5

carbohydrates isomers ketone starch lipid protein amine

Biochemistry 2

Doctor 2018 | Medicine | JU

◉ Sheet ○ Slides

Done By

Abdullrahman + Rand Assaf

Contributed in the Scientific Correction

Abdullrahman + Rand Assaf

Contributed in the Grammatical Correction

Abdullrahman + Rand Assaf

Doctor

Dr. Faisel Alkhateeb

UDP

-Uridine diphosphate has a very high affinity to carry monosaccharides such as glucose, so it can serve as a glucose donor in many biochemical reactions

-UDP has a very important role (as a glucose donor) in the process of glycogenesis (The synthesis of glycogen in the liver) by carrying a (Glucose-1-phosphate) and adding it to the existing glycogen

-The following figure illustrates the structure of UDP-glucose molecule

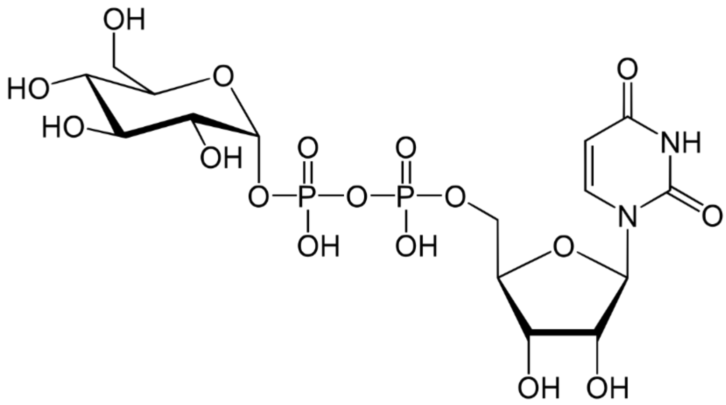
It consists of

1-Ribose sugar

2-Two phosphate molecules

3-Nitrogenous base (Uracil)

4-The carried glucose molecule



Glycogen (n) + UDP-glucose $\longrightarrow$ **Glycogen (n+1) + UDP**

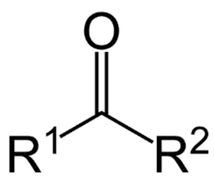
*where ‘n’ indicates the number of the glucose molecules which are present in the Glycogen polymer

Acetyl Co-Enzyme A

-Acetyl Co-A is considered to be a high energy molecule during several anabolism reactions in our body, as the **Co-enzyme A** is considered to be the universal carrier of the acetyl (**Acetyl donor**)

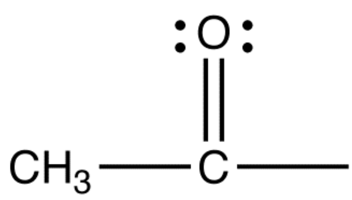
Q-What is the Acyl group?

A-It is a molecule consists of a carboxyl group (C=O) and an alkyl group (alkene)

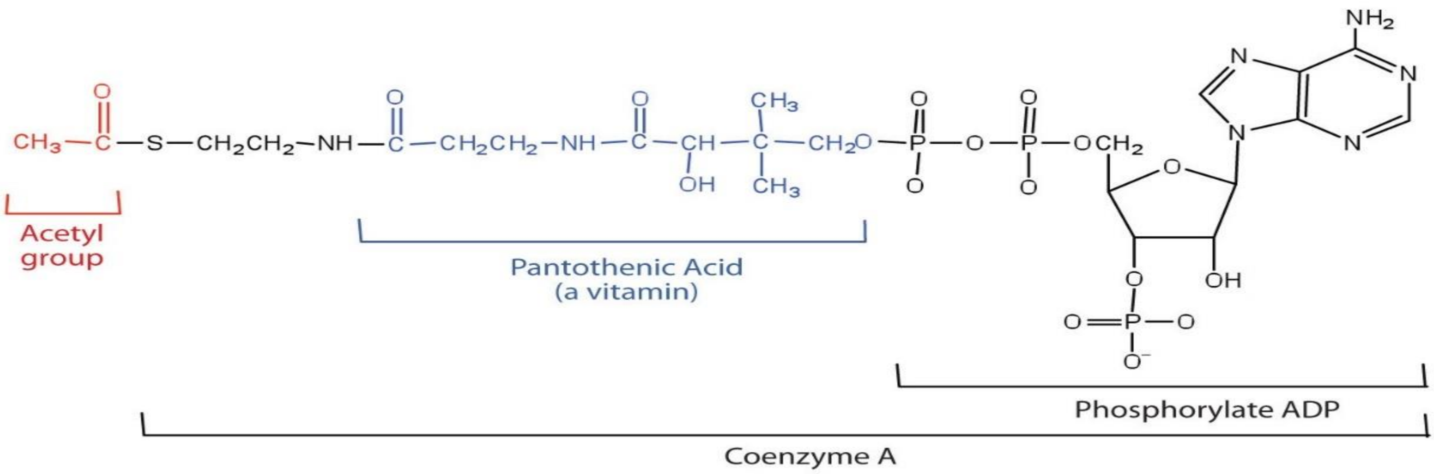


Q-What Is the Acetyl group?

A-It is a specific type of acyl groups in which the alkene is a methyl group (-CH_3)



-The following figure illustrate the structure of the Acetyl Co-A



-**The Co-A consists of**

1-ADP

2-Pantothenic acid (Vitamin B5)

3-Beta Mercabtoethylamine

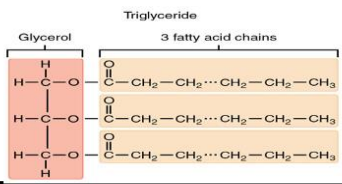
4- Thiol group (-Thiol group Is the binding Group in the Co-A and the bond that its forms is Called Thioester bond).

**Detailed structure of the Co-A is not required and won't be examined, but you must be able to recognize its general features.

-**During synthesis of fats** (Triacyl glycerides), acyl groups cannot be directly added to the glycerol molecule, otherwise, they must be converted to the active form (Acetyl Co-A), then they can be added to the glycerol molecule by Acyl transferase

Recall the structure of Fats

-One glycerol molecule attached to 3 fatty



- **Acetyl Co-A and Exergonic-Endergonic coupling**

As it is considered a high energy molecule, Degradation of it yields a high amount of energy which can be used to carry other endergonic reactions

-For example, Acetylcholine is a neurotransmitter that is degraded in the nerve synapse according to the following reaction 3

Remember all hydrolysis reactions tend to be Exergonic

Acetylcholine + H_2O $\rightarrow$ Acetate + Choline $\Delta G = -3Kcal$

-In order to resynthesize the Ach, it will be an Endergonic reaction with ΔG of +3 Kcal so it must be coupled with the reaction that breaks down the Acetyl-coA as following

Acetate + Choline $\rightarrow$ Acetylcholine + H_2O $\Delta G = +3Kcal$

Acetyl Co-A + H_2O $\rightarrow$ Acetate + Co-A $\Delta G = -7.5$ Kcal

---

Choline + Acetyl Co-A $\rightarrow$ Co-A + Acetylcholine $\Delta G = -4.5$ Kcal

---

Oxidation-Reduction reactions

-Oxidation is loss of electrons and reduction is gain of electron, this is why they always occur together (Electrons cannot be lost)

Some misunderstood concepts

Reducing Agent: A molecule that will be oxidized and will reduce other molecules (Electron donor)

Oxidizing Agent: A molecule that will be reduced and will oxidize other molecules (Electron acceptor)

Reduced: Had gained electrons

Oxidized: Had lost electrons

**Rather than memorizing these terms, it would be better to understand the movement of electrons in these different stages

-Electrons have many forms in order to be transmitted

1-Free electrons

2-Hydrogen atom (one proton + one electron)

3-Hydride (one proton + two electrons) (H-)

-Oxidation of molecules occurs in 2 stages

1-Transfer the electrons from molecules to electron carriers

2-Transfer of electrons from the carrier to an oxygen molecule

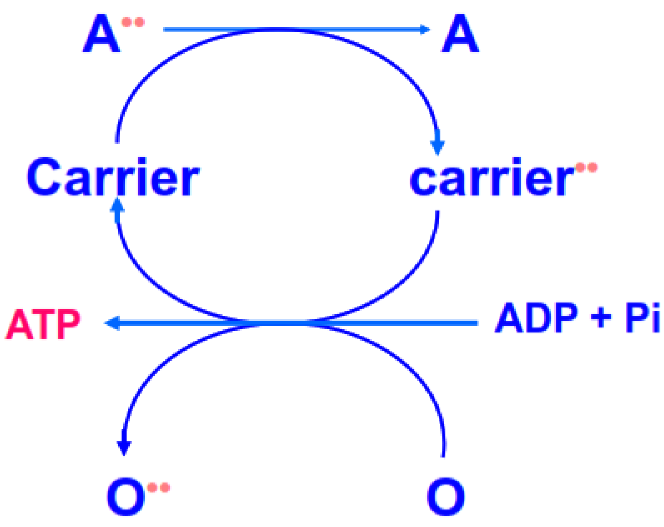
Let's consider the following example:

Stage I

-(A) acts as fuel (electron donor) and it will be oxidized (loss of electrons)

-The carrier will accept these electrons and it will be reduced (end of stage I)

Here the 'A' acts as reducing agent



Stage II

-The carrier will lose its electrons (oxidized)

-The oxygen will gain these electrons (Reduced)

*In the 2nd stage the oxygen molecule acts as an oxidizing agent, however the oxygen is considered to be a very strong oxidizing agent so that the 2nd stage will have a highly negative ΔG (Compared to stage I), so it can be coupled with endergonic reaction of ADP phosphorylation in order to produce ATP .

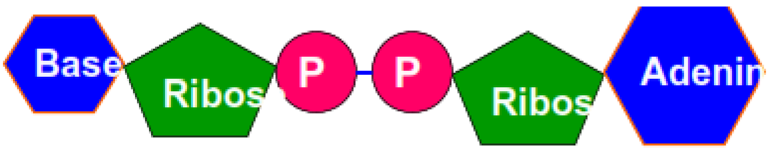
Electron carriers

-Electron carriers are usually dinucleotides (2 nucleotides connected through phosphate groups)

-Nucleotide is formed by phosphate group, ribose, Nitrogenous base

-Among the two nitrogenous bases within the dinucleotide, one of them must be Adenine

-NAD+, FAD



NAD+

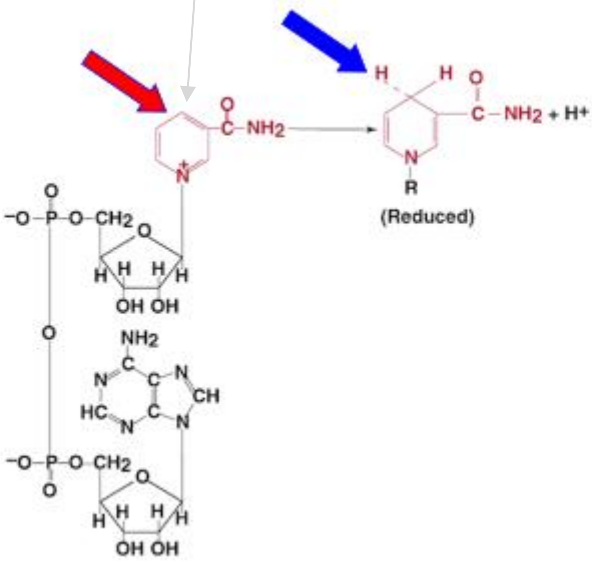
-Nicotinamide Adenine Dinucleotide

-Notice that the nitrogen molecule within the nicotinamide ring had formed 4 covalent bonds to become(N+) and this is why NADH is positively charged when it is oxidized

-It accepts the electron is the form of hydride ion (H-)

-The fuel loses two neutral hydrogen atoms (2 protons and 2 electrons)

Nicotinamide



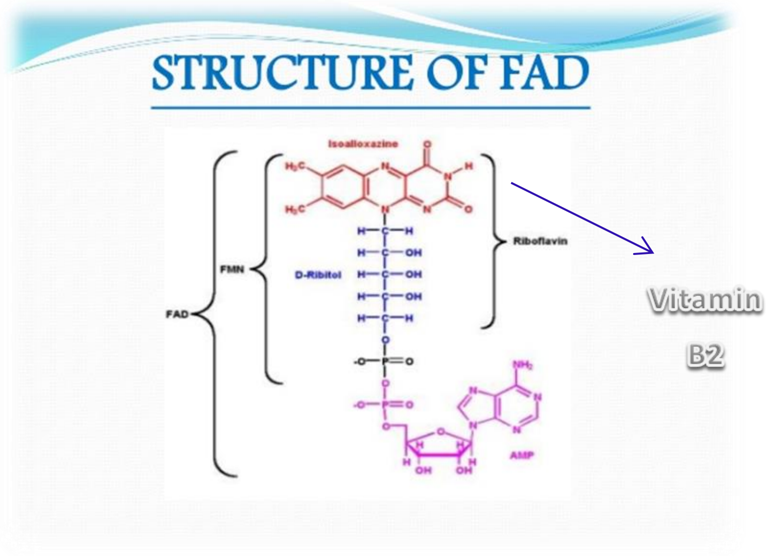
-The NAD+ accepts a hydride ion (one proton and two electrons), and one remaining protons will be released

FAD

It contains adenine, ribose, 2 phosphate groups , riboflavin (ribitol + isoalloxazin)

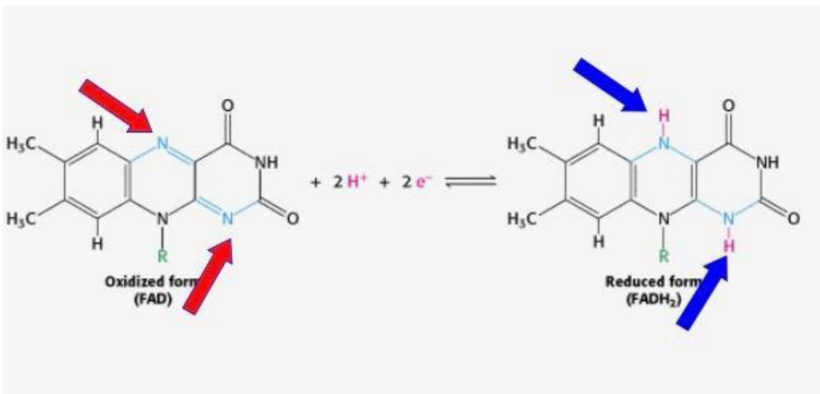
*Ribitol is the reduced form of ribose

**ribitol isn't pentose sugar



How FAD gets reduced?

Two hydrogen atoms are accepted (2 electrons and 2 protons) at the reactive site (by nitrogen) and the two double bonds are converted to two single bonds.



Electron carriers are used among different catabolism reactions in our bodies and on different stages in order to generate ATP.

1st stage →Carbohydrates, Amino Acids and Fatty Acids are converted to CO_2 and H_2O and the electron carriers are converted to their reduced form

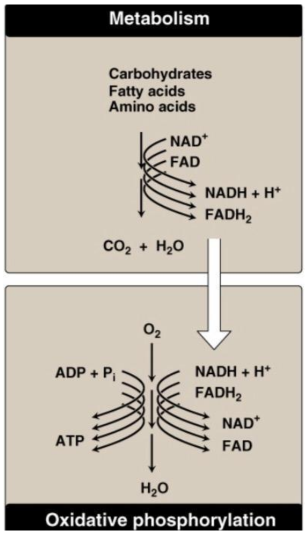
2nd stage→ NADH/$FADH_2$ moves the electrons to oxygen and ATP is synthesized by the released energy

Oxidative phosphorylation is phosphorylation that depends on oxidation

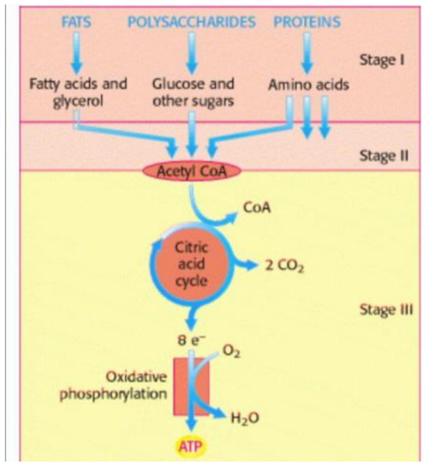
→**In order to add a phosphate we need energy and in Oxidative phosphorylation the source of energy is <u>oxidation</u>**

1st

2nd



The General Map of Metabolism



Large molecules are converted to simple building blocks, which will be further converted to Acetyl COA, which can be oxidized in citric acid cycle releasing the two carbons of acetyl group as CO_2

The electrons released from this oxidation are passed through oxidative phosphorylation and ATP is produced here.

*Don't be overwhelmed with this part as it will be further illustrated Later on

---

Reduction Potential

-Let's shift gears and introduce this new concept, in order to do it lets discuss the following EX:

$$A\text{-}P + B \longrightarrow A + B\text{-}P \quad \Delta G-$$

Reaction Type: (transfer of phosphate group), and the direction is determined by the sign of the Delta G

-The previous reaction is an exergonic reaction, as the 'B' molecule had accepted the phosphate group in such spontaneous conditions so we can say that 'B has higher affinity than A to accept the phosphate group'

-Now let's discuss the following reaction to understand the **Reduction potential**

$$A^{++} + B^{++} \text{-------->} A^{+} + B^{+++} \quad \Delta G-$$

Direction of Reaction

Is determined by Δ G

Reaction Type: Oxidation-Reduction reduction reaction (gaining & losing electrons)

-This is a spontaneous reaction in which B had released an electron, which was accepted by A, as the reaction was spontaneous, A is said to have a higher affinity to accept electrons than B, so it tends to be **reduced**, and has a higher **Reduction Potential**

Reduction potential: Measurement of the molecule's ability to accept electrons (Be reduced)

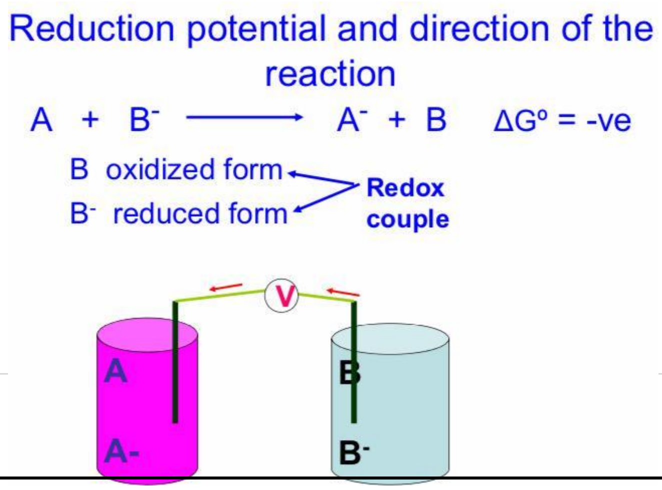
→if ΔG was positive it means that the reverse reaction will occur

A has higher tendency to give electrons than B

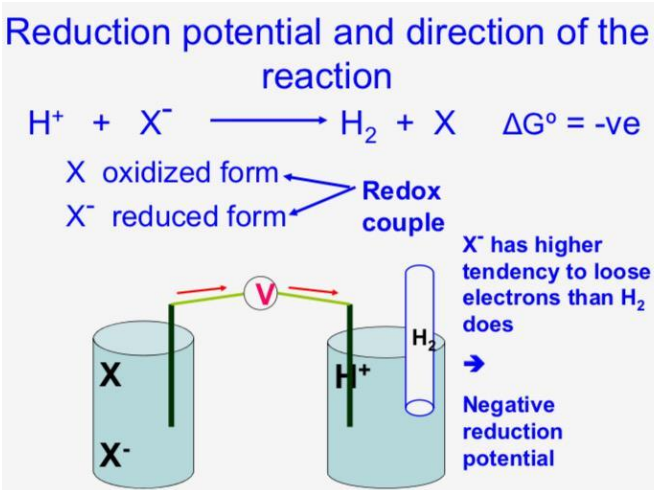
Same concept

-A has higher tendency to gain electrons than B

Electrons will move from B to A as current and the reduction potential is measured by the voltmeter



In order to compare between molecules reduction potentials, we need a standard value (The zero point) to know each molecule's reduction potential($\Delta E°$)



This standard (reference) value is set to be the hydrogen. So that :

-Any molecule is reduced in the prescence of hydrogen in a spontanous reaction is said to have a **Positive reduction potential**

- Any molecule is oxidized in the prescence of hydrogen in a spontanous reaction is said to have a **Negative reduction potential**

-The following table shows some Delta E node values compared to hydrogen

Increasing strength as oxidizing agent

Oxidized + e^-	------->REDUCED	$\Delta E°$
Succinate	α ketoglutarate	-0.67
Acetate	Acetaldehyde	-0.60
NAD^+	**NADH**	**-0.32**
Acetaldehyde	Ethanol	-0.20
Pyruvate	Lactate	-0.19
H^+	H_2	0.00
Fumarate	Succinate	+0.03
Cytochrome $^{+3}$	Cytochrome^{+2}	+0.22
Oxygen	Water	+0.82

Increasing strength as reducing agent

-The stronger the Oxidizing agent -The more the positive reduction potential value

-The stronger the Reducing agent-The more the negative reduction potential value

**No need to memorize the previous table, just be aware how to deal with it regarding to different arrangement possibilities.

NOTE: Any molecule that can take electrons from H^+ (standard) is located below it and any molecule that can give electrons to H^+ is located above it.

Calculating delta E node from Delta G node

$$\Delta G^o = -nF\Delta E^o$$

-Where 'n' represents the number of the transferred electrons and 'F' represents the Faraday constant = 23.06 Kcal/Volt

- Calculate ΔG^o of the following reaction

$$NADH + 1/2O_2 \longrightarrow NAD^+ + H_2O$$

$$NADH \longrightarrow NAD+ + 2e^- \quad \Delta E^o = +0.32$$

$$O + 2e^- \longrightarrow O^{2-} \quad \Delta E^o = +0.82$$

ΔG^o = - 52.6 kcal/mol

-This is a sample calculation on how to use the previous equation

-Notes regarding to the illustrated equation

1-In order to properly use the previous law, the reaction must be separated into 2 halves (Reduction and oxidation halves), then balance them

2-Note that the sign of the reduction potential of the NADH is reversed, because it is now an oxidation reaction rather than reduction (compare the reaction mentioned in the table with this one and you will notice that the second one represents the backward reaction)

The reaction is spontaneous, NADH is oxidized rather than reduced so we need to covert the sign of it's E

The oxygen gets reduced so it maintains it's E

$$\Delta G^o = -nF\Delta E^o$$

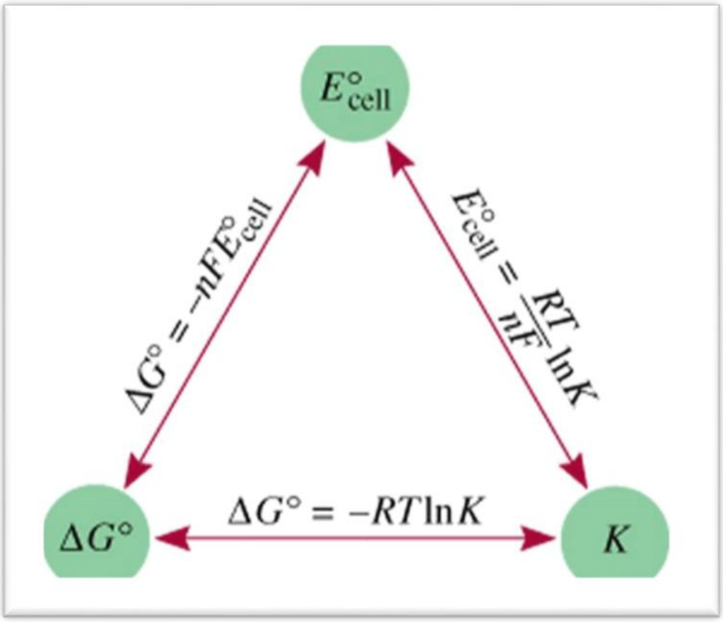
= - (2* 23.06* (0.32 + 0.82))

= - 52.6 Kcal/mol

** Changing the stoichiometric coefficients of a half reaction doesn't affect the value of 'E' **BECAUSE ELECTRODE POTENTIALS ARE INTENSIVE PROPERTIES.**

**** always check that the half reactions are balanced.**

Relationships between k,ΔG°, ΔE°



With a strong why, there is no hard how

Good Luck