CONCEPT MAP

SPECIFICATION OF CONFIGURATION

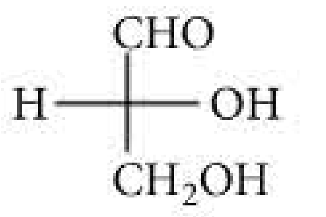
CONFIGURATION

The arrangement of atoms or groups in space that characterises a stereoisomer is called its configuration. The sign of rotation of a stereoisomer is not related to its configuration.

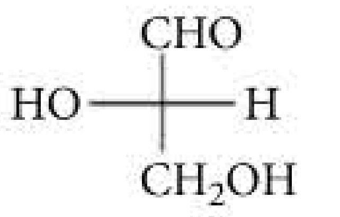
Relative Configuration

The configuration of the (OH) group at penultimate carbon of various stereoisomers are studied with respect to glyceraldehyde.

- The configuration with —OH group at right side is given *D*-configuration arbitrarily whereas the configuration with —OH group at left side is given *L*-configuration.
  Chiral molecules which can be chemically related to *D*-glyceraldehyde were designated as *D*-isomer and the molecules related to *L*-glyceraldehyde are designated as *L*-isomer.



D(+)-Glyceraldehdye



L(–)-Glyceraldehdye

- In polyhydroxy compounds (sugars) having more than one chiral center, the configuration of stereocenter farthest from carbonyl group is compared with glyceraldehyde configuration.

Absolute Configuration

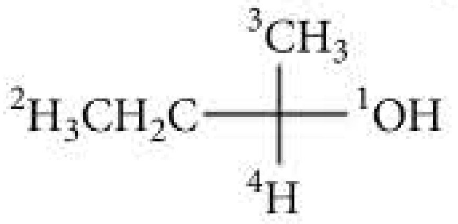
Cahn-Ingold-Prelog system has been developed to assign absolute configuration.

Rules for Assigning Configuration

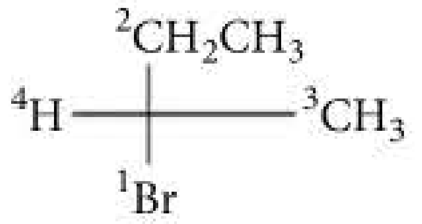
STEP I : Order of Priority

Rule 1 : If all the four atoms attached to chirality centre are different, their priority numbers are decided on the basis of their higher atomic numbers.
e.g., —I > —Br > —Cl > —F > —O > —N > —C > —H

Rule 2 : If two of the atoms attached to chirality centre are same then the relative priorities can be decided by comparing the second (or even third) atom of the respective group.

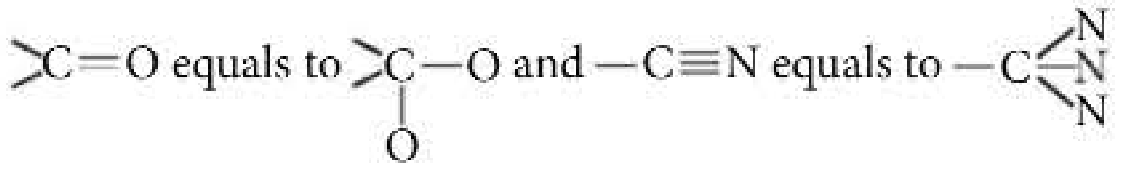


Butan-2-ol



2-Bromobutane

Rule 3 : This is an extension of rule II. If the second atoms is attached by double bond or triple bond, then double bonds are treated as they have two single bonds and triple bonds as they have three single bonds *i.e.*,

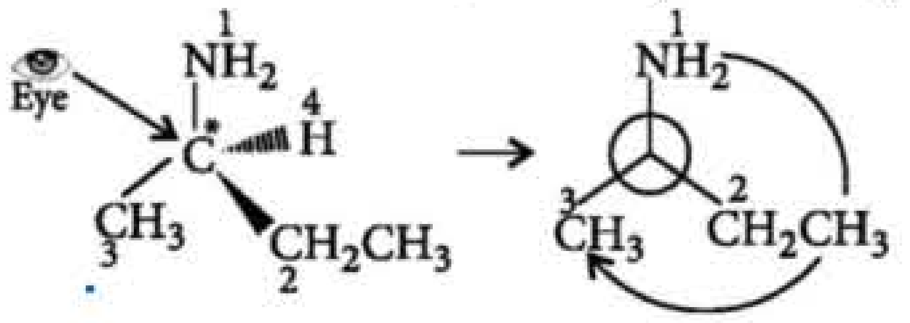


$$>C{=}O \text{ equals to } >\underset{\displaystyle O}{\underset{|}{C}}{-}O \text{ and } {-}C{\equiv}N \text{ equals to } {-}C\!\!<\!\!\begin{smallmatrix}N\\N\\N\end{smallmatrix}$$

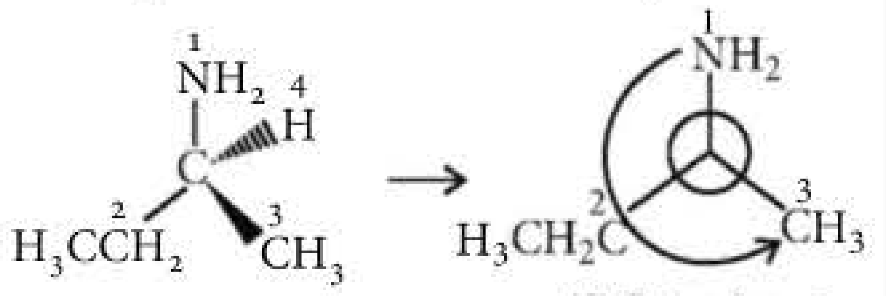
Thus, priority order is $C_6H_5{-} > {-}C{\equiv}CH > {-}CH{=}CH_2 > {-}CH(CH_3)_2$

STEP II

After deciding the priority of four atoms or groups attached to the chirality centre, the molecule (formula) is now rotated so that the group of lowest priority (4) is directed away from the eye (viewer). The arrangement of remaining three groups is viewed in decreasing order of their priorities, *i.e.*, from 1 to 2 to 3. In looking so, if the eye travels in a clockwise direction, the configuration is specified as *R* (from *rectus* Latin for right), while in case if eye travels in the anticlockwise direction, the configuration is specified as *S* (from *sinister* Latin for left).



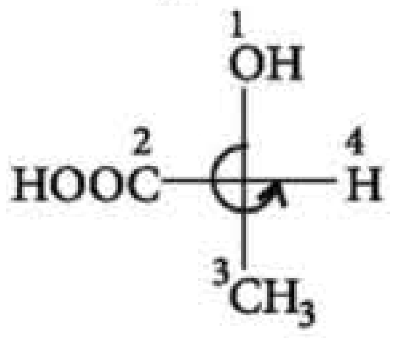
(*R*)-Butan-2-amine
(Clockwise)



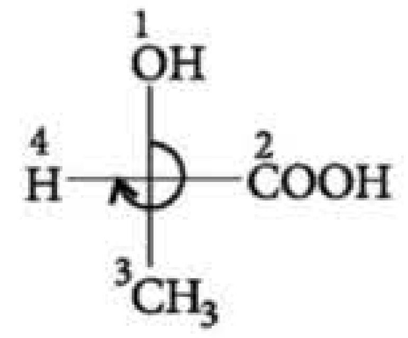
(*S*)-Butan-2-amine
(Anti-clockwise)

Golden Rule

If the lowest priority group occupies horizontal position (left or right) in the Fischer projection formula, then change the configuration obtained from (*R*) to (*S*) or (*S*) to (*R*).
For example,



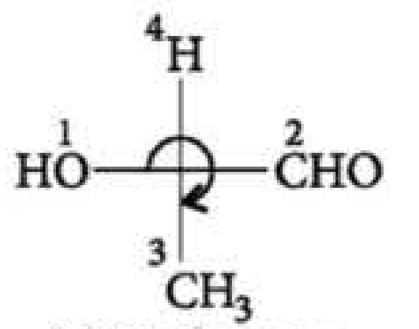
(*R*)-Configuration
(Anticlockwise)



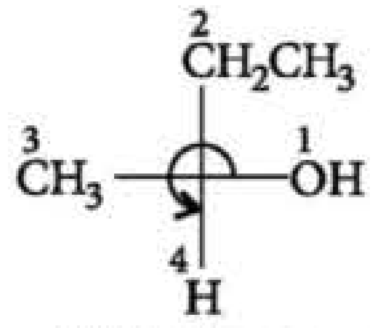
(*S*)-Configuration
(Clockwise)

Assigning *R*, *S* Configuration in Fischer Projection

- **When atom or group of lowest priority is at the bottom of vertical line :**
  There is an easy way of assigning *R* and *S* configuration to optical isomers represented by Fischer projection formula. Firstly assign priorities to the groups/atoms attached to chiral centre without making any change/interchange in the strength. Find out the configuration. Now if the lowest priority group occupies vertical (upward or downward) position in the original Fischer projection, then the configuration obtained above gives the actual configuration of the molecule. For example,

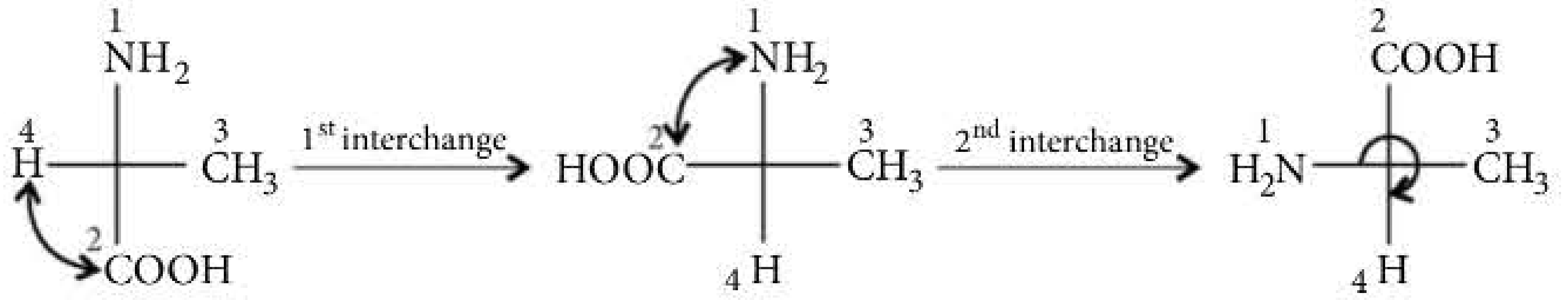


(*R*)-Configuration
(Clockwise)



(*S*)-Configuration
(Anticlockwise)

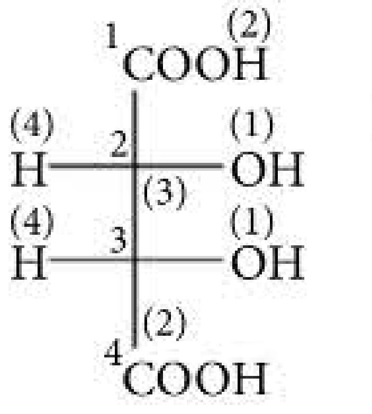
- **When atom or group of lowest priority is not on the vertical line :**
  If the lowest priority group/atom does not lie at vertical downward or upward position (bottom or above), then make two interchanges of atoms or groups in such a way that the atom or group of lowest priority is placed either vertically upward or downward. Now, assign the configuration according to path followed in decreasing order of priority.



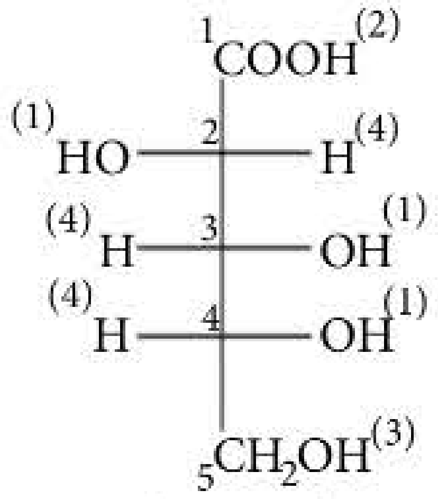
(*R*)-2-Aminopropanoic acid (*R*)-2-Aminopropanoic acid

Assigning *R*, *S* configuration of the compounds with more than one chiral centres

If a compound has two or more chiral carbon atoms, separate configuration is assigned to each carbon atom on the basis of sequence rule. In such compounds, application of golden rule is more convenient.
For example,



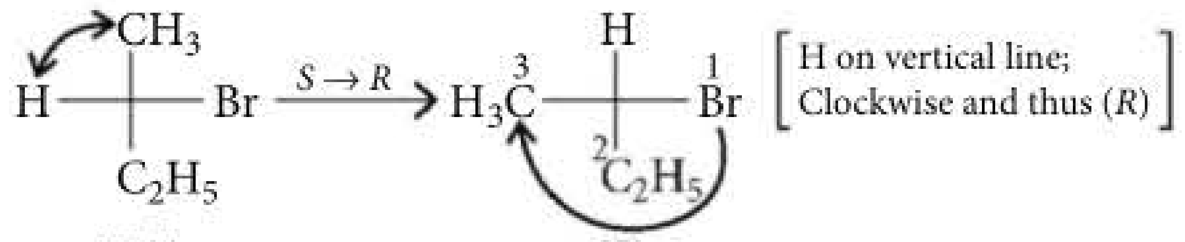
(2*R*, 3*S*)-Tartaric acid



(2*S*, 3*R*, 4*R*)

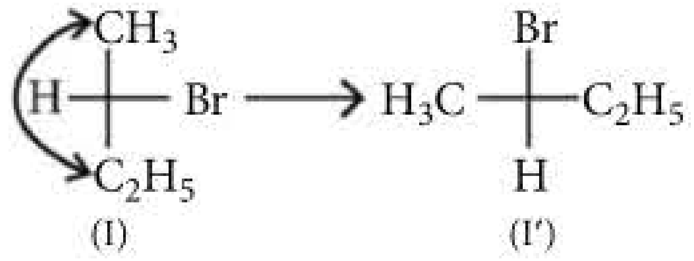
Effect on the configuration

- **By exchanging a horizontal and vertical ligand :**



(*S*) (I) (*R*)

- **By 180° vertical or horizontal rotation outside the plane of paper :** This type of operation is not allowed in Fischer projection because any flipping out of the plane of paper (side to side or top to bottom) would change the ligands formerly projecting behind the plane of paper to projecting towards the observer. Those ligands formerly pointing towards the observer would change to behind the paper.
- **By a 90° rotation on the plane of paper :**
  This type of operation is also not allowed in Fischer projection. For example,



(I) (I′)

In (I), H and Br project behind the plane, but a 90° rotation on the plane does not change the projection of bonds towards or away from the observer.