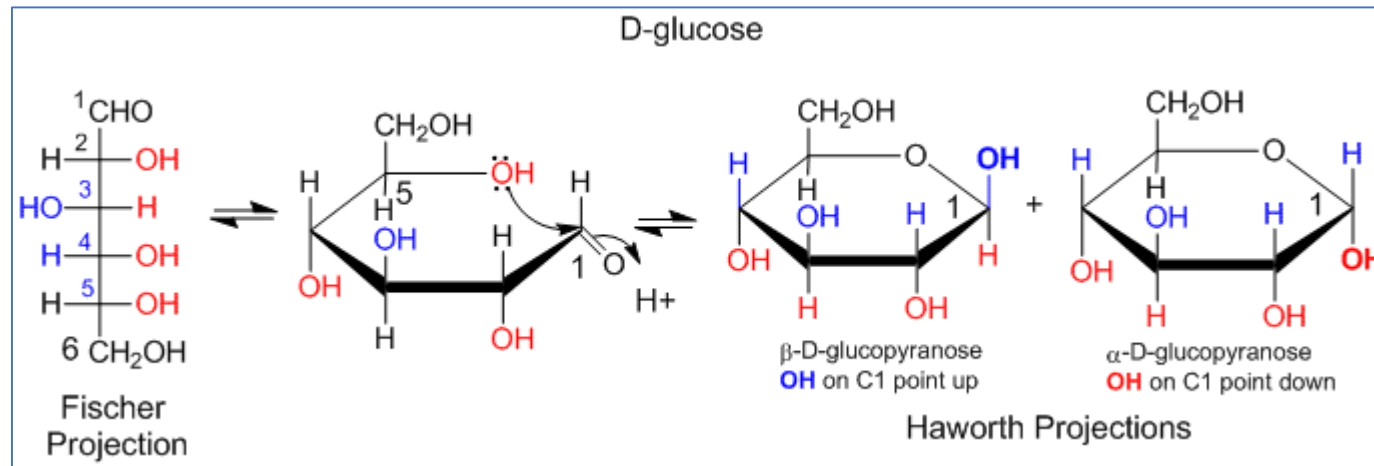
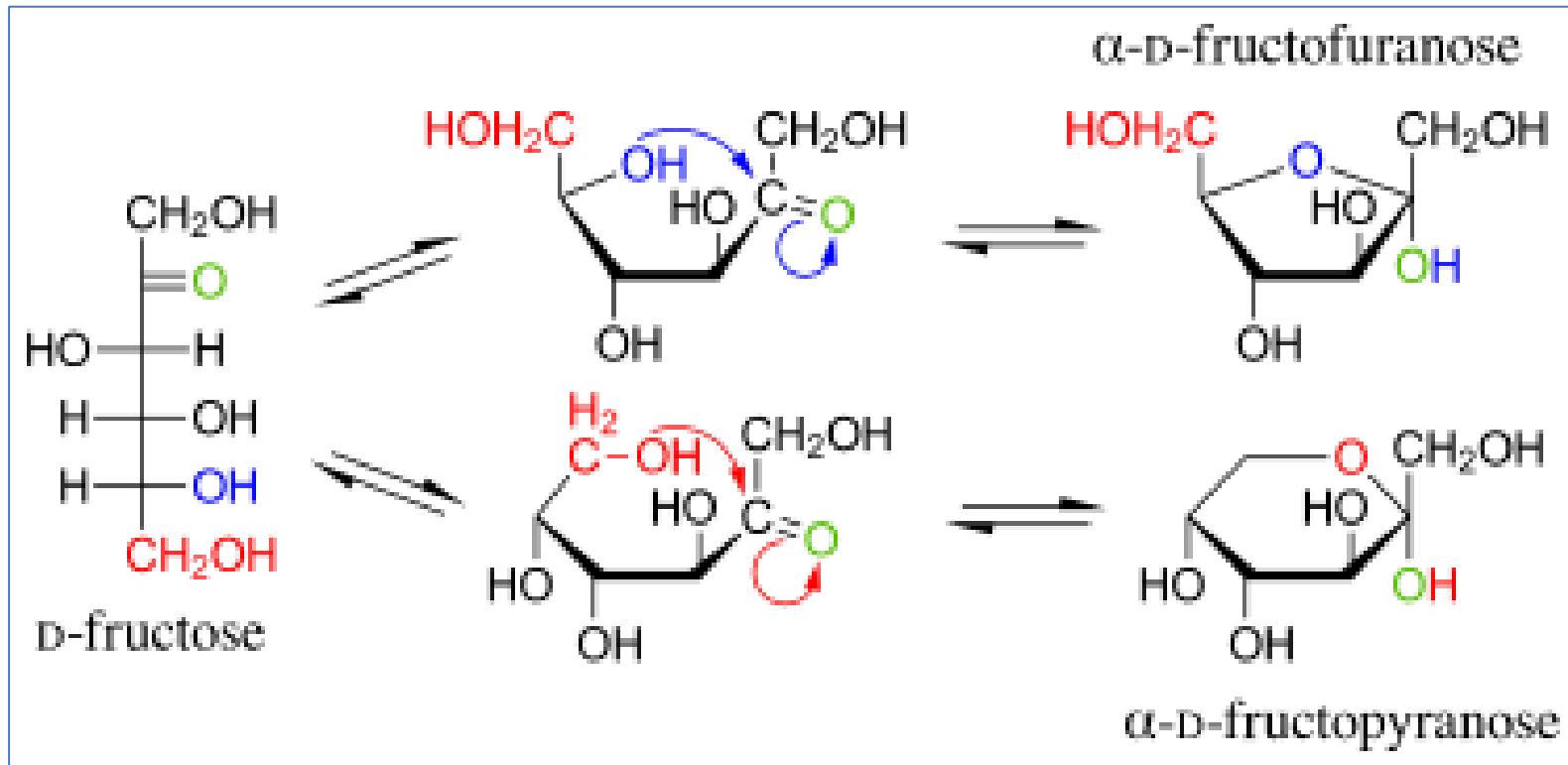


Haworth projection

- Haworth projection is "flattened" diagrams used to represent the stereochemistry carbohydrates.
- The six-membered ring of D-pyranose is represented as flat and is viewed edge on.
- The ring oxygen is always placed in the back right-hand corner of the ring, with the anomeric carbon (C-1) on the right-hand side and the primary alcohol group drawn up from the back left-hand corner (C-5).
- Groups on the *right* in a Fischer projection are *down* (below the ring) in a Haworth projection.



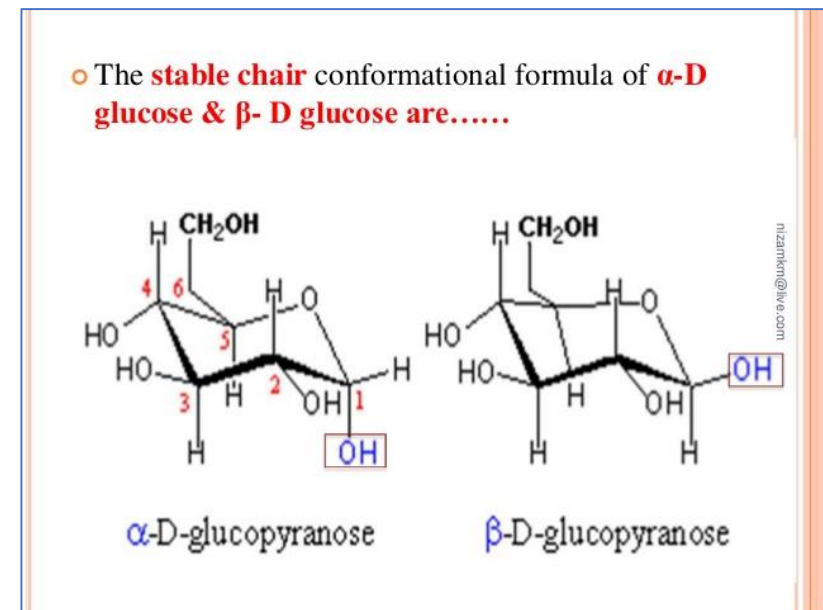
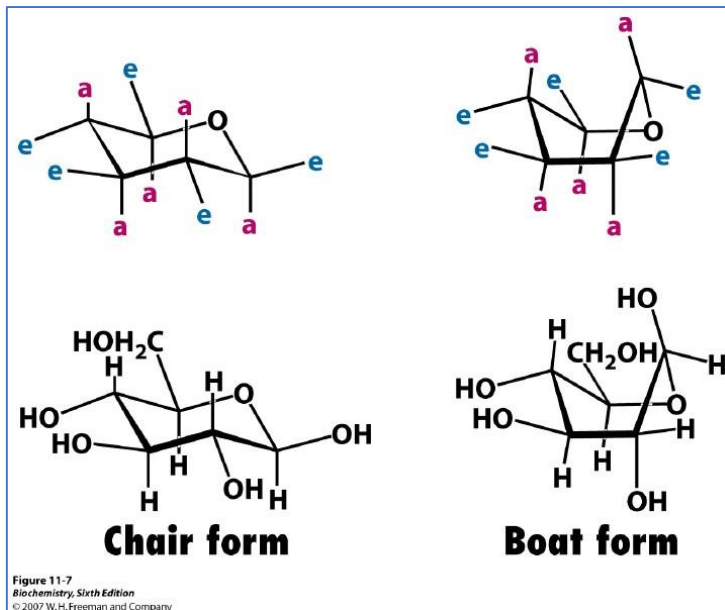
- Groups on the *left* in a Fischer projection are *up* (above the ring) in a Haworth projection.
- D-Furanose is viewed edge on, with the ring oxygen away from the viewer.
- The anomeric carbon is on the right-hand side of the molecule, and the primary alcohol group is drawn up from the back left-hand corner



Conformational Structure of Glucose

- Depending on the type of sugar, the cyclic forms of them can assume '**boat**' or '**chair**' conformations. For example, glucose
- Observing the arrangement of atoms about the structure, **chair conformation** is often more stable. Since substituents on:
 - C 2,3,5 and 6 lie on the same plane
 - While C 1 lies above the plane & C 4 below
 - This allows bond angles to be 110.9 degrees from each other, rather than 109.5 degrees away from each other, allowing more freedom and reduces electron repulsion
 - C-H bonds are all staggered and eliminates torsion
- In the **boat conformation**, however, groups facing upwards are brought close enough by Van der Waal forces of attractions, which cause steric crowding.
- Bulky groups are too close to each other making the structure unstable and energetically unfavorable.
- Thus, chair conformation is more stable, energetically feasible and preferred.

- α -D-glucopyranose exists with the -OH substituents on the anomeric carbon putting out of the structure – **axial** orientation (down/perpendicular to the ring)
- Where as, β -D- glucopyranose exists with -OH substituent on anomeric carbon in the **equatorial** orientation. (up/parallel to the plane)
- Because the former is axial, it allows substituents larger than H (-OH groups) closer together, increasing steric
- The latter,-OH is further away from the neighboring like substituent, the increased freedom of Crowding.
- The substituent from electron cloud repulsion decreases steric crowding.
- This allows the structure to be more energetically feasible and more stable.



Interconversion of aldoses to ketoses

Lobry de Bruyn–Alberda van Ekenstein rearrangement

- ❖ Lobry de Bruyn–Alberda van Ekenstein rearrangement involves the reciprocal interconversion of carbohydrates into their isomers in an alkaline solution through the enediolic intermediate.
- ❖ It is a glycochemical reaction catalyzed by hydroxide, irrespective of the counterions, and depends only on the base concentration and temperature. The reaction mechanism takes place via the transformation reactions.
- ❖ This reaction is used in the preparation of carbohydrate isomers on the basis of available carbohydrate molecules.
- ❖ The rearrangement reaction also occurs in between the aldose glyceraldehyde and the ketose dihydroxyacetone in a chemical equilibrium.

Aldose-Ketose Transformation

- ❖ The equilibrium or the *reactant to product ratio* depends on concentration, solvent, pH and temperature.
- ❖ At equilibrium the aldose and ketose form a mixture which in the case of the glyceraldehyde and dihydroxyacetone is also called **glycerose**.
- ❖ A related reaction is the alpha-ketol rearrangement.

