

Enzymes

MECHANISM OF ACTION

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Enzymes

Small amounts are effective

Stomach produces approx.
80 mg of pepsin
for one serving of meal

1/125 of sugar cube



Enzymes

Not changed irreversibly in reaction

- Can be recycled

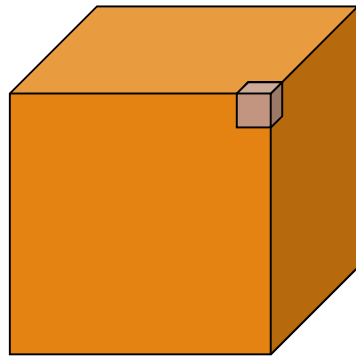
Enzymes

Do NOT change thermodynamics of reaction

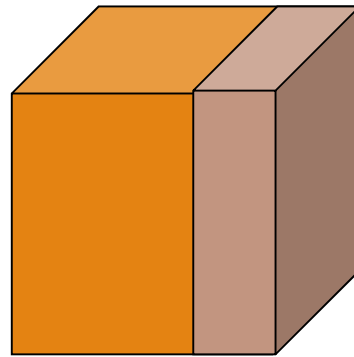
- K , ΔG

Increase the reaction rate

Catalytic activity

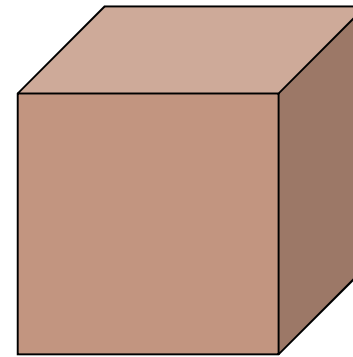


Without catalyst
(per year)



"Classical" catalyst
(per year)

100-1000_x



Enzyme
(per second)

10⁸-10²³_x



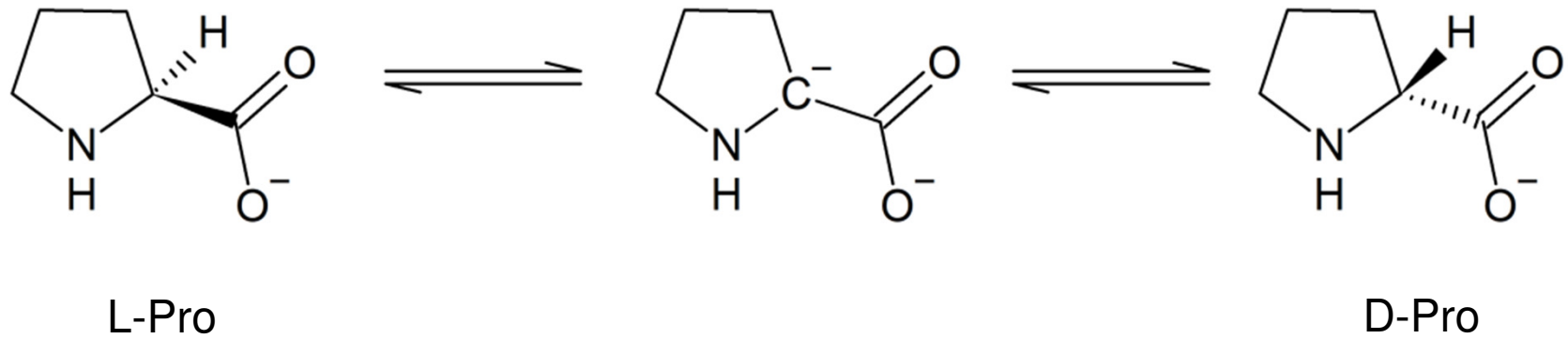
How does enzyme
work?



Decreasing activation energy



Transitive state



Enzyme-substrate complex



Entry of the substrate to the active center

Substrate dehydration

Binding the substrate to the surface of enzyme

Conformational changes



Binding the substrate to the enzyme

Non-covalent interactions

- Ionic
- Hydrogen bridges
- Hydrophobic

Binding the substrate

Lock and key

Induced fit



Mechanism of catalysis



Catalysis by proximity

High local concentration

Orientation of substrates

Low entropy



Acid-base catalysis

Acidic or basic residues in the active center

- Aminoacids of the enzyme
- Prosthetic groups

Catalysis by tension

Covalent bond under tension,
more susceptible to break-down

Stabilisation of the transitive state

Lytic reactions



Covalent catalysis

A functional group covalently bond to the enzyme or its co-enzyme

E.g. transaminases

Often „ping-pong“ mechanism

In active center:

- Cys
- Ser
- (His)

Enzyme specificity



Enzyme specificity

Substrate

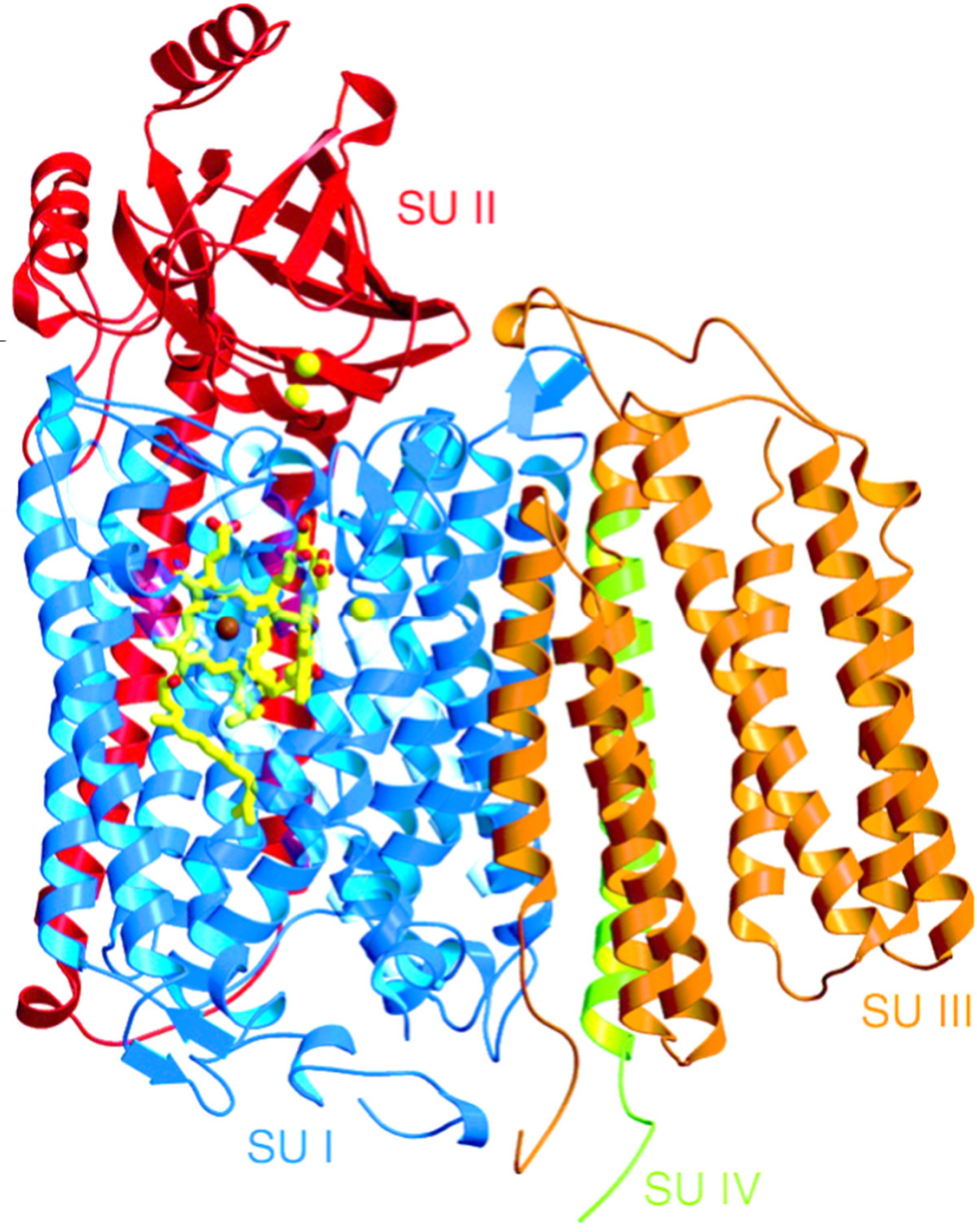
- Strict for optical isomers
- Less strict to length of chain

Reaction



Composition of an enzyme





Composition of enzyme

Holo-enzyme

- Apo-enzyme
- Non-proteinaceous moiety

Non-proteinaceous part

- Prosthetic group
- Cofactor
- Co-enzyme

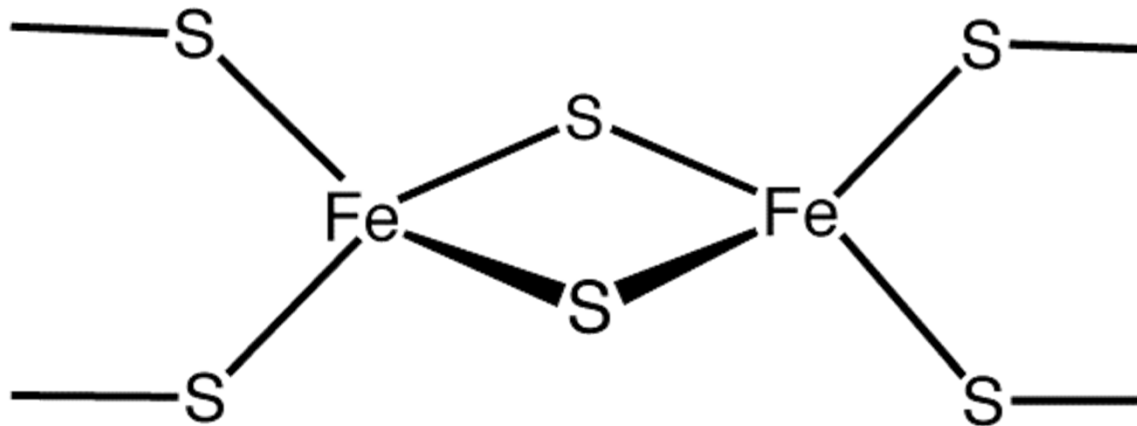
Prosthetic group

Covalently bond to apo-enzyme

Metals

- About 1/3 of enzymes (metalloproteins)
- Often in
 - hem
 - clusters

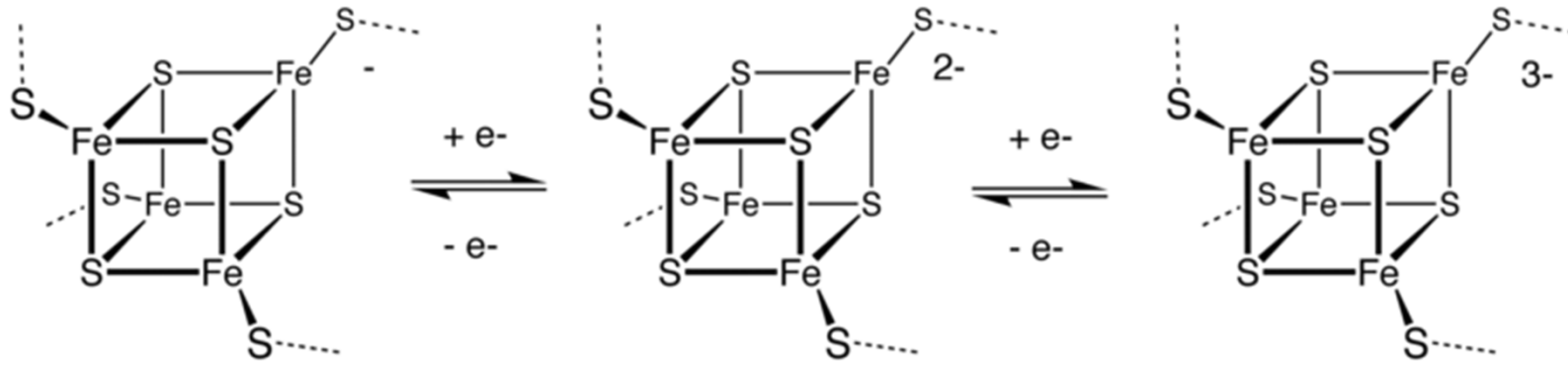
Fe-S clusters [Fe₂S₂]



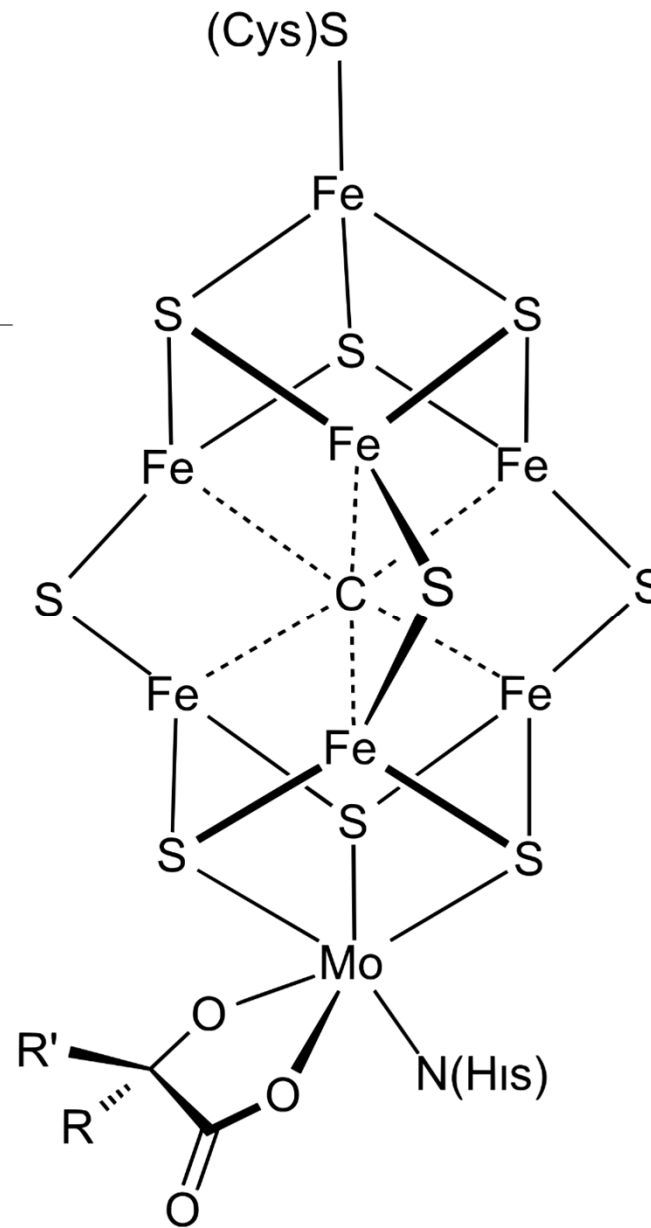
2-/3-



$[\text{Fe}_4\text{S}_4]$ - ferredoxins



Fe-S clusters



Cofactors

Can be dissociated

Must be present near the enzyme

Metallic ions

- Metal activated enzymes

Co-enzymes

Often derived from vitamins

Carriers of functional groups and substrates

Stabilise high-reactive groups (e.g. H)



Enzyme nomenclature



Names of enzymes

-ase

International Union of Biochemistry

- Name and code

Names of enzymes

Hexokinase

ATP:D-hexose-6-phosphotransferase

E.C. 2.7.1.1

- 2 = transferases
- 7 = transfer of phosphate
- 1 = alcohol is the acceptor
- 1 = serial number

Translocases

7th class of enzymes since October 2018

- Proton channels
- Ion channels
- Channels and transporters for aminoacids, peptides, saccharides...

Isoenzymes

Different enzymes catalysing the same reaction

Different localisation

Different regulation



Expressing the
amount of an
enzyme



Enzyme activity

Katal, kat

- The amount of an enzyme that catalyses conversion of 1 mol of substrate per 1 s

Enzyme unit, U

- 1 μmol per 1 min

International unit, IU

- „Biologic activity“, not only enzymes
- Different definition for every enzyme

Enzyme activity

Specific activity

- kat / mg prot.

Activity concentration

- kat / L