  to  $\text{I}^-$ , thus lattice energy decreases from NaCl to NaBr to NaI.

**1(b)(ii)**

| Ion              | $\text{Na}^+$ | $\text{Mg}^{2+}$ |
|------------------|---------------|------------------|
| Ionic radius /nm | 0.095         | 0.065            |

The electrostatic attraction between doubly charged ions in MgO is stronger than the singly charged ions in sodium halides. In addition, the ionic radii of  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  are smaller than that of  $\text{Na}^+$  and the halide

ions. Since  $L.E. \propto \frac{q^+ q^-}{r^+ + r^-}$ , thus lattice energy of

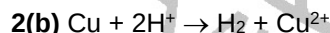
MgO is considerably larger than those of sodium halides.

**1(c)** The theoretical lattice energy assumes 100% ionic character for the compound. However, there is considerable covalent character in AgI than in AgF since the electron cloud of  $\text{I}^-$  is larger and more polarisable than  $\text{F}^-$ , hence the model used to calculate the theoretical value of the LE of AgI is unsuitable.

**1(d)(i)** Co-ordination number of an ion in an ionic crystal lattice structure is the number of its nearest oppositely charged neighbouring ions surrounding it.

**1(d)(ii)**  $\text{Cs}^+$  has a much larger ionic size than  $\text{Na}^+$  and  $\text{K}^+$  ions, thus it more  $\text{Cl}^-$  ions could be packed around this larger  $\text{Cs}^+$  ion.

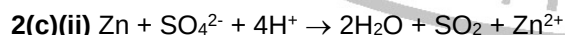
**2(a)** Cu and Zn



$$E^\ominus_{\text{cell}} = (+0.00\text{V}) - (+0.34\text{V}) = -0.34\text{V} \text{ (not feasible)}$$

Residue formed is copper.

**2(c)(i)** oxidising agent

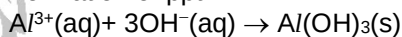


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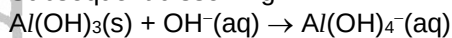
**2(d)(i)**  $\text{Al}(\text{OH})_3$

**2(d)(ii)**

Formation of ppt:



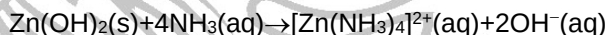
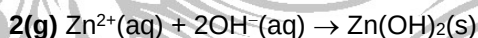
Subsequent dissolving:



**2(e)** Zn has electronic configuration of  $[\text{Ar}]3\text{d}^{10}4\text{s}^2$ , thus its fully filled d-orbitals makes its compound white and solution of its compound colourless. It also has only one fixed oxidation state of +2.



**2(f)(i)** From Data Booklet, radius of  $\text{Mg}^{2+}$  is 0.065nm. The charge density or polarising power of  $\text{Zn}^{2+}$  is lower than that of  $\text{Mg}^{2+}$  since both  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  are doubly charged. The C–O bond in  $\text{ZnCO}_3$  is polarised or weakened to less extent than that in  $\text{MgCO}_3$ , thus  $\text{ZnCO}_3$  will decompose at a higher temperature than  $\text{MgCO}_3$ .



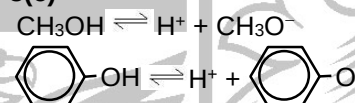
**3(a)** Ethanoic acid and benzoic acid

**3(b)** Assuming equilibrium  $[\text{phenol}] \approx \text{initial} [\text{phenol}]$ ,

$$[\text{H}^+] = \sqrt{0.10 \times 1.3 \times 10^{-10}} = 3.60 \times 10^{-6} \text{ mol dm}^{-3}$$

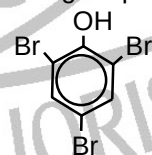
$$\text{pH} = -\log(3.60 \times 10^{-6}) = 5.44$$

**3(c)**



The phenoxide anion is more stable than the methoxide anion as the negative charge of the oxygen atom in the phenoxide anion can be delocalised into the benzene ring.  $\text{CH}_3$  group is electron-donating and will intensify the negative charge on the oxygen atom, thus destabilizing the methoxide anion. Hence, phenol is a stronger acid than methanol.

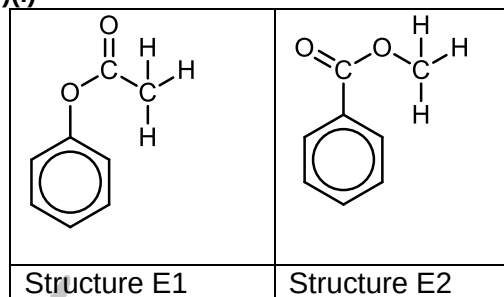
**3(d)** White ppt will be formed and decolourisation of orange aqueous bromine is observed.



**3(e)(i)** Heat under reflux the reaction mixture of methanol and benzoic acid with catalytic amount of concentrated sulfuric acid.

**3(e)(ii)** Add phosphorus pentachloride,  $\text{PCl}_5$ , to ethanoic acid at room temperature and pressure to convert it into ethanoyl chloride,  $\text{CH}_3\text{COCl}$ . After that, add ethanoyl chloride to phenol at the room temperature and pressure to synthesise phenyl ethanoate.

**5(b)(i)**



**4(a)(i)** A, C, D

**4(a)(ii)** A, D

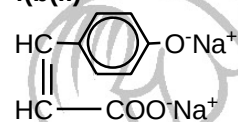
**4(a)(iii)** A, D

**4(a)(iv)** A, D

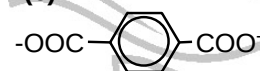
**4(a)(v)** D

**4(b)(i)** (a)(v)

**4(b)(ii)**



**4(c)**



**4(d)**

| A produces                                                           | D produces                                                           |
|----------------------------------------------------------------------|----------------------------------------------------------------------|
| $^+\text{Na}^+\text{OOC}-\text{C}_6\text{H}_4-\text{CH}=\text{CHOH}$ | $\text{HO}-\text{C}_6\text{H}_4-\text{CH}=\text{CHCOO}^-\text{Na}^+$ |

**5(b)(ii)**

| E1 produces                                                                                                                                             | E2 produces                                                                                                                                  |
|---------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{O}^-\text{Na}^+$<br><br>& $\text{CH}_3\text{COO}^-\text{Na}^+$ | $\text{COO}^-\text{Na}^+$<br><br>& $\text{CH}_3\text{OH}$ |

**5(c)**

| Mixture from E1 produces                                                                                                     | Mixture from E2 produces |
|------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| <br>& $\text{CH}_3\text{COO}^-\text{Na}^+$ | No reaction              |

**Explanation:**

$\text{CO}_2$  dissolves in water to form carbonic acid,  $\text{H}_2\text{CO}_3$  ( $K_a = 4.5 \times 10^{-7} \text{ mol dm}^{-3}$ ).

Since  $\text{H}_2\text{CO}_3$  is a stronger acid than phenol (refer to  $K_a$  table), hence phenoxide is a stronger base than  $\text{HCO}_3^-$  and it will be protonated by  $\text{H}_2\text{CO}_3$ .

**5(a)(i)**

| C:                                                     | H:                | O                   |
|--------------------------------------------------------|-------------------|---------------------|
| $\frac{70.6}{12.0}$                                    | $\frac{5.9}{1.0}$ | $\frac{23.5}{16.0}$ |
| 4                                                      | 4                 | 1                   |
| Empirical Formula of E: $\text{C}_4\text{H}_4\text{O}$ |                   |                     |

**5(a)(ii)**  $PV = nRT$

$$(101.7 \times 10^3 \text{ Pa})(60.4 \times 10^{-6}) = \left(\frac{0.344 \text{ g}}{M_r}\right)(8.31)(21 + 273) \text{ K}$$

$$M_r = 136.8 = n(4 \times 12.0 + 4 \times 1.0 + 16.0)$$

$$\Rightarrow n = 2, \therefore \text{Molecular formula of E is } \text{C}_8\text{H}_8\text{O}_2$$

**Suggested Solns for N2009 H2 Chemistry Paper 3 (9746/03)**

**i) Primary Structure**

The primary structure refers sequence of the amino acids in the polypeptide chain. Amino acids are held together by peptide bonds.

**ii) Secondary Structure**

The secondary structure of a protein is defined as the local spatial arrangement of a polypeptide's backbone atoms with regard to the conformations of its side chains. These local conformations are called  $\alpha$ -helices and  $\beta$ -pleated sheets which are stabilised by hydrogen bonds between C=O and N-H groups.

**iii) Tertiary Structure**

The tertiary structure of a protein is three-dimensional structure of an entire polypeptide. The native 3D conformation is held by side chain R group interactions (electrostatic) ionic attractions, van der Waals' interactions, disulfide bonds and hydrogen bonds.

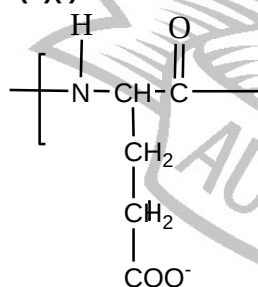
**iv) Quaternary Structure**

The quaternary structure refers to the spatial arrangements and association of the polypeptide subunits of proteins. The bonds holding the subunits together originate from the side-chain R groups, and can involve disulfide links, ionic interactions, hydrogen bonding and van der Waals' forces.

**Key Example: Haemoglobin**

- consists of four polypeptide chains fitting together to form a compact, globular assembly of considerable stability.
- two  $\alpha$ -subunits and two  $\beta$ -subunits.
- each subunit is bonded to a haem residue.
- the iron in the haem group binds to oxygen.
- each subunit has an irregularly folded conformation.
- considerable amount of side chain group interactions (hydrogen bonds, van der waals forces and ionic interactions) between an  $\alpha$ -subunits and the neighbouring  $\beta$ -subunit.

**1(b)(i)**



**1(b)(ii) van der waals' (id-id) interactions**

\*Note hydrophobic interactions are NOT acceptable.

**1(b)(iii)** Normal haemoglobin do not have favourable interactions with one another due to repulsion of the negative charged  $\text{COO}^-$  group, thus they do not attract each other.

$$\text{1(c)(i)} \quad K_C = \frac{[\text{Hb}(\text{O}_2)_4]}{[\text{O}_2]^4[\text{Hb}]} \text{ mol}^{-4} \text{ dm}^{12}$$

**1(c)(ii)**

$$K_C = \frac{[\text{Hb}(\text{O}_2)_4]}{[\text{O}_2]^4[\text{Hb}]} = \frac{x}{[7.6 \times 10^{-6}]^4 x} = 3.00 \times 10^{20} \text{ mol}^{-4} \text{ dm}^{12}$$

**1(c)(iii)**

$$\frac{0.99x}{[\text{O}_2]^4(0.01x)} = 3.00 \times 10^{20} \text{ mol}^{-4} \text{ dm}^{12}$$

$$[\text{O}_2] = 2.40 \times 10^{-5} \text{ mol dm}^{-3}$$

**1(d)**

Let % of  $\text{MbO}_2$  be  $y\%$  &  $[\text{MbO}_2]_{\text{eqm}}$  be  $\frac{xy}{100}$

Let % of Mb be  $(100-y)\%$  &  $[\text{Mb}]_{\text{eqm}}$  be  $\frac{(100-y)x}{100}$

$$K_C = \frac{[\text{MbO}_2]}{[\text{O}_2][\text{Mb}]} = \frac{\frac{xy}{100}}{[7.6 \times 10^{-6}](\frac{100-y}{100})x} = 1 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$$

% of  $\text{MbO}_2$  in the Mb- $\text{MbO}_2$  mixture,  $y = 88.4\%$

**2(a)(i) -2**

**2(a)(ii)**

HCHO

A

HCOOH or CO

B

$\text{H}_2\text{CO}_3$  or  $\text{CO}_2$

C

**2(a)(iii)**

| Reaction                                       | Reagents & Conditions                                                                                                 |
|------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| $\text{CH}_3\text{OH} \rightarrow \text{HCHO}$ | $\text{H}_2\text{SO}_4(\text{aq})$ & $\text{K}_2\text{Cr}_2\text{O}_7$ , heat with immediate distillation             |
| $\text{CH}_3\text{OH} \rightarrow \text{CO}$   | Limited $\text{O}_2$ , heat                                                                                           |
| $\text{CH}_3\text{OH} \rightarrow \text{CO}_2$ | $\text{H}_2\text{SO}_4(\text{aq})$ & $\text{KMnO}_4$ , heat<br>OR<br>Excess $\text{O}_2$ , heat to give $\text{CO}_2$ |

2(b)(i)

$$\Delta H_c = - \frac{(200g)(4.18Jg^{-1}K^{-1})(30.0^{\circ}C)}{(1.50g / (2 \times 12.0 + 6 \times 1.0 + 16.0)gmol^{-1})}$$

$$\Delta H_c(\text{ethanol}) = -769kJmol^{-1}$$

2(b)(ii)

Heat loss to environment or container.

Temperature change is smaller than the actual value.

2(c)(i)

$$\Delta H_r = (5(410) + 350 + 360 + 460 + \frac{1}{2}(496))$$

$$-(2(460) + 740 + 350 + 4(410))$$

$$\Delta H_r = -182kJmol^{-1}$$

2(c)(ii)

$$\Delta H_r = \Sigma \Delta H_c(\text{rxts}) - \Sigma \Delta H_c(\text{prdts})$$

$$-182 = -1367 - \Delta H_c(\text{ethanol})$$

$$\Delta H_c(\text{ethanol}) = -1185kJmol^{-1} = -1190kJmol^{-1} (3s.f.)$$

The enthalpy change of combustion of ethanol was given as  $-1185 kJ mol^{-1}$  by UCLES.

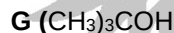
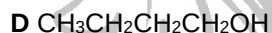
2(c)(iii)

The enthalpy change of combustion of ethanoic acid is expected to be less exothermic than that of ethanal. C–O and O–H bonds, which do not exist in ethanal, are strong and have to be broken during the combustion of ethanoic acid. Additional energy will have to be expended, leading to a less exothermic enthalpy change of combustion.

OR

As ethanal is more oxidised than ethanol and so it  $\Delta H_c$  is less exo., the even more oxidised ethanoic acid will have an even less exothermic  $\Delta H_c$ .

2(d)(i)



2(d)(ii)

**D** and **E** are primary alcohols, **F** is a secondary alcohol and **G** is a tertiary alcohol.

2(d)(iii) Alcohol **F**

2(d)(iv) Alcohol **F**, Products:  $CH_3CH_2COO^-$  &  $CHI_3$

2(d)(v) Alcohol **F**, Product:  $CH_3COCH_2CH_3$

| Equations of reaction               | Observations                             |
|-------------------------------------|------------------------------------------|
| $2Mg + O_2 \rightarrow 2MgO$        | Bright white flame to give white residue |
| $P_4 + 5O_2 \rightarrow 2P_4O_{10}$ | White flame                              |
| $S + O_2 \rightarrow SO_2$          | Blue flame                               |

3(b)

| Equations of reaction                    | Colour of universal indicator |
|------------------------------------------|-------------------------------|
| $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ | Red                           |
| $SO_2 + H_2O \rightarrow H_2SO_3$        | Red or Orange                 |

3(c)(i)

Total amt of  $OH^-$  in 25 cm<sup>3</sup> of soln **H** = Amt of HCl

$$= \frac{22.5}{1000} \times 0.100 = 2.25 \times 10^{-3} \text{ mol}$$

Total amt of  $OH^-$  in 100 cm<sup>3</sup> of soln **H**

$$= \frac{100}{25} \times 2.25 \times 10^{-3} = 9.00 \times 10^{-3} \text{ mol}$$

3(c)(ii)

Amt of  $MnO_4^-$  that reacted with 25 cm<sup>3</sup> of soln **H**

$$= \frac{10}{1000} \times 0.02 = 2.00 \times 10^{-4} \text{ mol}$$

Amt of  $H_2O_2$  in 100 cm<sup>3</sup> of soln **H**

$$= \frac{5}{2} \times 2.00 \times 10^{-4} \times \frac{100}{25} = 2.00 \times 10^{-3} \text{ mol}$$

3(c)(iii)

Amt of  $Na_2O_2$  = Amt of  $H_2O_2$  in 100 cm<sup>3</sup> of soln **H**

$$= 2.00 \times 10^{-3} \text{ mol}$$

$$\text{Amt of } Na_2O = \frac{1}{2} (9.00 \times 10^{-3} - 2(2.00 \times 10^{-3}))$$

$$= 2.50 \times 10^{-3} \text{ mol}$$

3(d)(i)

$$\text{rate of reaction} \propto \frac{1}{\text{time}}$$

3(d)(ii)

3(a)

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$$\text{rate of reaction, } R_2 = \frac{1}{\text{time}}$$

| Expt | Rate of rxn,<br>$R_2 / \text{s}^{-1}$ |
|------|---------------------------------------|
| 1    | 0.0303                                |
| 2    | 0.0100                                |
| 3    | 0.0149                                |
| 4    | 0.0200                                |

Compare Expt 2 and Expt 4, when conc of  $\text{H}_2\text{O}_2$  is doubled, rate of reaction doubles, thus rate of reaction is directly proportional to conc of  $\text{H}_2\text{O}_2$ . Order of reaction w.r.t.  $\text{H}_2\text{O}_2$  is 1.

Compare Expt 2 and Expt 3, when conc of  $\text{I}^-$  is increased to 1.5 times, rate of reaction increased to 1.5 times, thus rate of reaction is directly proportional to conc of  $\text{H}_2\text{O}_2$ . Order of reaction w.r.t.  $\text{I}^-$  is 1.

Compare Expt 1 and Expt 4, when conc of  $\text{H}_2\text{O}_2$  is increased to 1.5 times, rate of reaction increased to 1.5 times. However, the rate of reaction is unchanged despite the fact that conc of  $\text{H}^+$  is halved. Order of reaction w.r.t.  $\text{H}^+$  is 0.

**3(d)(iii)** rate =  $k[\text{H}_2\text{O}_2][\text{I}^-]$

units of rate constant is  $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$

**4(a)** Any three of the list below will suffice.

- Gases consist of small particles of **negligible volumes**. The particles are widely separated and can move anywhere in the container.
- The gas particles **exert no attractive forces** on each other.
- Collisions between the gas particles are perfectly **elastic**, ie there is no loss of kinetic energy upon collision.

**4(b)(i)** Both  $\text{CH}_4$  and  $\text{NH}_3$  are covalent simple molecules. During boiling, less amount of energy is required to overcome the weaker instantaneous dipole-induced dipole interactions between  $\text{CH}_4$  molecules than the stronger hydrogen bonding between  $\text{NH}_3$  molecules, thus  $\text{CH}_4$  has lower boiling point than  $\text{NH}_3$ .

**4(b)(ii)** Entropy change is negative or entropy decreases when gaseous methane is liquefied as the system becomes more orderly due to the decrease in amount of gaseous particles.

**4(b)(iii)**  $\Delta G = \Delta H - T\Delta S$

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$$0.0 = +23.3 - (273 - 33)K(\Delta S)$$

$$\Delta S = +97.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

**4(c)(i)** Ethylamine is the strongest base of the three compounds due to presence of electron-donating ethyl group that increases the availability of the lone pair of electrons on the N atom of the cation or stabilises conjugate acid of ethylamine by de-intensifying its positive charge.

Phenylamine is the weakest base of the three compounds due to delocalization of lone pair of electrons on the nitrogen atom into the aromatic ring. This decreases the electron density on the nitrogen atom of the cation or destabilizes the conjugate acid of phenylamine by intensifying its positive charge.

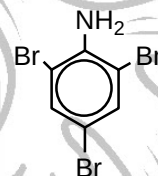
**4(c)(ii)** Assuming  $[\text{OH}^-]_{\text{eqm}} \approx [\text{OH}^-]_{\text{initial}}$

$$[\text{OH}^-] = \sqrt{6.4 \times 10^{-4} \times 0.100} = 8.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log[\text{OH}^-] = 2.10$$

$$\text{pH} = 14 - 2.10 = 11.9$$

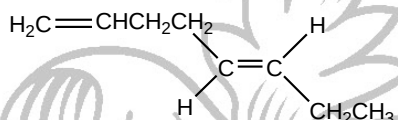
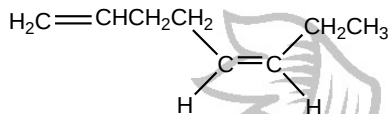
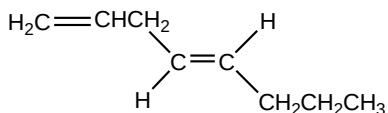
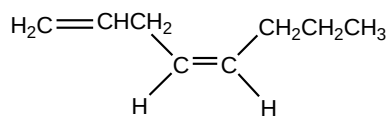
**4(c)(iii)**



**4(d)(i)** Nucleophilic substitution



4(d)(iii)



5(a) Down the group, volatility decreases and the colour of the halogen darkens.

| Halogen  | Colour of halogen | Physical state at r.t.p |
|----------|-------------------|-------------------------|
| Fluorine | Pale yellow       | Gas                     |
| Chlorine | Yellow-green      | Gas                     |
| Bromine  | Reddish brown     | Liquid                  |
| Iodine   | black             | Solid                   |

5(b)

|                       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Cl<sup>-</sup></b> | $\text{NaCl} + \text{conc H}_2\text{SO}_4 \rightarrow \text{HCl} + \text{NaHSO}_4$<br>White fumes of HCl are observed.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| <b>Br<sup>-</sup></b> | $\text{NaBr} + \text{conc H}_2\text{SO}_4 \rightarrow \text{HBr} + \text{NaHSO}_4$<br>$2\text{HBr} + \text{conc H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$<br>White fumes of HBr are observed. Upon oxidation of HBr, reddish brown Br <sub>2</sub> vapour is observed. Acidic and pungent SO <sub>2</sub> gas is produced too.                                                                                                                                                                                                                                                           |
| <b>I<sup>-</sup></b>  | $\text{NaI} + \text{conc H}_2\text{SO}_4 \rightarrow \text{HI} + \text{NaHSO}_4$<br>$2\text{HI} + \text{conc H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$<br>$6\text{HI} + \text{conc H}_2\text{SO}_4 \rightarrow 3\text{I}_2 + \text{S} + 4\text{H}_2\text{O}$<br>$8\text{HI} + \text{conc H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$<br>White fumes of HI are observed. Upon oxidation of HI, violet I <sub>2</sub> vapour is observed and yellow solid of sulfur may be observed after prolonged reaction with excess concentrated sulfuric acid |

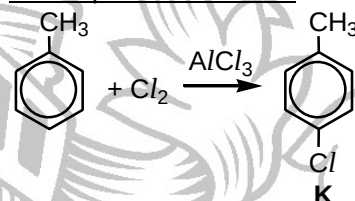
5(c)

The hydroxyl group is 2,4-directing and strongly activating. The delocalisation of lone pair of electrons on oxygen into the benzene ring enhances the electron density in the ring.

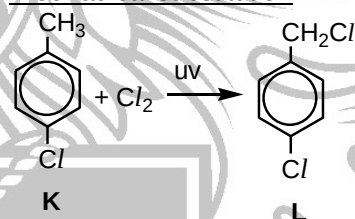
Phenol undergoes electrophilic substitution much more readily than methylbenzene, without the need for a strong electrophile NO<sub>2</sub><sup>+</sup>. The methyl group is weakly activated as it is electron-donating via the inductive effect. Hence, a more adverse condition as well as a halogen-carrier (Lewis acid) is required for electrophilic substitution for methylbenzene.

5(d)

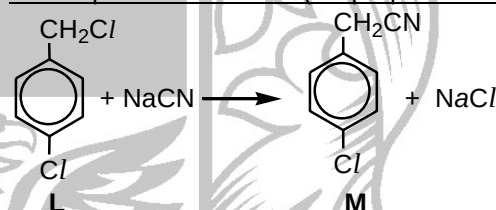
Electrophilic substitution



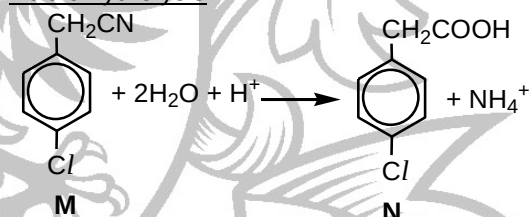
Free radical substitution



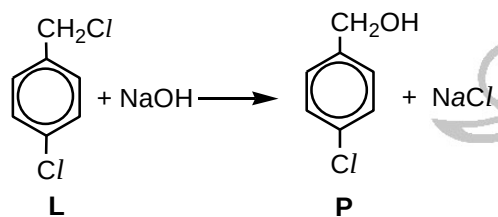
Nucleophilic substitution (Step-up is not acceptable)



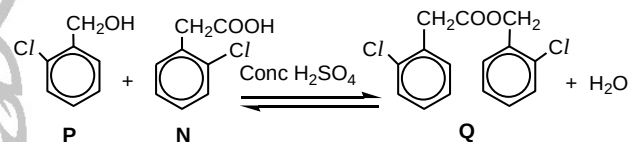
Acidic hydrolysis



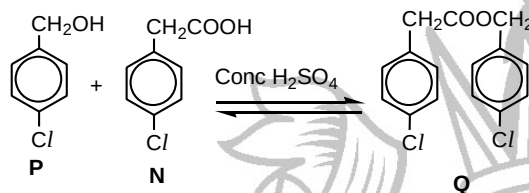
### Nucleophilic substitution



### Esterification (nucleophilic substitution)

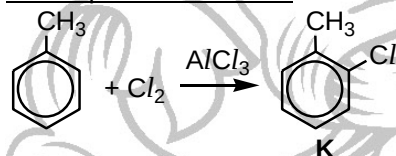


### Esterification (nucleophilic substitution)

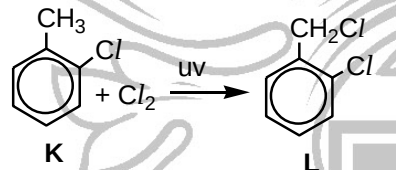


### Alternative Solution

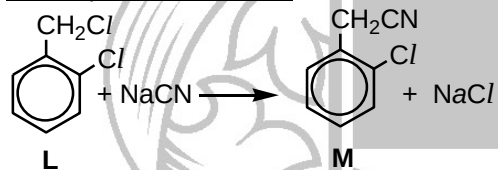
#### Electrophilic substitution



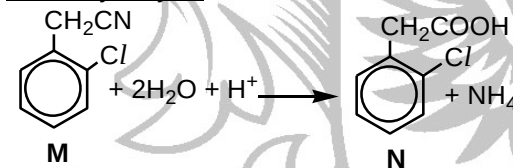
#### Free radical substitution



#### Nucleophilic substitution



#### Acidic hydrolysis



#### Nucleophilic substitution

