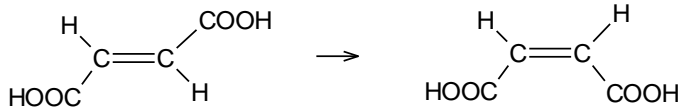
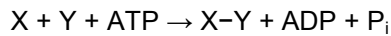


- dehydratases: $\begin{array}{c} | & | \\ -C & -C- \\ | & | \\ OH & H \end{array} \rightarrow$
- decarboxylases: $HOOC-COOH \rightarrow$

- **Isomerases** – catalyse intramolecular changes

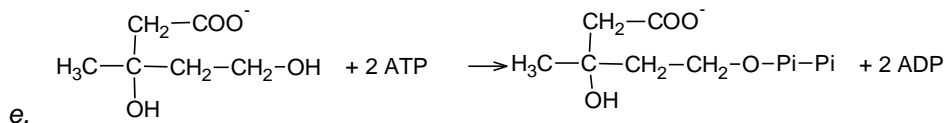
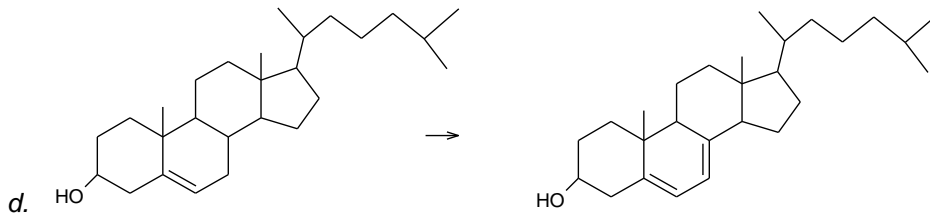


- **Ligases** – catalyse bond formations connected with the breakdown of energy rich phosphate bonds.



1. What types of enzymes catalyse the following reactions?

- $^-OOC-CH_2-CO-COO^- \rightarrow CH_3-CO-COO^-$
- $CH_2=C(CH_3)-CH_2-CH_2-O-P_i-P_i \rightarrow CH_3-C(CH_3)=CH-CH_2-O-P_i-P_i$
- lipids + $H_2O \rightarrow$ glycerol + fatty acids



Structure of an enzyme molecule

Enzymes = mostly proteins

Some enzymes (HOLOENZYMES) consist of a protein part (APOENZYME) and a non-protein part (COFACTOR)

HOLOENZYME (catalytically active complex) = APOENZYME + COFACTOR

Cofactors:

- Metal ions in metalloenzymes
 - Components of the active site of the enzyme

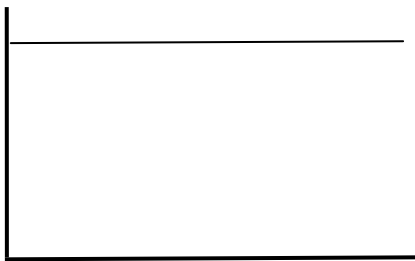
- Bridges for bonding the substrate
 - Stabilise the structure of the enzyme
- Organic molecule :
 - COENZYMES = carriers of functional groups, atoms or electrons in the reactions they catalyse, bonded by a weak force to the enzyme
 - PROSTHETIC GROUP = permanently bonded to the enzyme
 - Some coenzymes:
 - NAD⁺ (nicotinamide adenine dinucleotide) – derived from nicotinic acid (vitamin PP)
 - NADP⁺ (phosphate of NAD⁺)
 - FAD (flavin adenine dinucleotide) – derived from riboflavine (vitamin B₂)
 - Coenzyme A – derived from panthotenic acid (vitamin B₅)

Enzyme kinetics

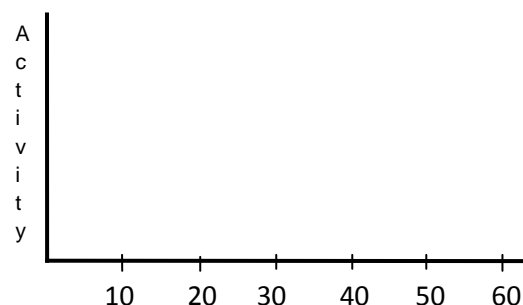
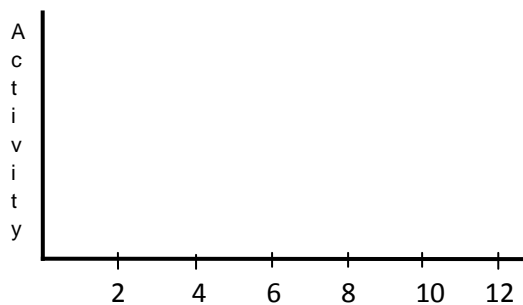


Rate of the reaction depends on the concentration of the substrate.

At a certain concentration of a substrate the enzyme is saturated by the substrate and the rate of the reaction cannot be further increased by adding more substrate. The reaction reaches the maximum velocity.

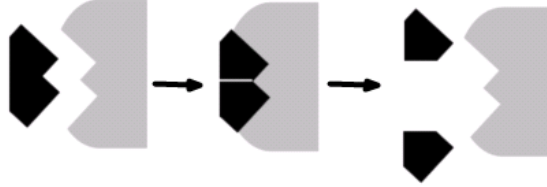


The concentration of a substrate at which the reaction goes at half of the maximum velocity is Michaelis constant (for the enzyme). It depends on the structure of the substrate, temperature and pH.



The mechanism of an enzyme function

The lock and key theory: an enzyme contains an ACTIVE SITE = BINDING SITE + CATALYTIC SITE.



2. Suggest the type of forces which may occur between the substrate and the binding site of the enzyme.

Induced fit theory

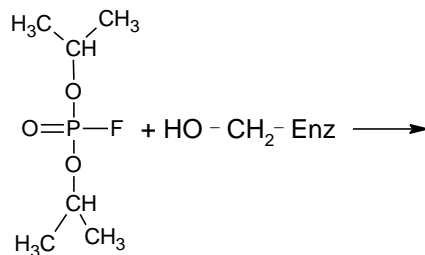
Specificity of an enzymatic reaction is based on a FLEXIBLE RESPONSE of the active site to the substrate.

http://www.teachertube.com/viewVideo.php?video_id=134992

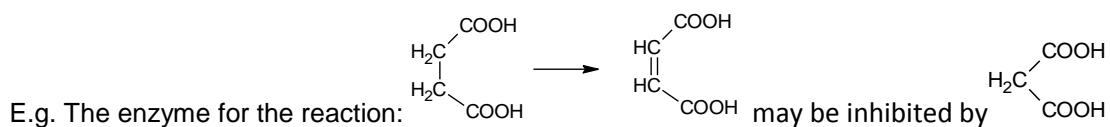
Enzyme inhibition

INHIBITOR = substance decreasing the catalytic action of an enzyme

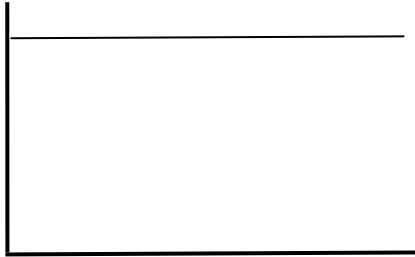
- IRREVERSIBLE: the inhibitor binds irreversibly to the enzyme by covalent bonds. The functional groups of an enzyme are changed and the enzyme loses its catalytic function.



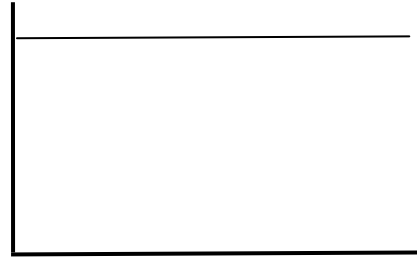
- REVERSIBLE: the inhibitor binds reversibly to the enzyme by weak forces
 - Competitive: the inhibitor combines with the active site of the enzyme and compete for it with a substrate



- Non-competitive: in most cases the inhibitor doesn't bind to the active site of the enzyme, it binds to a different part of the enzyme



competitive inhibition



non-competitive inhibition

<http://www.youtube.com/watch?v=PILzvT3pCQ&feature=related>

feedback control: the final product of a sequence of enzyme catalysed reactions is an inhibitor of the enzyme catalysing the first step of this sequence. This mechanism enables to maintain certain concentrations of the produced substances.

$A \rightarrow B \rightarrow C \rightarrow D$... D is an inhibitor of E_1

<http://www.youtube.com/watch?v=rHDp4wJ1U0w&NR=1>

Enzymes and biotechnologies

It is expensive to isolate enzymes from cells → whole cells are used.

Proteases: hydrolyse

- Biological detergents
- Baking industry
- Brewing industry

Amylases: hydrolyse

- Baking industry
- Brewing industry
- Paper industry

Fermentation of glucose:

Using enzymes from: yeast →
bacteria →
mould →

BIOCHEMICAL PROCESSES – METABOLISM

Bioenergetics = obtaining, transfer and use of energy in living organisms

Energy is used for:

- Chemical synthesis
- Electric and osmotic work
- Mechanical work
- Heat
- Light
- Information and regulation work

Living systems do work at constant temperature and pressure \Rightarrow the energy changes may be described by Gibbs free energy.

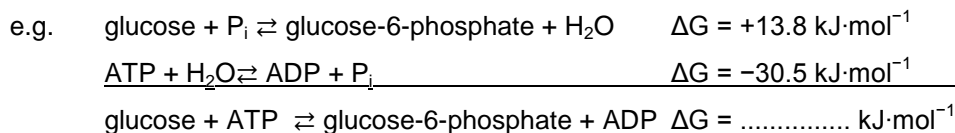
$\Delta G < 0$... exergonic reaction – thermodynamically more probable

$\Delta G > 0$ reaction – thermodynamically less probable

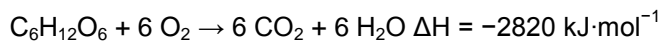
CATABOLIC PROCESSES: decompositions, energy is liberated, ΔG $0 \text{ kJ}\cdot\text{mol}^{-1}$

ANABOLIC PROCESSES: synthetic, energy is required, ΔG $0 \text{ kJ}\cdot\text{mol}^{-1}$

The reactions in living organisms do not occur separately, they occur in systems. Endergonic reactions take place together with exergonic. The resulting $\Delta G < 0$.



The metabolism of glucose:

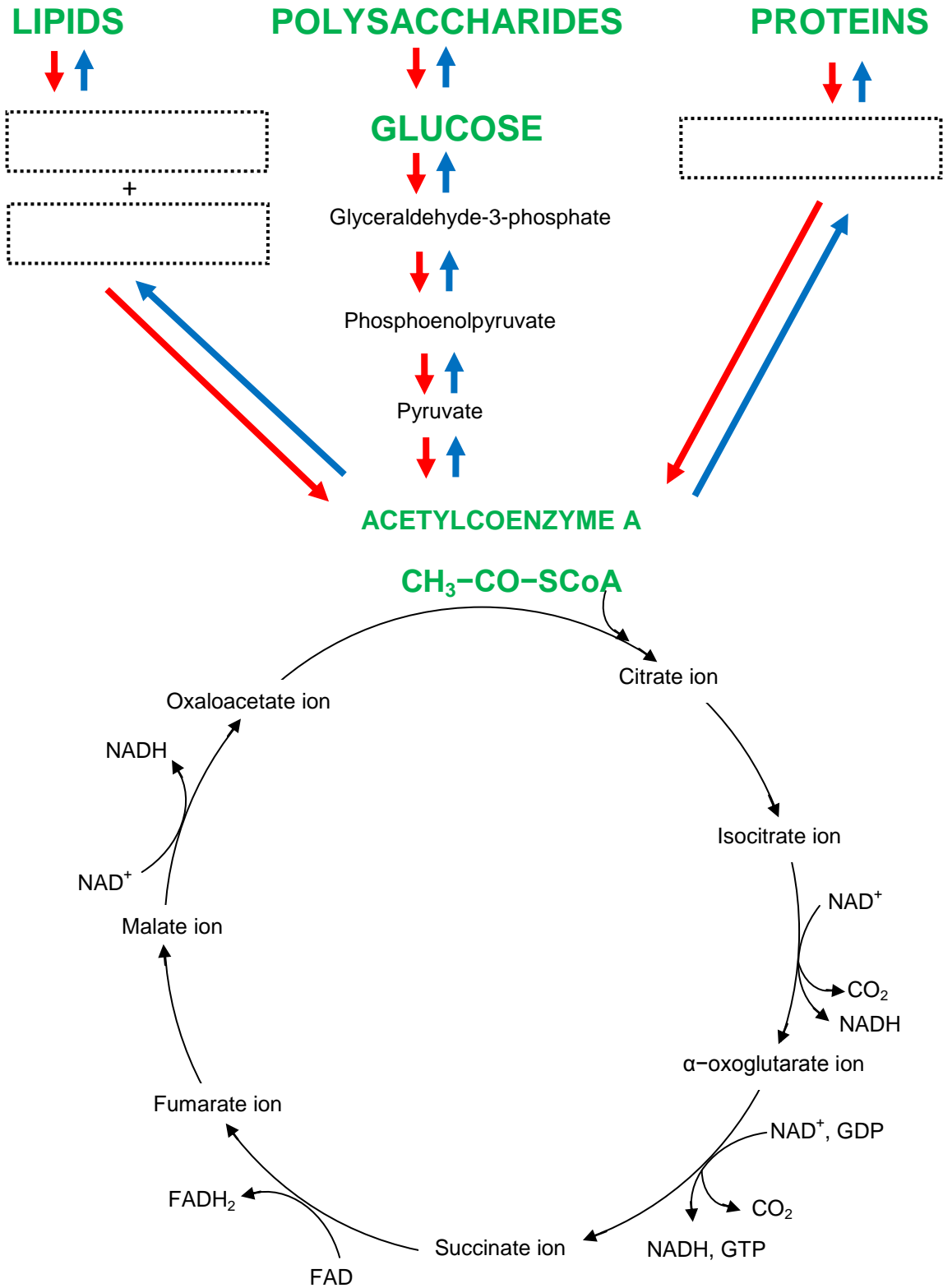


In the cells it takes place as a sequence of steps, which is divided into three parts:

- **Glycolysis:** from glucose to acetyl (bonded to coenzyme A)
- **Citrate (tricarboxylic) cycle:** from acetyl to CO_2 and hydrogen bonded to NAD (FAD)
- **Electron transport chain:** hydrogen on NAD (FAD) is oxidised to water

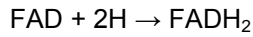
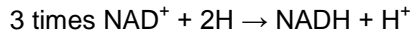
The energy liberated in all these steps is stored in ATP (GTP): $\text{ADP} + \text{P}_i \rightarrow \text{ATP} \quad \Delta H = 32 \text{ kJ}\cdot\text{mol}^{-1}$

The energy is then liberated where it is needed: $\text{ATP} \rightarrow \text{ADP} + \text{P}_i \quad \Delta H = \dots\dots\dots \text{kJ}\cdot\text{mol}^{-1}$

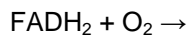
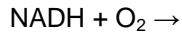


The electron transport chain (respiratory chain)

-there are four dehydrogenation steps in each citrate cycle:



The hydrogen atoms are oxidised by molecular oxygen to form water. The oxidation takes place by means of a series of electron transfers.



Energy is liberated and stored in

Most of the ATP formed through the oxidation of glucose is produced in the electron transport chain.

3. *Make the formulae for the ions taking part in the citric cycle:*

phosphoenolpyruvate

citrate

isocitrate

α -glutarate

succinate

fumarate

malate

oxaloacetate

knowing that: pyruvic acid = 2-oxopropanoic acid

α -glutaric acid = 2-oxopentanedioic acid

citric acid = 2-hydroxypropane-1,2,3-tricarboxylic acid

fumaric acid = trans butanedioic acid

succinic acid = butanedioic acid

oxaloacetic acid = oxobutanedioic acid

malic acid = hydroxybutanedioic acid

4. *Classify the enzymes catalysing the steps of the citric cycle:*

1

4

2

5

6