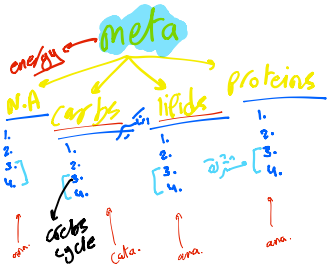
Bioenergetics



metabolism → cata. (energy released)
→ Ana. (energy stored)

effects

- [ ]
- Temp.
- Enzyme → ΔG dominant effect.

ΔG<0 → T↑ → speed↓
ΔG>0 → T↑ → speed↑

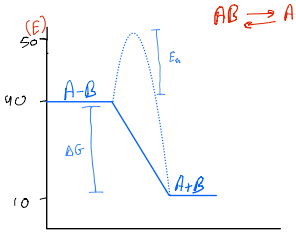
Energy

- light
- kinetic
- Potential
  - Chemical

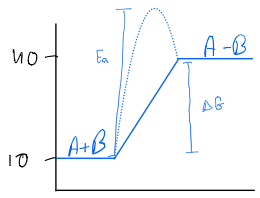
laws of thermodynamics:-
① conservation.
② entropy of universe always increase.

$$\Delta G = G_f - G_i$$

AB ⇌ A + B



40 - 10 → -30
ΔG → -ev → favorible
Catabolism (spontaneous)
doesn't happen spontaneously.
a.E ↓↓



10 - 40 → -30
ΔG → +ev → non favorible
non-spontaneous
Anbolism.

$$\Delta G = \Delta H - T.\Delta S$$

ΔH → enthalpy
ΔS → entropy

H = G + S
↓ ↓ ↓
total energy of system | free energy | randomness

[ ]↑ → ΔG↑
ΔG° (in std. conditions, not given)

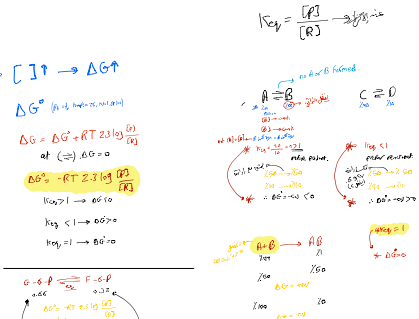
$$\Delta G = \Delta G^\circ + RT\,2.3\log\frac{[P]}{[R]}$$

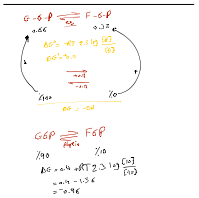
at (⇌) ΔG = 0

$$\Delta G^\circ = -RT\,2.3\log\frac{[P]}{[R]}$$

$K_{eq} > 1 \rightarrow \Delta G^\circ < 0$
$K_{eq} < 1 \rightarrow \Delta G^\circ > 0$
$K_{eq} = 1 \rightarrow \Delta G^\circ = 0$

$$K_{eq} = \frac{[P]}{[R]}$$





BIOENERGETICS

- Dr. NABIL Bashir
- Metabolism ,Ist semester, 2023

Energy & why do we need it?

without it we couldn't survive → important in biological systems.
→ we get it from metabolism.

- **Definition: Capacity to perform work**

✗ The cell in order to have energy the cell must doing metabolism.

- **What for? Mechanical, Active transport, Biosynthesis, Heat**
- **Types of energy:** → that could be transduse from one type to another. (energy never destroyed
  - ✓ **1- Kinetic: Energy in the process of doing work or Energy of motion**
  - ✓ **2- Potential: Energy content stored in a matter**
- **Whether a reaction occurs or not!**
- **metabolism vs. energy**

The major purpose of metabolism

to synthesis of many type of polymers or even monomers.

- **Metabolism: Sum of all biochemical reactions in living organisms**, that are regulated by specific mechanism's & controlled by thermodynamics roll's
  - anabolism (biosynthises)
  - catabolism (degredation) (oxidation) → usually in catabolism part there is circales of energy.
- **Mainly for energy generation**

There is a consumed in order to synthesise polymers.

- **Other purposes:**
  - Synthesis of building blocks
  - Synthesis of macromolecules
  - Degradation of biomolecules → to monomers (synthesis of monomers like: A.A. & glucose.)

all of these synthesis & degredation done by biochemical rxns.

- **Bioenergetics: Energy transformations in the cell**

The different free energy terms

- ΔG = the free energy difference of a system at any condition

- ΔG^{o} = the free energy difference of a system at standard conditions (25C^{o} & 1 atmospheric pressure, 1M concentration of reactants & products, pH = 7)

* in the cell we don't have these conditions.
(the conditions is varies).

Gibbs free energy, ΔG

$A \rightleftharpoons B$

* ΔG will determine the dirctionality of the rxn as well as indirectly also determine the equilibrium.

- this equilibrium is not determined by enzyme but determined by thermodynamics.
- more equilibrium to the A, you will not change the equilibrium by adding any amount of enzyme to the reaction.
- What determine the equilibrium between them? Gibbs free energy.
- ΔG which is related to equilibrium constant, can be used to determine if the reaction is favorable or not:
- if ΔG< 0, reaction is spontaneous, → for ex $A \rightleftharpoons B$ → the eq. is more to the A, (from B → A) → ΔG is -ev. (لأنه هذه المادة هي اللي بتفضلها التفاعل)
- if ΔG> 0, reaction is not spontaneous → A → B, ΔG is +ev.
- if ΔG= 0, reaction is at equilibrium → no more B or A is formed.

Standard free energy change ΔG^o

- Concentrations of reactants and products = 1 mole/L

- $\Delta G = \Delta G^o + RT \ln \frac{[Products]}{[Reactants]}$

natural logarithem

* concerning the [product] of [reactent] you are looking at the ratio of the product & the reactent not the absolut concentration of them.

* $\Delta G < 0$ → energy realeser (exothermic)

- $\Delta G = \Delta G^o + RT\ 2.3 \log \frac{[Products]}{[Reactants]}$

* $\Delta G > 0$ → energy absorber (endothermic)

* any change in $\frac{[Products]}{[Reactants]}$, change the the ΔG.

* DG doesn't affected by the rate, the rate that affected by the enzyme, the enzyme won't change the value of ΔG.

Standard free energy change (ΔG^o) and equilibrium constant Keq

K_{eq} is obtained by dividing [products] by [reactants] when the reaction reaches equilibrium

$$K_{eq} = \frac{[Products]}{[Reactants]}$$

- At equilibrium
- $\Delta G = 0$

$$0 = \Delta G^o + RT \ln K_{eq}$$

$$\Delta G^o = - RT \ln K_{eq}$$

* if K_{eq} is high, the ΔG will be (-ev) & that will affect the ΔG°, & that give us an idea about the rxn where to go until it reaches the eq.

ΔG & Keq

K'_{eq}	$\Delta G^{o'}$ kJ/mol	Starting with 1 M reactants & products, the reaction:
10^4	- 23	proceeds forward (spontaneous)
10^2	- 11	proceeds forward (spontaneous)
$10^0 = 1$	0	is at **equilibrium**
10^{-2}	+ 11	reverses to form "reactants"
10^{-4}	+ 23	reverses to form "reactants"

highe ← 10^4 → -ev

log 1=0 ← $10^0 = 1$

low ← 10^{-4} → +ev

For a reaction $A + B \leftrightarrow C + D$

$$\Delta G = \Delta G^{o'} + RT \ln \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

*Keq = 1

ΔG° = 0

$$\Delta G = \Delta G^{o'} + RT \ln \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

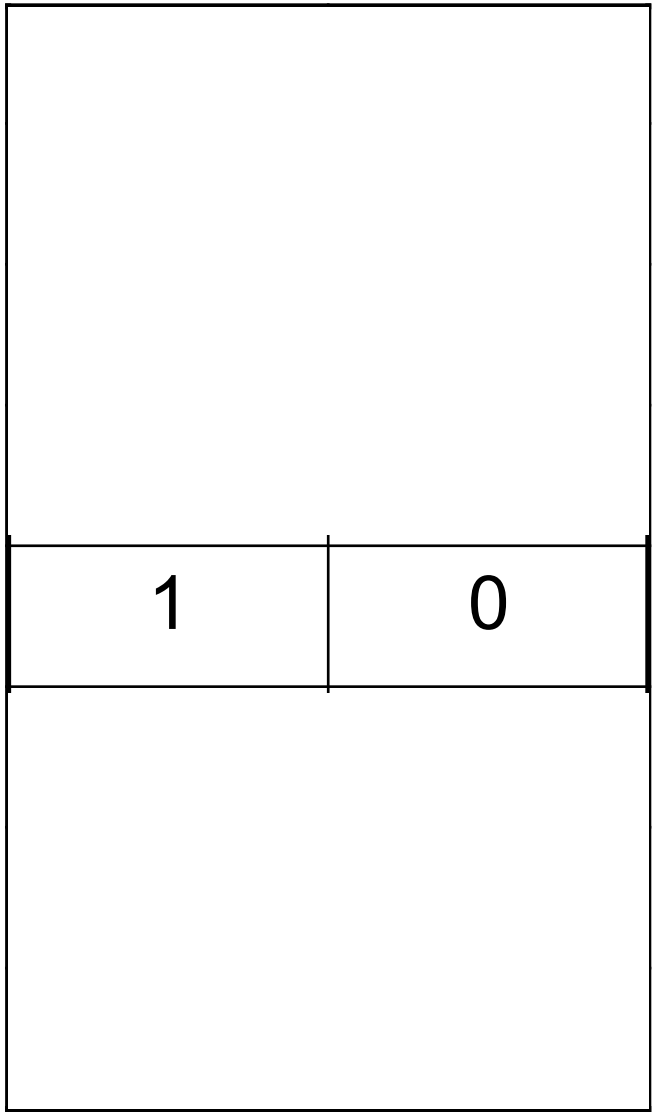
$$0 = \Delta G^{o'} + RT \ln \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

$$\Delta G^{o'} = -RT \ln \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$$

defining $K'_{eq} = \left(\frac{[C]\,[D]}{[A]\,[B]} \right)$

$$\Delta G^{o'} = -RT \ln K'_{eq}$$

ΔG^{o} and K_{eq}



How much change in delta G compared to changes in Keq

If $K_{eq} = 1$, then $\Delta G^{o} = 0$

If $K_{eq} > 1$, then $\Delta G^{o} < 0$

If $K_{eq} < 1$, then $\Delta G^{o} > 0$

Gibbs free energy conditions & ΔG`0

- ΔG depends on conditions: equilibrium & concentration
- A↔B at equilibrium, [A] and [B] are not changing. ΔG=0.
- If we add more A, leads to production of B,
- ΔG A→B <0, until you establish the equilibrium.
- If we add more B, leads to production of A, ΔG B→A <0, until you establish the equilibrium, or ΔG A→B >0.
- Does not matter how much A or B added, the equilibrium depends on the ratio of [B]/[A] not the absolute concentration of each species.

Sometimes in the cell will increas or decreas the [ ] of reactant or product, it could decrease the amount of product by finding another rxn's, that it will pull it always in the forward rxn, so the product of the 1st rxn always its [ ] is low, so the reactant will be converted to that product even is was unfavorable, so it's a strategy used in the cell to change the [product] or the [reactant] in order to pull or to lit the unfavorable rxn to happen, & this is very important.

Direction of a reaction

- If $\Delta G_{A-B} = 0$, $\Delta G`0 = -RT \ln [B]/[A]$, so you can calculate the equilibrium constant if you know the ratio or the concentrations of A and B.
- A → B
- If $\Delta G`0 < 0$, then B is favored over A at equilibrium → [B] > [A].
- If $\Delta G`0 > 0$, then A is favored over B at equilibrium → [A] > [B].
- So $\Delta G`0$ is the convenient way to determine the direction of the reaction → [A] = [B]
- ΔG depends on conditions: $\Delta G`0$ and the concentration of B &A
- If $\Delta G < 0$, then, the RX is spontaneous, energy is released,
- If $\Delta G > 0$, then, there is no RX without energy input

* in the cell also there are many rxn's in the metabolic pathways in which ΔG is (+ve) but energy input as in ATP hydrolysis will help this rxn to take place.

Stages of catabolism

extract energy from food in different places for the cell to take benifit of those energy releases in different places.

the energy will dissipated as heat & the cell won't take advantage much as if stepwise. ← one step old

no energy

digestion & absorbtion of food.

1st stage: Large molecules in food are broken down into smaller units. Preparation stage without capture of energy.

- Proteins -> amino acids,
- Polysaccharides -> monosaccharides (glucose, ...)
- Fats -> glycerol, fatty acids.

glu. & some simple sugar converted to 2 Pyruvic acid ← contain 2 C

converted to acetyl coA by Pyruvat dehydrogenase complex.

2nd stage: Molecules are degraded to simple units that play a central role in metabolism. Most of them are converted into the acetyl unit of acetyl CoA (acetyl + co enzyme A). Some ATP is generated in this anaerobic stage, but amount is small compared with 3rd stage.

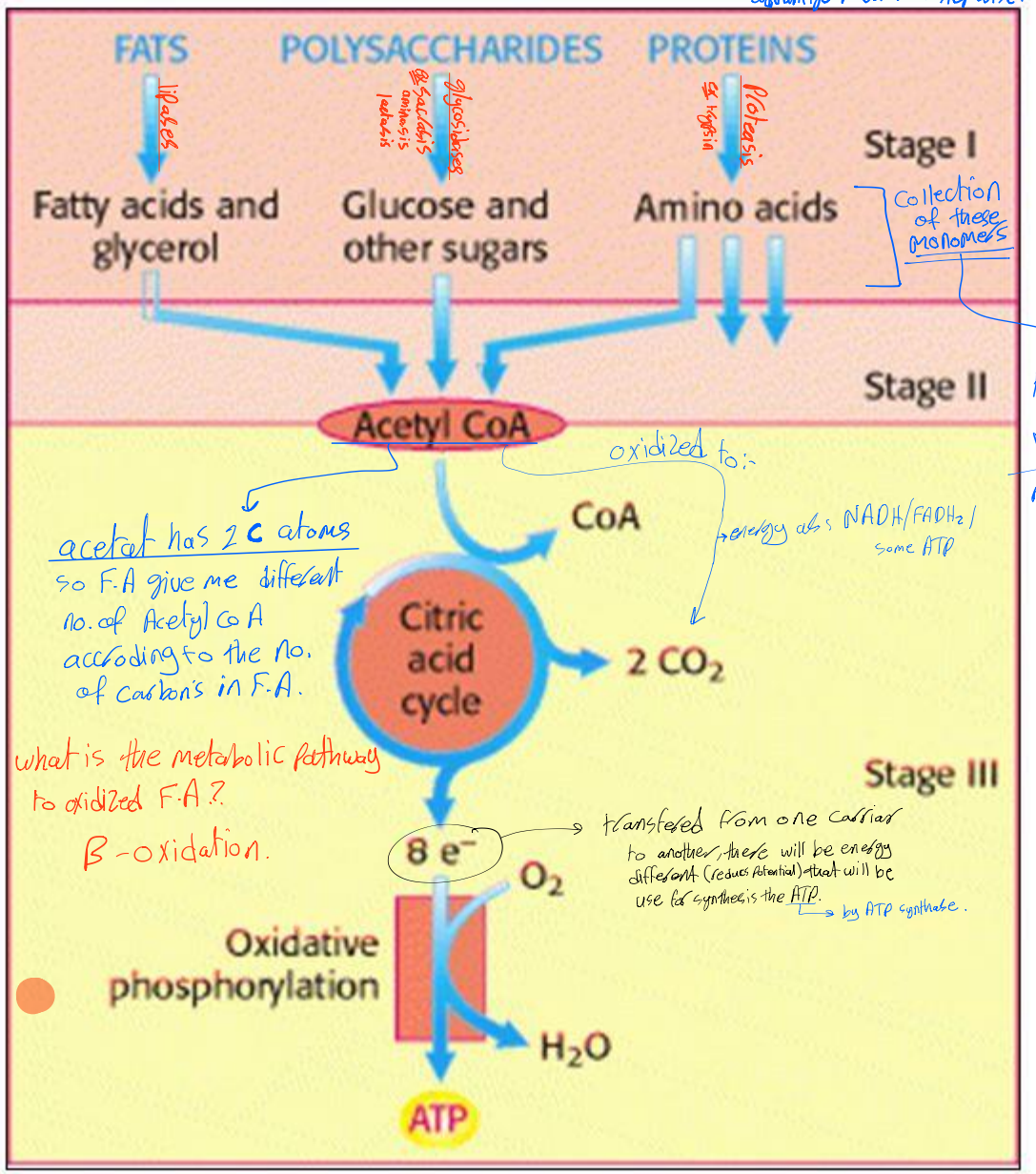
amino acids: some of the oxidized to acetyl coA or Pyrophat or intermediat that will be oxidized later.

* ketogenic a.a → acetyl coA.
* glucogenic a.a → Pyruvate.

* usually ketogenic a.a you can't synthesized glucose from it. but you can synthesized glucose from glucogenic. because in our system acetyl coA can't be converted to Pyruvate in order to synthesized glucose.

we can't synthesized glucos from the fat. (the same reason).

3rd stage: ATP is produced from the complete oxidation of the acetyl unit of acetyl CoA. Acetyl CoA brings acetyl units into the citric acid cycle, where they are completely oxidized to CO_2. Four pairs of electrons are transferred (three to NAD^+ and one to FAD) for each acetyl group that is oxidized. Then, a proton gradient is generated as electrons flow from the reduced forms of these carriers to O_2, and this gradient is used to synthesize ATP.



glycosidases hydrolys:- α-1-4 bond not β 1-4 bond so we didn't eat wood.

converted to Acetyl CoA via different:- metabolic pathways & rxn's & DG's not standered.

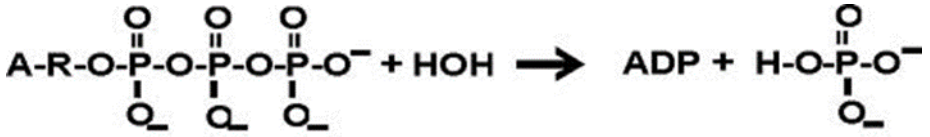
ATP is the energy currency of the cell

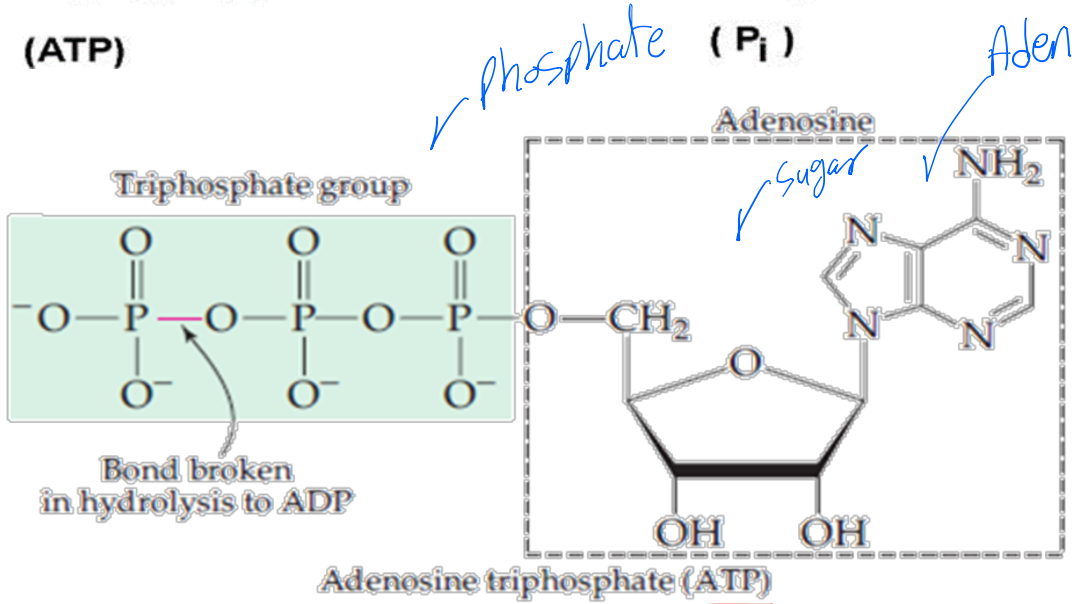
the energy form in meta.

What is a high energy molecule? Phosphoenol Pyruvate.

Why ATP? because hydrolysis of ATP it most easier than others

Has an intermediate energy value, so can be coupled





Nucliotide (nucloside triphosphat)

this type of ATP formation called the substrat level phosphorylation, in which ATP reproduced from high energy compound & ADP.

Compound +H_2O	Product + phosphate	ΔG° in kcal/mol
Phosphoenol pyruvate	glycolysis → Pyruvate	-14.8
1,3 bisphosphoglycerate	3 phosphoglycerate	-11.8
Creatine phosphate	Creatine	- 10.3
ATP	→ ADP + Pi	- 7.3
Glucose 1- phosphate	Glucose	-5.0
Glucose 6- phosphate	Glucose	-3.3

used to synthesized ATP not at stage 3, but at stage 2, in which glycolysis take place. & it will be used as coublles to do unfavorable

could be used as an input energy for biosynthesis or for other purposes (transport, making unfavorable rxn).

we couldn't store it!

because its easier for the cell to make metabolisms? Produce ATP than the cell to be busy to synthesing ATP → we need 7.3 kcal/mol

How ATP hydrolysis provide energy to make unfavorable reactions to occur

For any polymer synthesis: **unfavorable**

ATP is hydrolyzed as:

ATP→AMP +PPi **HIGHLY FAVORABLE**

PPi→2pi ≈ ΔG`0 for both rxs <<0

Two tricks are done here:

- 2 favorable reaction to drive unfavorable polymer synthesis
- keeping ppi concentration very low

* ATP hydrolysis to make unfavorable rxn will happen (synthesis of polymers)
  - used in this form: ATP → AMP + PPi, ΔG << 0
    - another molecule can't do this so this is reason to why use it.
    - will be hydrolized to 2 inorganic phosphate also with ΔG<<0. ⟹ so we have 2 rxn's in ATP hydrolysis & give highly -ev ΔG.
      - used to overcome the energy input for synthises polymer.

* we need to keep the [PPi] very low. so lowering the [product] or [reactant] help ATP to keep going to forward direction.

Glucose Trapping by Phosphorylation:

* in the first rxn of glycolisis the glucose must be phosphorylated. → unfavorible
→ to trappin the glu. inside the cell.

ATP → ADP + Pi $\Delta G`0 = -7.5$ Kcal/mol

Glucose + Pi → glucose-p $\Delta G`0 = 3.3$ Kcal/mol, Equilibrium is toward glucose + Pi - no trapping.

Coupling

Make ΔG -ve

If you couple these two reactions:

Glucose + ATP → glucose-p + ADP $\Delta G`0 = -4.2$ Kcal/

$$\Delta G = \Delta G`0(\text{glucose} \rightarrow \text{glucose-p}) + \Delta G`0(\text{ATP} \rightarrow \text{ADP}) + RT\ln\frac{[\text{glucose-p}][\text{ADP}]}{[\text{glucose}][\text{ATP}]}$$

if this is <4.2, favorable

+3.3 + -7.5= -4.2 >-4.2