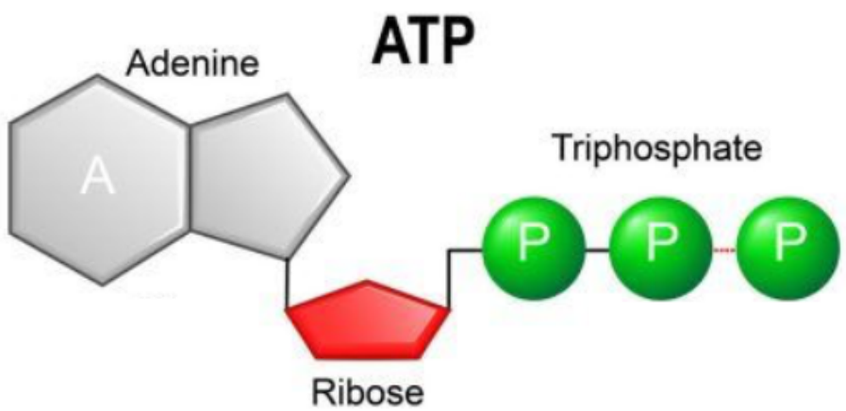
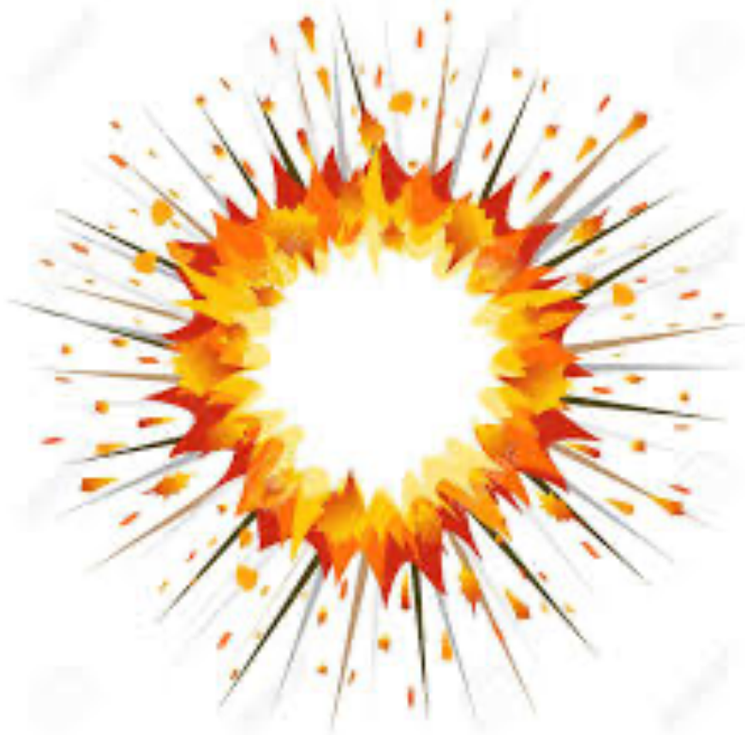
BIOL2107, Fall ’23

Lecture 19





Glucose Metabolism, Redox and Water …

Term Paper:

1. "Evolution is a man-made myth"

2. "An understanding of Genetics is **fundamental** to our understanding of how an organism works."

3. "Virus are alive"

Choose one of the statements above, and provide **two arguments** for me; one **for** and one **opposed** to the statement that you chose.

Minimally, each of your arguments should be **half a page** of **11pt**, single-spaced writing (450 words).

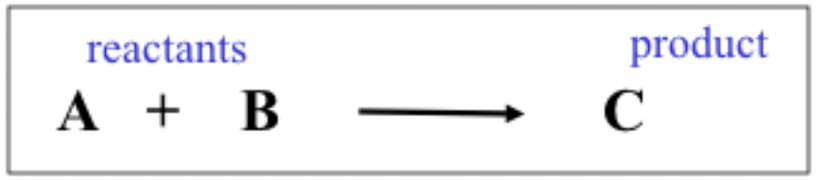
Maximally, each of your arguments should be no more than **one page** of **11pt**, single-spaced writing (900 words).

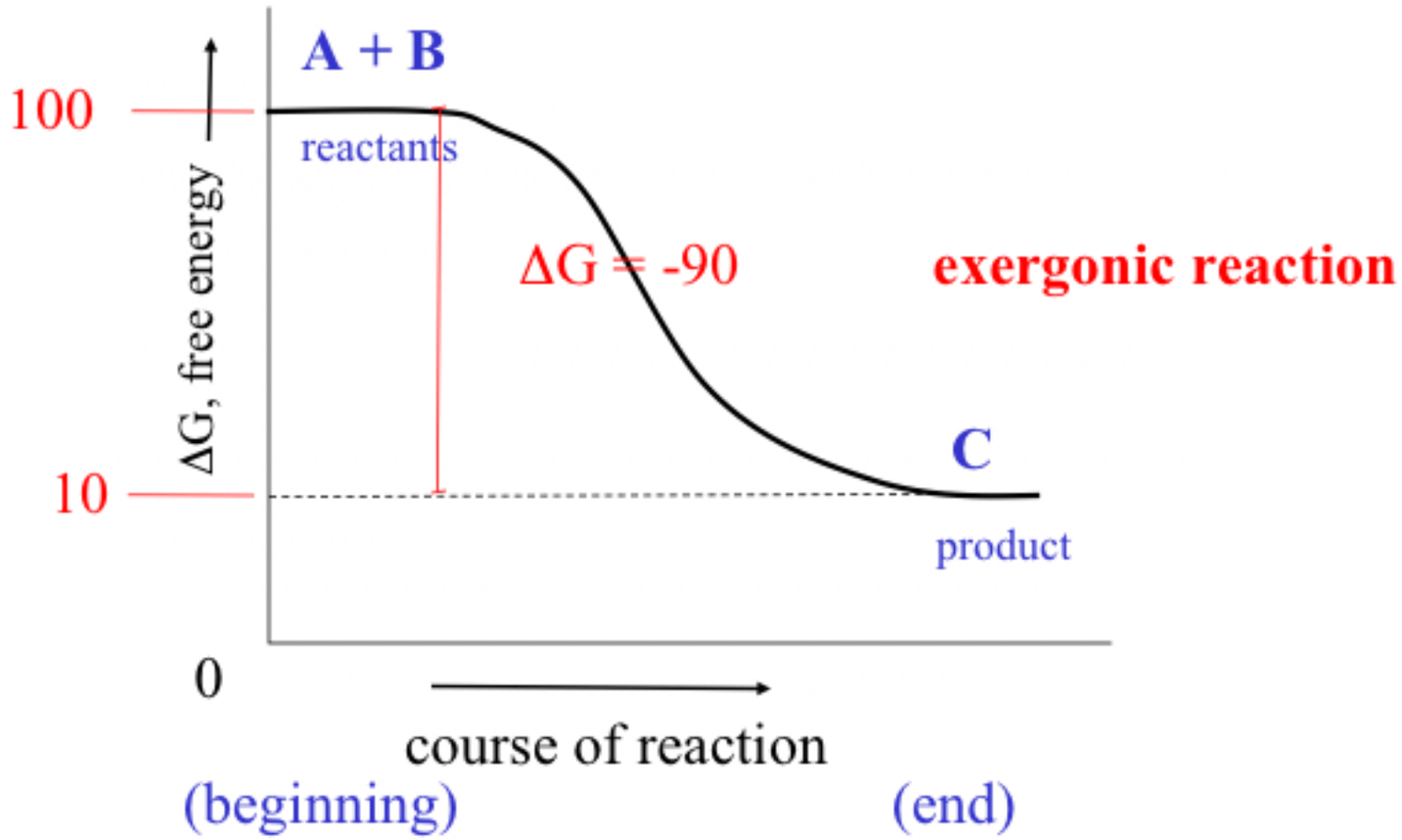
In addition: you will need to put down references for all the sources of information that you cite.

You will submit your paper as a typed document (E-MAIL)... by **NOV 18th**!!

When you do e-mail me your paper, please ensure that you give the title **"BIO2107 Term Paper"** in the subject line of the email.

- free energy example

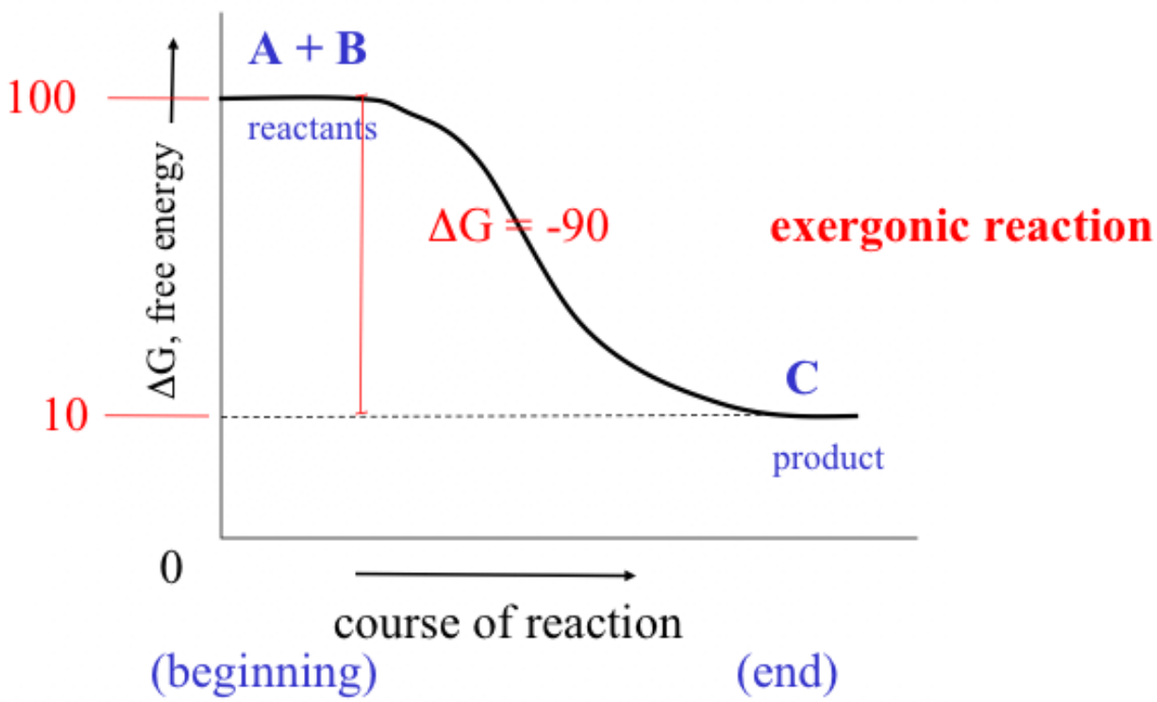




- free energy example

reactants product

A + B ⟶ C



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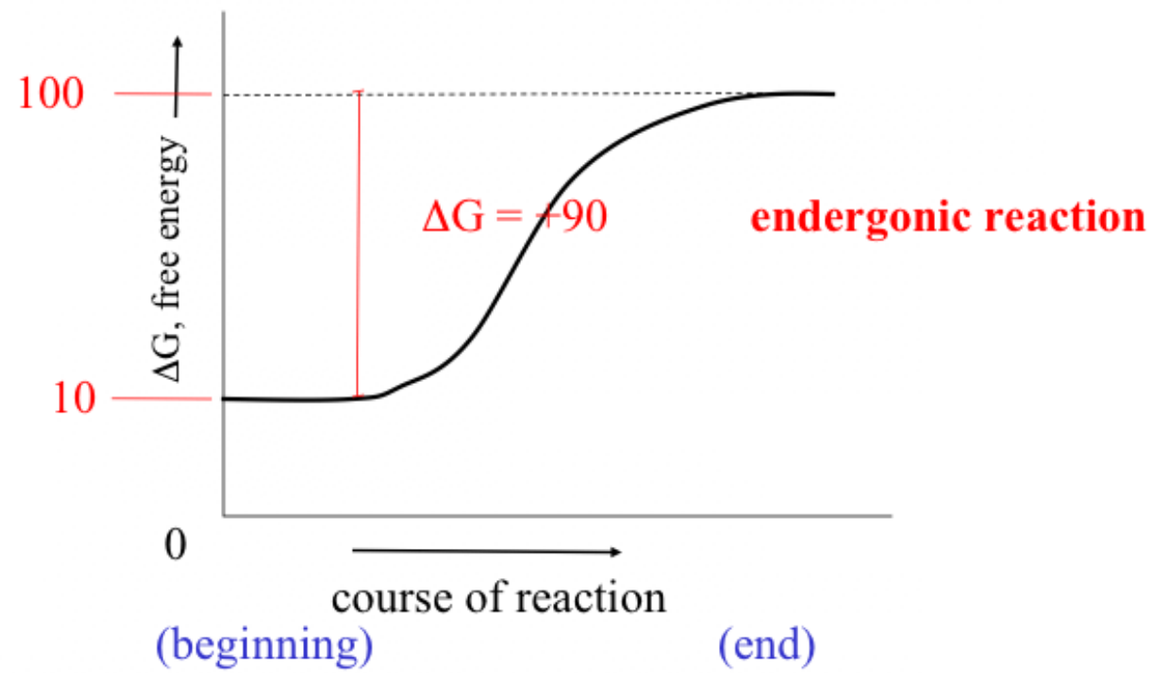
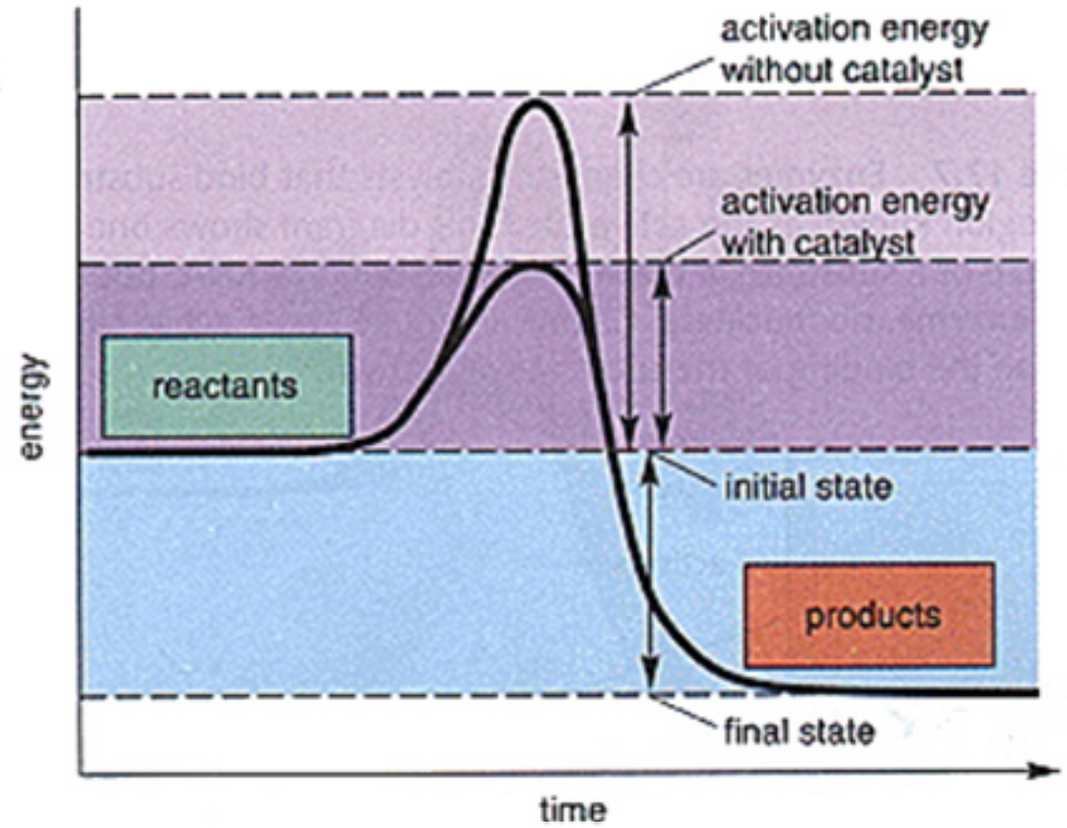


While it is easy to predict the direction that a spontaneous reaction will go, it is not so easy to predict the "likelihood" or rate of the reaction.

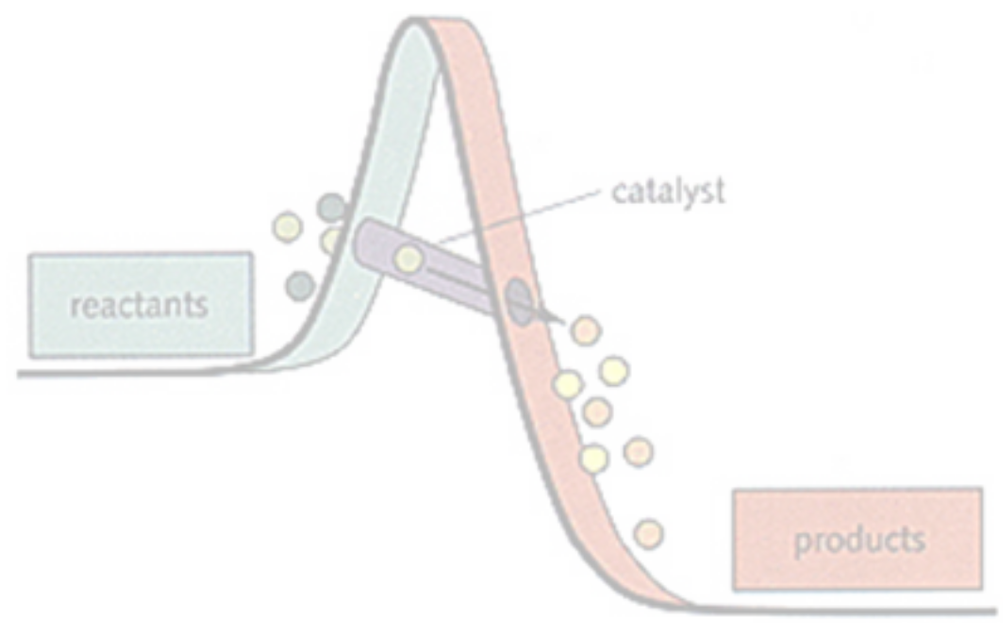
Energy of Activation

The energy required to start a chemical reaction.



Lowering the Energy of Activation

This is the way in which chemical catalysts speed up chemical reactions.



Types of enzymes (Biological catalysts)

- "_____-ase" implies an enzyme

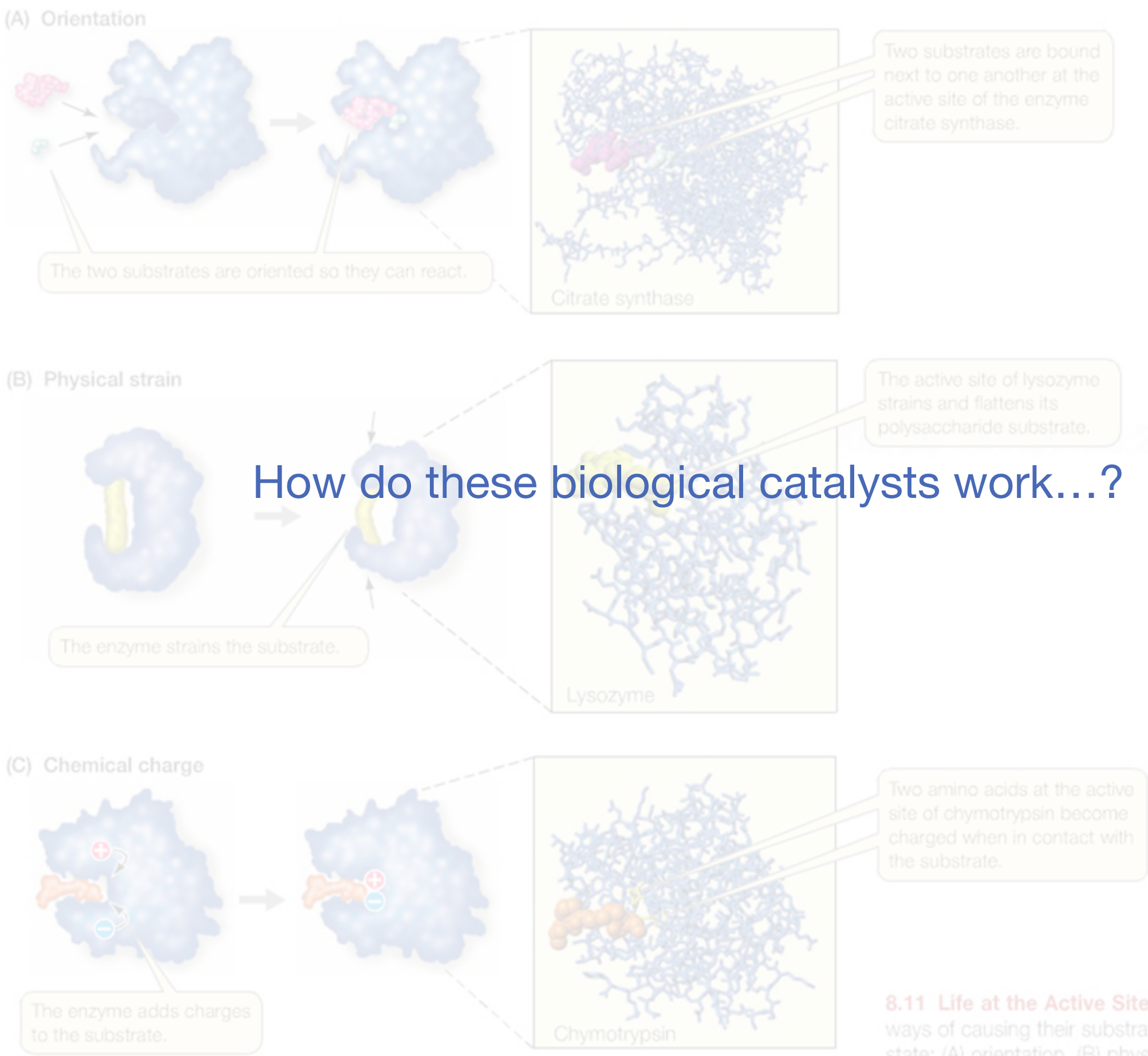
examples:

kinase adds phosphate (phosphorylates) another molecule

isomerase rearranges a molecule's structure

dehydrogenase oxidizes a compound (removes electrons)

reductase reduces a compound (adds electrons)



How do these biological catalysts work…?

8.11 Life at the Active Site Enzymes have several ways of causing their substrates to enter the transition state: (A) orientation, (B) physical strain, and (C) chemical charge.

6.1 A Few Examples of Nonprotein Molecular "Partners" of Enzymes

TYPE OF MOLECULE	ROLE IN CATALYZED REACTIONS
Cofactors	
Iron	Oxidation/reduction
Copper	Oxidation/reduction
Zinc	Helps bind NAD
Coenzymes	
Biotin	Carries $—COO^-$
Coenzyme A	Carries $—CH_2—CH_3$
NAD	Carries electrons
FAD	Carries electrons
Prosthetic groups	
Heme	Binds ions, O_2, and electrons; contains iron cofactor
Flavin	Binds electrons
Retinal	Converts light energy

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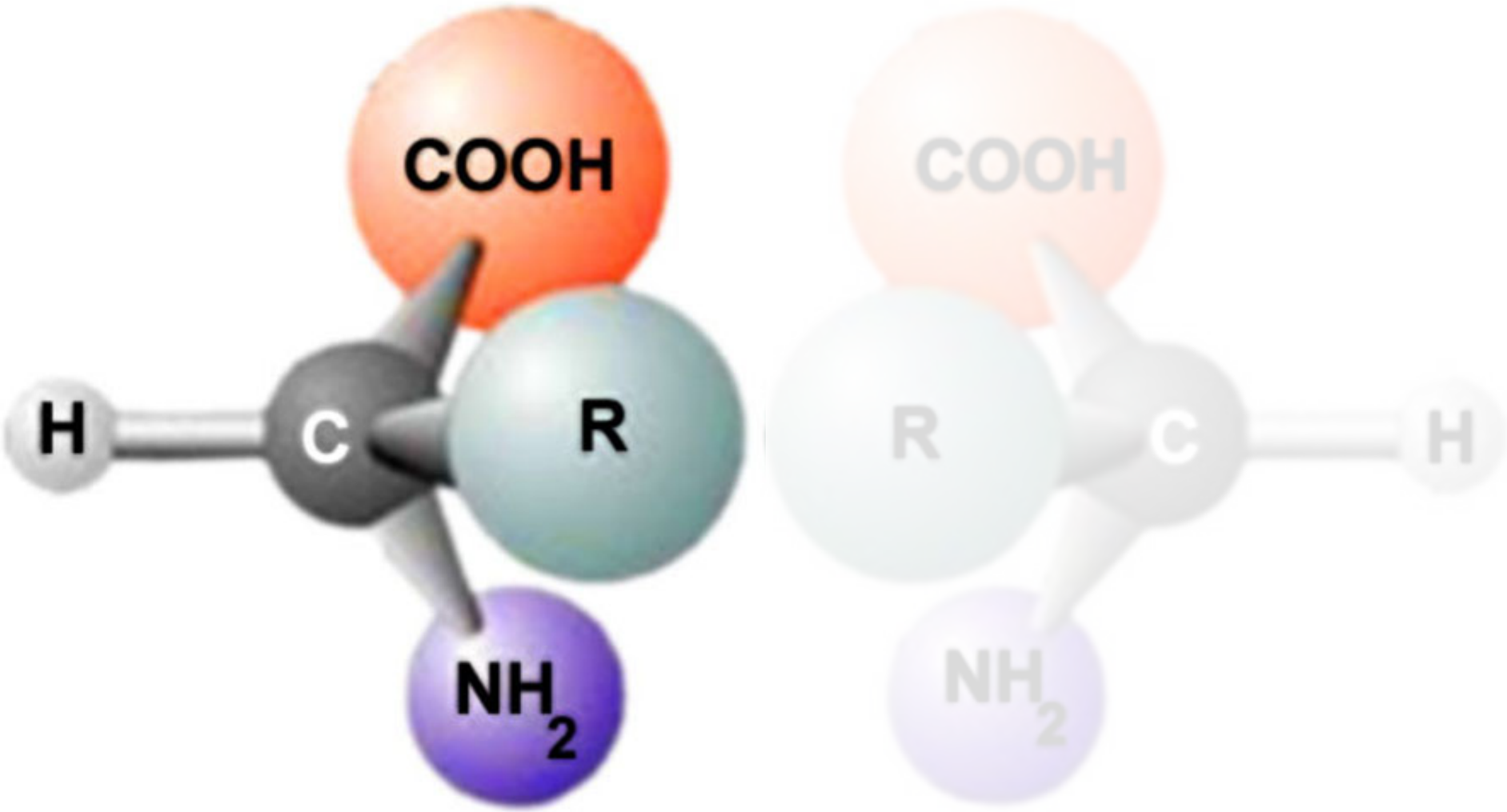
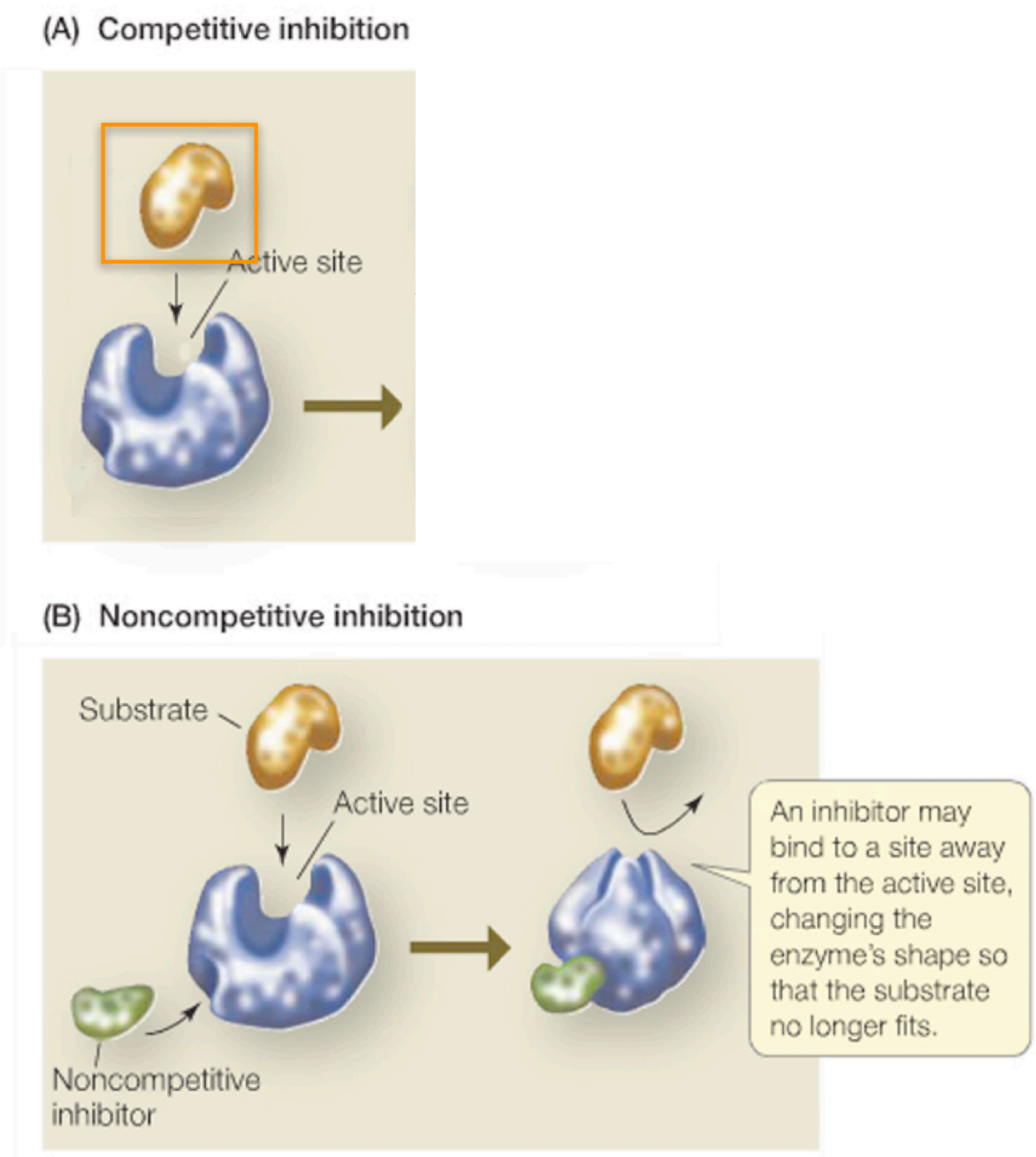
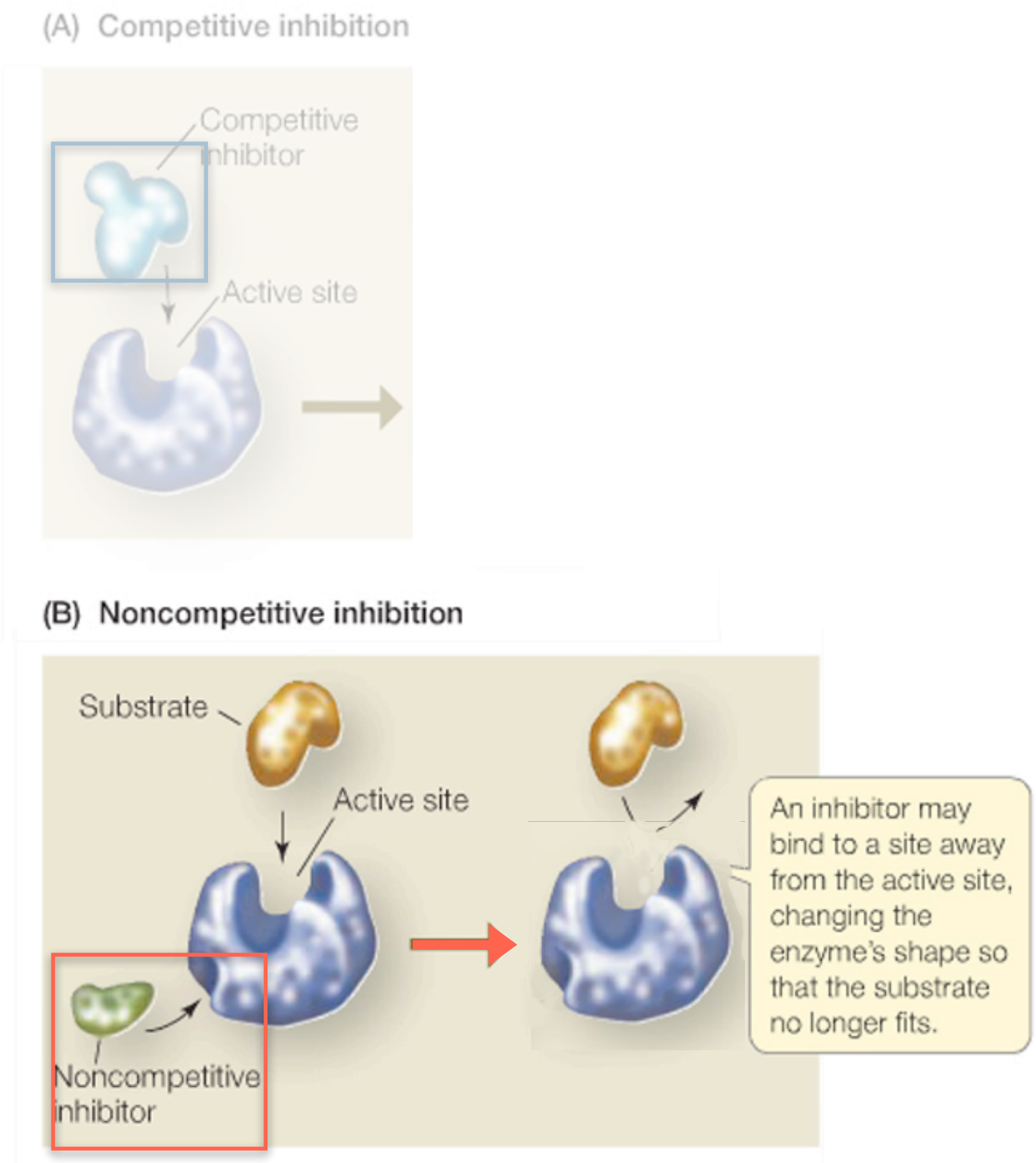

COOH
H
C
R
NH2
COOH
R
C
H
NH2



8.16 Reversible Inhibition (A) A competitive inhibitor binds temporarily to the active site of an enzyme. (B) A noncompetitive inhibitor binds temporarily to the enzyme at a site away from the active site. In both cases, the enzyme's function is disabled for only as long as the inhibitor remains bound.



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Metabolism can be divided into two types of “collective” enzymatic activities: **anabolic** and **catabolic** reactions.

Anabolic reactions are those that link simple molecules together to make complex ones. These are energy-storing reactions.....(e.g.condensation reactions?)

Anabolic reactions, which make single products from many smaller units; reactions **"consume" the useable energy.**

Catabolic reactions may reduce an organized substance, such as a glucose molecule, into smaller more randomly distributed substances, such as carbon dioxide and water; such reactions generally **"release" useable energy.**

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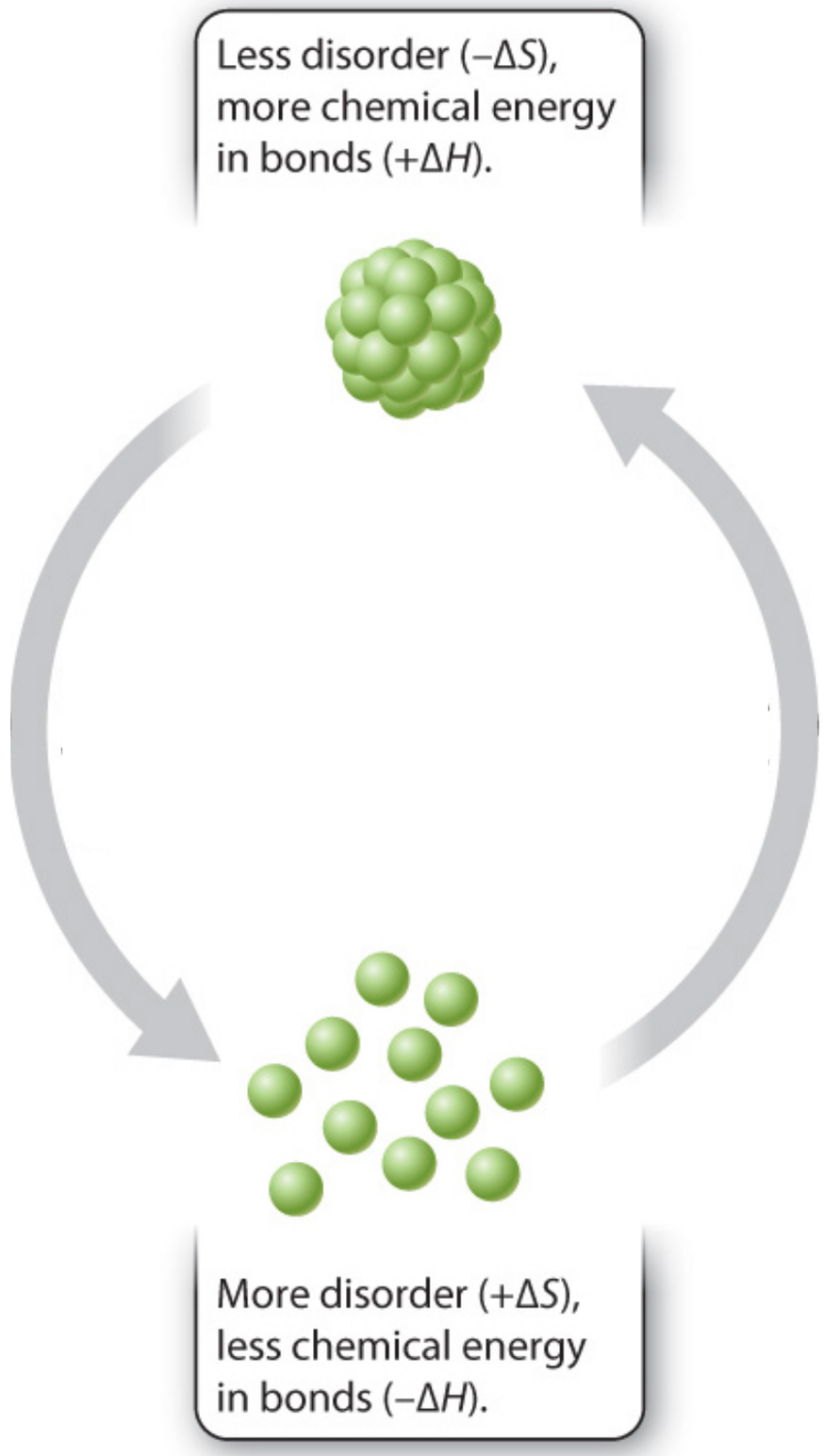
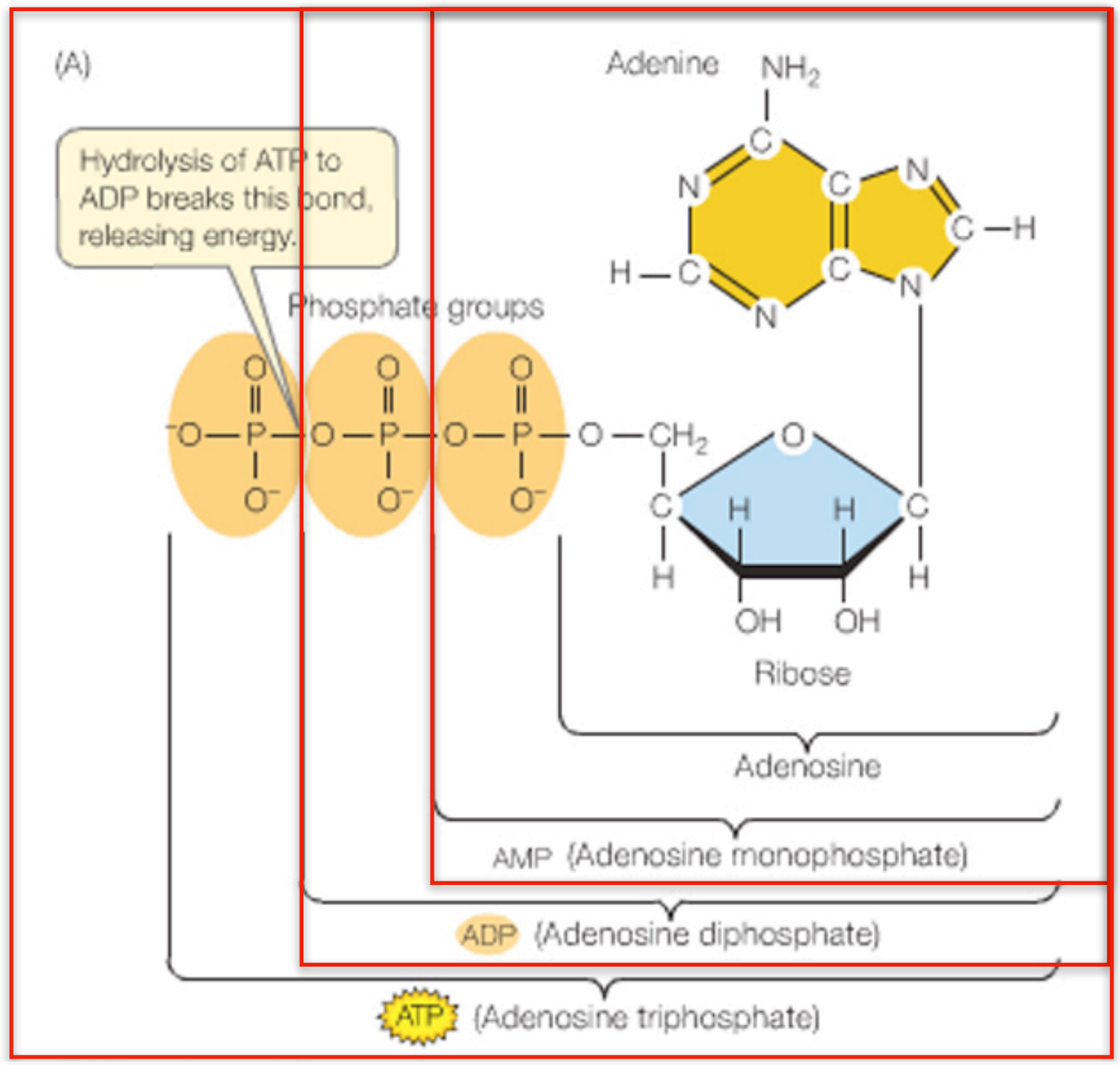

Less disorder (−ΔS), more chemical energy in bonds (+ΔH).
More disorder (+ΔS), less chemical energy in bonds (−ΔH).

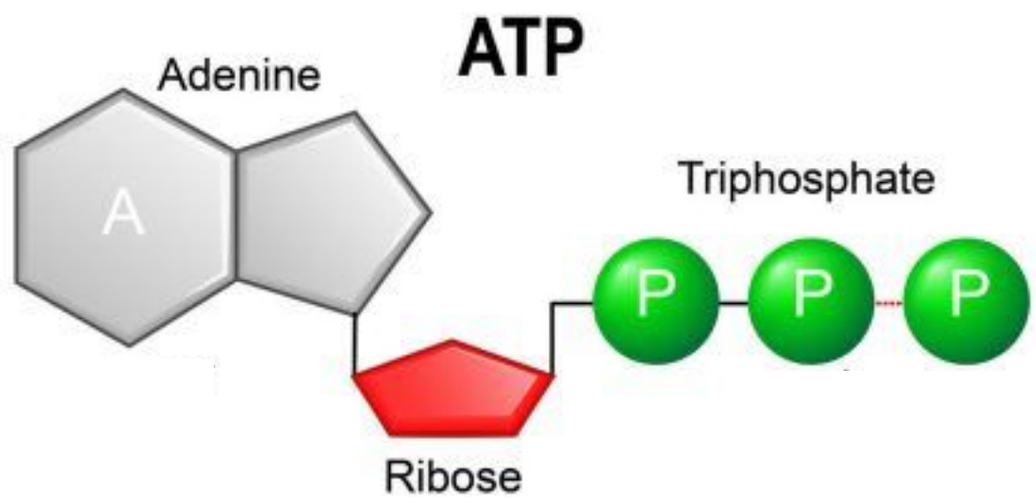
Metabolism:

ATP + H_2O ----> ADP + Pi + free energy.

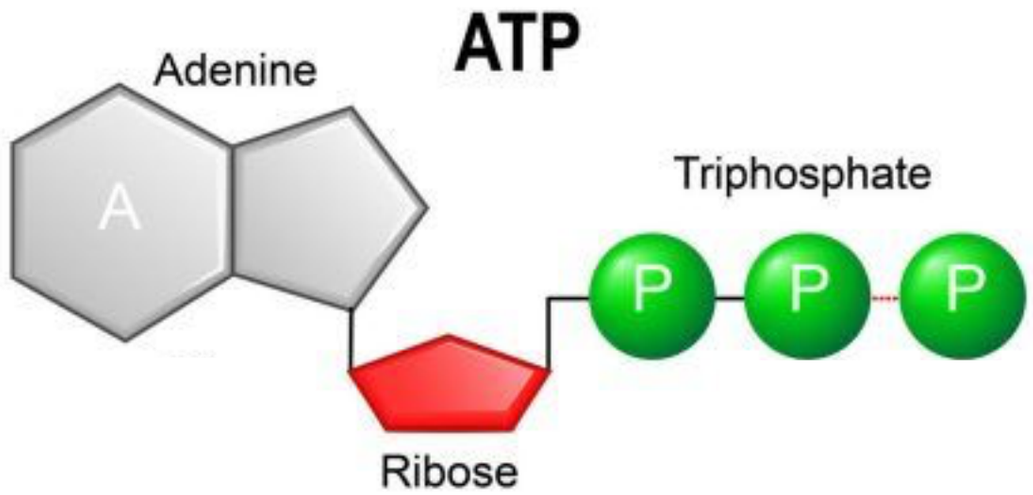


(B) *Luciola cruciata*

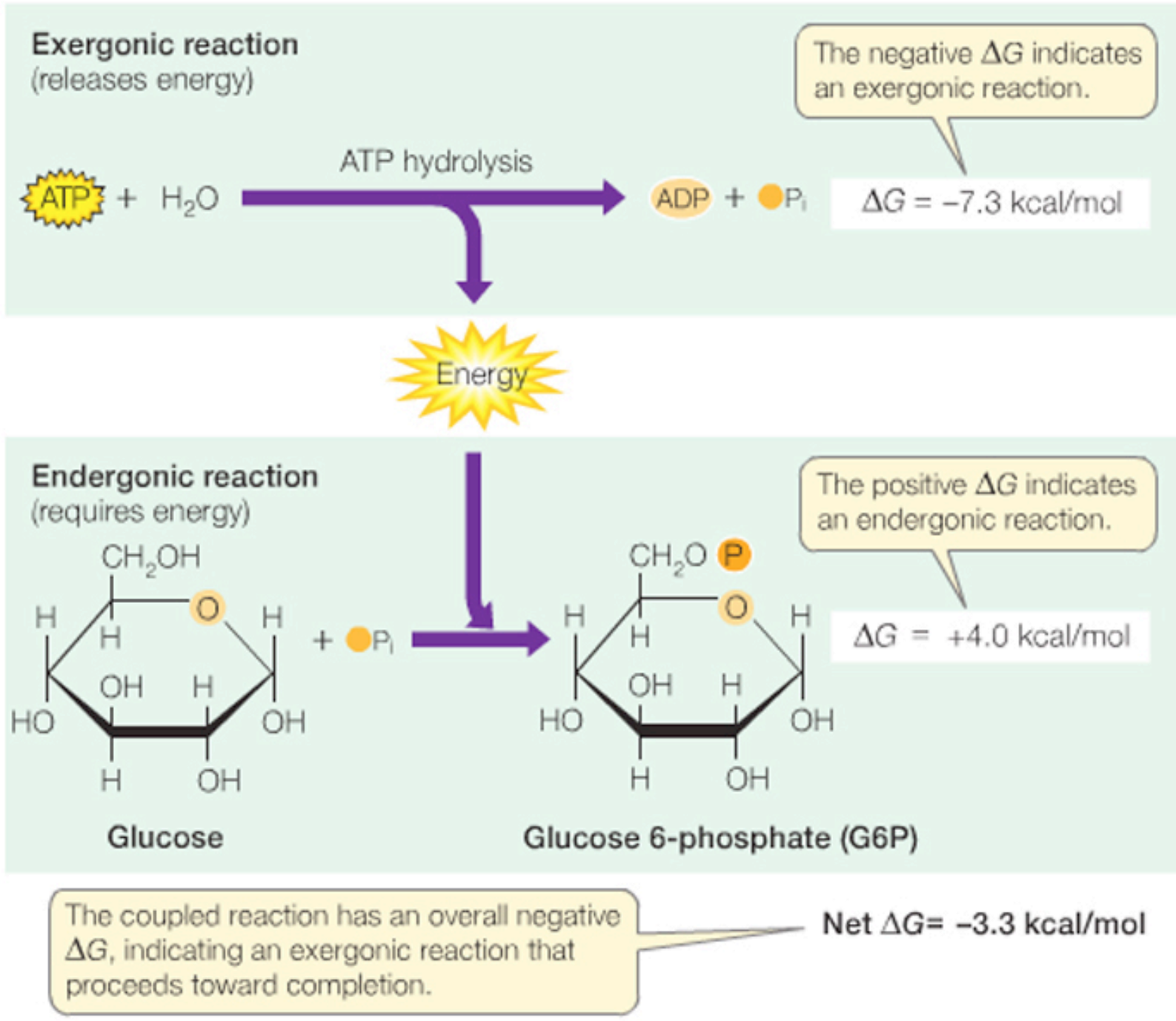
Metabolism:



Metabolism:



Metabolism:



8.7 Coupling of ATP Hydrolysis to an Endergonic Reaction The addition of phosphate derived from the hydrolysis of ATP to glucose forms the molecule glucose 6-phosphate (in a reaction catalyzed by hexokinase). ATP hydrolysis is exergonic and the energy released drives the second reaction, which is endergonic.

Metabolism:

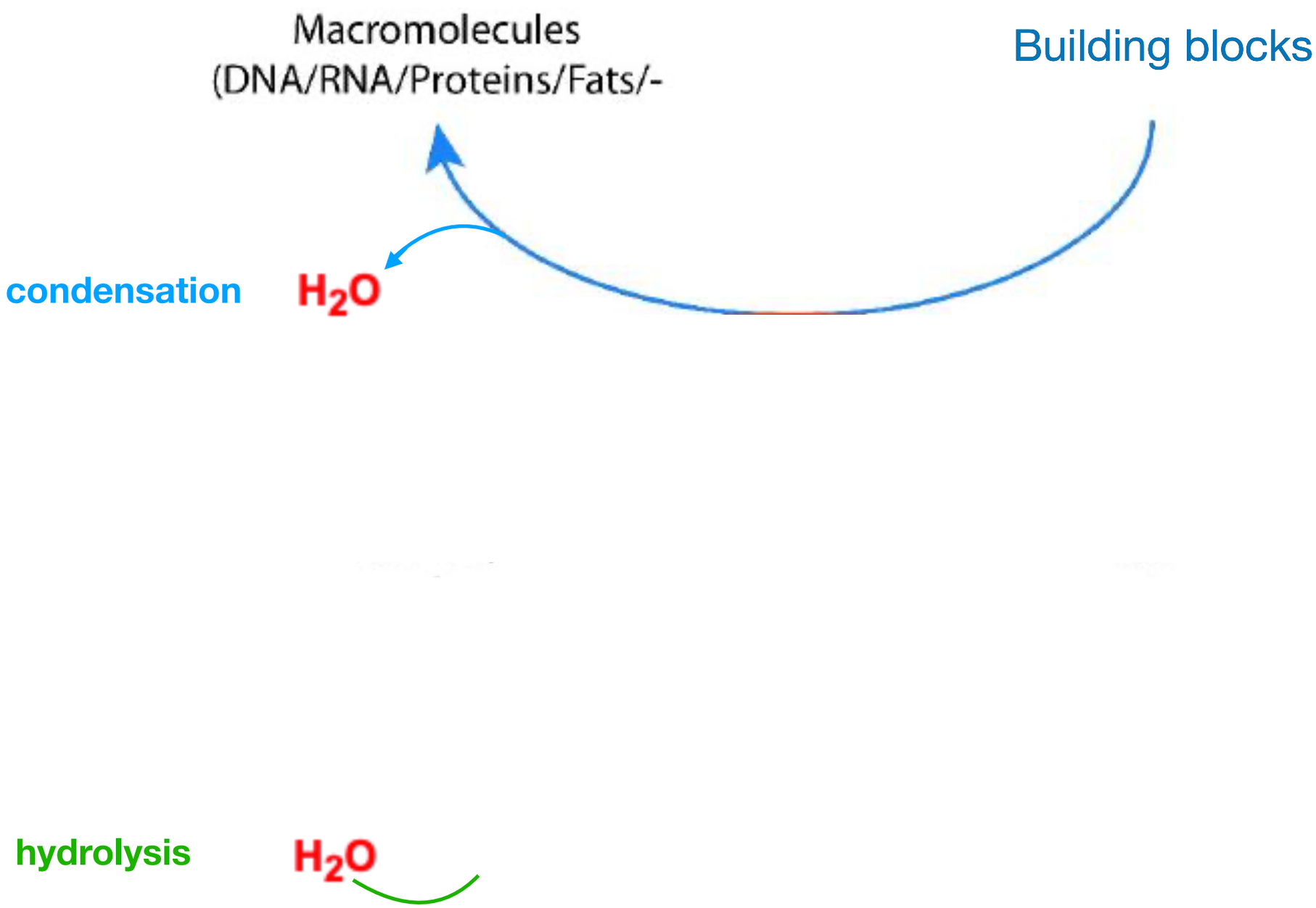
$$ATP + H_2O \text{ ----> } \boxed{ADP + Pi + \text{free energy}}$$

The change in standard free energy ($\Delta G^{o\prime}$) ~ **7.3 kcal/mol** at a living cell's typical temperature and pH.

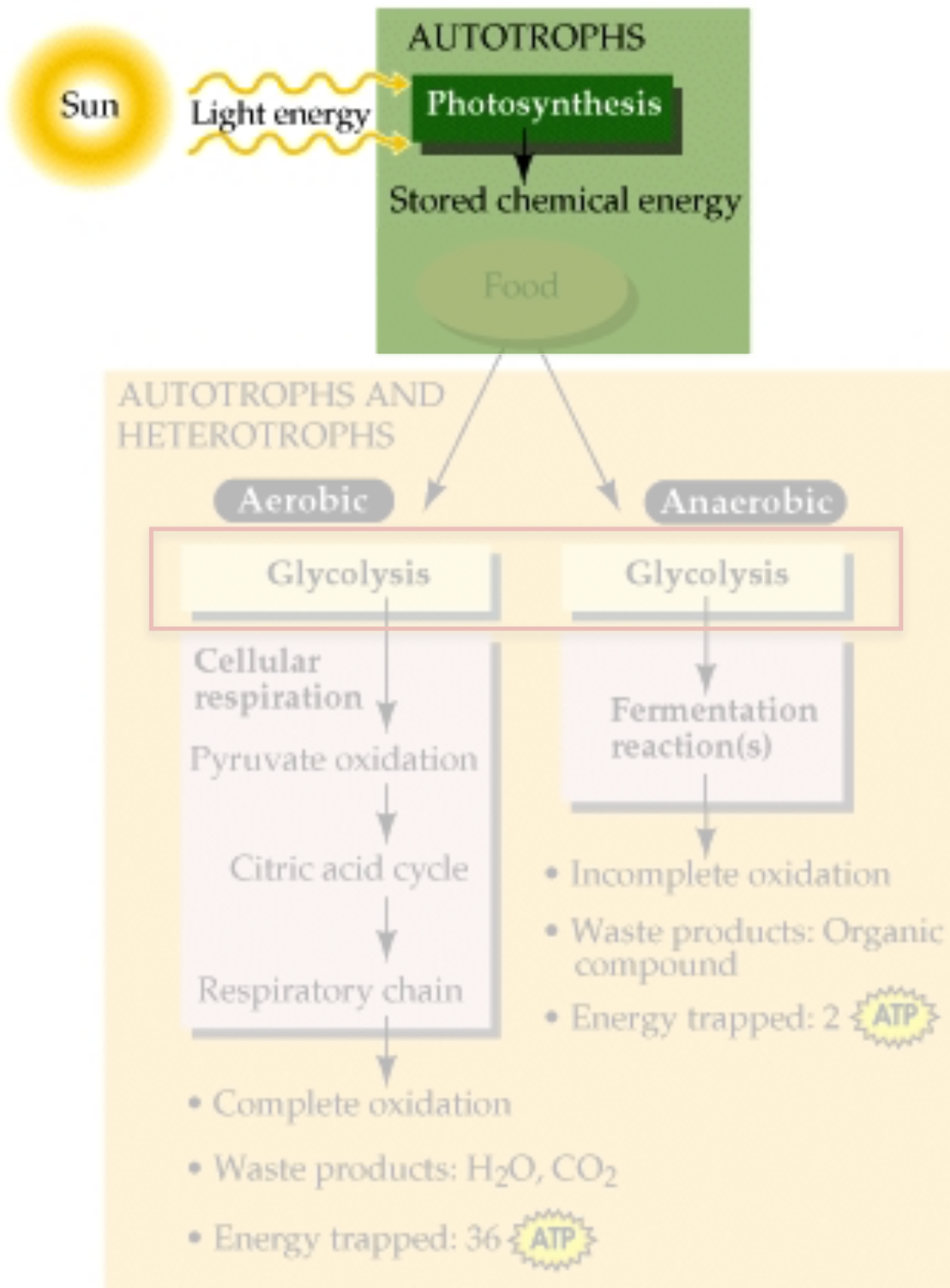
The equilibrium for this reaction is far to the right of the equation shown above, greatly favouring the **production of ADP**;

So much so that there are approximately 1×10^7 ADP molecules to each remaining ATP.

Making ATP from ADP (anabolic reaction) involves overcoming repulsive negative charges on the phosphates to be joined, the very same forces that provide the "free energy" released when ATP is broken apart to form ADP.


Macromolecules
(DNA/RNA/Proteins/Fats/-
Building blocks
condensation
H_2O
hydrolysis
H_2O

Metabolism: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Photosynthesis
Stored chemical energy
Food
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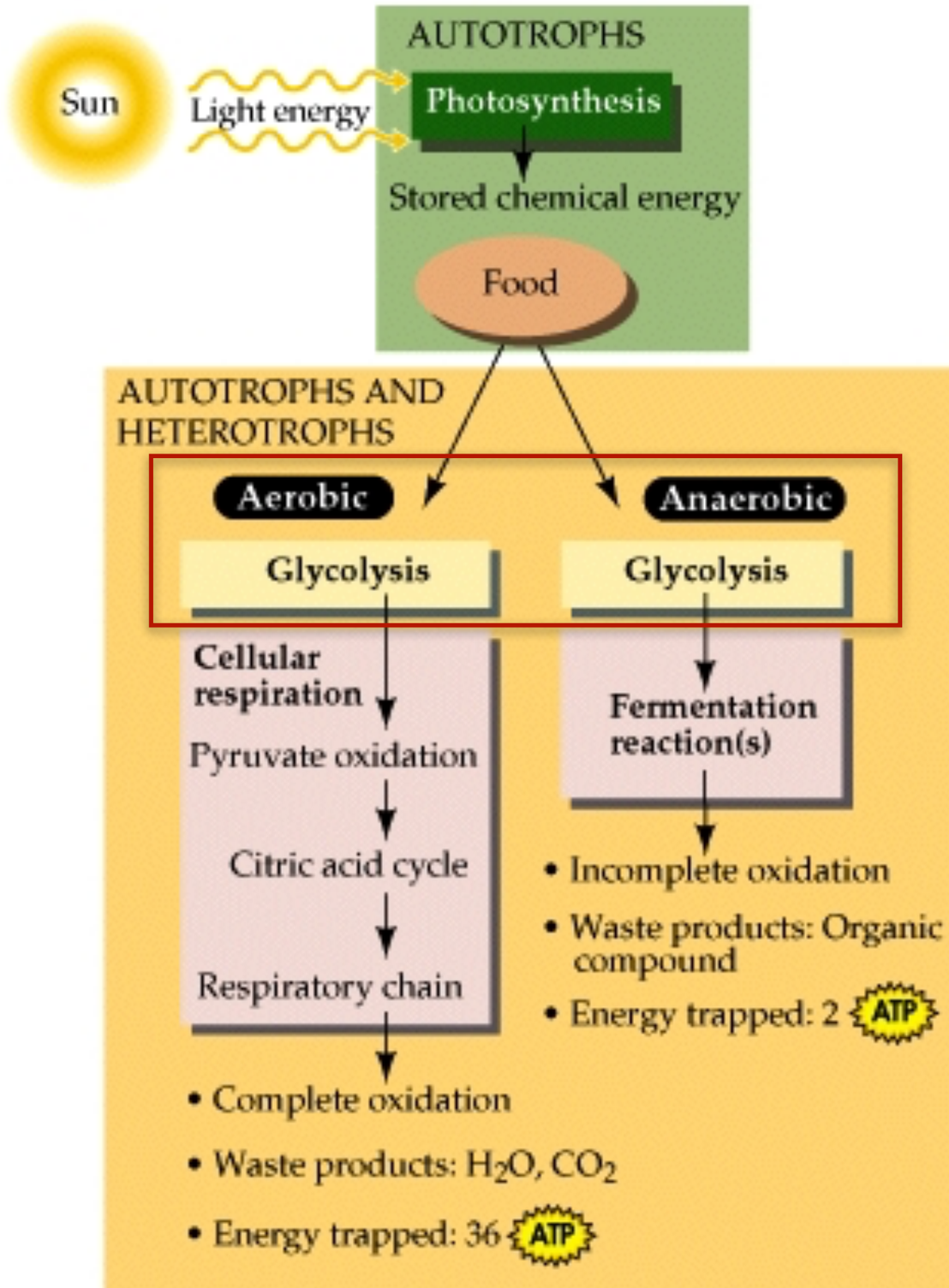
Fermentation reaction(s)
• Incomplete oxidation
• Waste products: Organic compound
• Energy trapped: 2 ATP
• Complete oxidation
• Waste products: H_2O, CO_2
• Energy trapped: 36 ATP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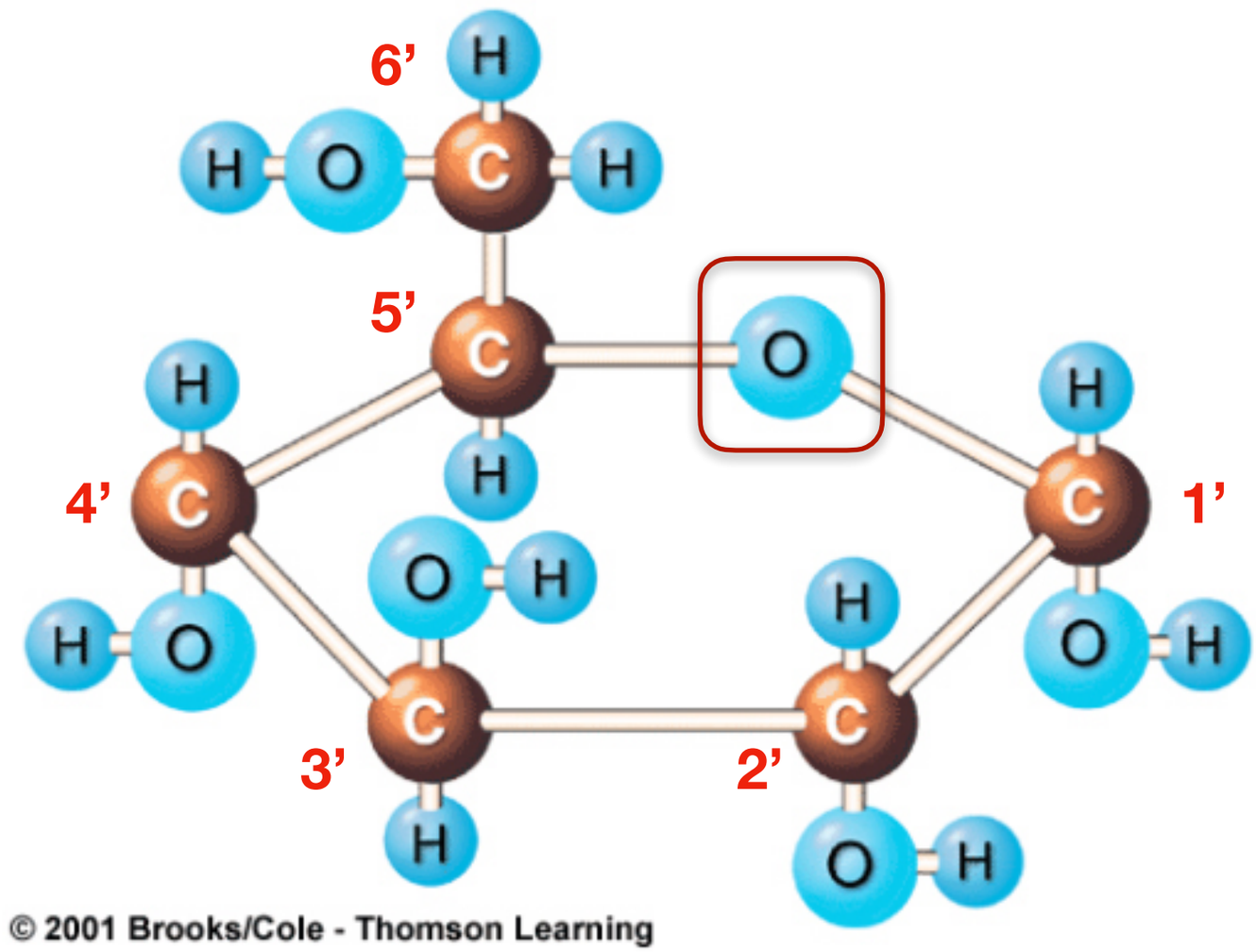
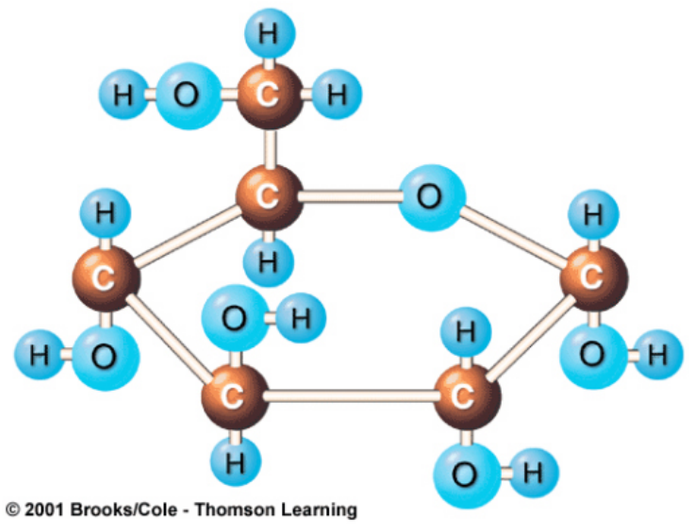


GLUCOSE



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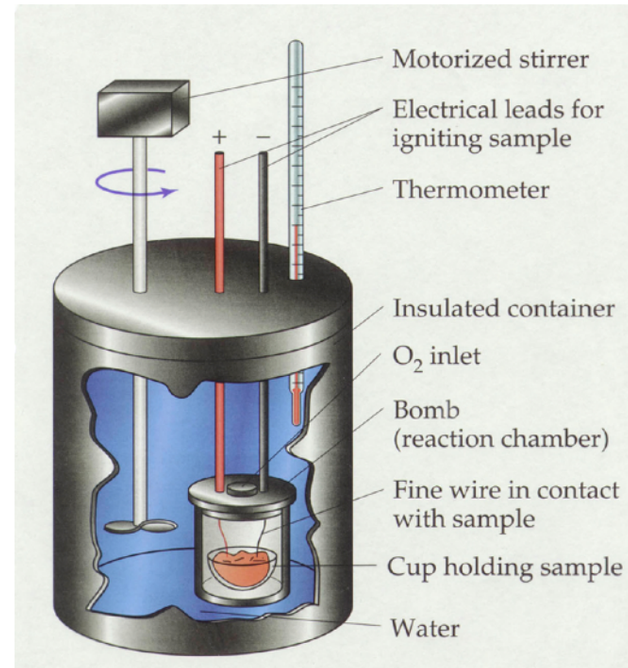


- 686 kcal/mol.

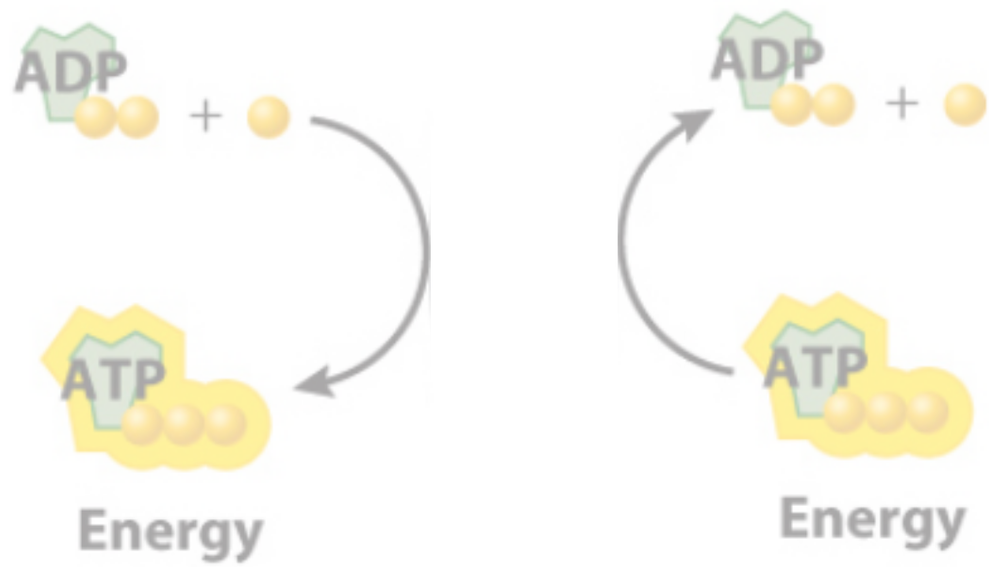
$$C_6H_{12}O_6 + 6\ O_2 \text{ --->} 6\ CO_2 + 6\ H_2O + \text{energy (heat and light).}$$

Respiration

- 686 kcal/mol

Metabolism:

1 mole of Glucose —> - 686 kcal/mol

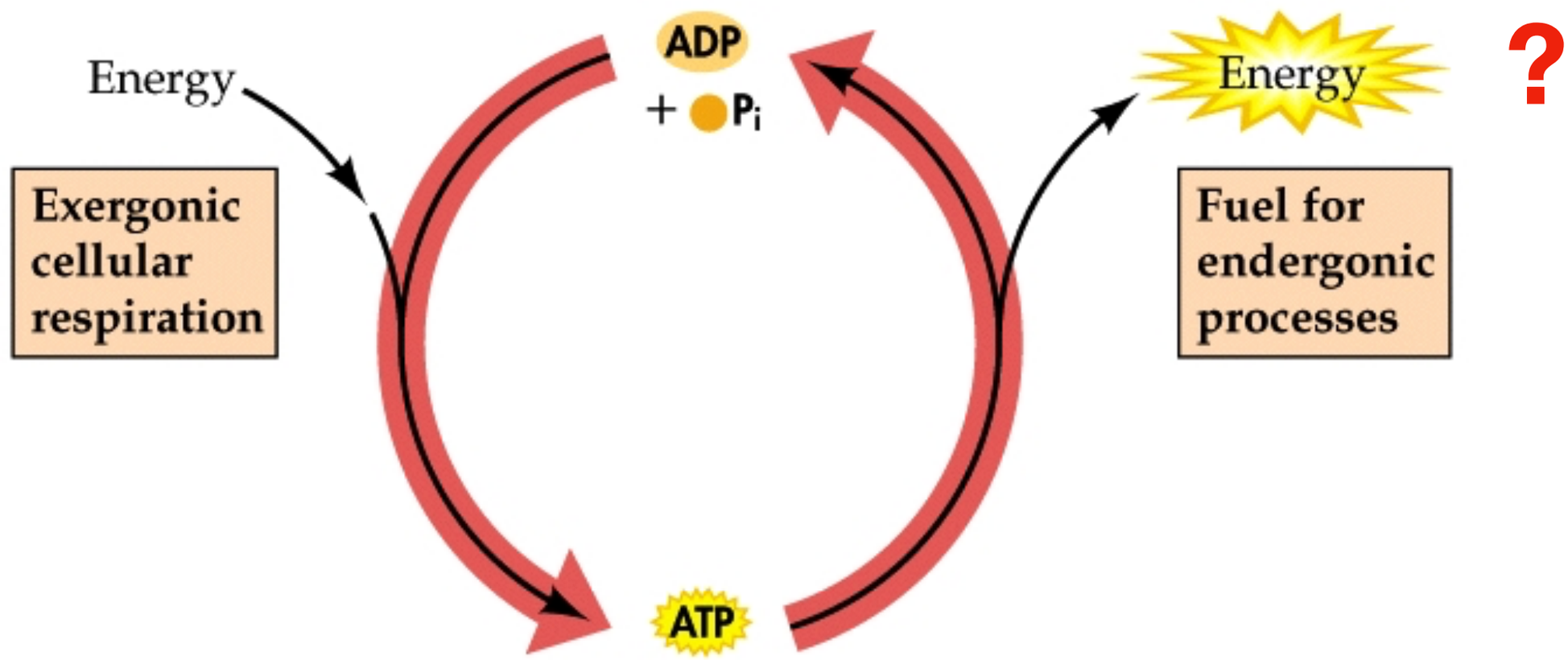


- 7.3 kcal/mol

1 mole of Glucose —> ~~~94~~ ATP's worth of energy

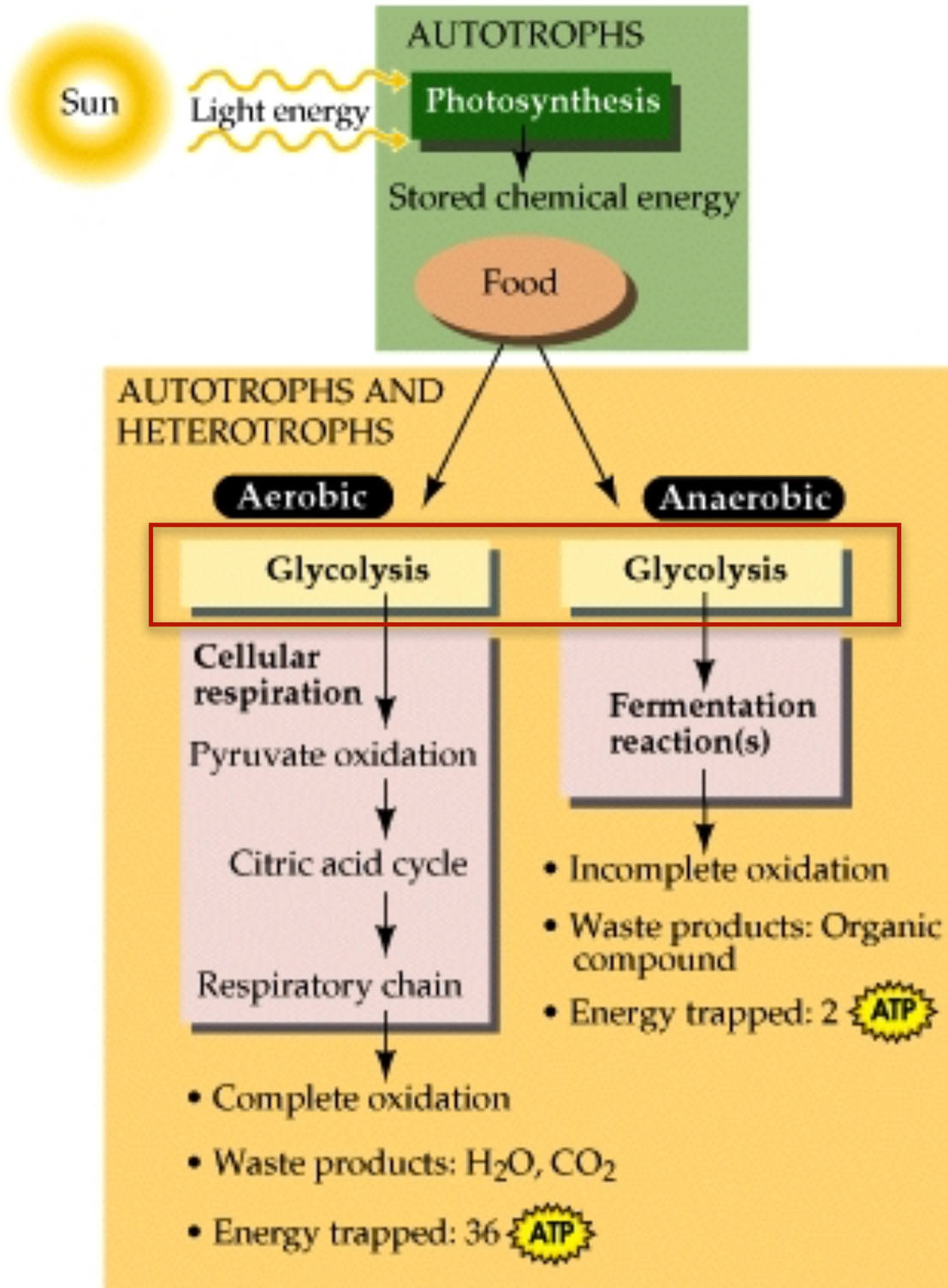
Metabolism:

- **686 kcal/mol**



Some kinds of cells metabolize glucose **incompletely**, and others do a much more efficient job and metabolize it **completely**.

Metabolism: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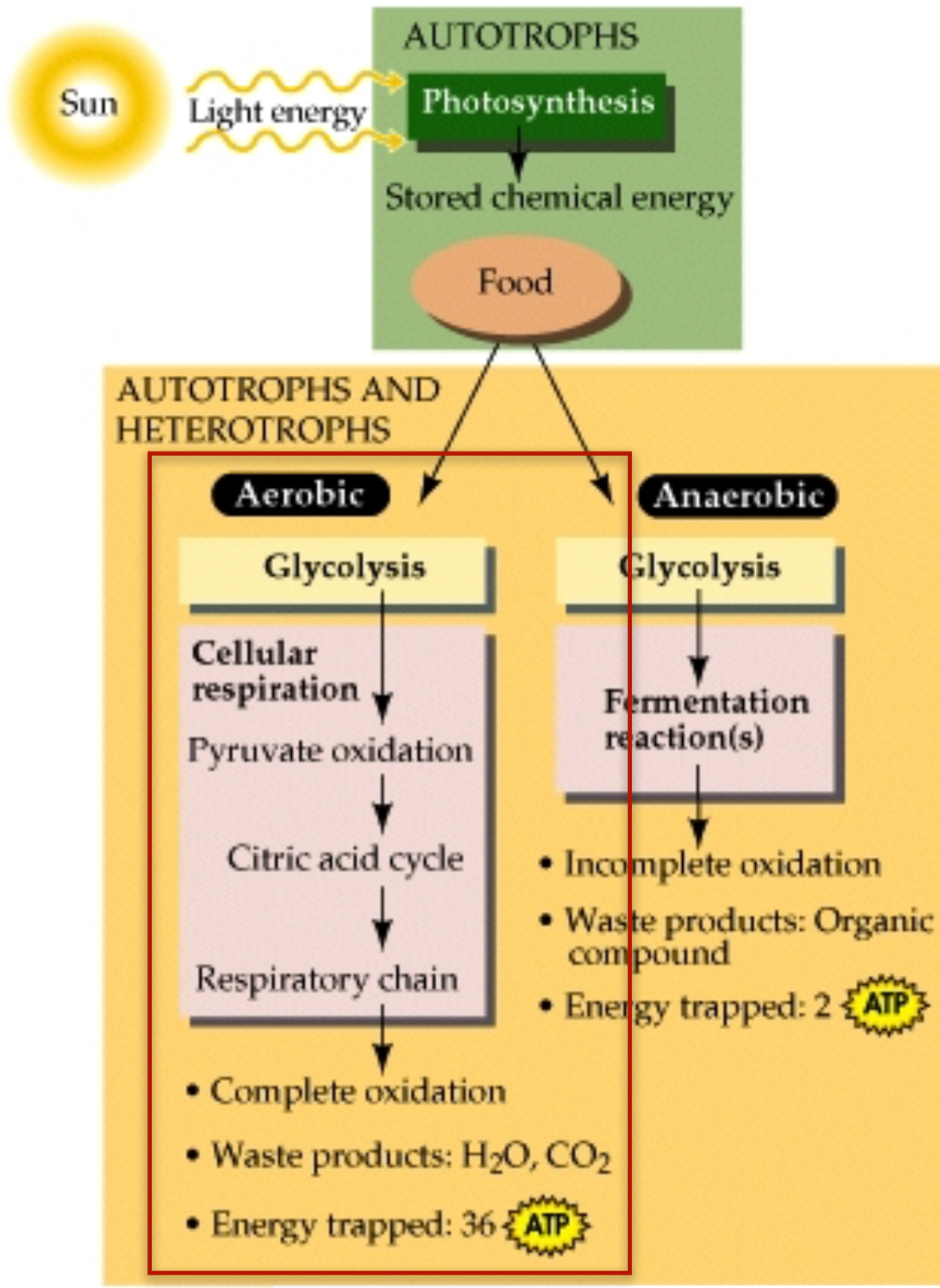
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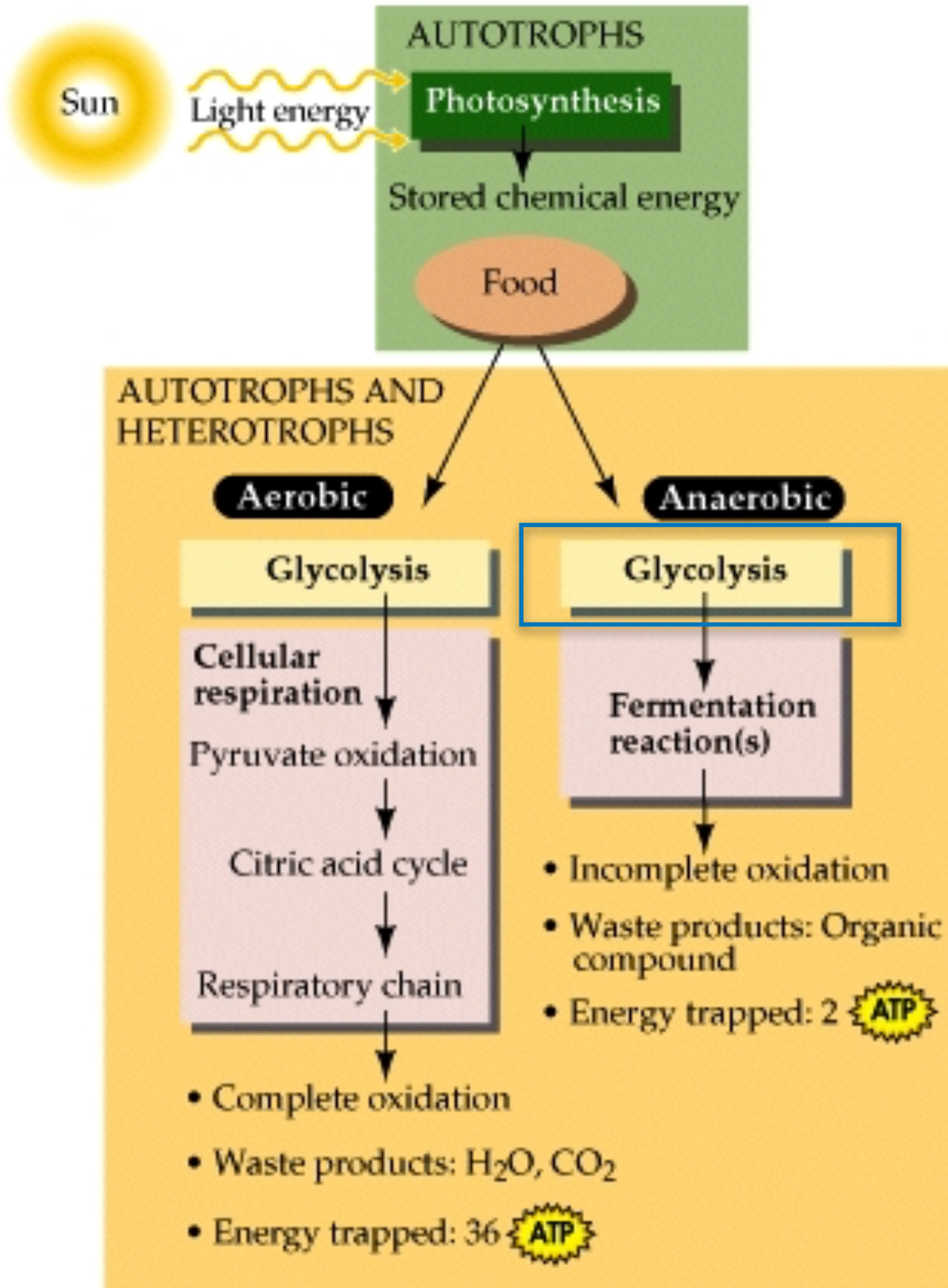
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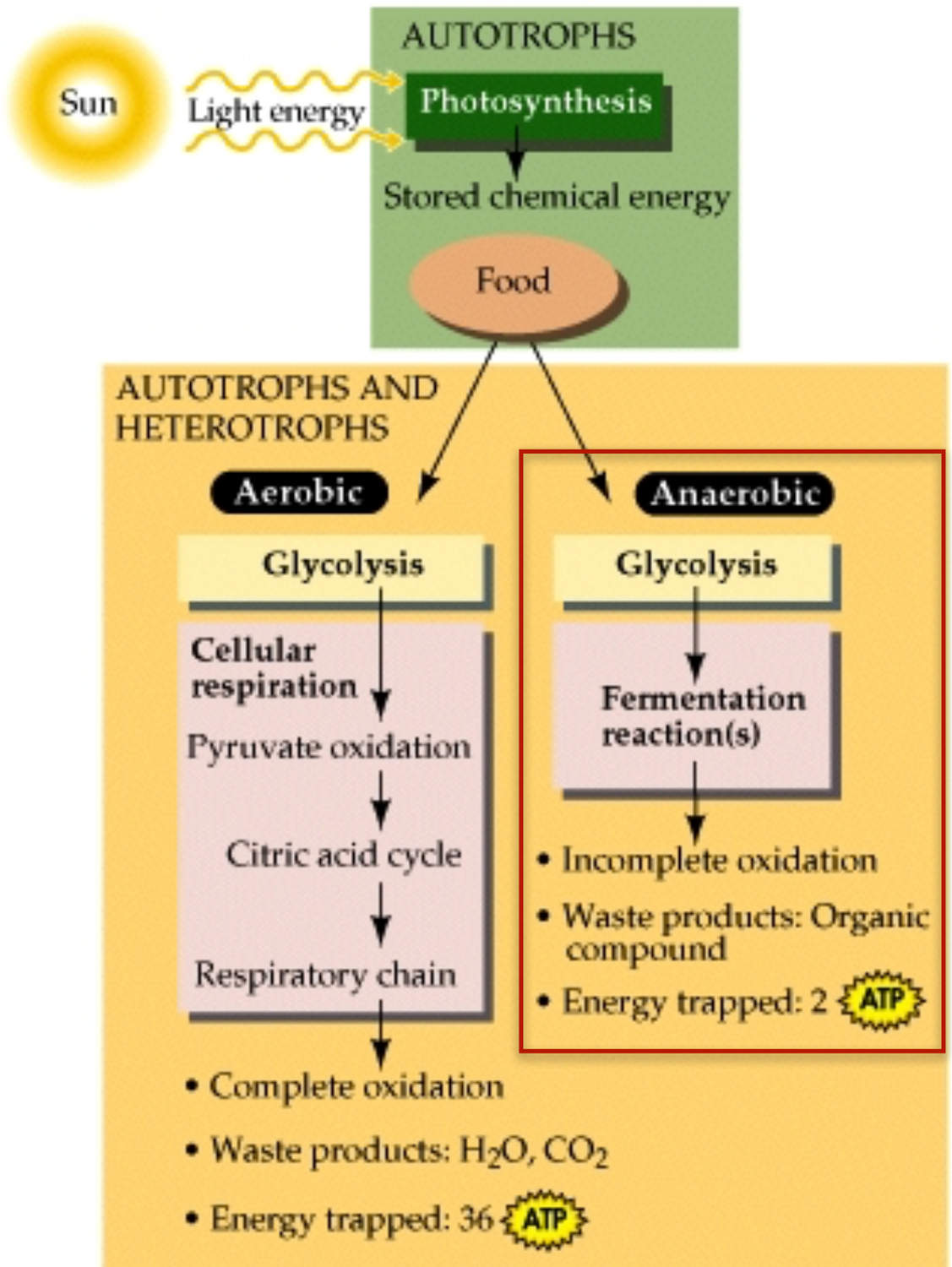
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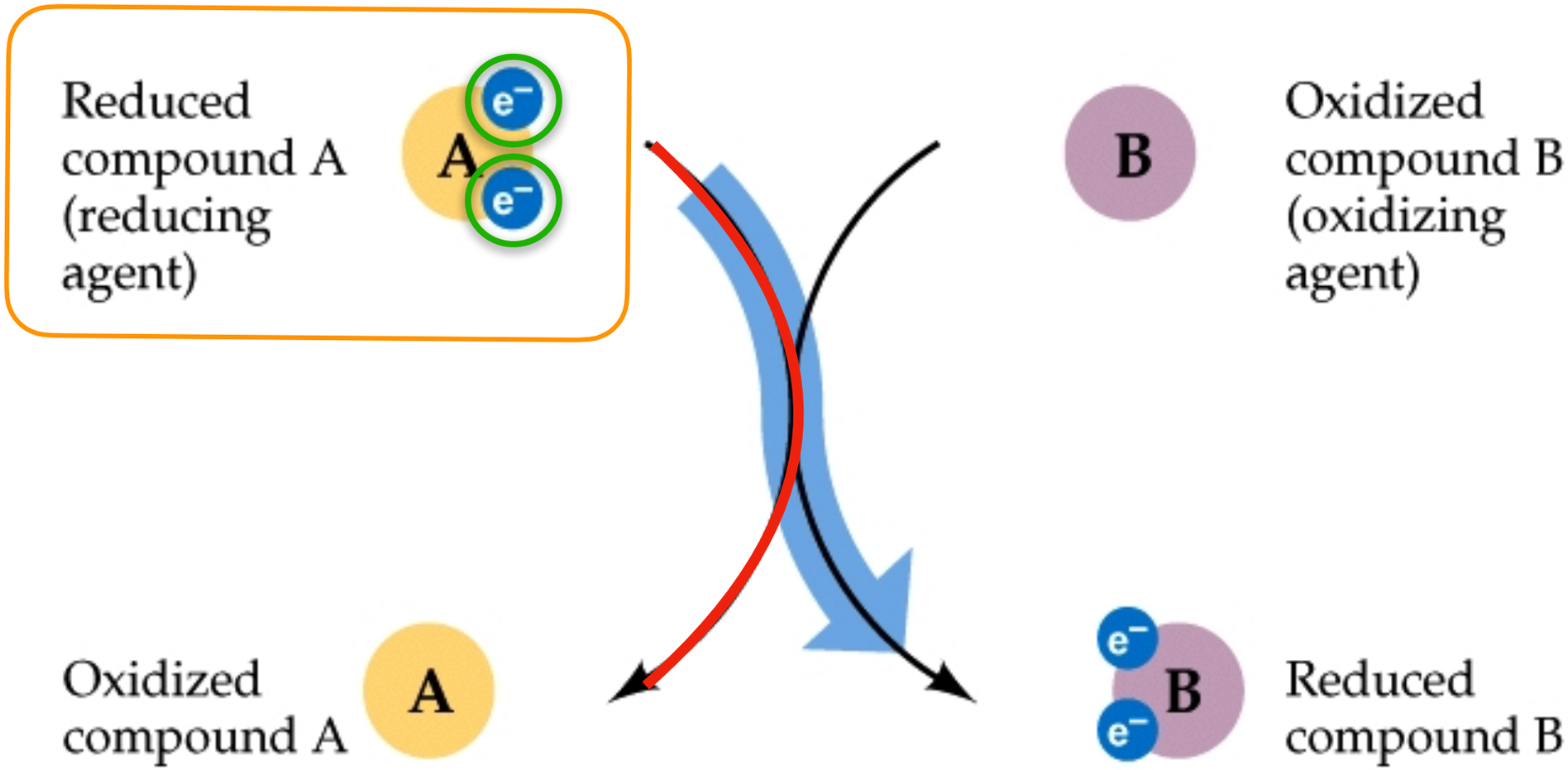
REDOX REACTIONS



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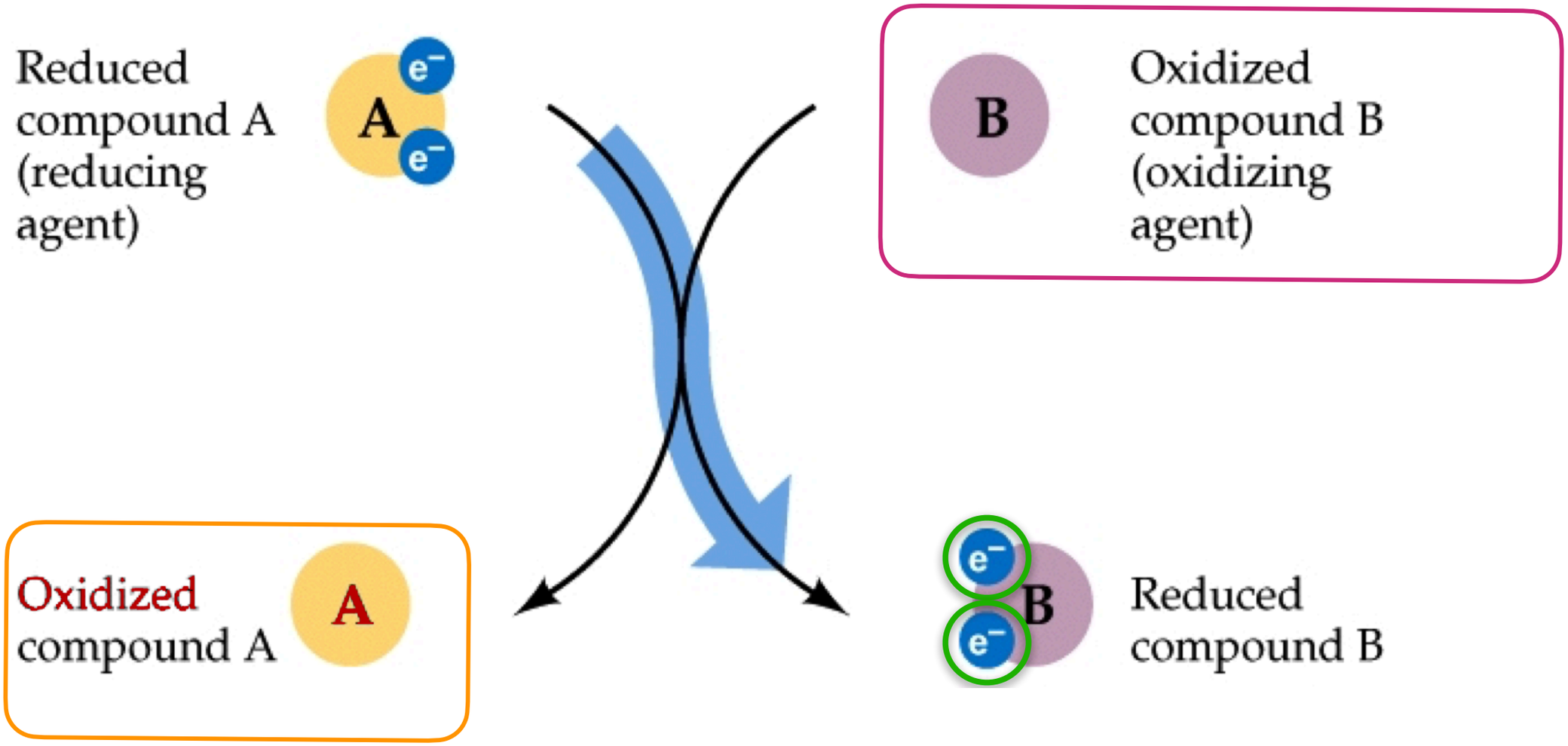

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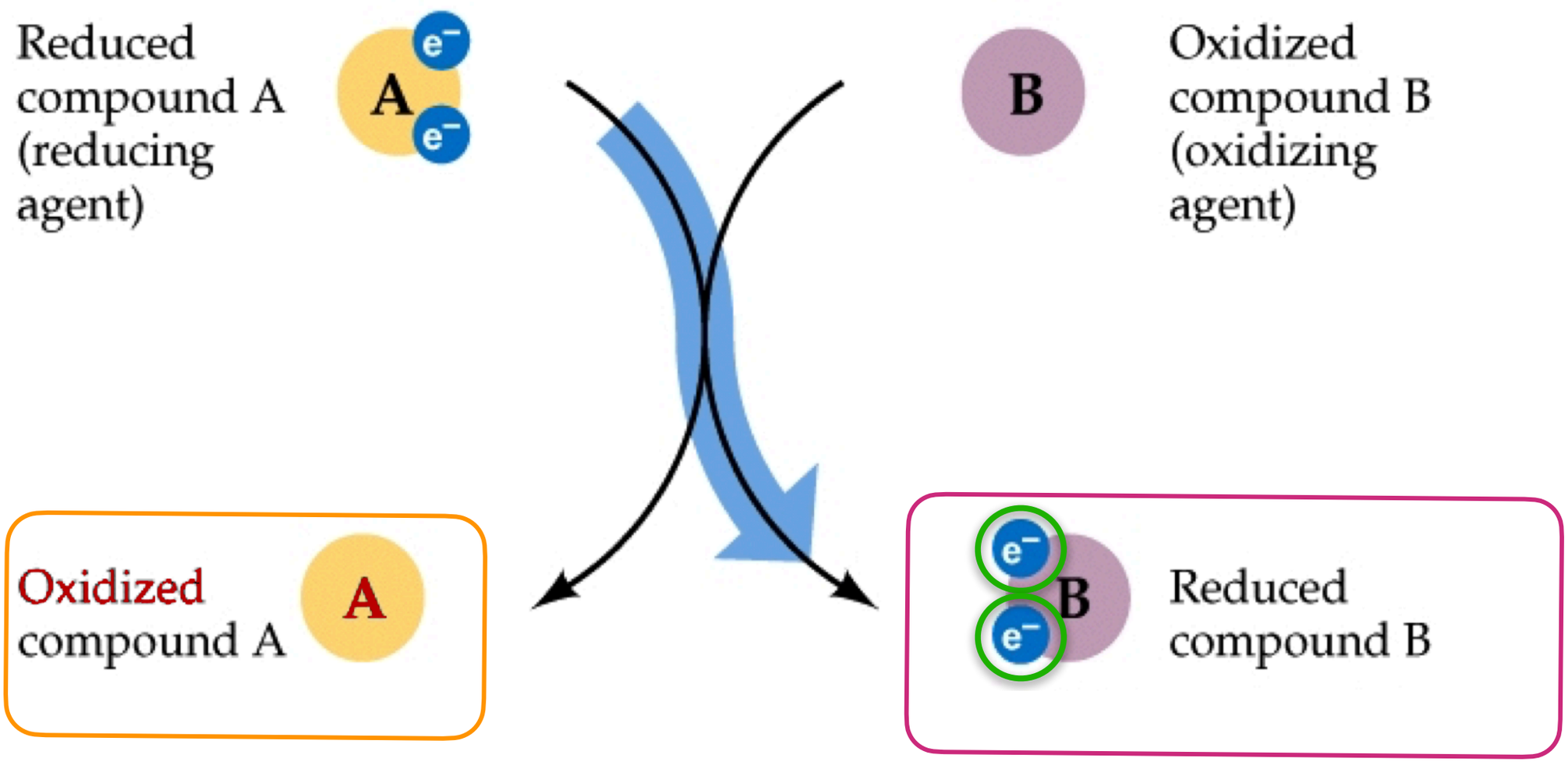


REDOX REACTIONS

….which involve that rather important element "hydrogen" and the transfer of energy of reactions from one form to another.

Simply put:

A **GAIN** of one or more **electrons** or **hydrogen atom(s)** is called **reduction.**

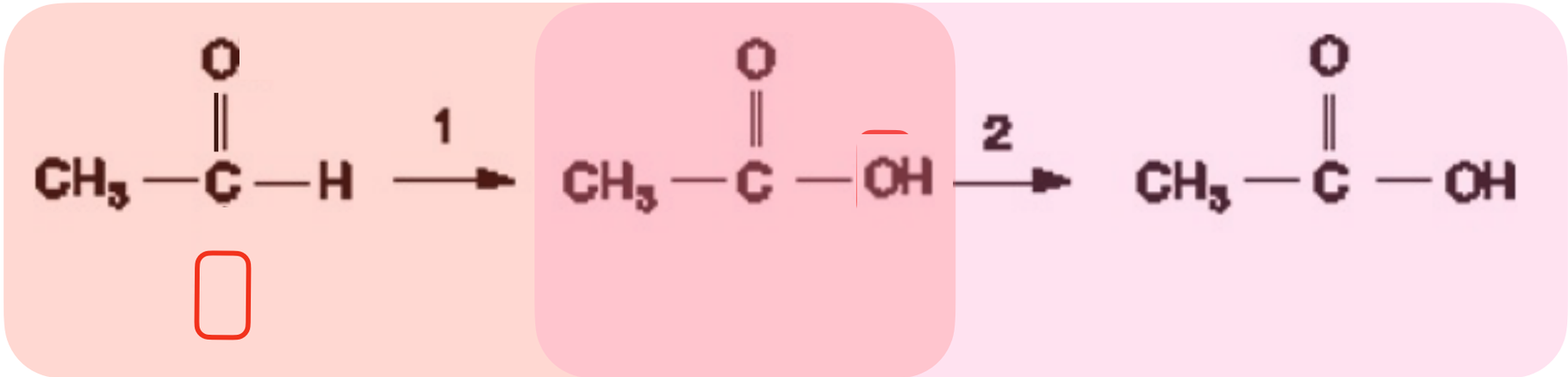
The **LOSS** of one or more **electrons** or **hydrogen atom(s)** is called **oxidation.**

Whenever one material is reduced, another is oxidized.

REDOX REACTIONS

If a carbon compound gains a bond with hydrogen, the compound is reduced.

If a carbon compound loses a bond with hydrogen, the compound is ***oxidized****.*



Reaction 1 of the above diagram is oxidation because the changed carbon loses a bond with hydrogen.

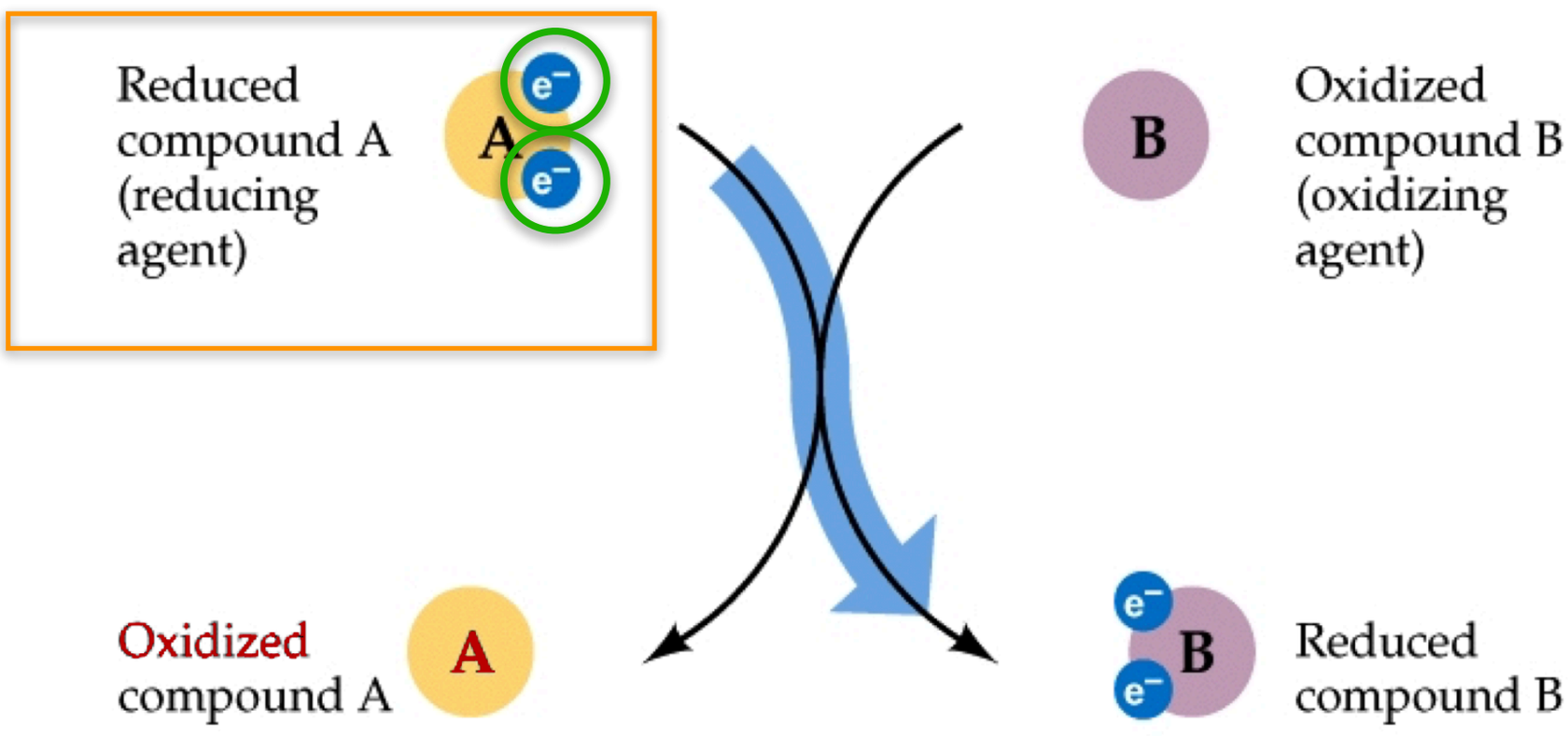
Reaction 2 is also oxidation because the central carbon in the reactant loses a hydrogen bond (even though the compound as a whole still has the same amount of hydrogens).

REDOX REACTIONS

As a result of all this…..

An **OXIDIZING agent** **ACCEPTS** an electron **OR** hydrogen atom **(a proton + electron)**.

A **REDUCING agent** **DONATES** an electron **OR** hydrogen atom **(a proton + electron)**.



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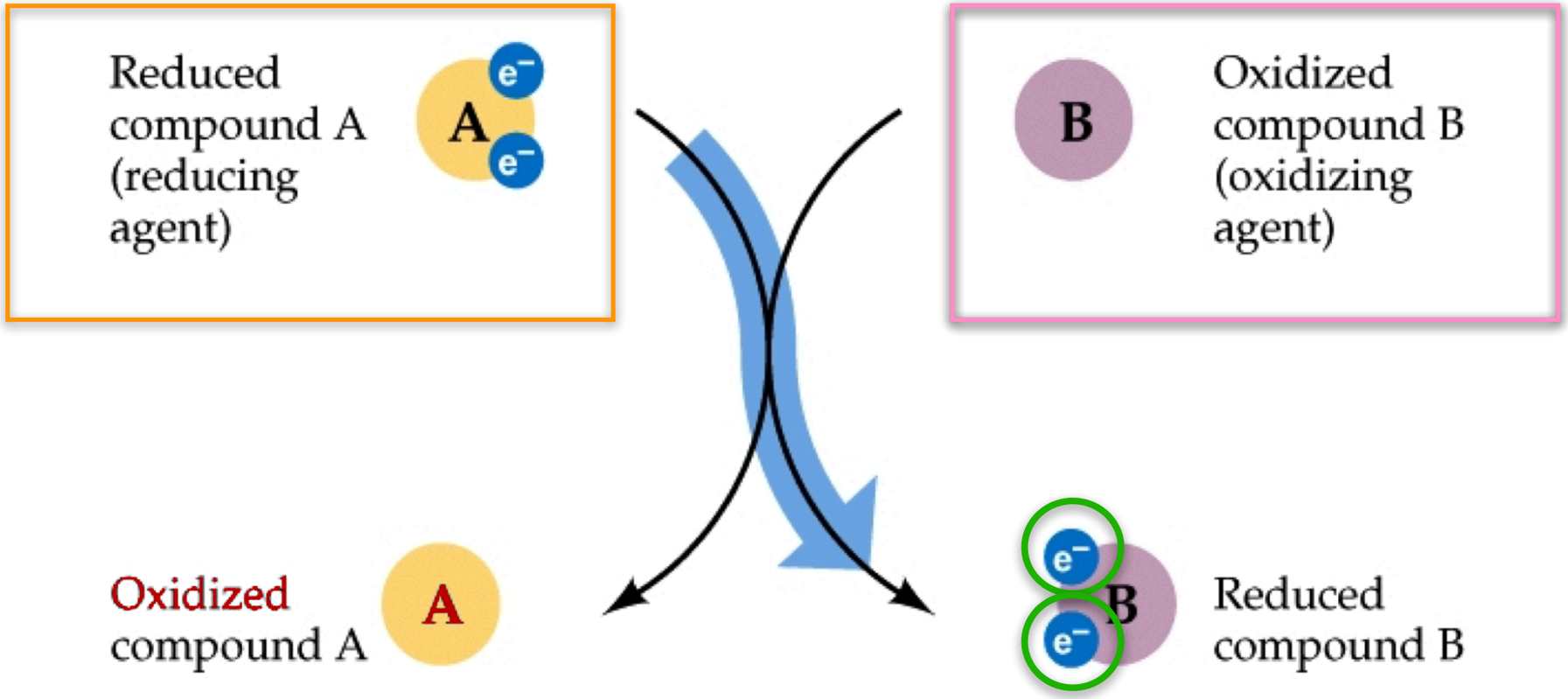

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REDOX REACTIONS

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Indeed the ultimate **RED OX** reaction (in the biological world) is the formation of

If you mix **Hydrogen** gas and **Oxygen** together in a sealed glass beaker…
but if you add just a little bit of heat (activation energy)…

REDOX REACTIONS

Cells don't just explode

Moreover, cells do not have any Hydrogen molecules hanging around (or else they/ we would all float away…).

Even so, cells are able to harness the energy of sugar metabolism to create an almost equivalent reaction… to produce (of all molecules)…

$$C_6H_{12}O_6 + 6\ O_2 \text{ ---> } 6\ CO_2 + 6\ H_2O + \text{energy (heat and light)}$$

- 686 kcal/mol.

A major component of this energy is through **REDOX reactions**, as well as **ATP**

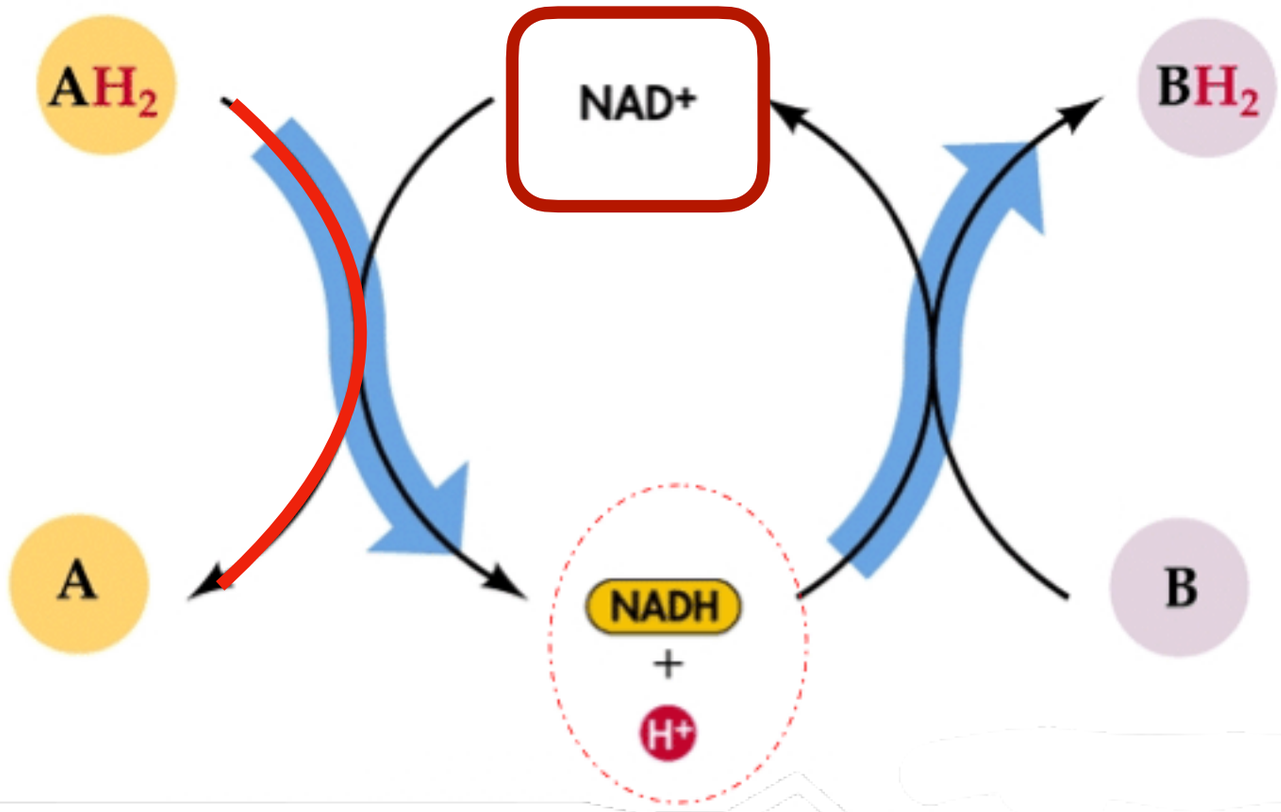
So, are there any molecules in the cell that are almost as explosive as Hydrogen when they **donate** their electrons…

6.1 A Few Examples of Nonprotein Molecular "Partners" of Enzymes

TYPE OF MOLECULE	ROLE IN CATALYZED REACTIONS
Cofactors	
Iron	Oxidation/reduction
Copper	Oxidation/reduction
Zinc	Helps bind NAD
Coenzymes	
Biotin	Carries $—COO^-$
Coenzyme A	Carries $—CH_2—CH_3$
NAD	Carries electrons
FAD	Carries electrons
Prosthetic groups	
Heme	Binds ions, O_2, and electrons; contains iron cofactor
Flavin	Binds electrons
Retinal	Converts light energy

Nicotinamide Adenine Dinucleotide (NAD^+)

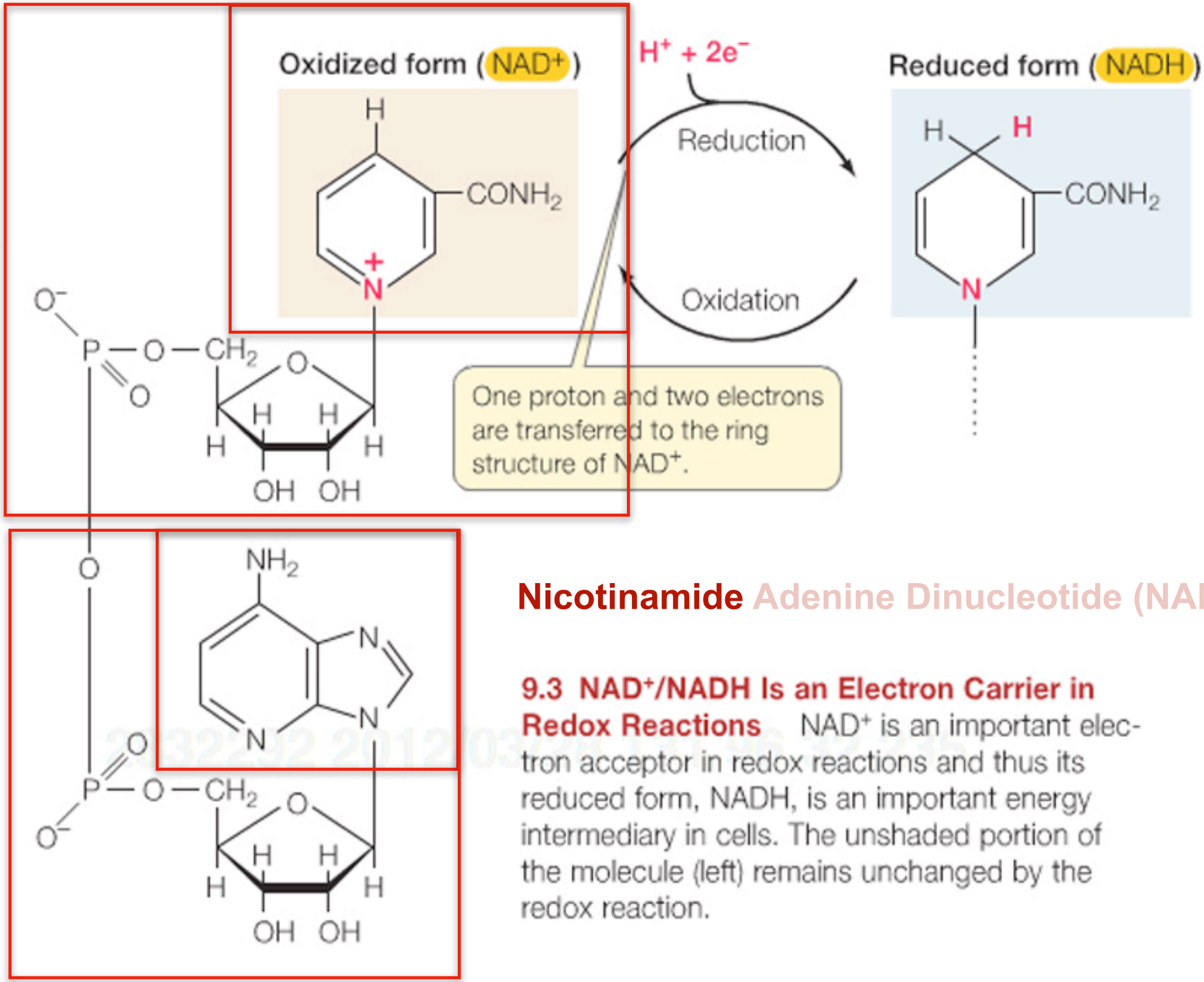
Example: electron carrier



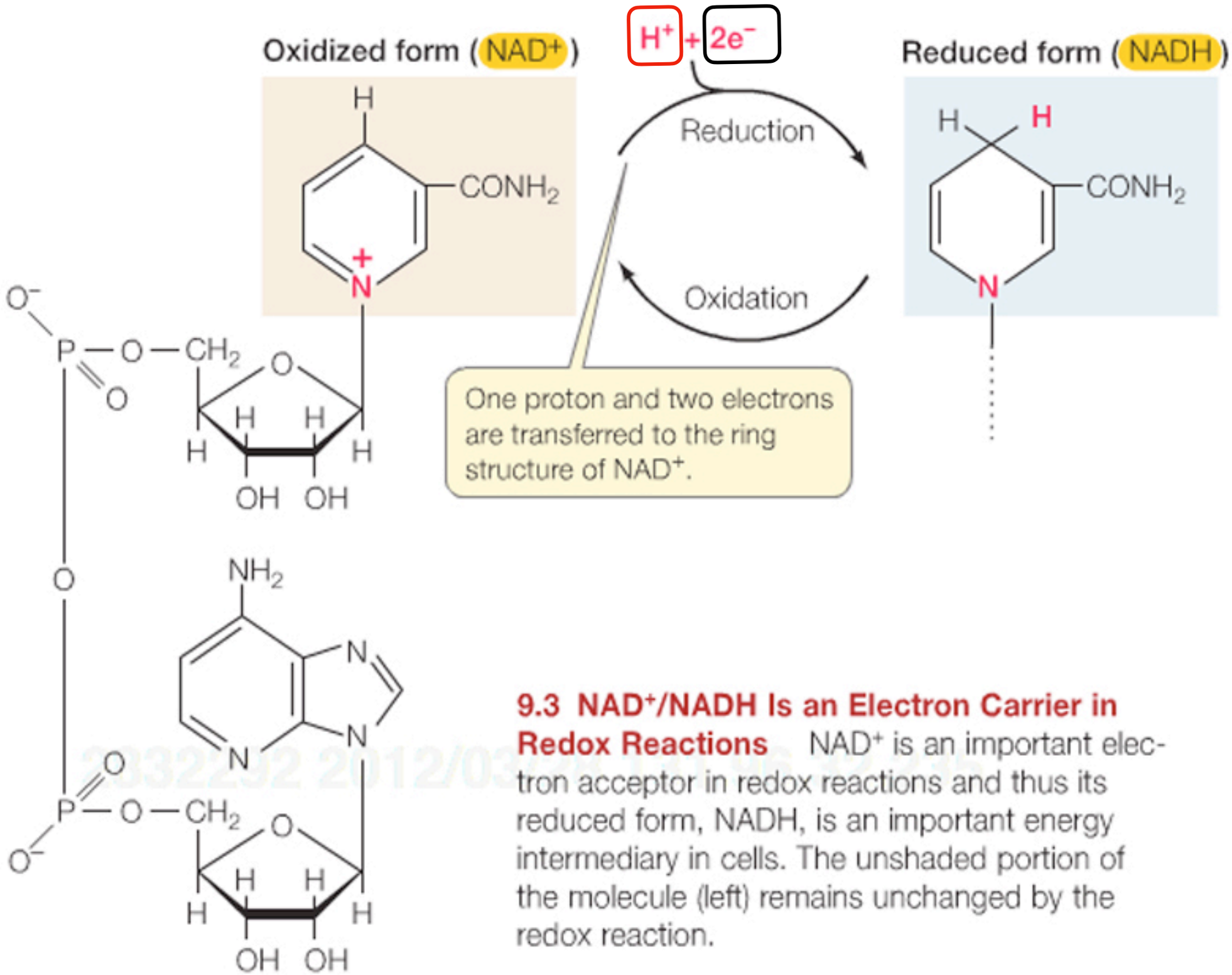
- each electron is associated with an H^+.

Molecule A $H \longrightarrow H^+ + e-$

$NAD^+ + 2e- (+H^+) \longrightarrow NADH + H^+$



9.3 NAD+/NADH Is an Electron Carrier in Redox Reactions NAD+ is an important electron acceptor in redox reactions and thus its reduced form, NADH, is an important energy intermediary in cells. The unshaded portion of the molecule (left) remains unchanged by the redox reaction.



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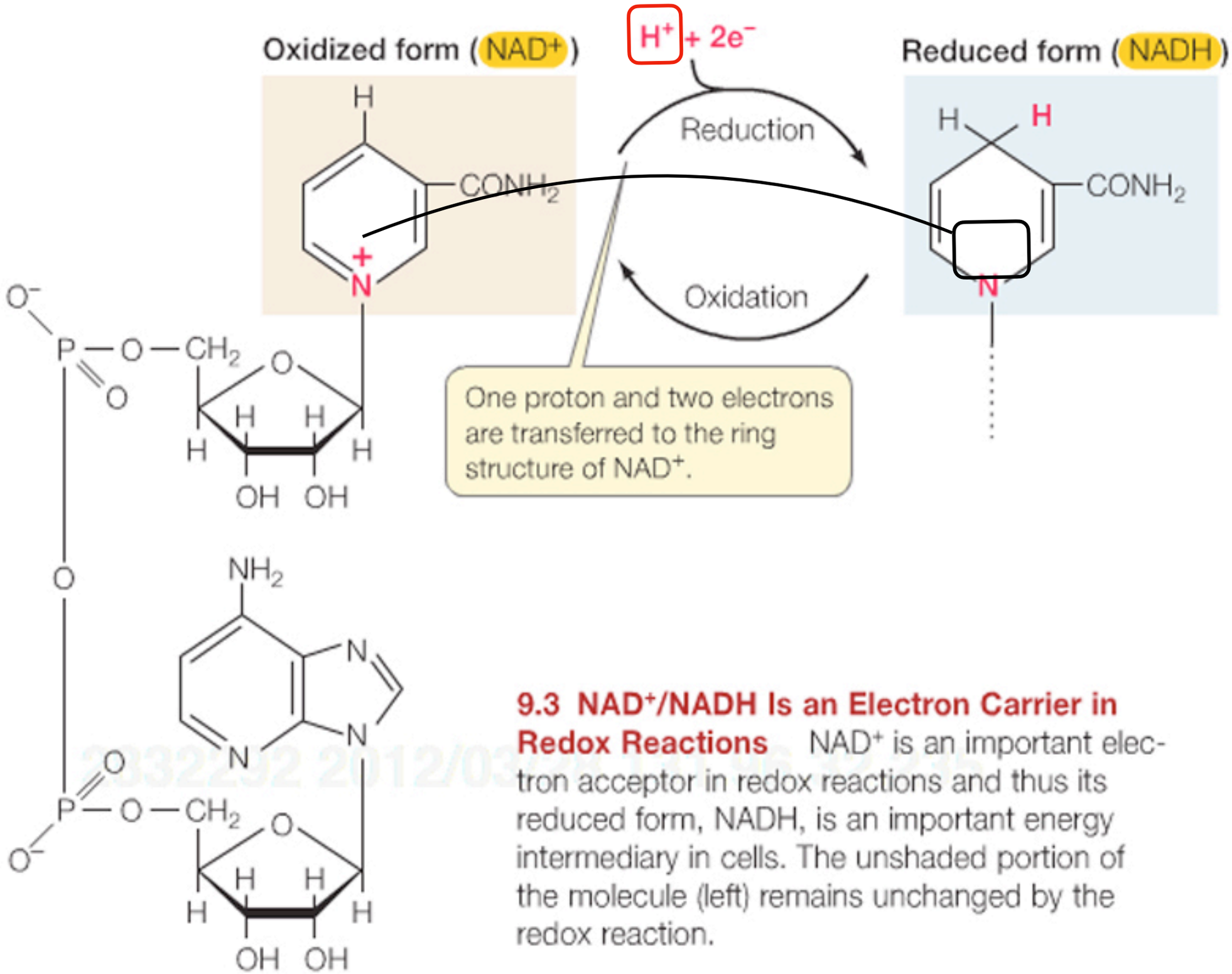

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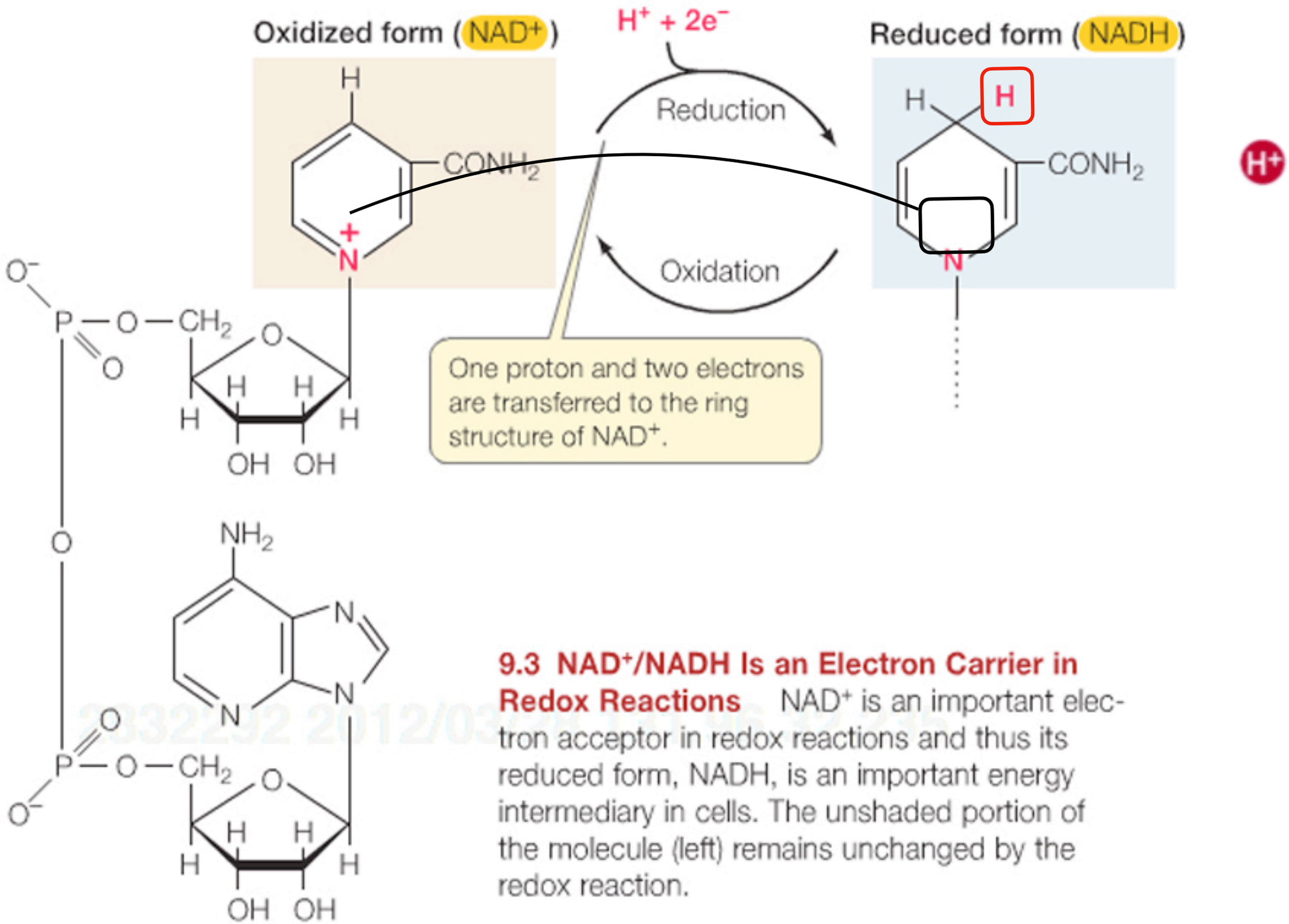
$NAD^+ + 2e^- + H^+ \longrightarrow NADH$



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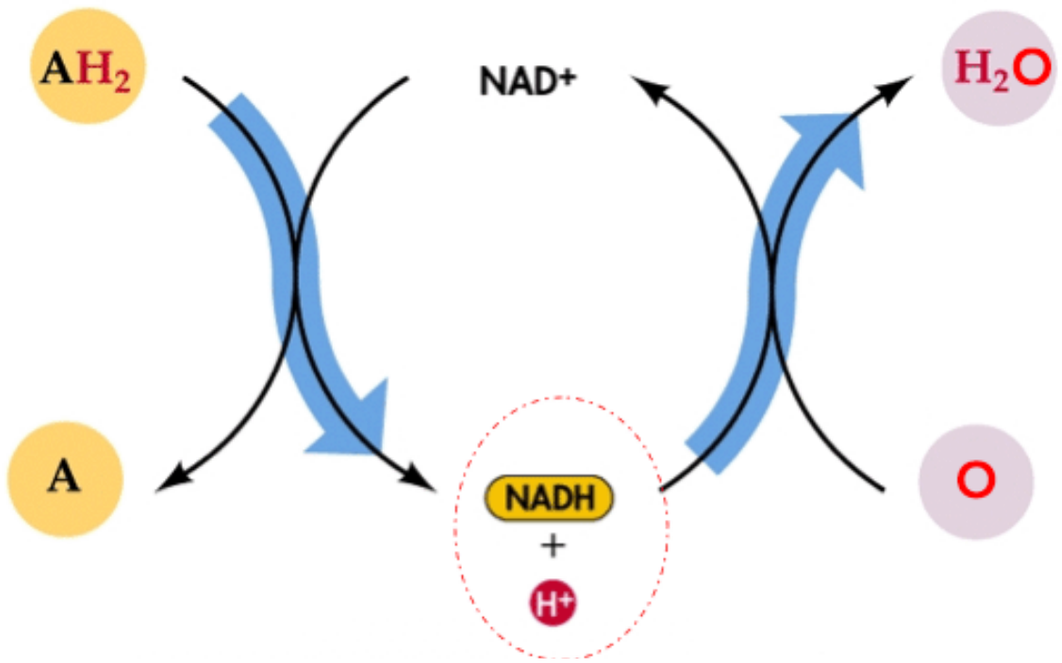
$NAD^+ + 2e^- + 2H^+ \longrightarrow NADH + H^+$

Example: electron carrier



The reduced form **(NADH + H^+)** can be converted back into the oxidized form in the presence of oxygen:

NADH + H^+ + 1/2 O_2----> NAD^+ + H_2O

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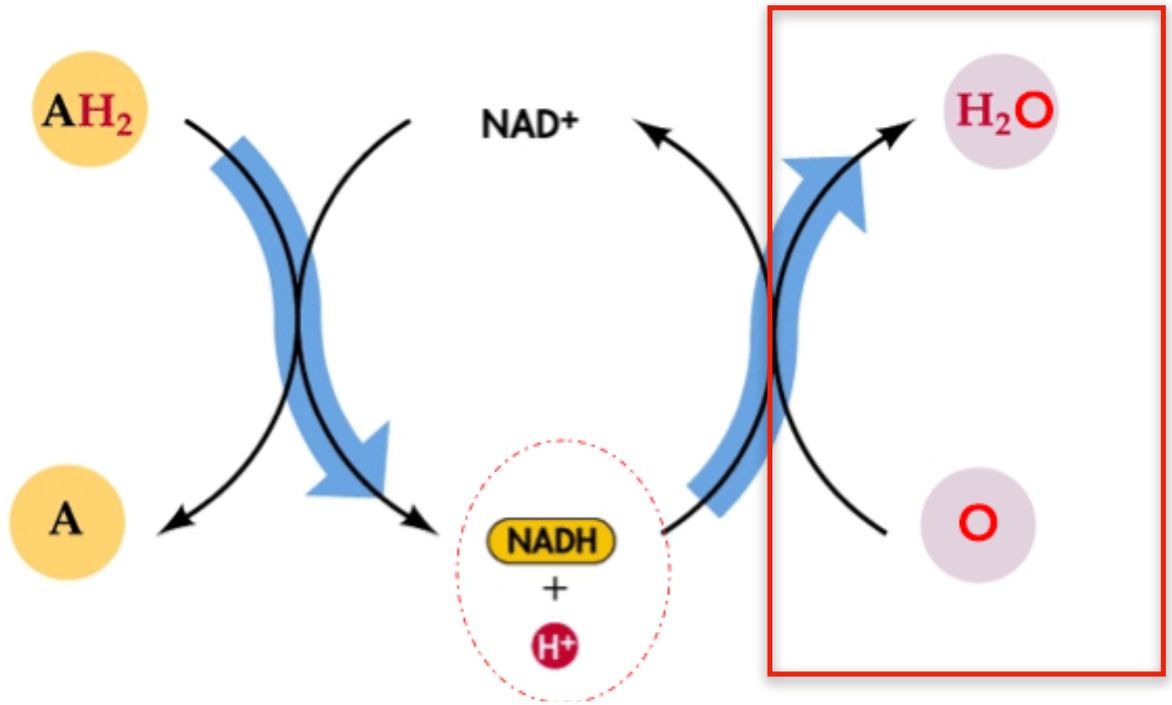

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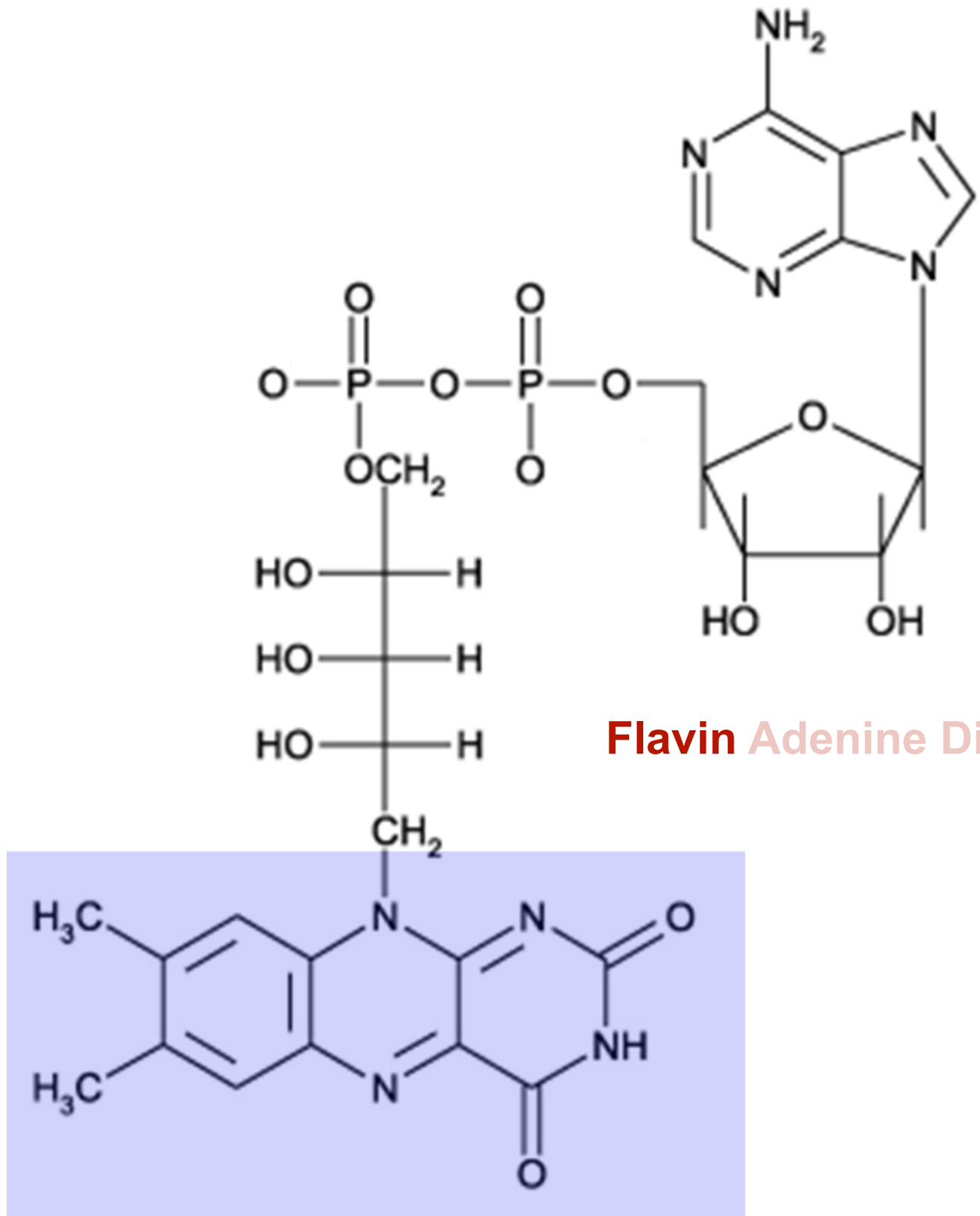
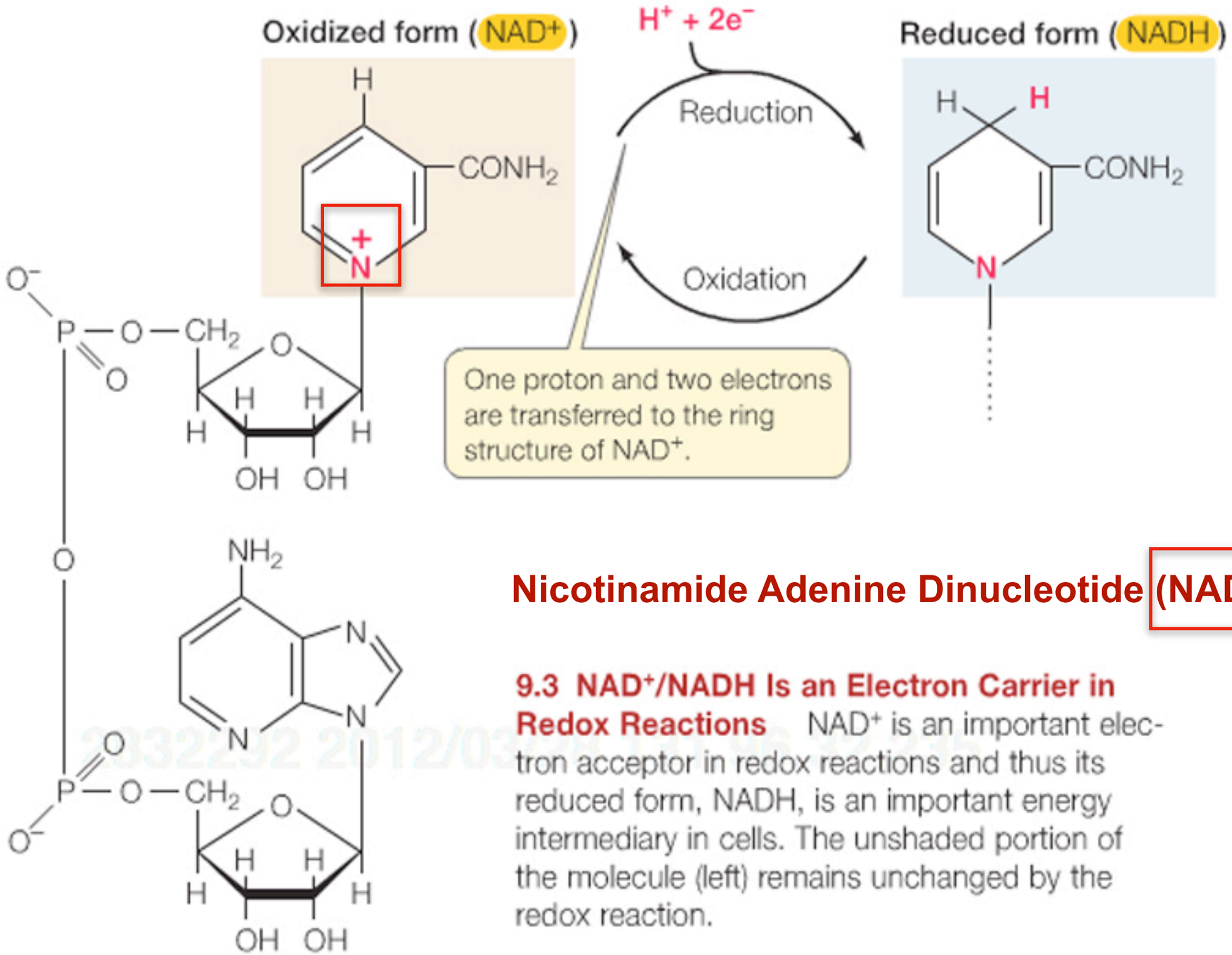
$$NADH + H^+ + 1/2\ O_2 \longrightarrow NAD^+ + H_2O$$

The $\Delta G^{o\prime}$ of this oxidation reaction is **-52.4 kcal/mol**.
(For comparisons sake, remember that the $\Delta G^{o\prime}$ of the ATP to ADP reaction is **~7.3 kcal/mol**)

Think of **NADH** + **H^+**, therefore, as a pre-packaged form of an available “Hydrogen carrier”, and is, therefore, a "potential" energy source that can eventually be turned into ATP and used to do work!!!



Flavin Adenine Dinucleotide (FAD)



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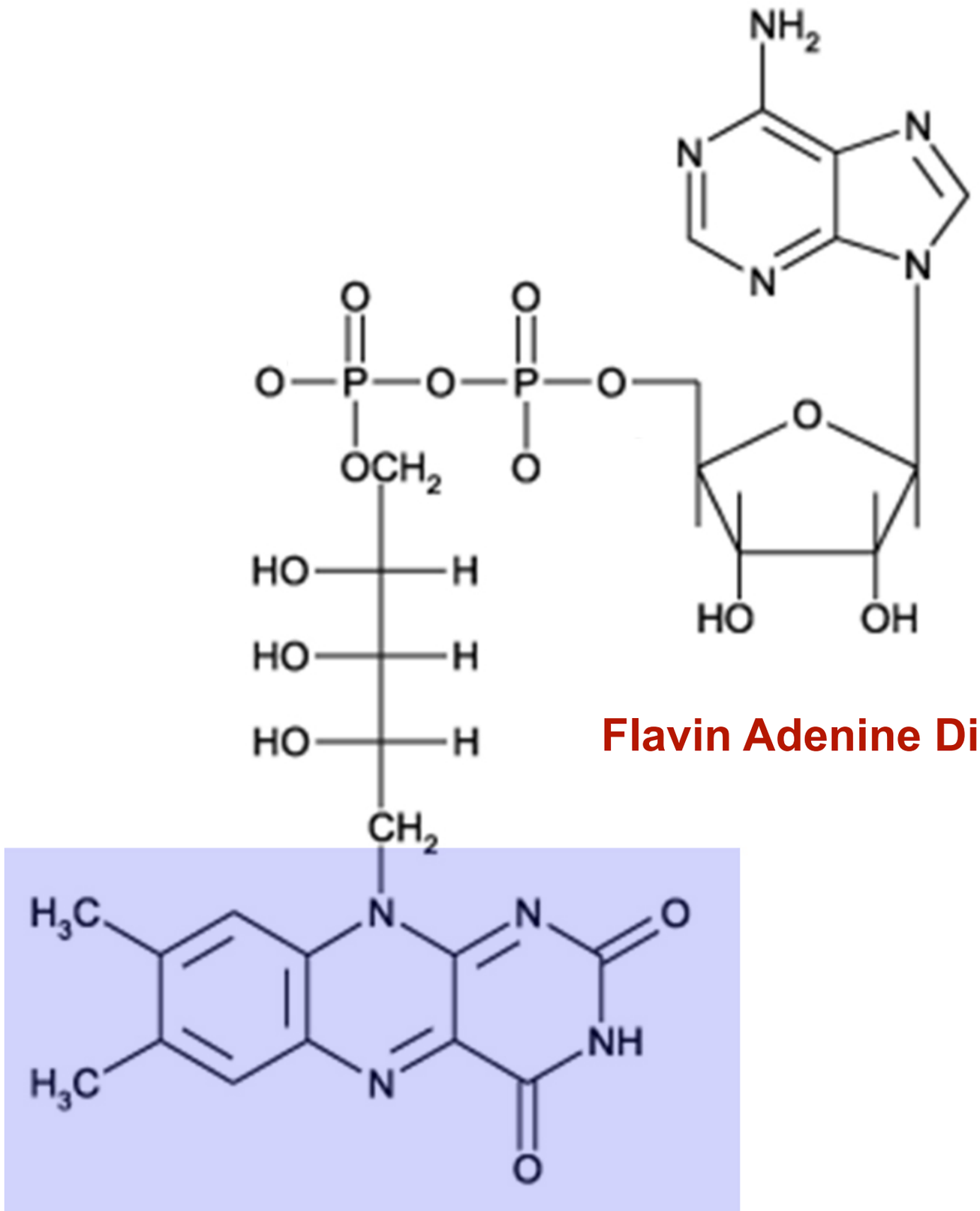

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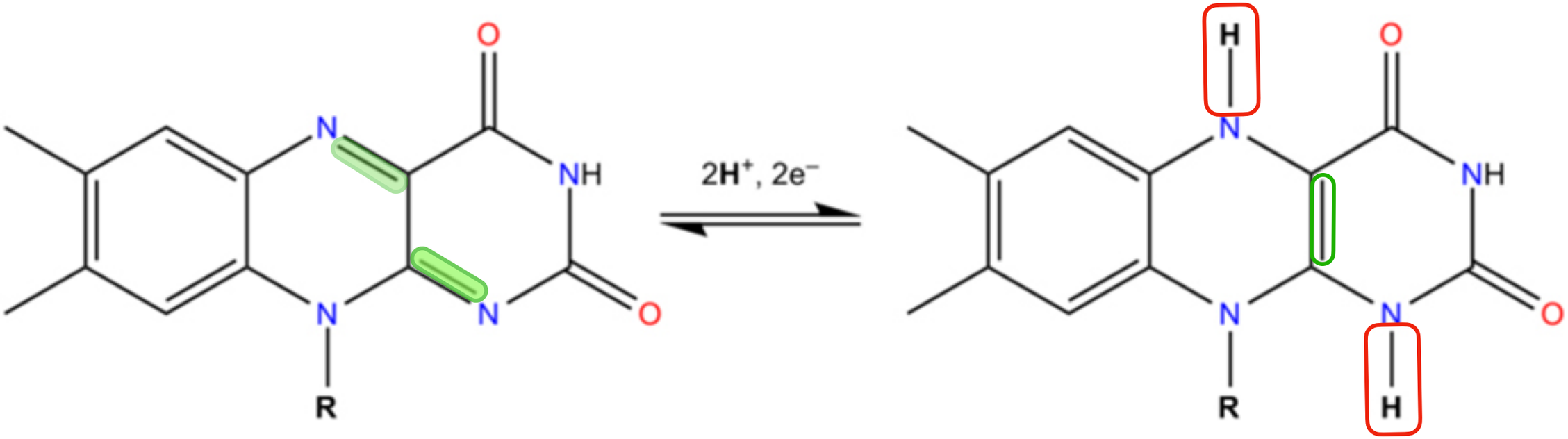


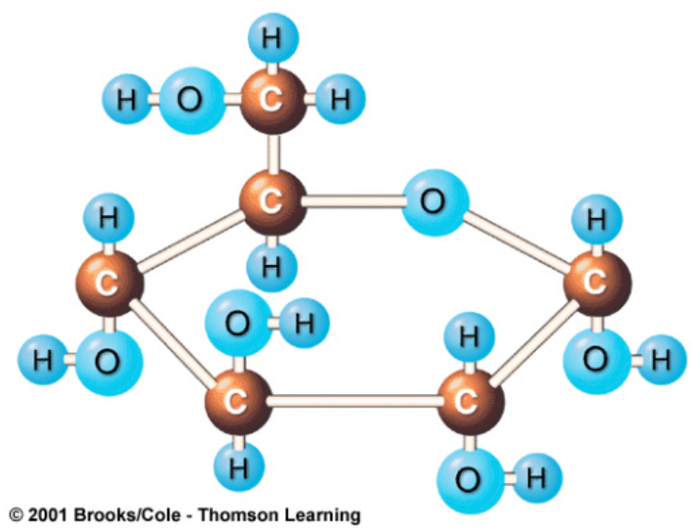
FAD + H_2 ----> $FADH_2$

$FADH_2$ + 1/2 O_2----> FAD + H_2O

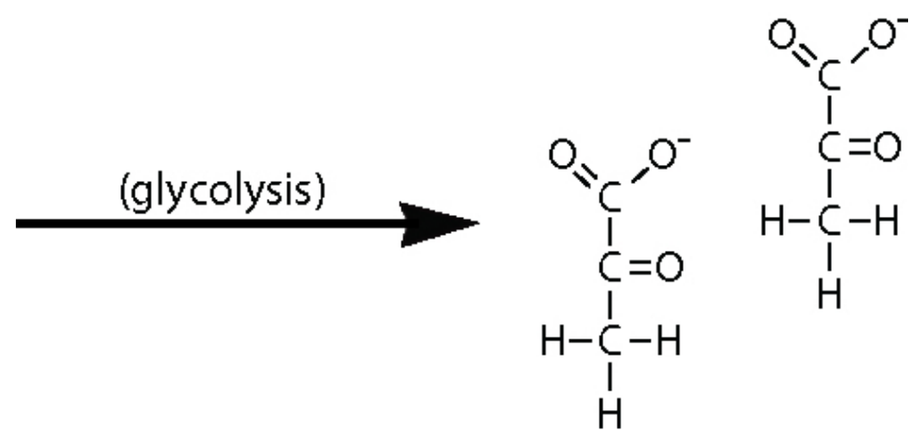
But what about the actual metabolism of Glucose:

It generally occurs in THREE stages

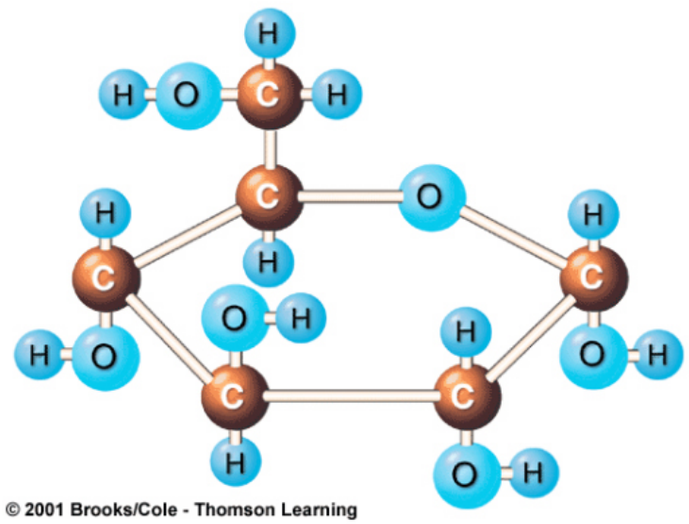
STAGE 1: Glycolysis -from Glucose to Pyruvate



GLUCOSE



2 Pyruvate



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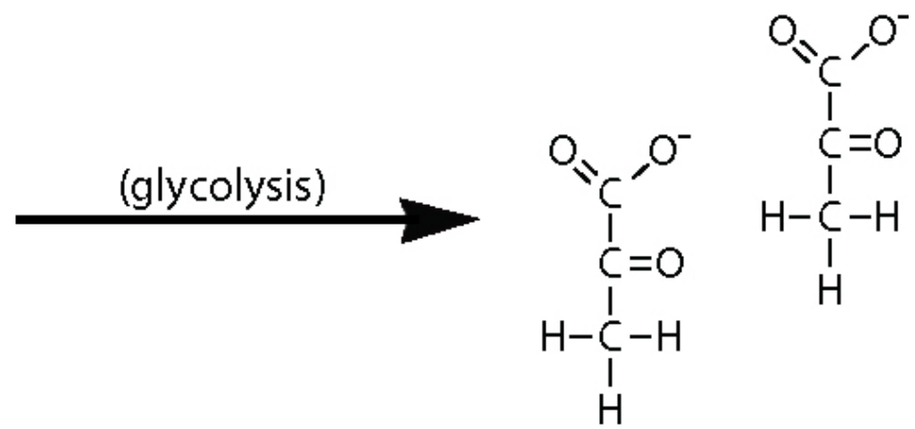


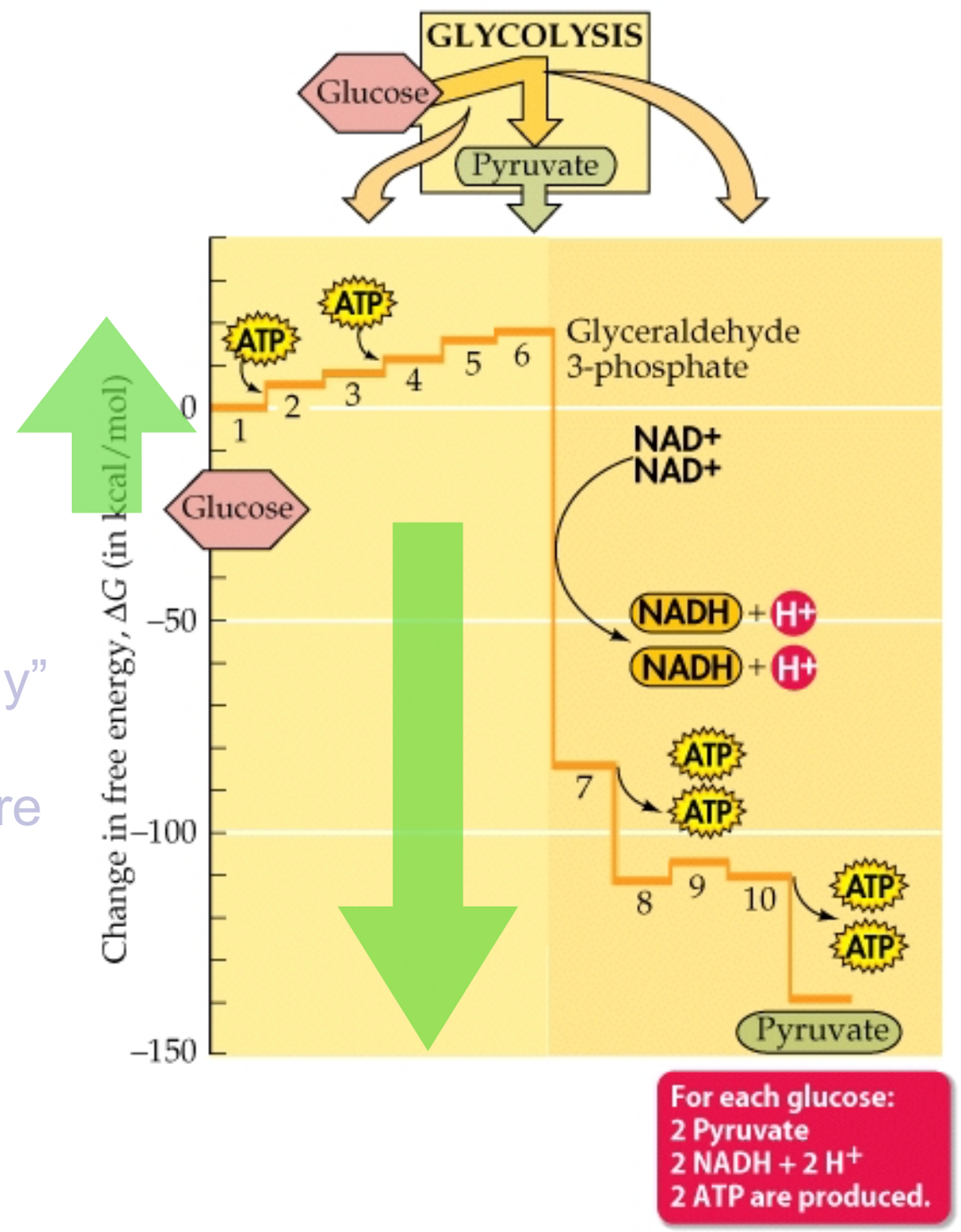
2 Pyruvate

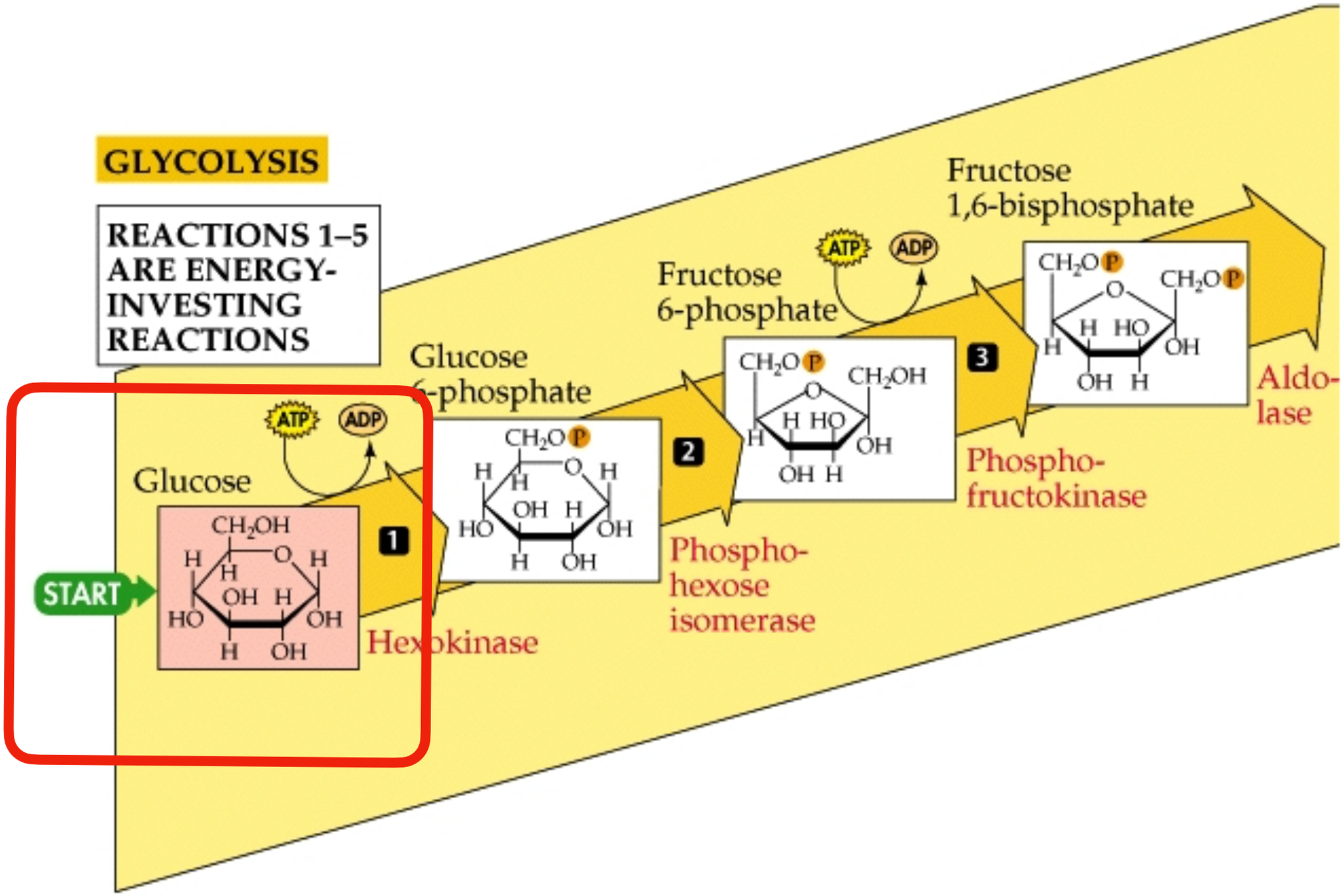
To get energy OUT of this overall reaction, energy first must be **invested** in the process.

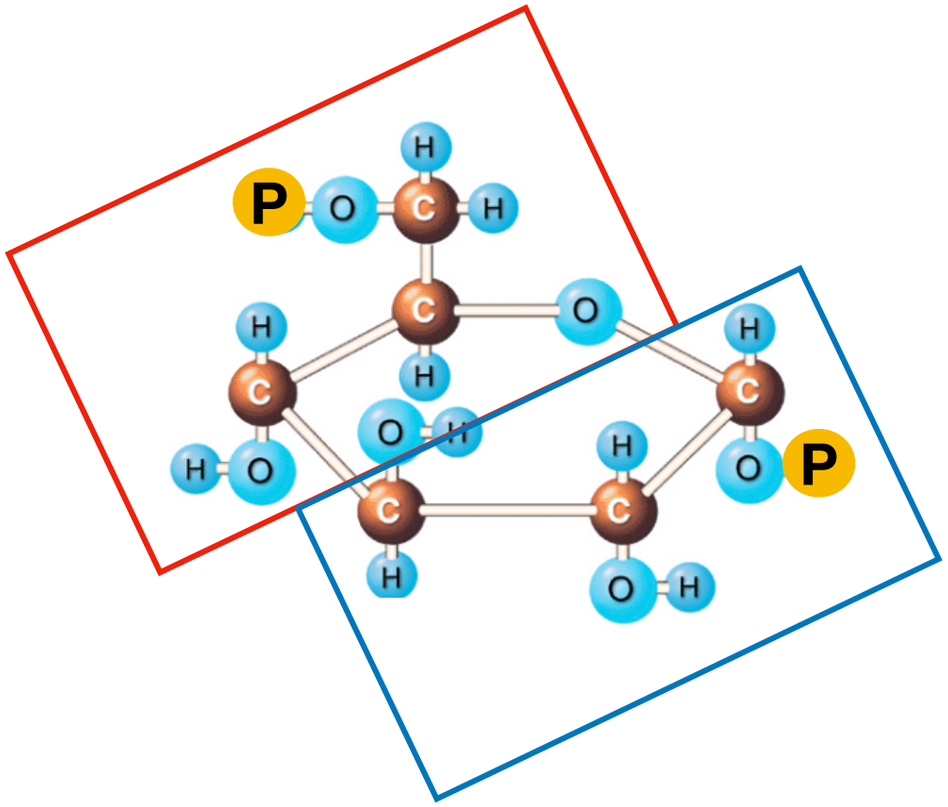
In separate reactions, **2 ATP molecules** are used to make **chemical modifications** to the glucose molecule.

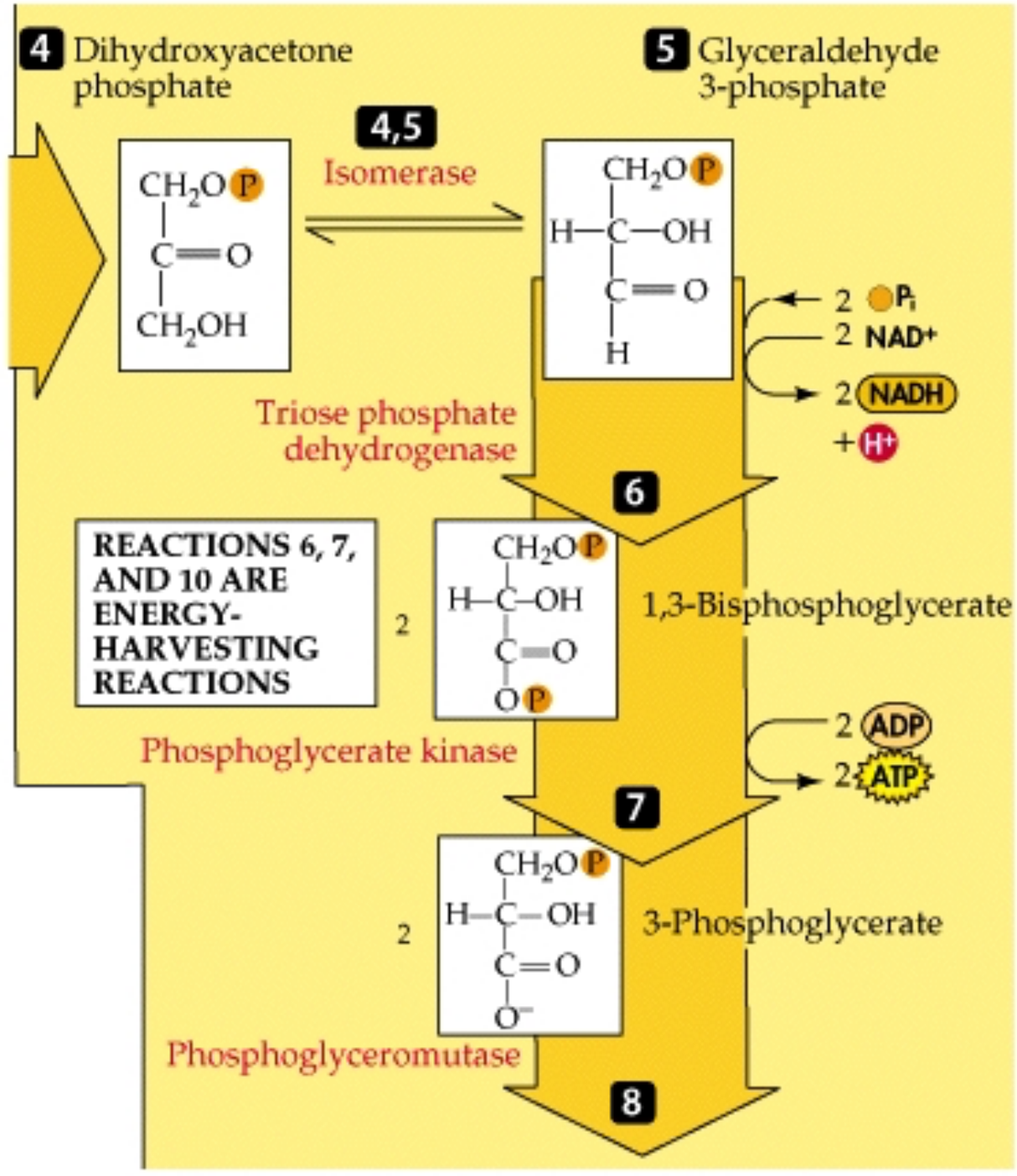
Phosphates from each **ATP** are added to the **carbon 6** and **carbon 1** skeleton of the glucose molecule.

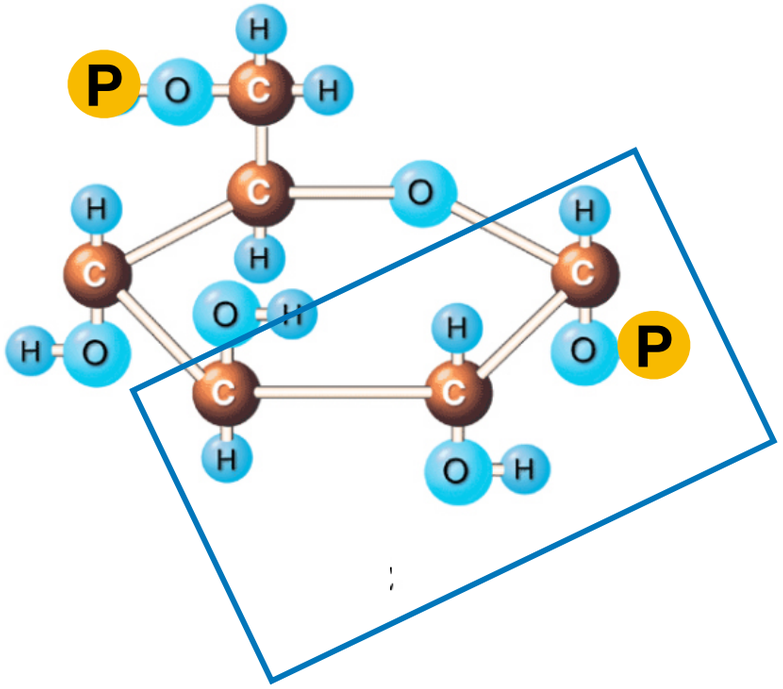
Note the change in "Gibbs Free energy" as phosphates are added to the glucose Carbon skeleton… it gets more **-ve**, as energy is "invested into the system




GLYCOLYSIS
REACTIONS 1–5 ARE ENERGY-INVESTING REACTIONS
Glucose
START
ATP
ADP
1
Hexokinase
Glucose 6-phosphate
2
Phospho-hexose isomerase
Fructose 6-phosphate
3
Phospho-fructokinase
Fructose 1,6-bisphosphate
Aldo-lase


P
P


4 Dihydroxyacetone phosphate
5 Glyceraldehyde 3-phosphate
4,5
Isomerase
Triose phosphate dehydrogenase
2 Pi
2 NAD+
2 NADH
+ H+
6
REACTIONS 6, 7, AND 10 ARE ENERGY-HARVESTING REACTIONS
2
1,3-Bisphosphoglycerate
Phosphoglycerate kinase
2 ADP
2 ATP
7
2
3-Phosphoglycerate
Phosphoglyceromutase
8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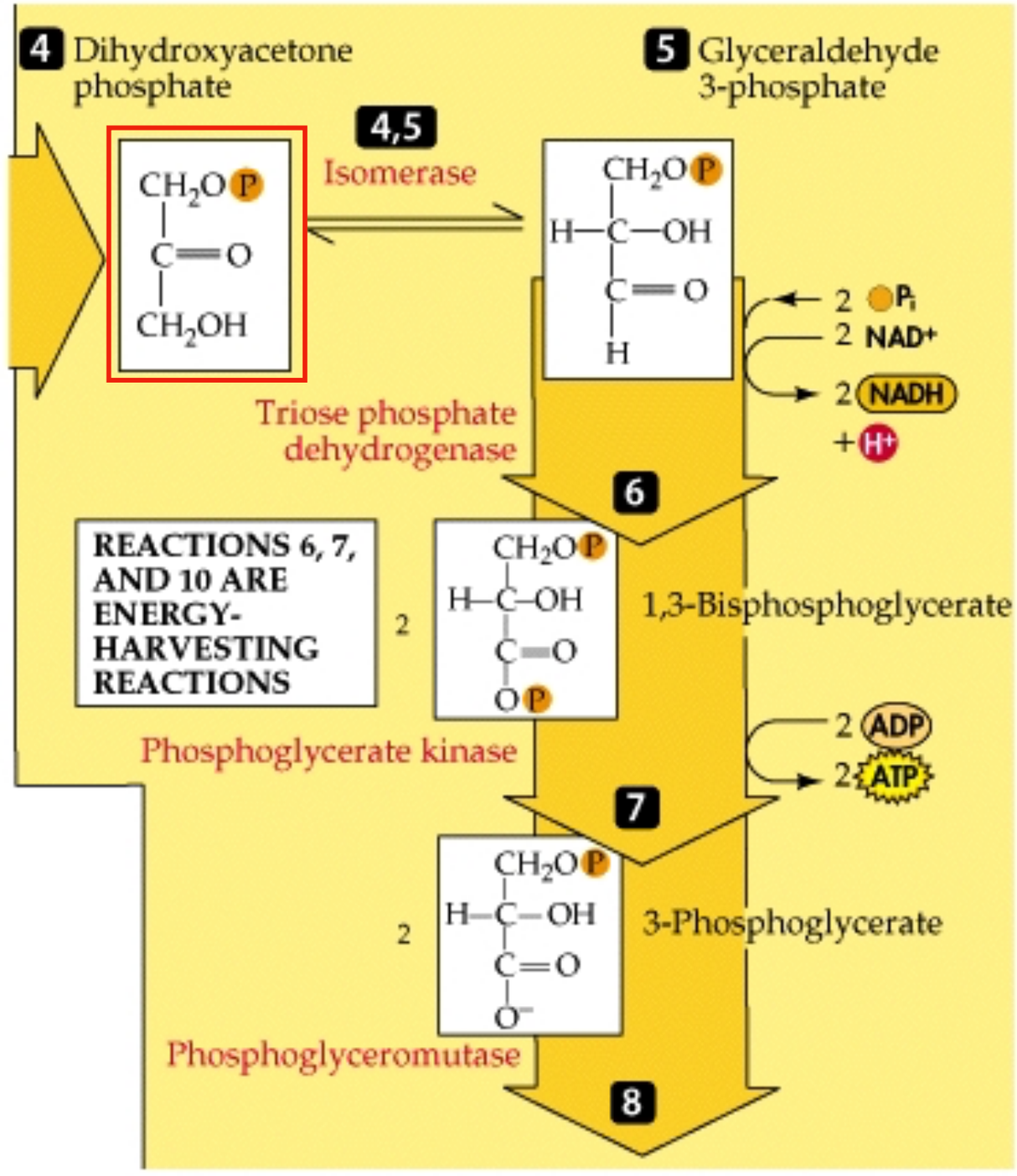
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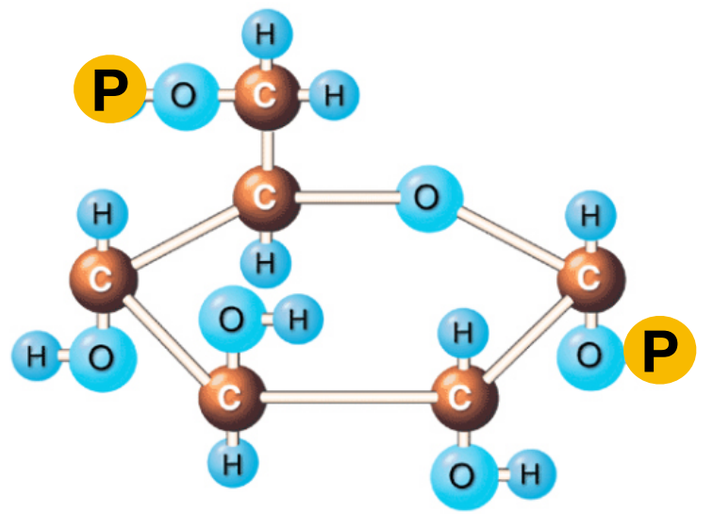
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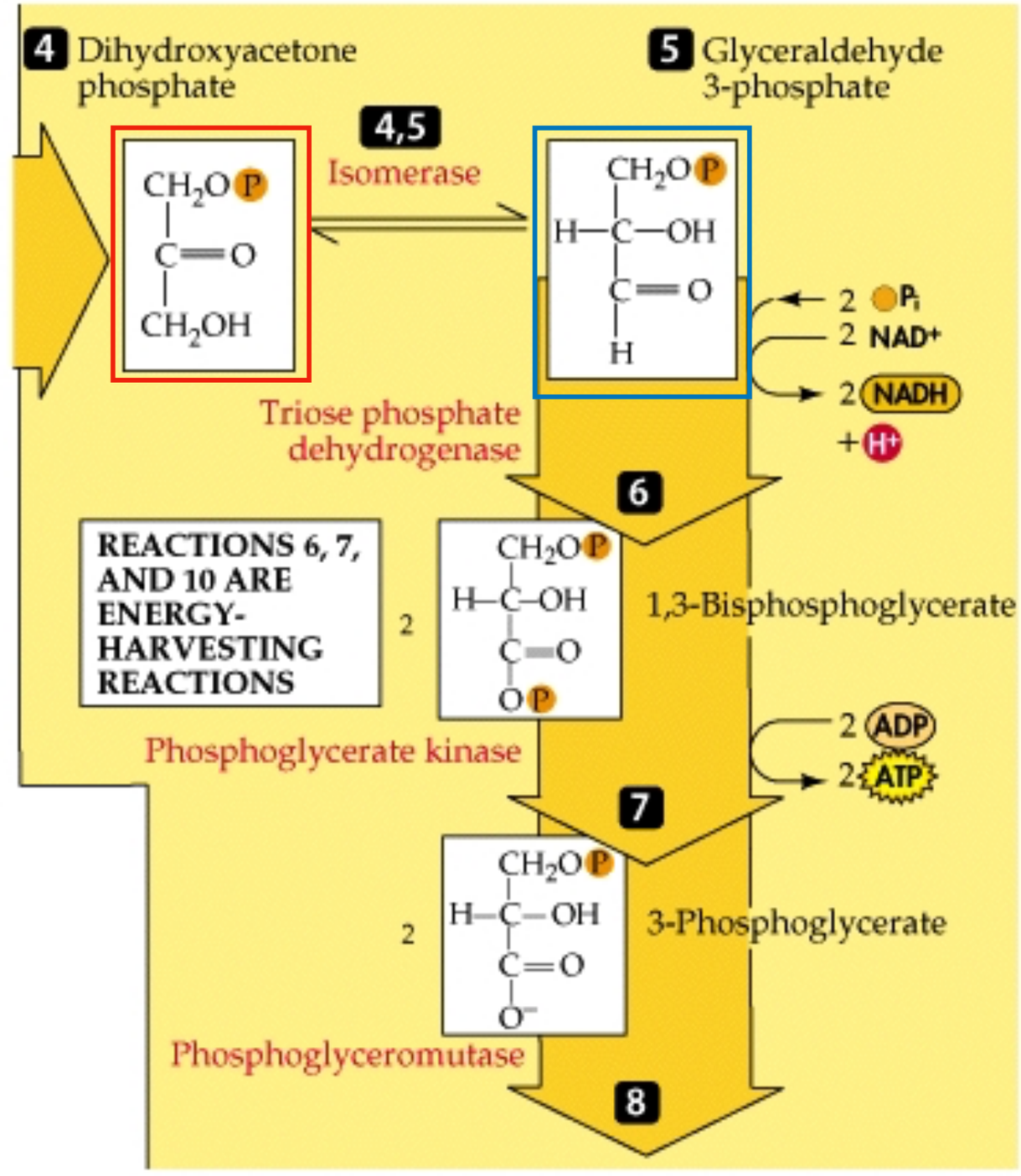
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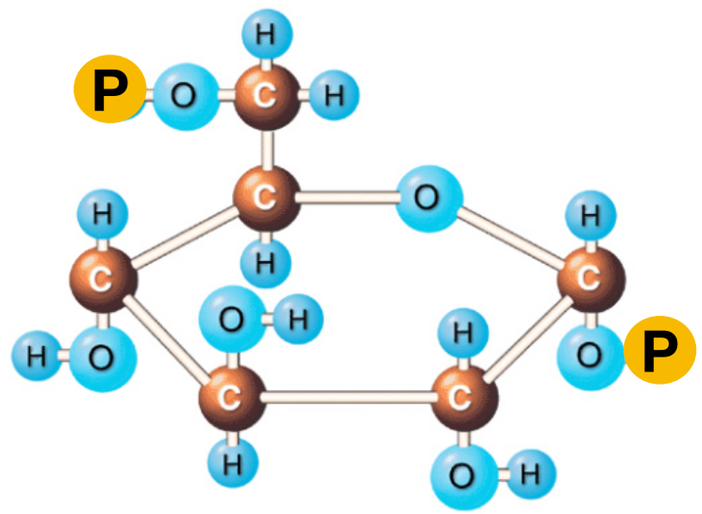
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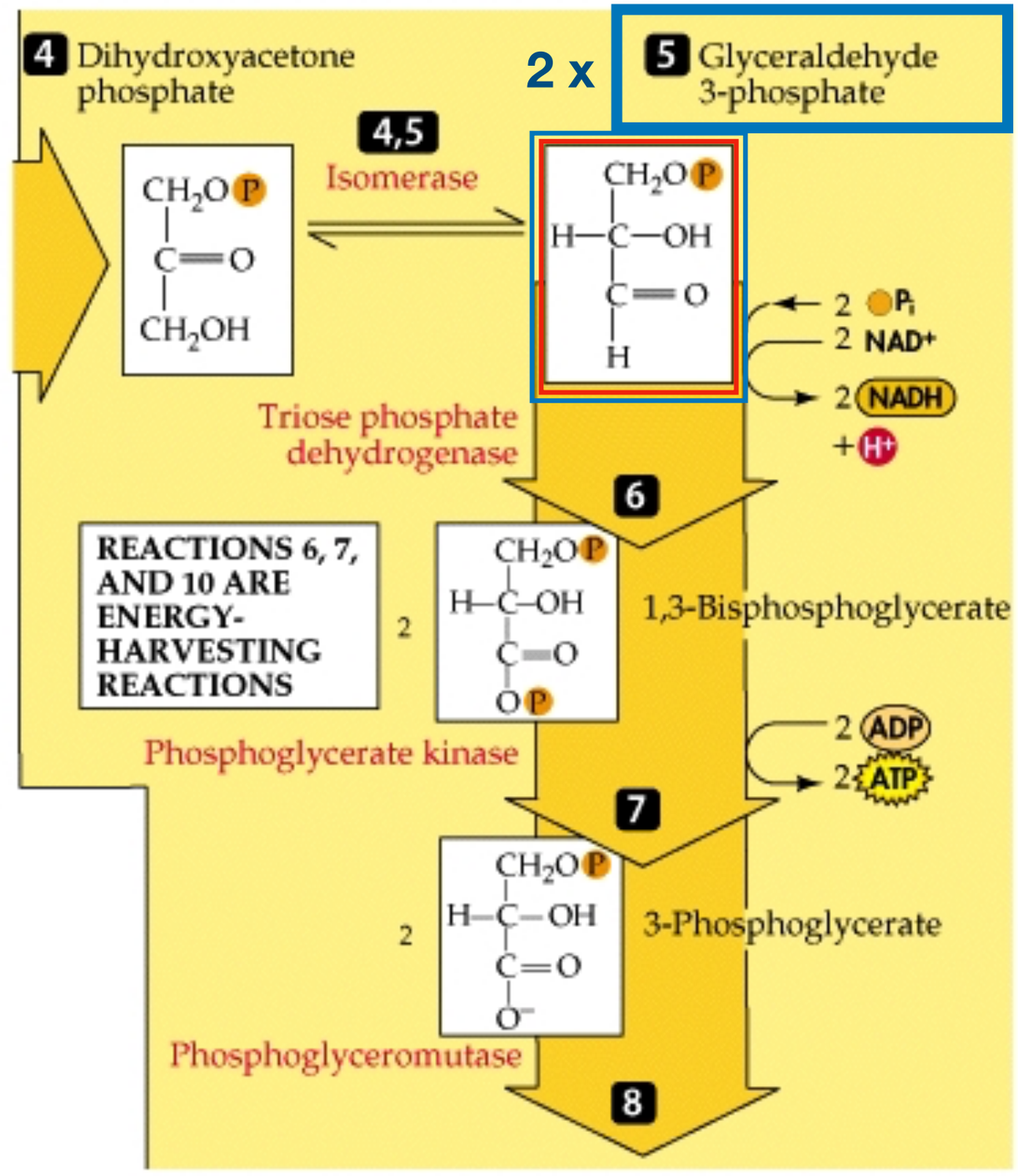
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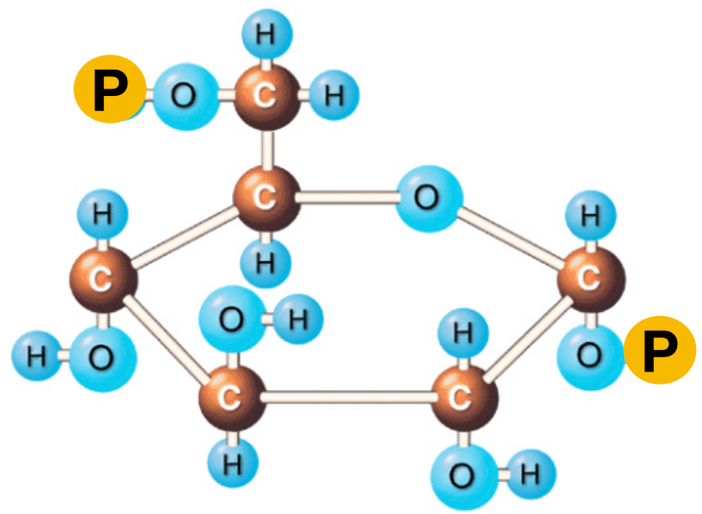

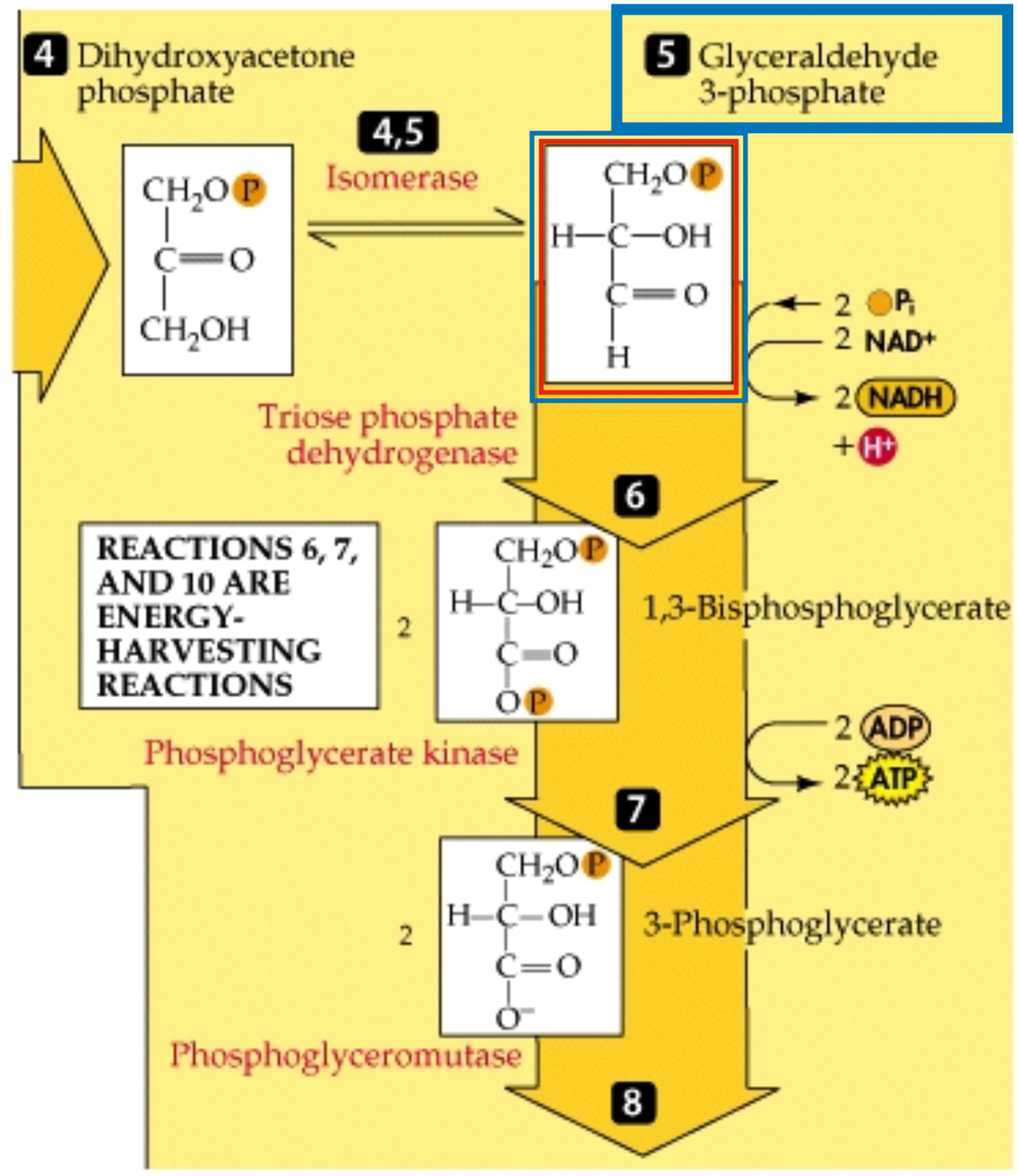
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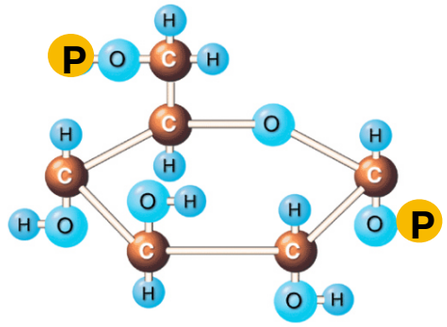
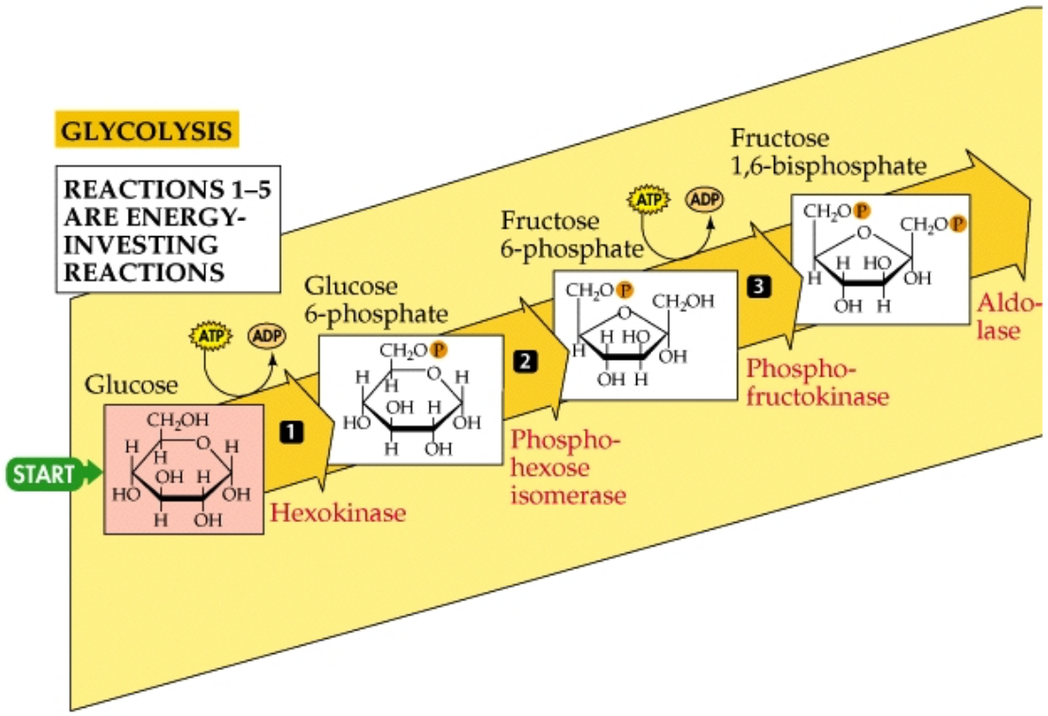
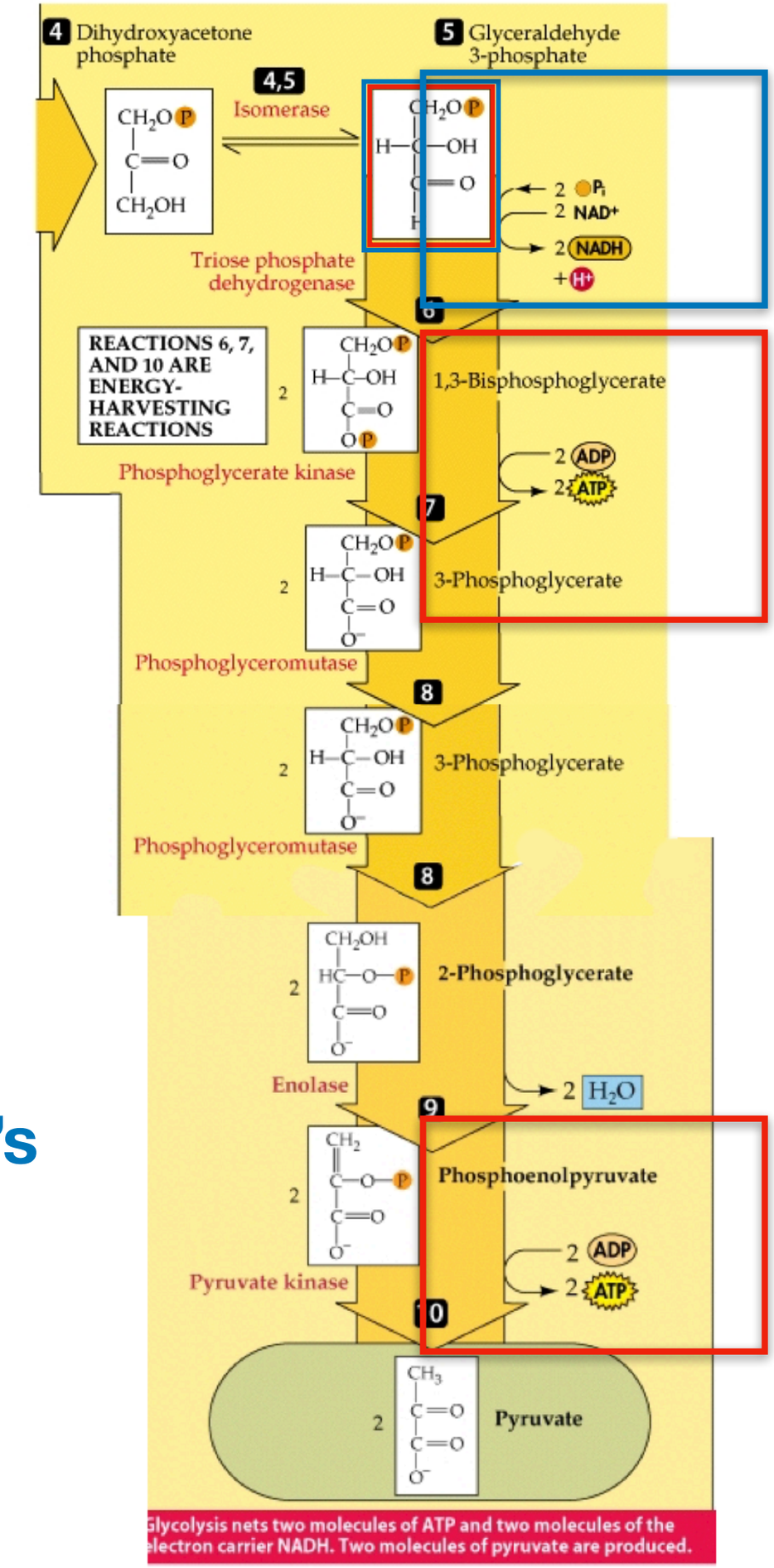
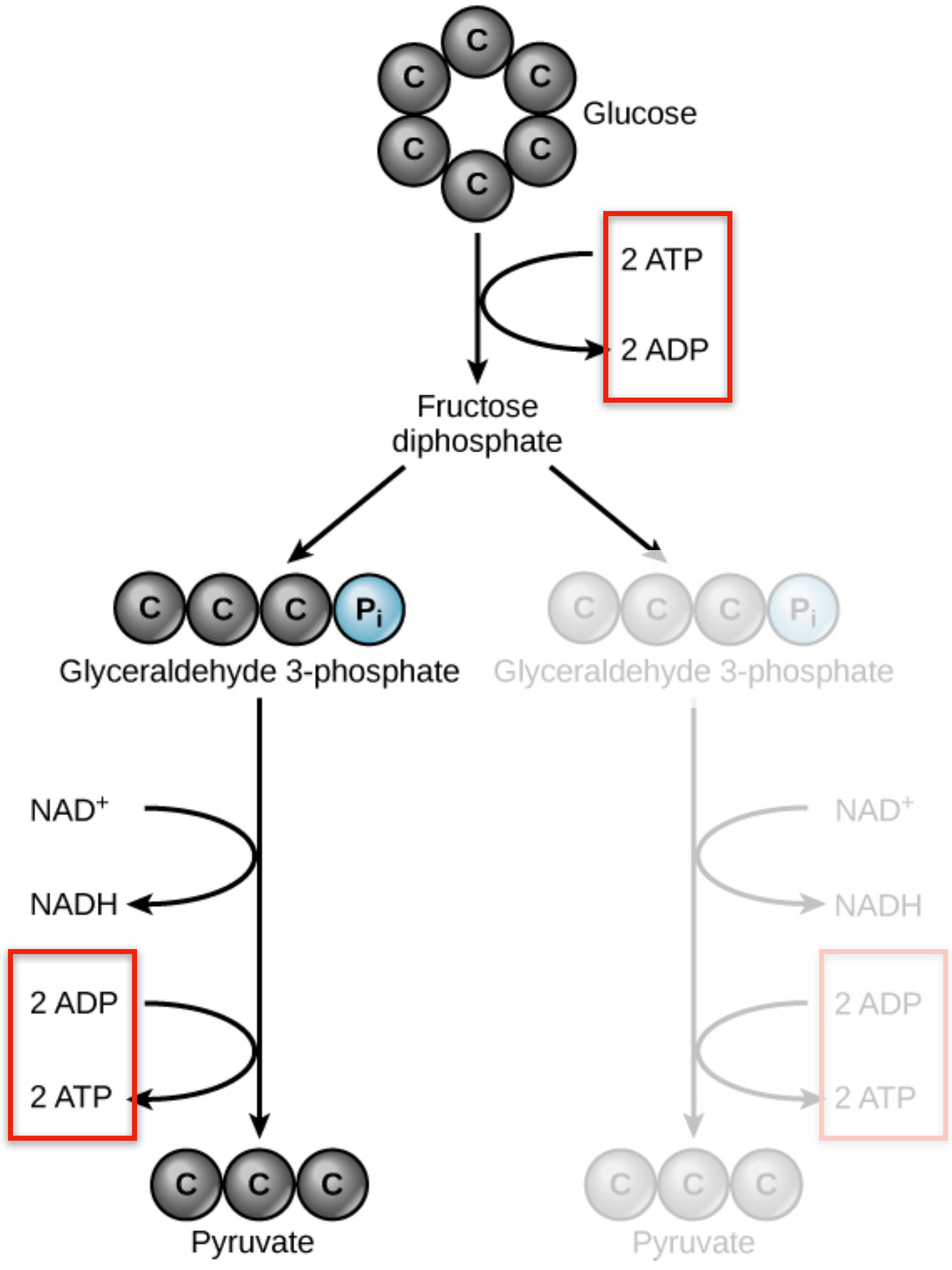
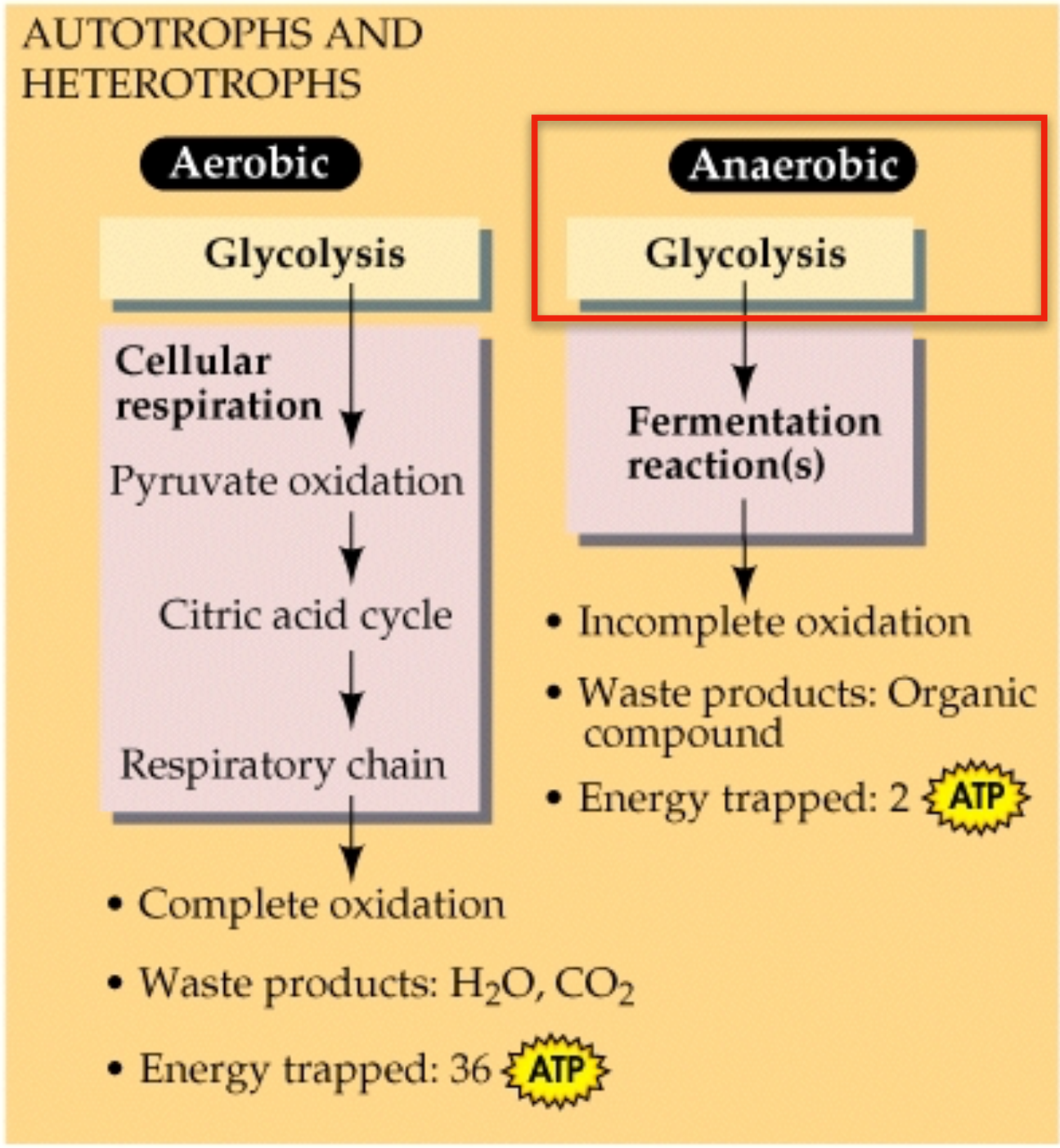


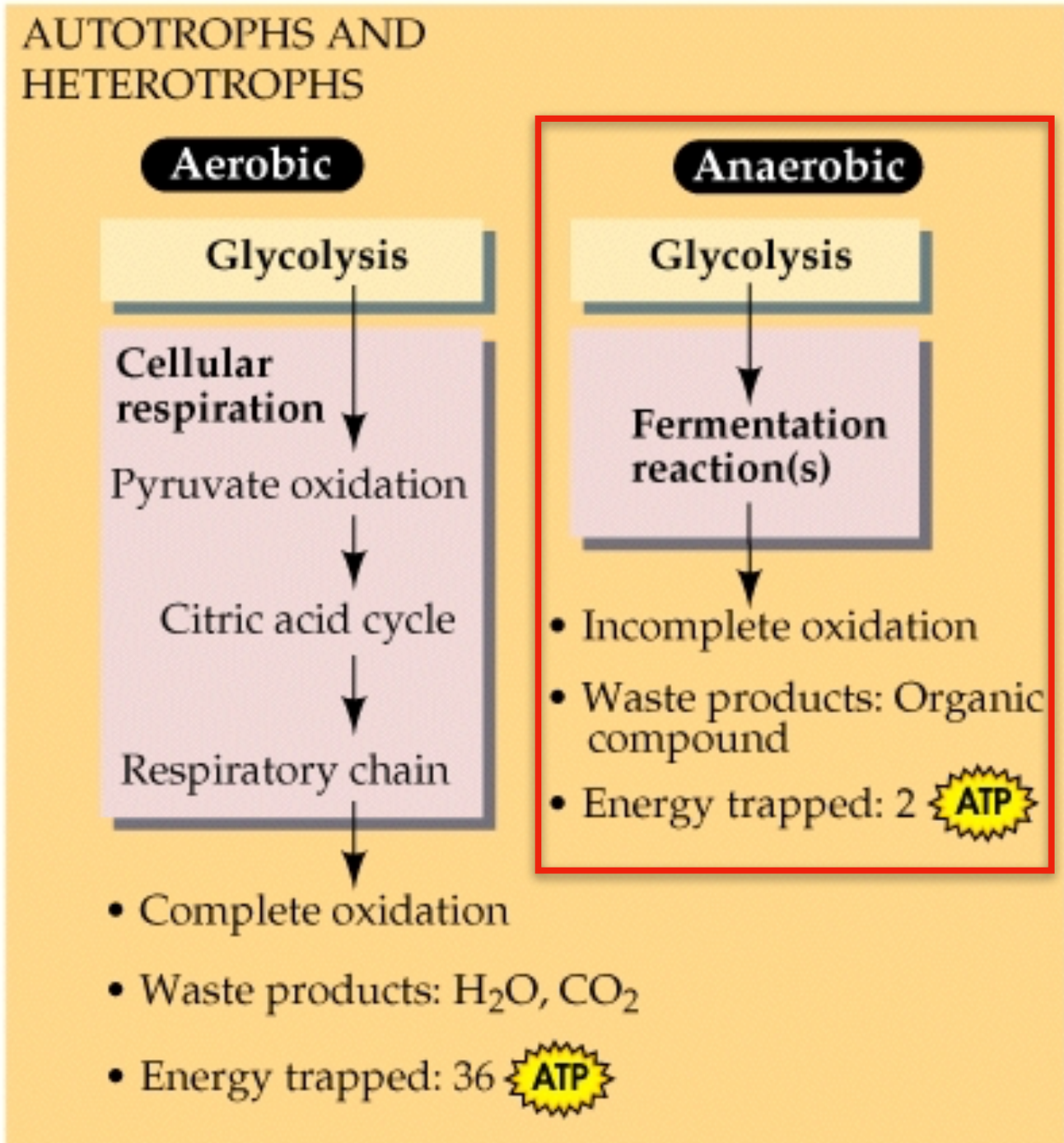




Net Gain of 2 ATP's


C
Glucose
2 ATP
2 ADP
Fructose diphosphate
C C C Pi
Glyceraldehyde 3-phosphate
NAD+
NADH
2 ADP
2 ATP
C C C
Pyruvate
C C C Pi
Glyceraldehyde 3-phosphate
NAD+
NADH
2 ADP
2 ATP
C C C
Pyruvate


AUTOTROPHS AND HETEROTROPHS
Aerobic
Glycolysis
Cellular respiration
Pyruvate oxidation
Citric acid cycle
Respiratory chain
• Complete oxidation
• Waste products: H_2O, CO_2
• Energy trapped: 36 ATP
Anaerobic
Glycolysis
Fermentation reaction(s)
• Incomplete oxidation
• Waste products: Organic compound
• Energy trapped: 2 ATP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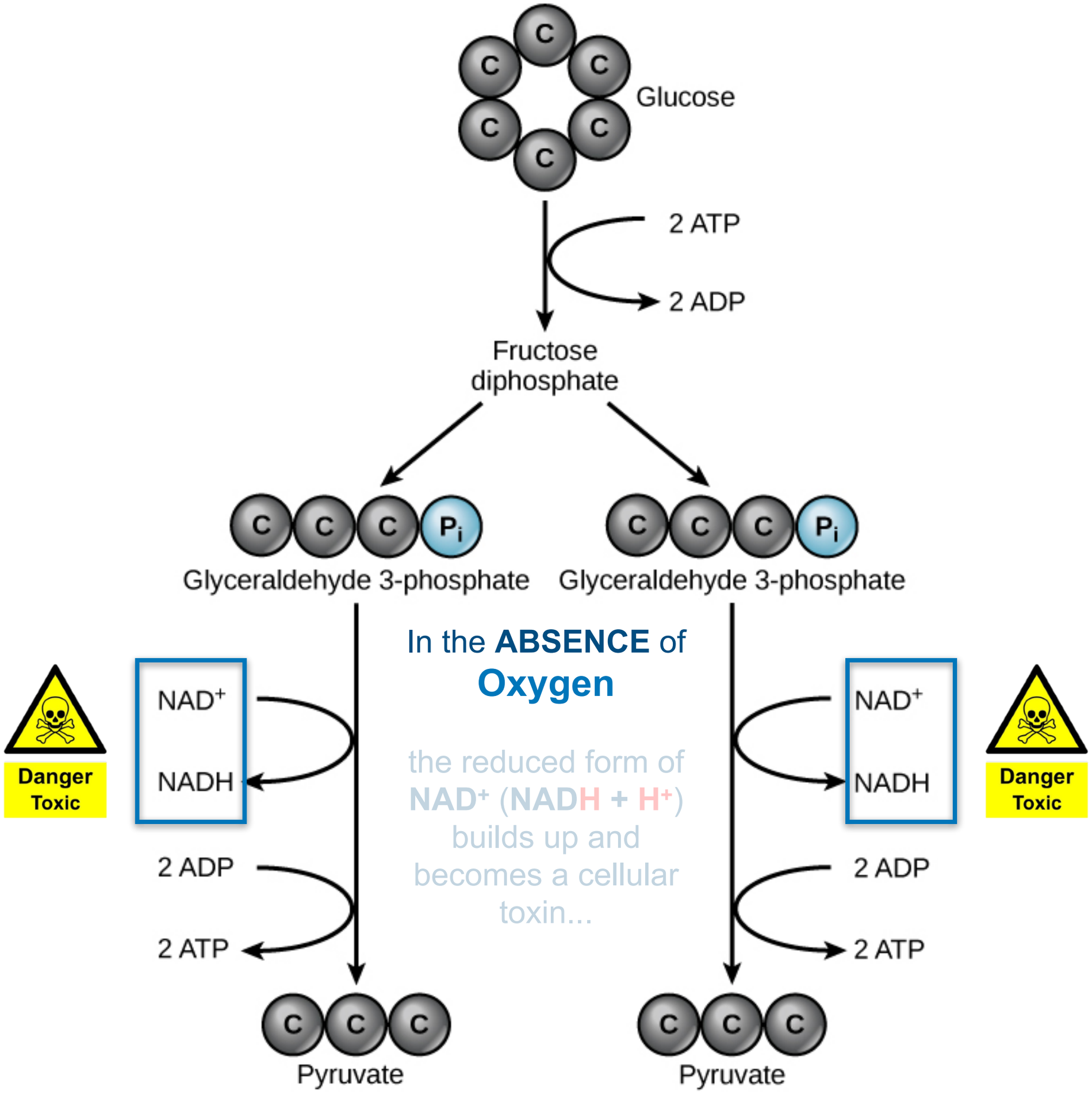
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Glucose
2 ATP
2 ADP
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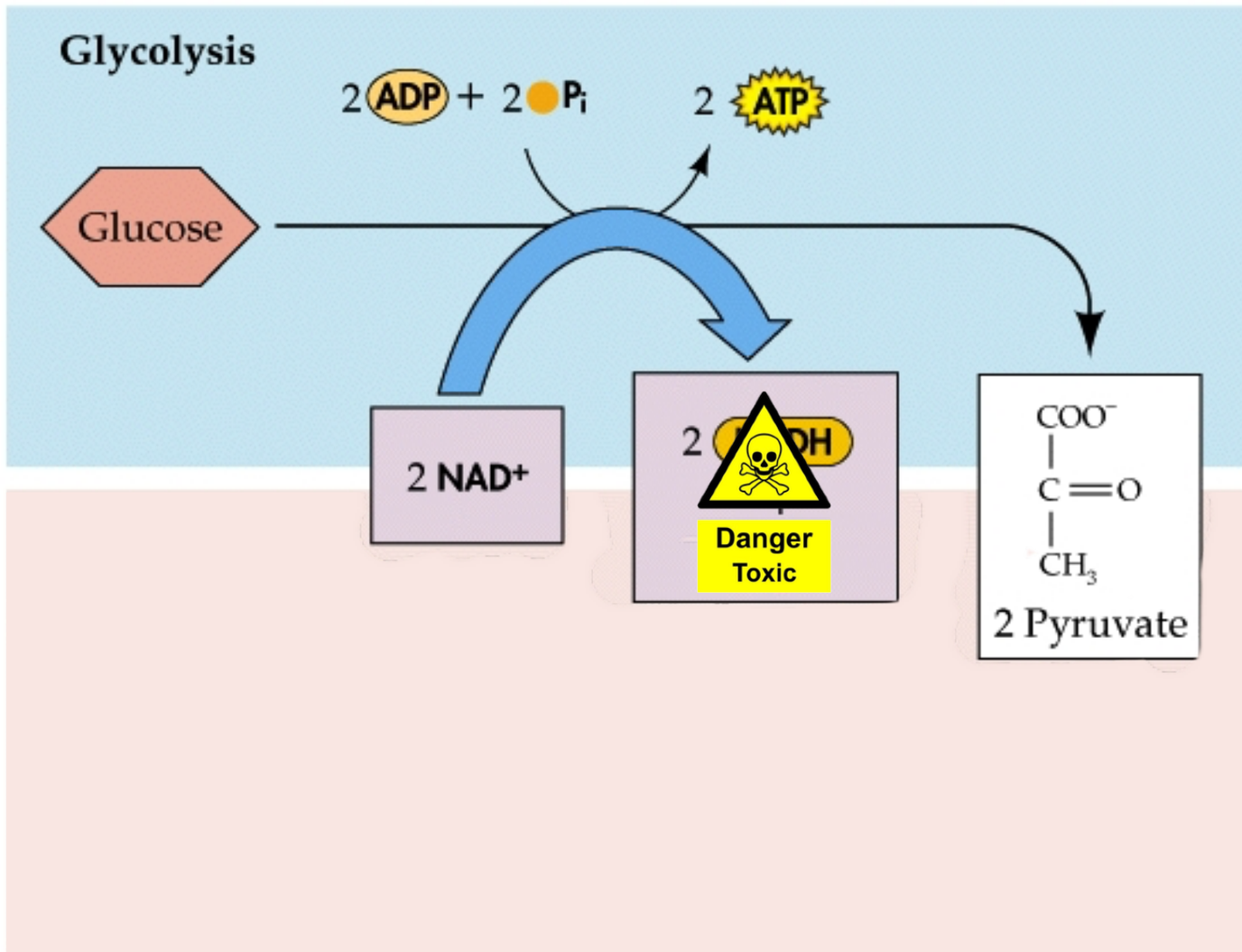
C C C Pi
Glyceraldehyde 3-phosphate
C C C Pi
Glyceraldehyde 3-phosphate
In the ABSENCE of Oxygen
the reduced form of NAD+ (NADH + H+) builds up and becomes a cellular toxin...
Danger Toxic
NAD+
NADH
2 ADP
2 ATP
C C C
Pyruvate
NAD+
NADH
2 ADP
2 ATP
Danger Toxic
C C C
Pyruvate

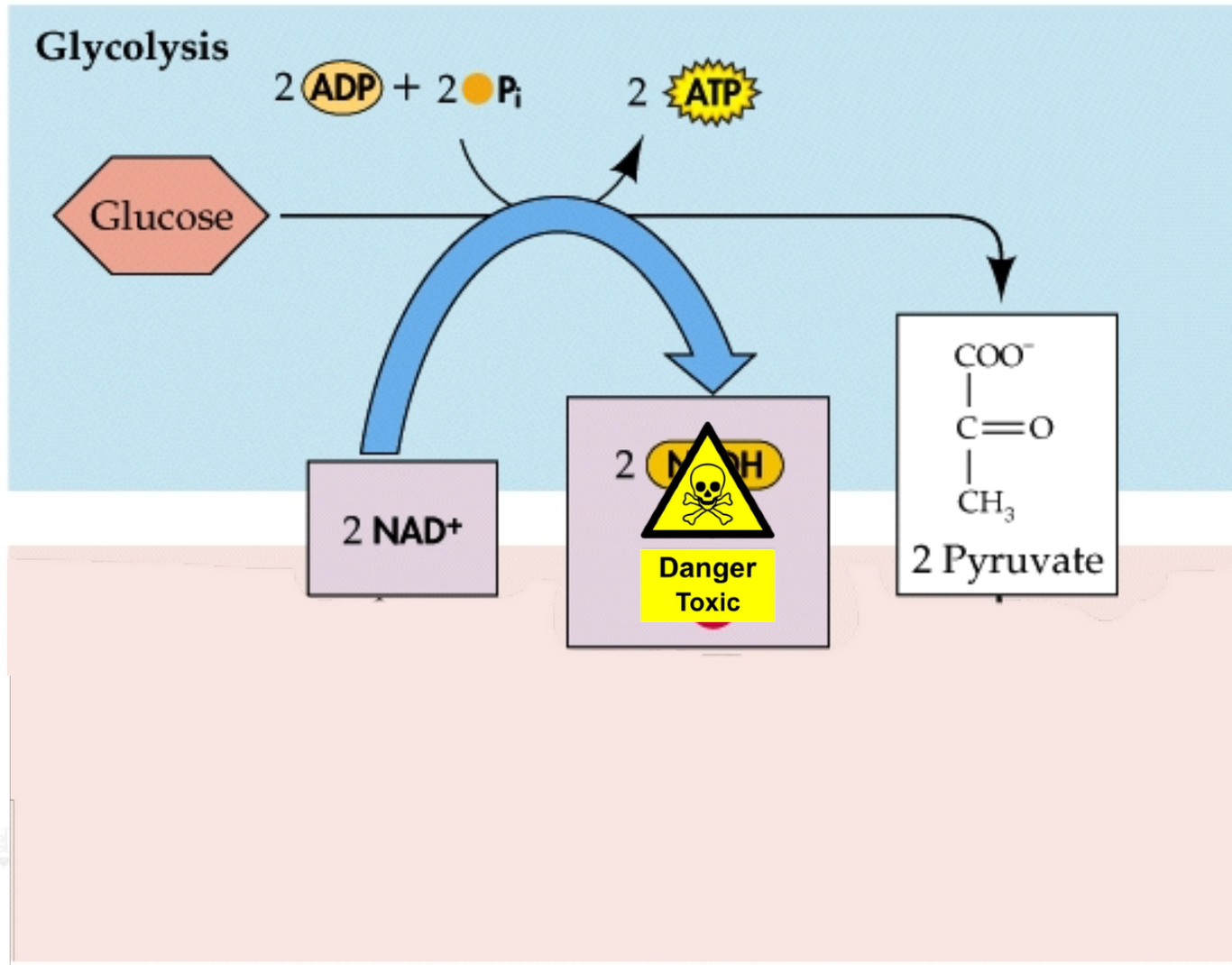
Anaerobic Conditions



In the ABSENCE of oxygen the reduced form of **NAD^+** (**NADH + H^+**) builds up and becomes a cellular toxin...

It, therefore, needs to be **RECYCLED...**

Anaerobic Conditions



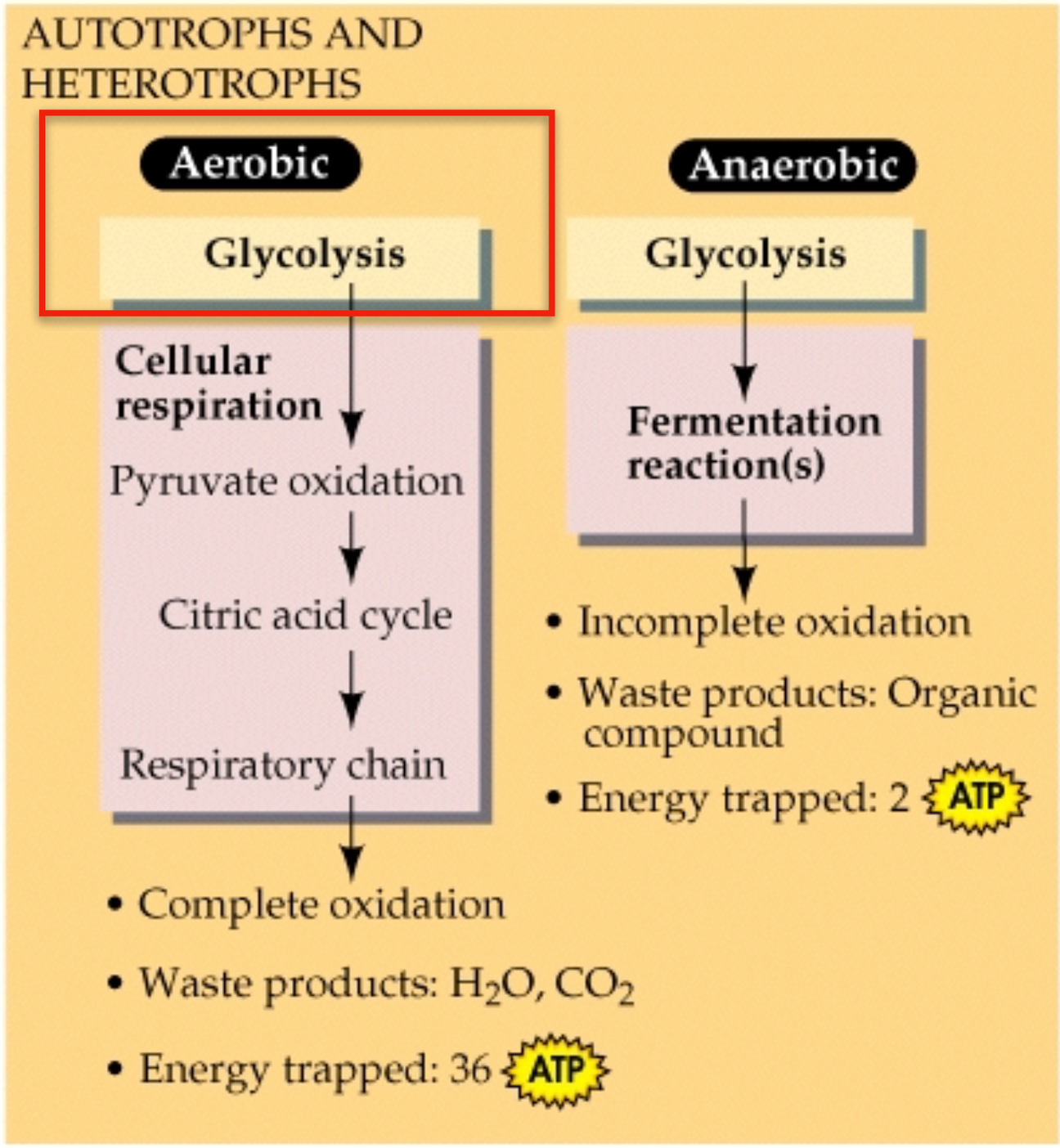
Aerobic Conditions

In the **presence of oxygen,** however, the reduced form of NAD^+ ($NADH + H^+$) can be converted back into the oxidized form…

$$\mathbf{NADH + H^+ + \boxed{1/2\ O_2} \dashrightarrow NAD^+ + H_2O}$$

…and just like the normal reaction this is an **ENERGY yielding reaction**... with almost the same energy yield.

$$\mathbf{H_2 + 1/2\ O_2 \dashrightarrow H_2O}$$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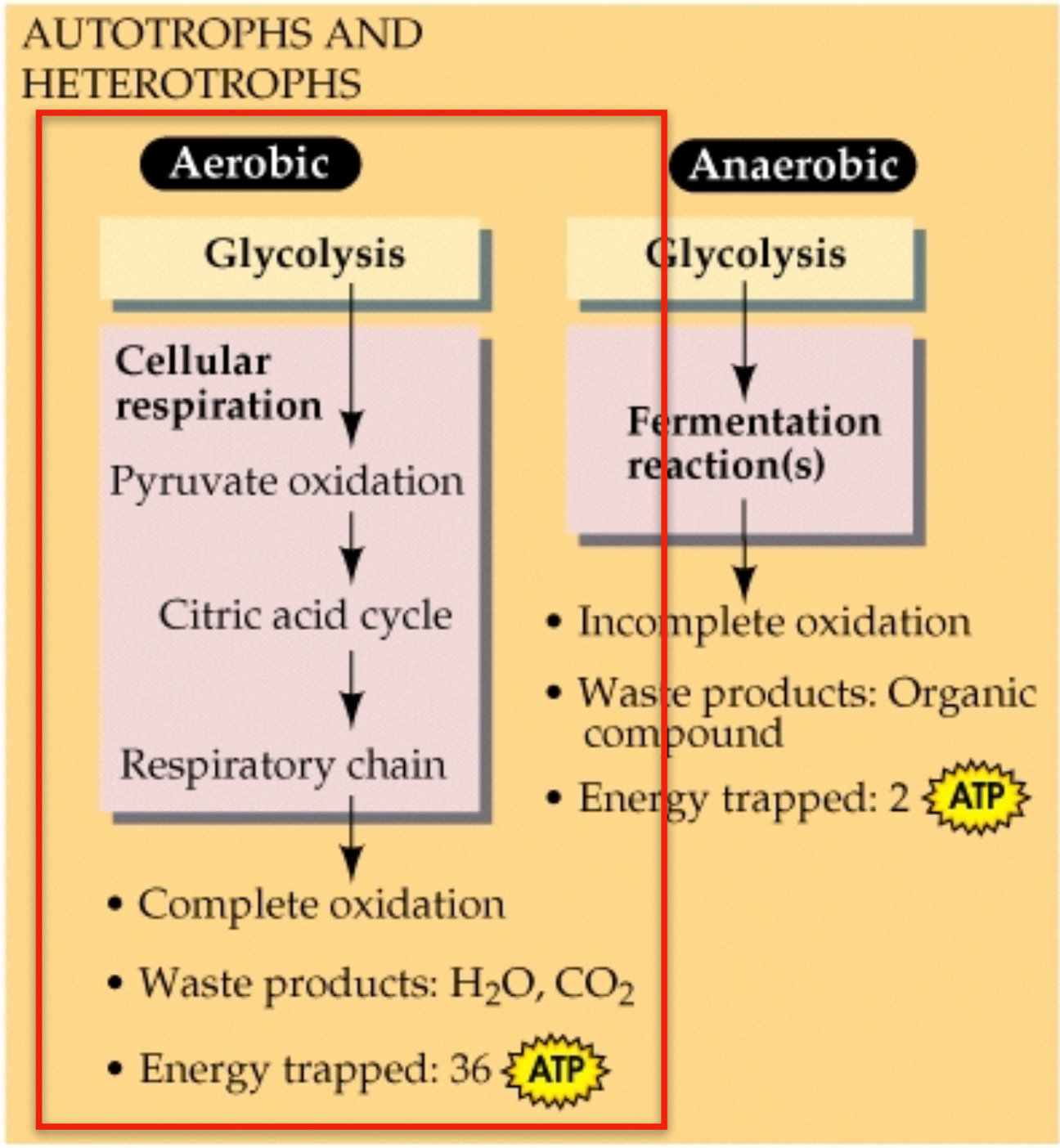
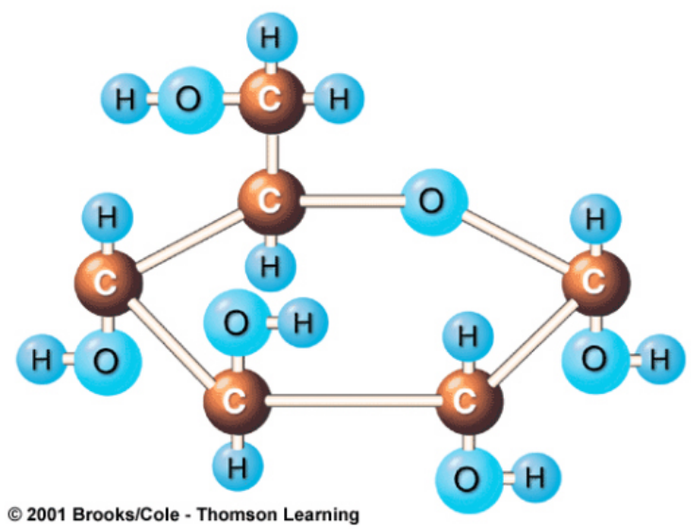
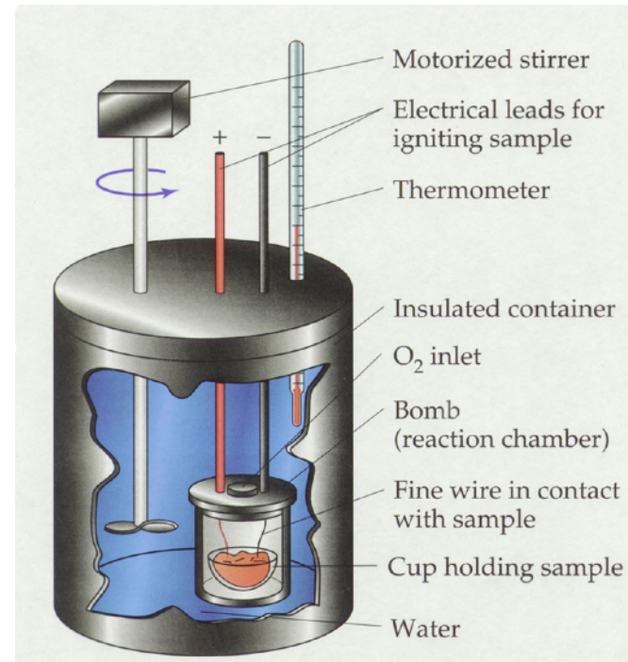
Fermentation reaction(s)
• Incomplete oxidation
• Waste products: Organic compound
• Energy trapped: 2 ATP


AUTOTROPHS AND HETEROTROPHS
Aerobic
Glycolysis
Cellular respiration
Pyruvate oxidation
Citric acid cycle
Respiratory chain
• Complete oxidation
• Waste products: H_2O, CO_2
• Energy trapped: 36 ATP
Anaerobic
Glycolysis
Fermentation reaction(s)
• Incomplete oxidation
• Waste products: Organic compound
• Energy trapped: 2 ATP



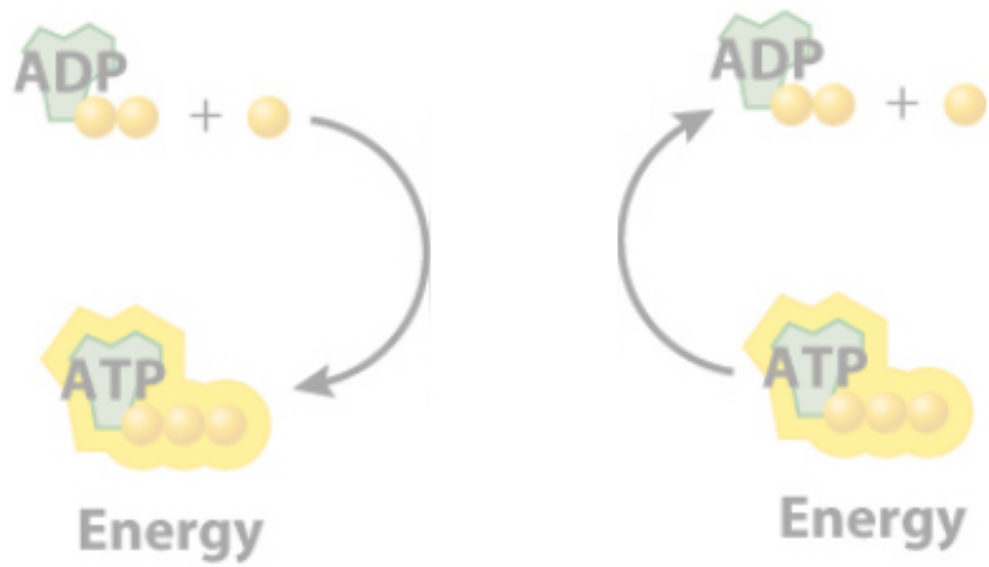
GLUCOSE



more than 1/3

- 686 kcal/mol.

1 mole of Glucose —> - 686 kcal/mol

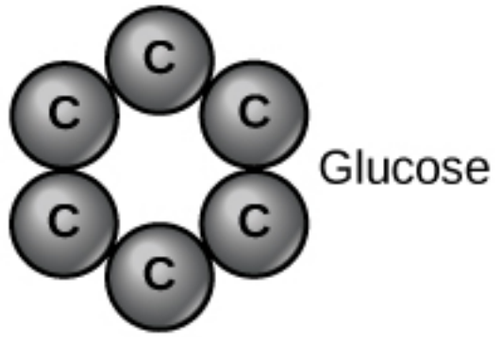


- 7.3 kcal/mol

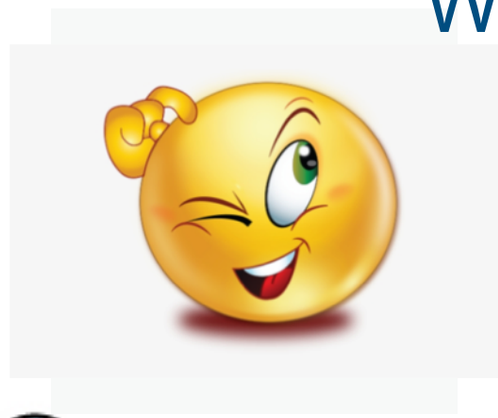
1 mole of Glucose —> ~~~94~~ ATP's worth of energy

36 …not too bad!!

STAGE 1: Glycolysis



Water !!!



2 ATP

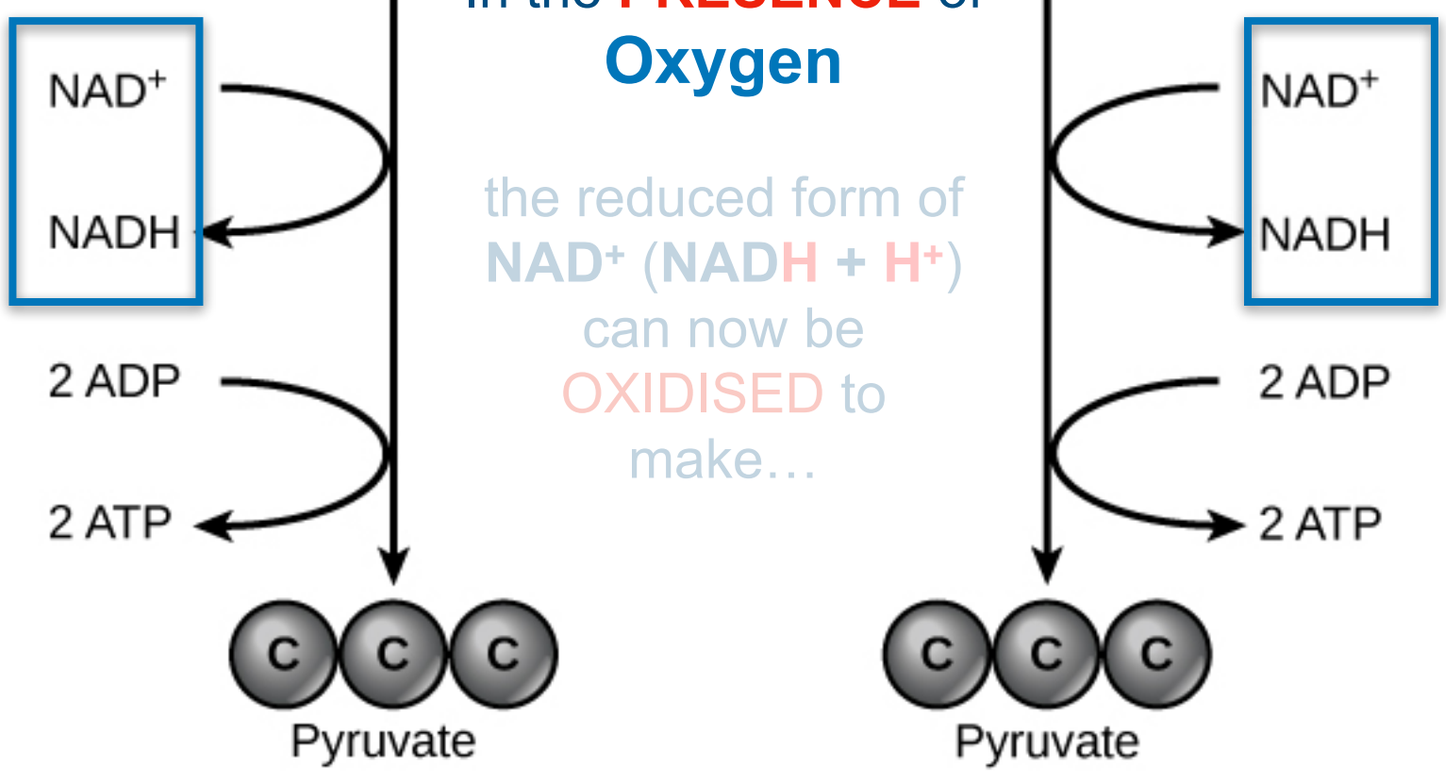
2 ADP

Fructose diphosphate

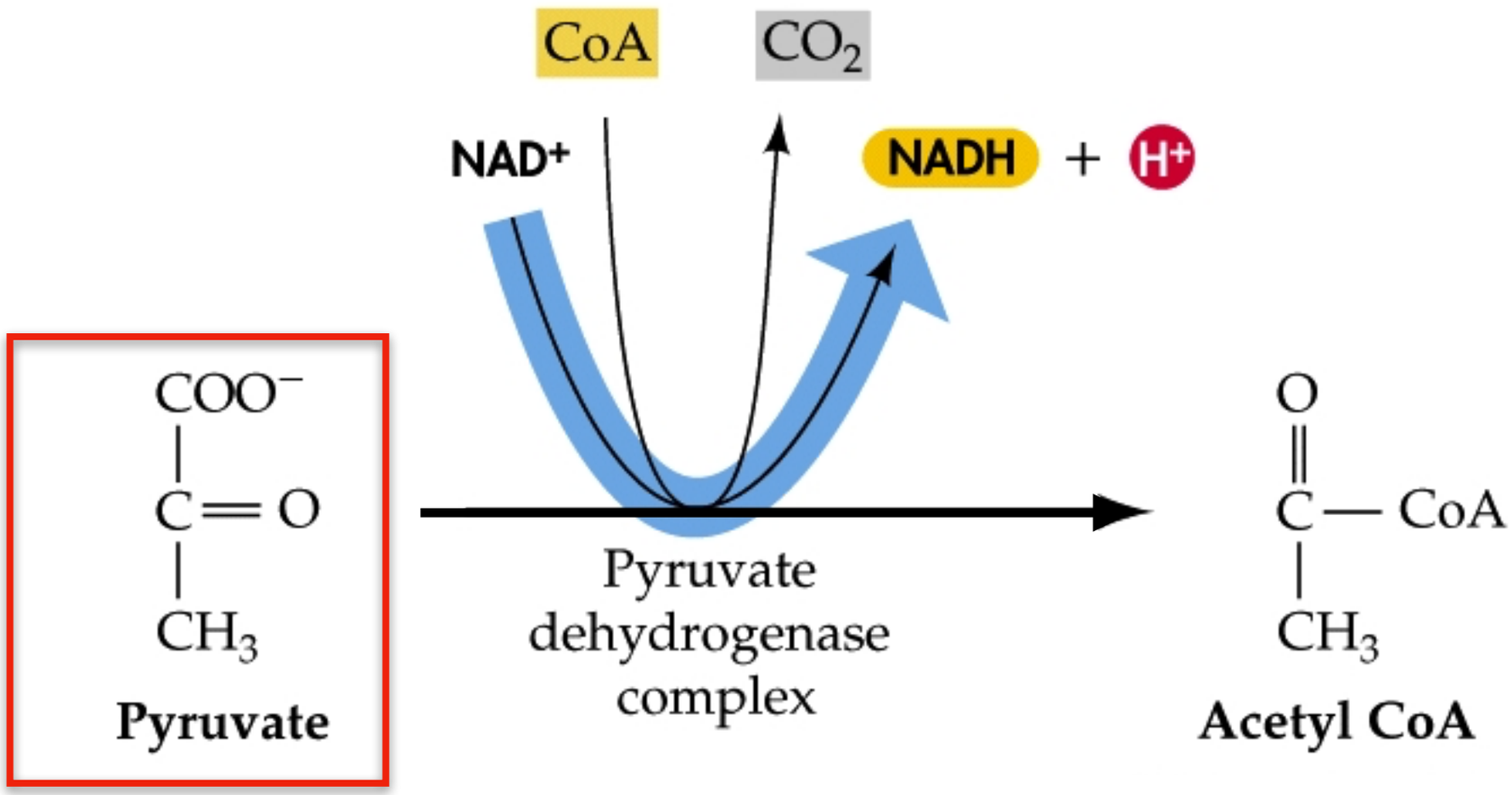
Glyceraldehyde 3-phosphate Glyceraldehyde 3-phosphate

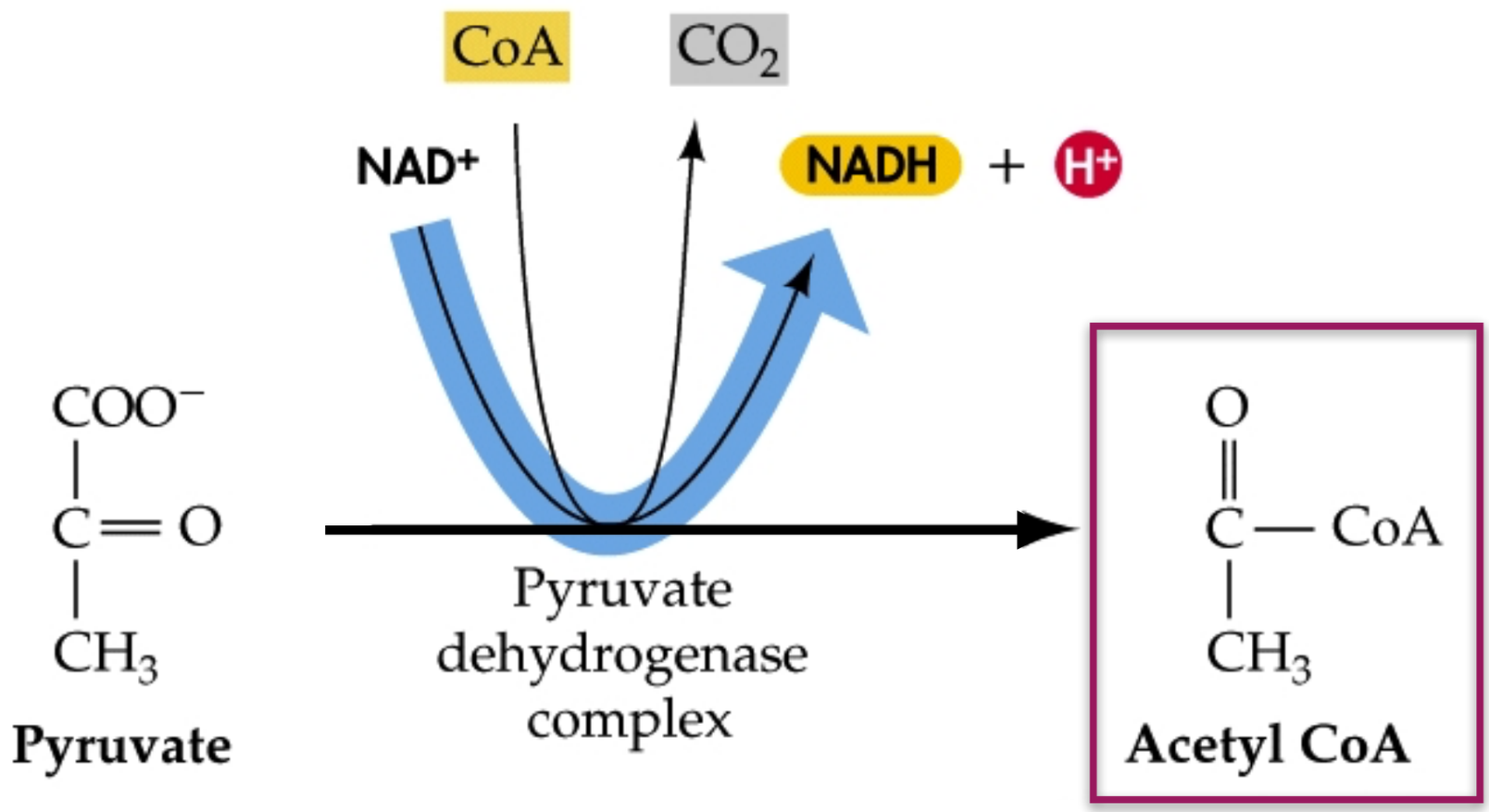
In the **PRESENCE** of **Oxygen**

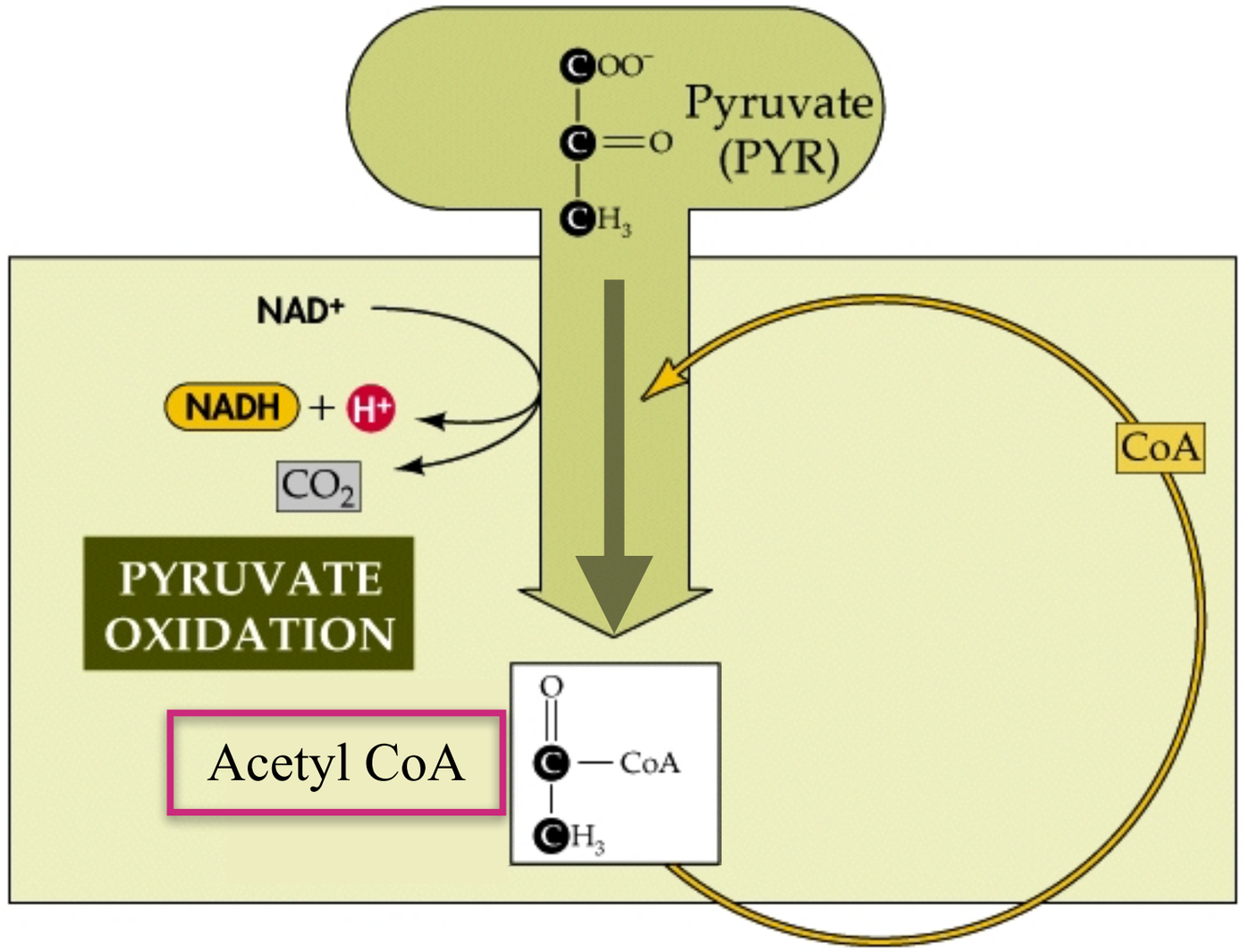
the reduced form of **NAD⁺** (**NADH + H⁺**) can now be OXIDISED to make…



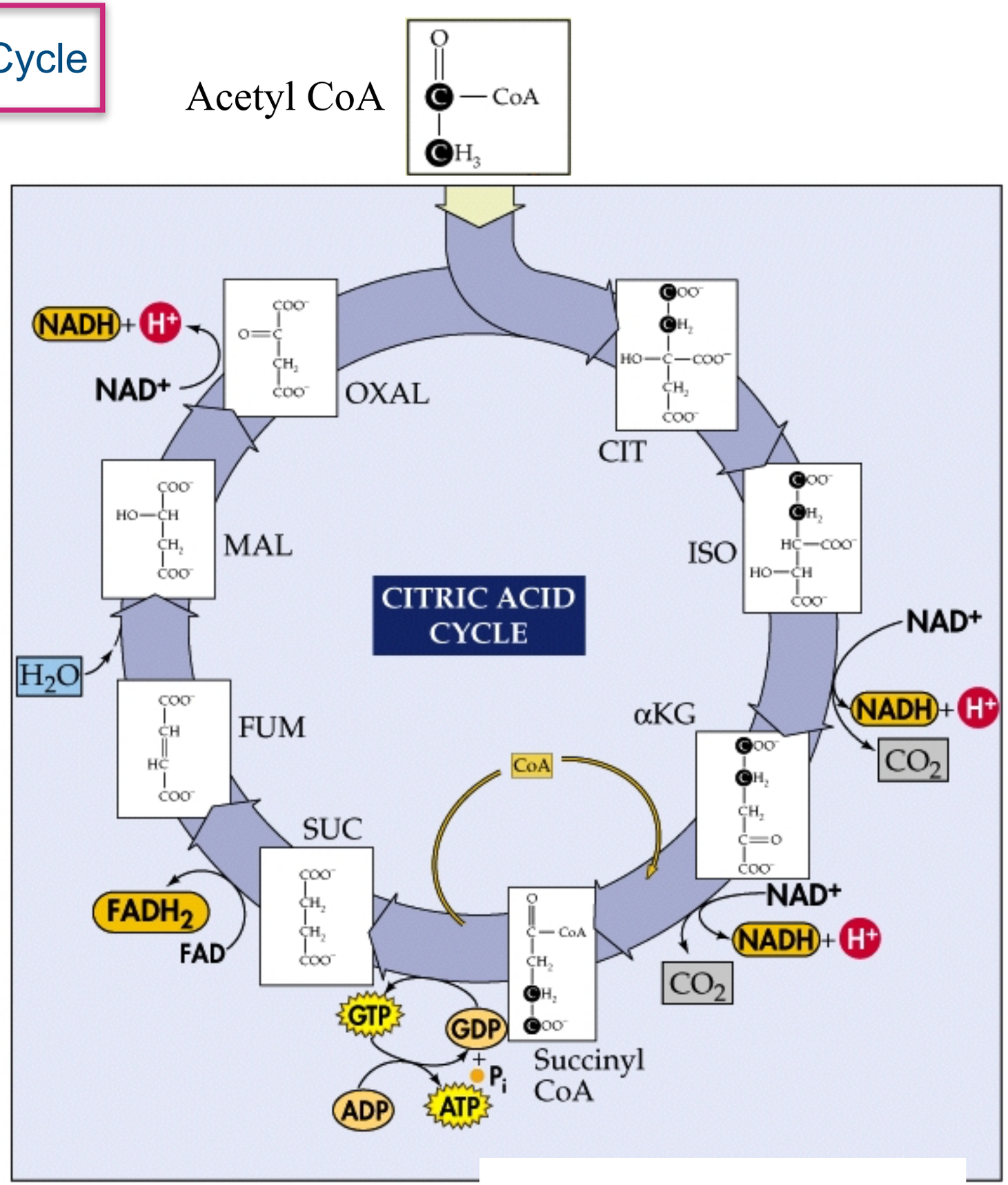
STAGE 2: Pyruvate Oxidation -from Pyruvate to AcetylCoA



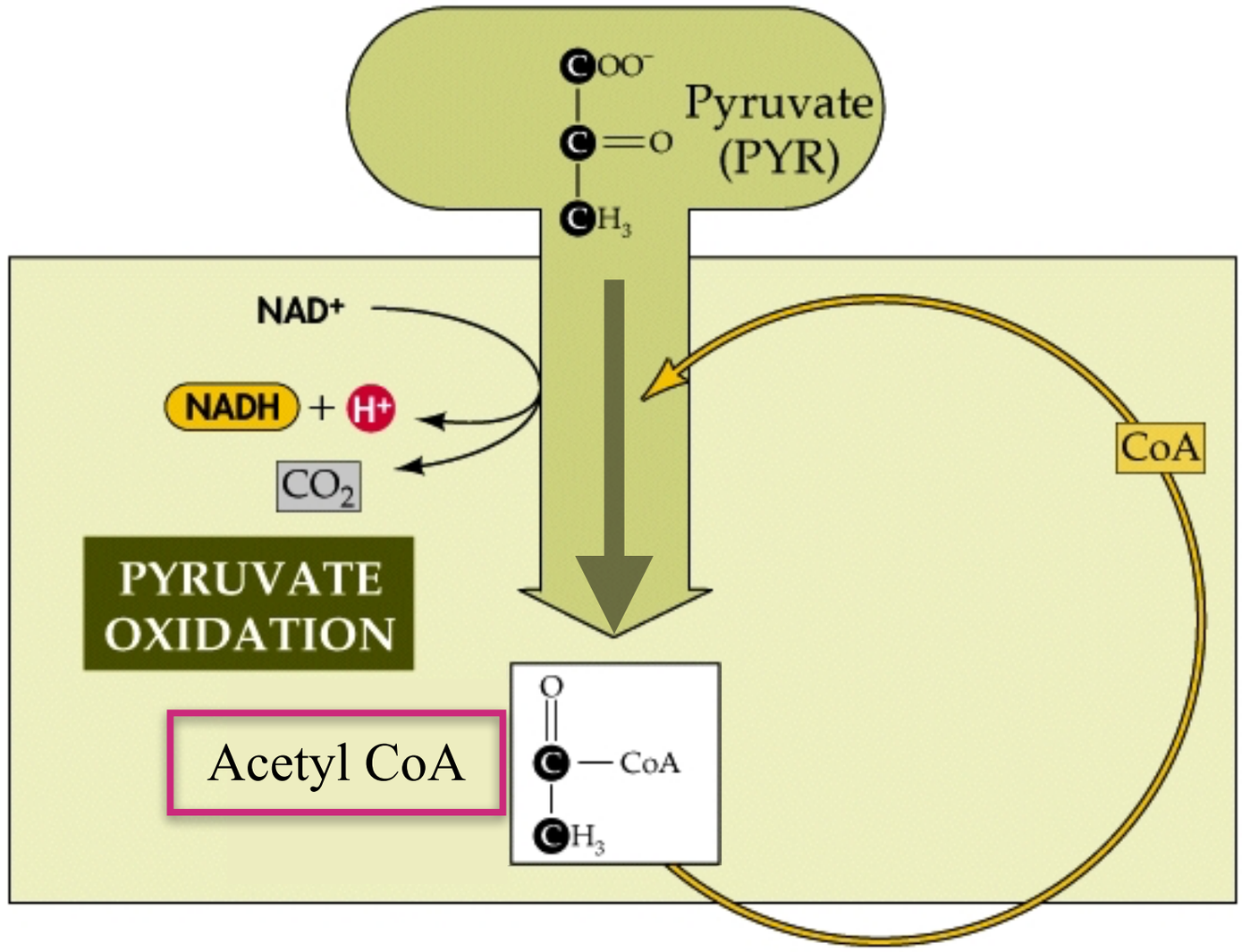

CoA
CO_2
NAD+
NADH + H+
COO⁻
C = O
CH_3
Pyruvate
Pyruvate dehydrogenase complex
O
C — CoA
CH_3
Acetyl CoA


COO⁻
C=O
CH3
Pyruvate
(PYR)
NAD+
NADH + H+
CO2
PYRUVATE
OXIDATION
CoA
Acetyl CoA
O
C — CoA
CH3

STAGE 3: Citric Acid Cycle

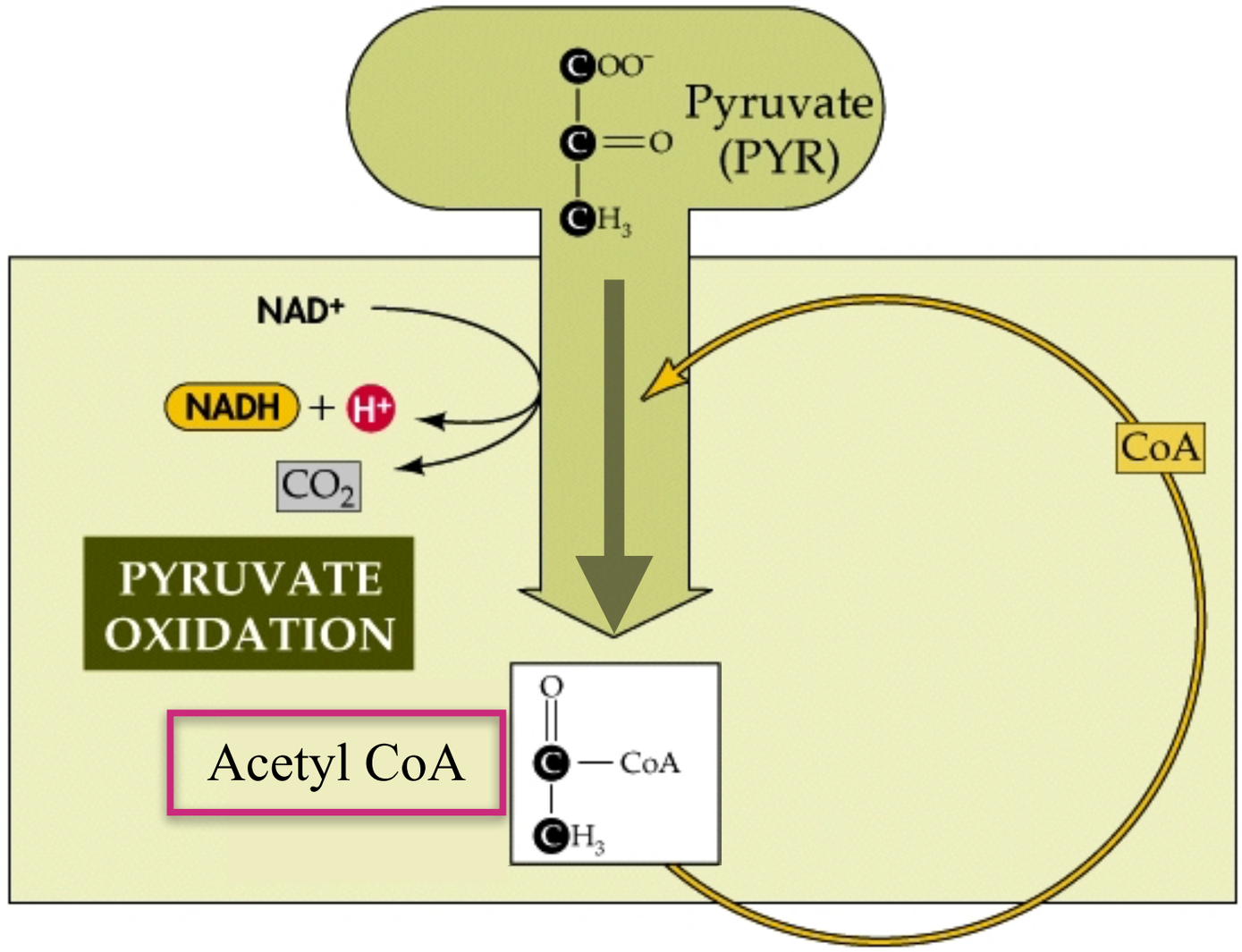


Inc.


COO⁻
C=O
CH3
Pyruvate
(PYR)
NAD+
NADH + H+
CO2
PYRUVATE
OXIDATION
CoA
Acetyl CoA
O
C — CoA
CH3

6.1 A Few Examples of Nonprotein Molecular "Partners" of Enzymes

TYPE OF MOLECULE	ROLE IN CATALYZED REACTIONS
Cofactors	
Iron	Oxidation/reduction
Copper	Oxidation/reduction
Zinc	Helps bind NAD
Coenzymes	
Biotin	Carries $—COO^-$
Coenzyme A	Carries $—CH_2—CH_3$
NAD	Carries electrons
FAD	Carries electrons
Prosthetic groups	
Heme	Binds ions, O_2, and electrons; contains iron cofactor
Flavin	Binds electrons
Retinal	Converts light energy


COO⁻
C=O
CH3
Pyruvate
(PYR)
NAD+
NADH + H+
CO2
PYRUVATE
OXIDATION
CoA
Acetyl CoA
O
C — CoA
CH3