1. Consider the following pairs of compounds:

(a) \[ \text{H} = \text{CH}_3 \quad \text{and} \quad \text{CH}_3 = \text{CH}_3 \]

Both compounds are C\(_4\)H\(_8\) but differ in the nature and sequence of bonding, hence *constitutional isomers*.

(b) \[ \text{CH}_3 \quad \text{HO} \quad \text{H} \quad \text{CH}_2\text{CH}_3 \quad \text{and} \quad \text{HO} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_2\text{CH}_3 \]

Same nature and sequence of bonding and not simply conformations of the same compound thus these compounds are *configurational isomers*. Interconversion of the two compounds can only be achieved by breaking one of the bonds and reforming the molecule in the opposite configuration. Non-superimposable mirror images, hence *enantiomers*.

(c) \[ \text{HOOC} \quad \text{COOH} \quad \text{and} \quad \text{HOOC} \quad \text{H} \quad \text{COOH} \]

Same nature and sequence of bonding and not simply conformations of the same compound thus these compounds are *configurational isomers*. Interconversion of the two compounds can only be achieved by breaking the double bond and reforming it in the opposite configuration. These are (E)/(Z)-isomers, a subset of the configurational isomers class: *diastereoisomers* (non-superimposable, not mirror-image related).

(d) \[ \text{Cl} \quad \text{CH}_3 \quad \text{H} \quad \text{COOH} \quad \text{and} \quad \text{H} \quad \text{Cl} \quad \text{CH}_3 \quad \text{COOH} \]

These are the *same* compound. Rotation of the first anticlockwise, around the C-COOH bond.

(e) \[ \text{Cl} \quad \text{H} \quad \text{pentagon} \quad \text{and} \quad \text{Cl} \quad \text{H} \quad \text{pentagon} \]

Both C\(_2\)H\(_7\)-Cl but the compounds differ in the nature and sequence of bonding, hence *constitutional isomers*.

(a) Which pair (or pairs) are constitutional isomers? *(a) and (e)*
(b) Which pair (or pairs) are diastereoisomers? *(c)*
(c) Which pair (or pairs) are enantiomers? *(b)*
(d) Which pair (or pairs) are (E)- / (Z)-isomers? *(c)*
2. Achiral - plane of symmetry passing through centre of C=C and CHCl group

\[
\text{\begin{align*}
\text{Cl} & \quad \text{H} \\
\text{Cl} & \quad \text{H}
\end{align*}}
\]

\[
\text{Cl} \quad \text{H}
\]

\[
\text{\begin{align*}
\text{**} & \quad \text{**} \\
\text{CH}_3\text{CH(OH)CH}_2\text{OH} = \text{H}_3\text{C} & \quad \text{\text{C}} & \quad \text{\text{H}} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH}
\end{align*}}
\]

\[
\text{\begin{align*}
\text{Cl} & \quad \text{**} \\
\text{CH}_3\text{OCH(OCH}_3\text{)CH}_3 & \quad \text{H}_3\text{C} & \quad \text{\text{C}} & \quad \text{\text{H}} \\
\text{OCH}_3 & \quad \text{OCH}_3
\end{align*}}
\]

Achiral - only three different groups around C

3. The sequence rules for assigning priorities to substituents on a stereogenic centre are:

(i) Look at the four atoms directly attached to the stereogenic centre and assign priorities in order of decreasing atomic number.

(ii) If a decision about priority cannot be reached by applying rule 1, compare atomic numbers of the second atoms of each substituent, continuing outwards if necessary until the first point of difference is reached.

(iii) Multiple-bonded atoms are considered as an equivalent number of single bonded atoms.

(iv) The structure is then viewed with the substituent with the lowest priority projecting backwards.

(v) If a curved arrow drawn from the highest to second-highest to third-highest priority substituent is clockwise, the configuration is \( R \). If the curved arrow is anticlockwise, the configuration is \( S \).
4. After assigning priorities to the groups on each end of the C=C bond as in question 3, the arrangement is $Z$ if both the substituents of higher priority are on the same side and $E$ if they are on opposite sides.
5. (a) The starting material is achiral and the reaction gives rise to the generation of a chiral carbon. Both faces of the alkene double bond are equally accessible to the Br₂ and hence compound (F) is obtained as the racemic mixture.

(b) The priorities of the substituents on the chiral carbon in F are:

\[ \text{Br} > \text{CH}_2\text{Br} > \text{CH}_2\text{CH}_3 > \text{H} \]

The \( R \) enantiomer has the configuration shown below in order to get a clockwise arrow from Br \( \rightarrow \) CH₂Br \( \rightarrow \) CH₃CH₃, with the H placed at the back:

\[ \text{Br} \quad \text{H} \quad \text{CH}_2\text{Br} \]
\[ \text{H}_3\text{CH}_2\text{C} \]
\[ \text{a} - \text{b} - \text{c} \text{ is clockwise: } \text{R} \]

6.

<table>
<thead>
<tr>
<th>Pyranose</th>
<th>Furanoce</th>
<th>Fischer projection</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>6-membered ring:</strong></td>
<td><strong>5-membered ring:</strong></td>
<td><strong>Change the stereochemistry at any stereogenic centre (but not at all). For example:</strong></td>
</tr>
<tr>
<td><img src="image" alt="β-D-glucopyranose" /></td>
<td><img src="image" alt="β-D-glucofuranose" /></td>
<td><img src="image" alt="β-D-glucopyranose" /></td>
</tr>
</tbody>
</table>
7. If the pH < pK of an ionisable group, then it will be predominantly in the conjugate acid form

If the pH > pK, then it will be predominantly in the conjugate base form.

The pI (i.e. the pH at which the predominant species has a net charge of zero) is the mean of the two pK values associated with the formation of the +1 and −1 species. In this case, the mean is \( \frac{1}{2} (2.10 + 4.07) = 3.09 \).

If the pH = pK, then 50% will be in the conjugate acid form and 50% in the conjugate base form.

(a) pH = 1.0:

\[ \text{pK}_a (\text{sidechain}) > \text{pH} \text{ so it will exist in the protonated (COOH) form.} \]
\[ \text{pK}_a (\alpha\text{-COOH}) > \text{pH} \text{ so it will also exist in the protonated (COOH) form.} \]
\[ \text{pK}_a (\text{NH}_3^+) > \text{pH} \text{ so it will also exist in the protonated (NH}_3^+ \text{ form).} \]

(b) pH = 4.0:

\[ \text{pK}_a (\text{sidechain}) > \text{pH} \text{ so it will exist in the protonated (COOH) form.} \]
\[ \text{pK}_a (\alpha\text{-COOH}) < \text{pH} \text{ so it will exist in the deprotonated (COO}^- \text{) form.} \]
\[ \text{pK}_a (\text{NH}_3^+) > \text{pH} \text{ so it will exist in the protonated (NH}_3^+ \text{ form).} \]

(b) pH = 12.0:

\[ \text{pK}_a (\text{sidechain}) < \text{pH} \text{ so it will exist in the deprotonated (COO}^- \text{) form.} \]
\[ \text{pK}_a (\alpha\text{-COOH}) < \text{pH} \text{ so it will exist in the deprotonated (COO}^- \text{) form.} \]
\[ \text{pK}_a (\text{NH}_3^+) > \text{pH} \text{ so it will exist in the deprotonated (NH}_3 \text{ form).} \]

<table>
<thead>
<tr>
<th>pH 1.0</th>
<th>pH 4.0</th>
<th>pH 12.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Chemical structure at pH 1.0" /></td>
<td><img src="image2.png" alt="Chemical structure at pH 4.0" /></td>
<td><img src="image3.png" alt="Chemical structure at pH 12.0" /></td>
</tr>
<tr>
<td><strong>+1 charge</strong></td>
<td><strong>0 charge</strong></td>
<td><strong>−1 charge</strong></td>
</tr>
<tr>
<td><strong>Major (over 50%)</strong></td>
<td><strong>Minor (under 50%)</strong></td>
<td><strong>−1 charge</strong></td>
</tr>
</tbody>
</table>