1

Chem 352 - Lecture 7
Introduction to Metabolism

2-1

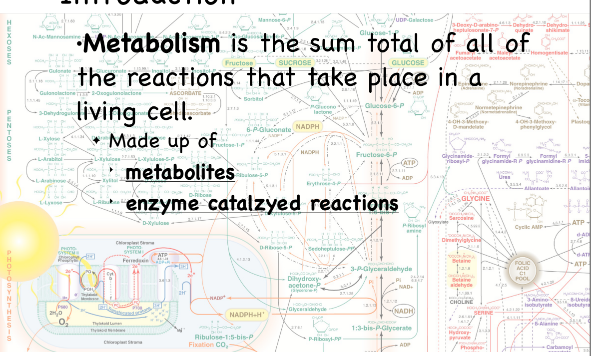
Introduction

·**Metabolism** is the sum total of all of the reactions that take place in a living cell.

- Made up of
  - **metabolites**
  - **enzyme catalzyed reactions**

2-2

Introduction



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2-3

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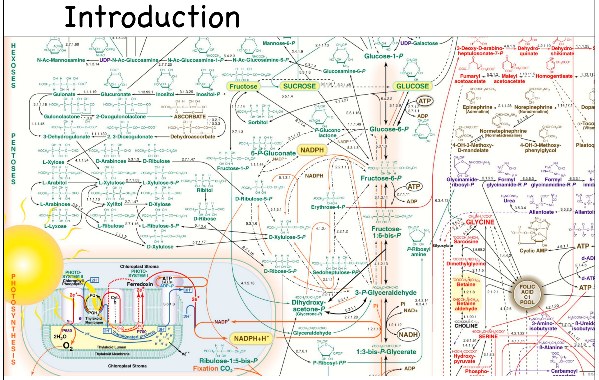
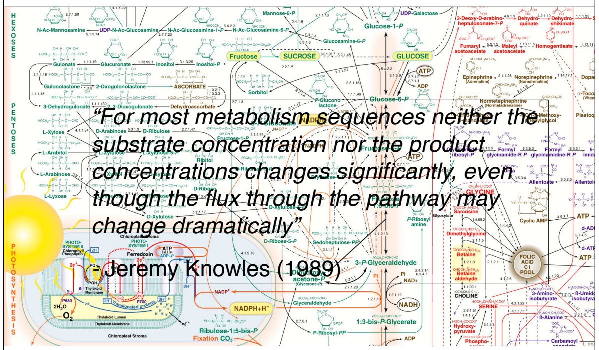


Introduction



"For most metabolism sequences neither the substrate concentration nor the product concentrations changes significantly, even though the flux through the pathway may change dramatically"

- Jeremy Knowles (1989)

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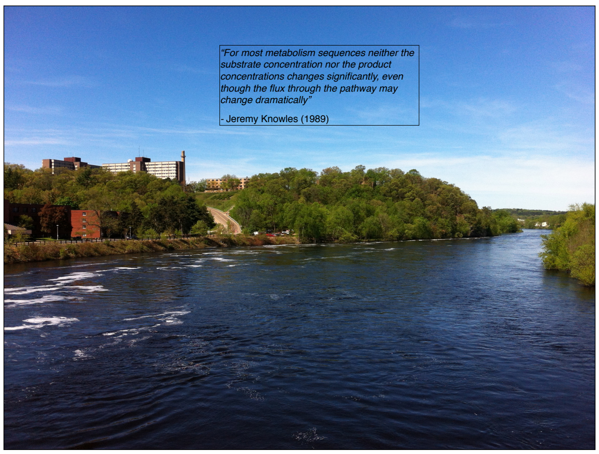

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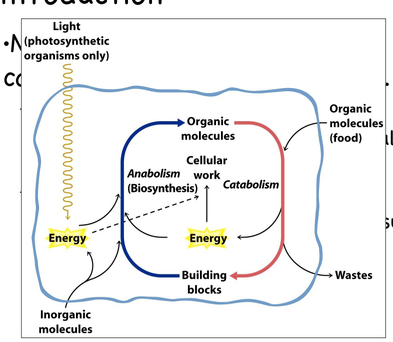
2-5

Introduction

- Metabolism is divided into two complimentary sets of reactions.
  - **Anabolic reactions (anabolism)**
    - The synthetic reactions, which usually require an input in free energy.
  - **Catabolic reaction (catabolism)**
    - The degradative reactions, which usually lead to a release of free energy.

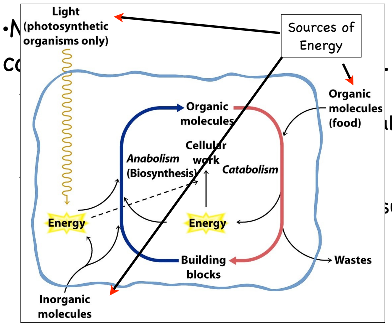
3-1

Introduction



3-2

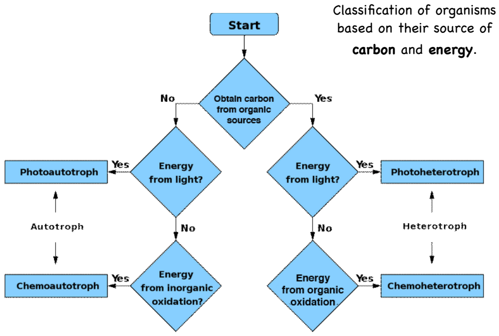
Introduction



3-3

Introduction

Classification of organisms based on their source of **carbon** and **energy**.



4

Metabolic Pathways

Common themes in metabolism:

5-1

Metabolic Pathways

Common themes in metabolism:

- Organisms or cells maintain specific internal concentrations of inorganic ions, metabolites, and enzymes. Cell membranes provide the physical barrier that segregates cell components from the environment.

5-2

Metabolic Pathways

Common themes in metabolism:

- Organisms extract energy from external sources to drive energy-consuming reactions. Photosynthetic organisms derive energy from the conversion of solar energy to chemical energy. Other organisms obtain energy from the ingestion and catabolism of energy-yielding compounds

5-3

Metabolic Pathways

Common themes in metabolism:

- The metabolic pathways in each organism are specified by the genes it contains in its genome.

5-4

Metabolic Pathways

Common themes in metabolism:

- Organisms and cells interact with their environment. The activities of cells must be geared to the availability of energy. Organisms grow and reproduce when the supply of energy from the environment is plentiful. When the supply of energy from the environment is limited, energy demands can be temporarily met by using internal stores or by slowing metabolic rates as in hibernation, sporulation, or seed formation. If the shortage is prolonged, organisms die.

5-5

Metabolic Pathways

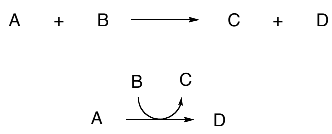
Common themes in metabolism:

- The cells of organisms are not static assemblies of molecules. Many cell components are continually synthesized and degraded, that is, they undergo turnover, even though their concentrations may remain virtually constant. The concentrations of other compounds change in response to changes in external or internal conditions.

5-6

Metabolic Pathways

The enzymes arrange the metabolites into pathways.



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Metabolic Pathways

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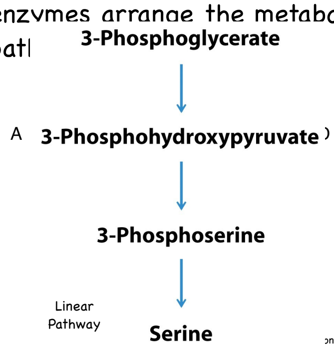

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Metabolic Pathways

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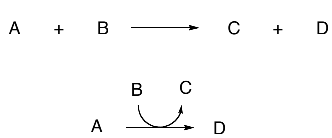

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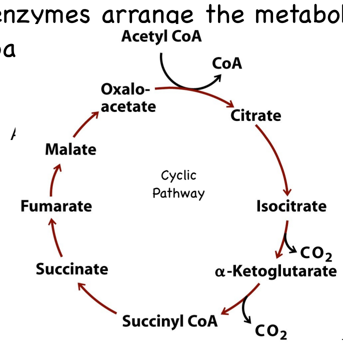

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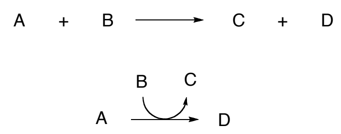

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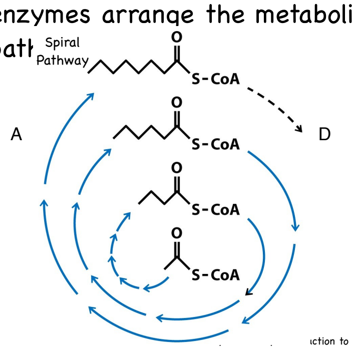

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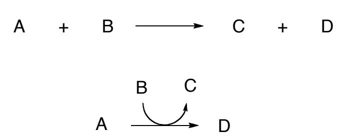

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Metabolic Pathways

Why pathways are broken down into little steps.

- Enzyme specificity allows only for breakage or formation of a few bonds at a time.
- Using pathways allows for multiple entry and exit points for metabolites.
- Pathways allow for finer control of energy input and output.
- Reactions are thermodynamically more efficient if carried out near equilibrium.

Metabolic Pathways

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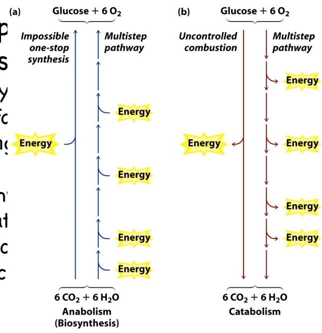

7-2

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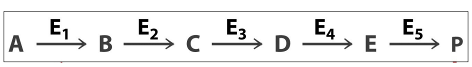
7-3

Metabolic Pathways

- Pathways are regulated
  - To control the flow of metabolites through a pathway



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Metabolic Pathways

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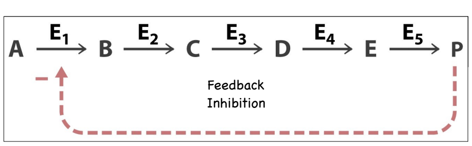

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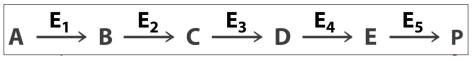

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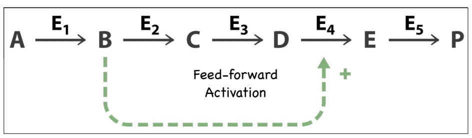

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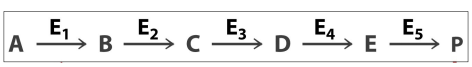

8-5

Metabolic Pathways

Pathways are regulated

- Allosteric regulation responds to immediate conditions within the cell,
  - And have short term response times.
- Reversible covalent modifications typically respond to extracellular signals,
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9-1

Metabolic Pathways

Pathways are regulated

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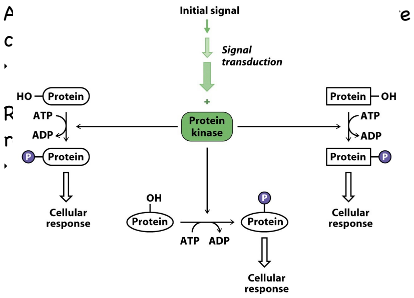

9-2

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9-3

Metabolic Pathways

Metabolic pathways represent the frontline for evolution.

- Genetic changes affect enzyme activities, which in turn, affect the flow of material through metabolic pathways.

10-1

Metabolic Pathways

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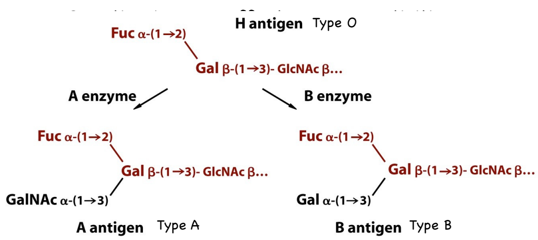

10-2

Metabolic Pathways

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10-3

Metabolic Pathways

Metabolic pathways represent the frontline for evolution.

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Andi Stempniak

Jennifer Czubakowski holds a picture of her brother, Tommy along with her parents Theresa and Ron in the living room of their Eau Claire home. Jenny Czubakowski held a picture of her late brother, Tommy, at the rural Eau Claire home she shares with their parents, Theresa and Ron. The family is trying to help people be aware of ornithine transcarbamylase deficiency, or OTC, which Tommy had.

10-4

Metabolic Pathways

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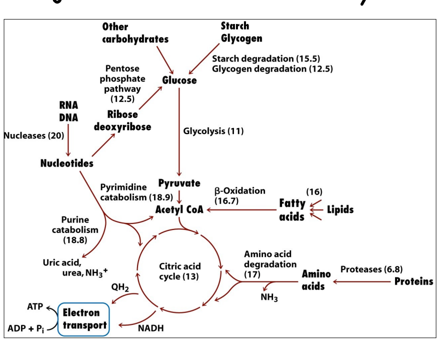
10-5

Major Metabolic Pathways



Catabolic Pathways

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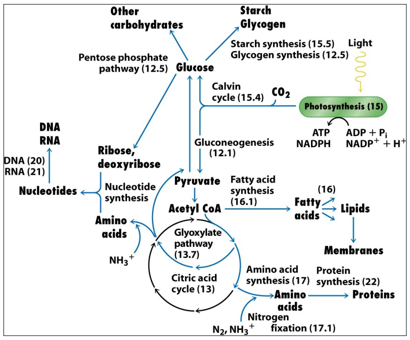
Major Metabolic Pathways



Anabolic Pathways

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Major Metabolic Pathways

- In many organisms, the various pathways are regulated through compartmentalization.

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Spontaneity of Metabolic Reactions

- The spontaneity (favorability) of a chemical reaction can be determined from its Gibbs Free Energy (ΔG)

$$\Delta G = \Delta G^{0'} + RT\ln\left(\frac{[\text{products}]}{[\text{reactants}]}\right)$$

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Spontaneity of Metabolic Reactions

Under conditions of constant temperature and pressure there are two contributions to the free energy change

- Enthalpy, H
- Entropy, S

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

15-1

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Change in heat content

15-2

Spontaneity of Metabolic Reactions

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- Enthalpy, H
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$$\Delta G = \Delta H - T\Delta S$$

Change in heat content   Change in disorder

15-3

Spontaneity of Metabolic Reactions

- The actual conditions within the cell must be considered when determining a ΔG value.

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

$Q = \left(\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}\right)$ is the mass action ratio

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Spontaneity of Metabolic Reactions

- When $Q \approx K_{eq}$ a reaction is reversible.
- When $Q < K_{eq}$ a reaction is spontaneous and irreversible.
- When $Q > K_{eq}$ a reaction is non-spontaneous and irreversible

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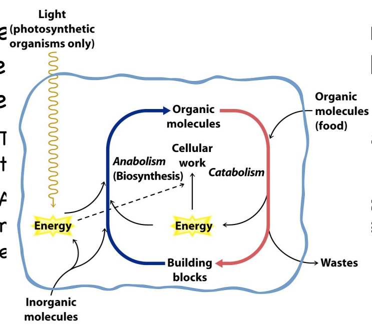
ATP

Adenosine Triphosphate (ATP) is one of the molecules used by a cell to store chemical energy.

- This energy is released by the hydrolysis of the two phosphate anhydride bonds.
- ATP is one of the ways that the energy released from catabolism is used to meet the energy requirements of anabolism

18-1

ATP



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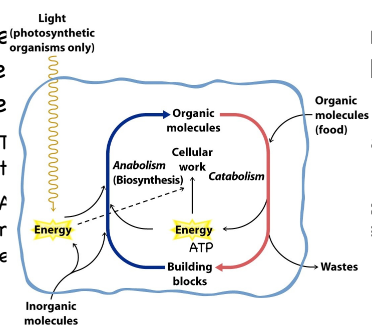
ATP



18-3

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18-4

18-5

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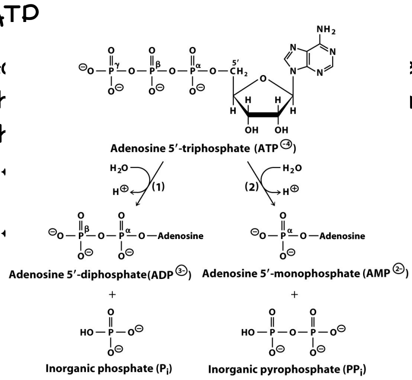

18-6

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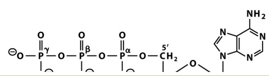
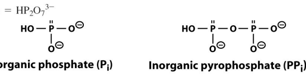


TABLE 10.1 Standard Gibbs free energies of hydrolysis for ATP, AMP, and pyrophosphate.

Reactants and products	$\Delta G^{\circ\prime}_{hydrolysis}$ (kJ mol^{-1})
$ATP + H_2O \rightarrow ADP + P_i + H^{\oplus}$	−32
$ATP + H_2O \rightarrow AMP + PP_i + H^{\oplus}$	−45
$AMP + H_2O \rightarrow$ Adenosine $+ P_i$	−13
$PP_i + H_2O \rightarrow 2\ P_i$	−29

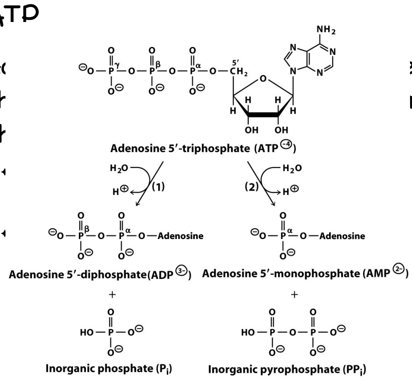
P_i (inorganic phosphate) = HPO_4^{2-}

PP_i (pyrophosphate) = $HP_2O_7^{3-}$



18-7

ATP



18-8

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19-1

ATP

- Adenosine Triphosphate (ATP) is just one of the molecules used by a cell to store chemical energy.
  - The other ribonucleotide triphosphates are also used for this same purpose.
    - Guanosine triphosphate (GTP)
    - Cytidine triphosphate (CTP)
    - Uridine triphosphate (UTP

19-2

ATP

- Adenosine Triphosphate (ATP) is just one of the molecules used by a cell to store chemical energy.

Question:
In a rat hepatocyte, the concentrations ATP, ADP and Pi are 3.4 mM, 1.3 mM and 4.8 mM, respectively. Calculate the Gibbs free energy for the hydrolysis of ATP in this cell. How does this compare to the standard free energy change?

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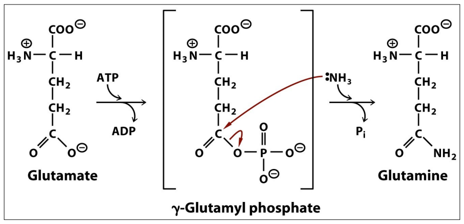
ATP

- The hydrolysis of ATP can be used to drive unfavorable reactions



21-1

ATP

- Phosphoryl-group-transfer potential

TABLE 10.3 Standard Gibbs free energies of hydrolysis for common metabolites

Metabolite	$\Delta G^{\circ\prime}_{hydrolysis}$ (kJ mol^{-1})
Phosphoenolpyruvate	−62
1,3-*Bis*phosphoglycerate	−49
ATP to AMP + PP$_i$	−45
Phosphocreatine	−43
Phosphoarginine	−32
Acetyl CoA	−32
ATP to ADP + P$_i$	−32
Pyrophosphate	−29
Glucose 1-phosphate	−21
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Glycerol 3-phosphate	−9

21-2

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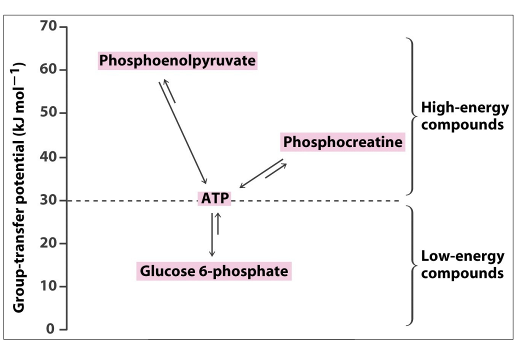
21-3

ATP



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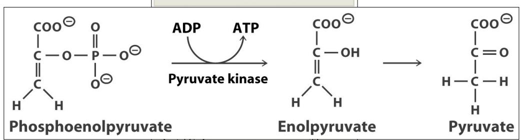

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21-4

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- Nucleotidyl group transfer
  - Used to activate substrates in ligase reactions

22-1

ATP

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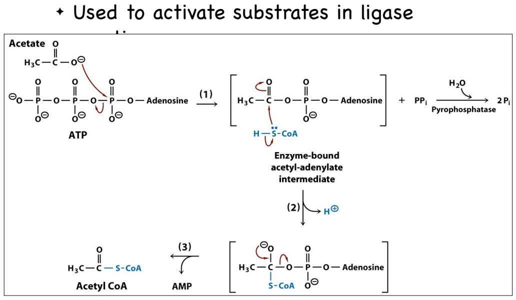

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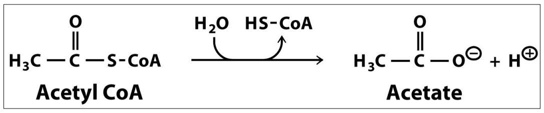
ATP

- Nucleotidyl group transfer
  - Used to activate substrates in ligase reactions

22-3

Thioesters as High Energy Compounds

- The thioester group also has a high energy for hydrolysis



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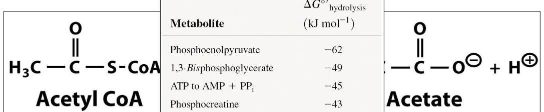

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23-2

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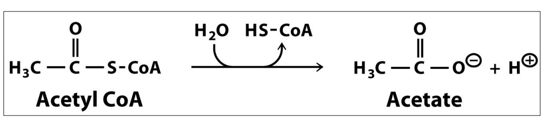

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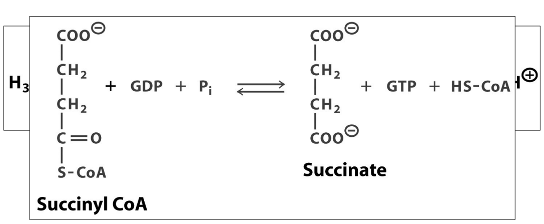

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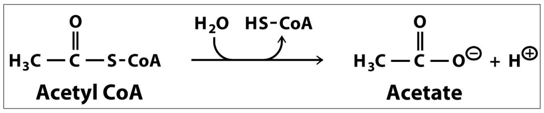
23-5

Thioesters as High Energy Compounds

- The thioester group also has a high energy for hydrolysis



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Chem 352 - Lecture 7 Introduction to Metabolism 2. April, 2014

Question for the Day: How is metabolism like a river?

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Reduced Coenzymes

- Reduced coenzymes (NAD, NADP, FAD, FMN, ubiquinone) provide another way to store chemical energy.
  - They can be used to store the free energy that is released in oxidation reactions.
  - The electrons released in these reactions are transferred to the coenzyme, usually in the form of a hydride ($H:^-$) ion.

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Reduced Coenzymes

- **Reduction potentials** can be used to measure the ability of a molecule to serve as a reducing agent in an oxidation/reduction reaction

$$A_{oxidized} + B_{reduced} \rightarrow A_{reduced} + B_{oxidized}$$

(B is the reducing agent in this reaction)

Reduced Coenzymes

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Reduction potentials can be measured with an electrochemical cell.

- The oxidation and reduction are separated by a wire.

The reduction of Cu^{2+} by Zn

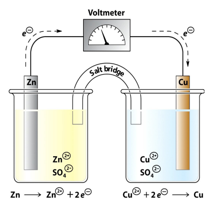
$Zn + Cu^{2+} \leftrightarrow Zn^{2+} + Cu$

$\Delta G' = -n\mathscr{F}\Delta E'$ (Nernst Equation)

$\Delta E'$ = potential measured by the voltmeter

n = number of electrons transferred

F = Faraday's constant (96,586 $JV^{-1}mol^{-1}$)



Reduced Coenzymes

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The change in the reduction potential for an oxidation/reduction reaction ($\Delta E^{o\prime}$) can be used to determine the change in Free energy for the reaction.

$$\Delta E^{o\prime} = E^{o\prime}_{\text{electron acceptor}} - E^{o\prime}_{\text{electron donor}}$$

$$\Delta G^{o\prime} = -n\mathscr{F}\Delta E^{o\prime}$$

n = number of electrons transferred

F = Faraday's constant (96,586 $JV^{-1}mol^{-1}$)

Reduced Coenzymes

29

Standard reduction potentials, Eo′, are usually measured with respect to the reduction potential for of $2\ H^+(aq) \rightarrow H_2(g)$

TABLE 10.4 Standard reduction potentials of some important biological half-reactions

Reduction half-reaction	$E^{\circ\prime}$ (V)
Acetyl CoA + CO_2 + $H^{\oplus}$ + $2e^{\ominus}$ → Pyruvate + CoA	−0.48
Ferredoxin (spinach), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	−0.43
2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2 (at pH 7.0)	−0.42
α-Ketoglutarate + CO_2 + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Isocitrate	−0.38
Lipoyl dehydrogenase (FAD) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Lipoyl dehydrogenase ($FADH_2$)	−0.34
$NADP^{\oplus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → NADPH + $H^{\oplus}$	−0.32
$NAD^{\oplus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → NADH + $H^{\oplus}$	−0.32
Lipoic acid + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Dihydrolipoic acid	−0.29
Glutathione (oxidized) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → 2 Glutathione (reduced)	−0.23
FAD + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $FADH_2$	−0.22
FMN + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $FMNH_2$	−0.22
Acetaldehyde + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Ethanol	−0.20
Pyruvate + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Lactate	−0.18
Oxaloacetate + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Malate	−0.17

TABLE 10.4 Standard reduction potentials of some important biological half-reactions

Reduction half-reaction	$E^{\circ\prime}$ (V)
Cytochrome b_5 (microsomal), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.02
Fumarate + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Succinate	0.03
Ubiquinone (Q) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → QH_2	0.04
Cytochrome *b* (mitochondrial), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.08
Cytochrome c_1, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.22
Cytochrome *c*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.23
Cytochrome *a*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.29
Cytochrome *f*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.36
Plastocyanin, Cu^{2+} + $e^{\ominus}$ → Cu^{+}	0.37
$NO_3^{\ominus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $NO_2^{\ominus}$ + H_2O	0.42
Photosystem I (P700)	0.43
Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.77
$\frac{1}{2}O_2$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2O	0.82
Photosystem II (P680)	1.1

Reduced Coenzymes

30-1

- Like ΔG, the observed change in the reduction potential for a reaction, (ΔE), can be determined relative to the change in the standard reduction potential, ($\Delta E^{o\prime}$):

$$\Delta E = \Delta E^{o\prime} - \frac{RT}{n\mathscr{F}}\ln\left(\frac{[A_{ox}][B_{red}]}{[A_{red}][B_{ox}]}\right)$$

Reduced Coenzymes

30-2

Problem:

Determine the standard free energy change for the oxidation of NADH + H^+ by O_2.

$$\tfrac{1}{2} O_2 + NADH + H^+ \rightarrow H_2O + NAD^+$$

- Like ΔG, the observed change in the reduction potential for a reaction, (ΔE), can be determined relative to the change in the standard reduction potential, ($\Delta E^{o\prime}$):

$$\Delta E = \Delta E^{o\prime} - \frac{RT}{n\mathscr{F}} \ln\left(\frac{[A_{ox}][B_{red}]}{[A_{red}][B_{ox}]}\right)$$

Reduced Coenzymes

30-3

Problem:

Determine the standard free energy change for the oxidation of NADH + H^+ by O_2.

$$\tfrac{1}{2} O_2 + NADH + H^+ \rightarrow H_2O + NAD^+$$

$$\Delta G^{\circ\prime} = -n\mathscr{F}\Delta E^{\circ\prime}$$

- Like ΔG, the observed change in the reduction potential for a reaction, (ΔE), can be determined relative to the change in the standard reduction potential, ($\Delta E^{o\prime}$):

$$\Delta E = \Delta E^{o\prime} - \frac{RT}{n\mathscr{F}} \ln\left(\frac{[A_{ox}][B_{red}]}{[A_{red}][B_{ox}]}\right)$$

Reduced Coenzymes

30-4

TABLE 10.4 Standard reduction potentials of some important biological half-reactions

Reduction half-reaction	$E^{\circ\prime}$ (V)
Cytochrome b_5 (microsomal), $Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.02
Fumarate + 2 H^+ + $2e^-$ → Succinate	0.03
Ubiquinone (Q) + 2 H^+ + $2e^-$ → QH_2	0.04
Cytochrome b (mitochondrial), $Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.08
Cytochrome c_1, $Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.22
Cytochrome c, $Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.23
Cytochrome a, $Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.29
Cytochrome f, $Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.36
Plastocyanin, $Cu^{2+} + e^- \rightarrow Cu^+$	0.37
$NO_3^- + 2 H^+ + 2e^- \rightarrow NO_2^- + H_2O$	0.42
Photosystem I (P700)	0.43
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$\tfrac{1}{2} O_2 + 2 H^+ + 2e^- \rightarrow H_2O$	0.82
Photosystem II (P680)	1.1

Pr ... fr ... re ... re ... st ... n ... o′):

Reduced Coenzymes

30-5

TABLE 10.4 Standard reduction potentials of some important biological half-reactions

Reduction half-reaction	$E^{\circ\prime}$ (V)
Acetyl CoA + CO_2 + H^+ + $2e^-$ → Pyruvate + CoA	−0.48
Ferredoxin (spinach), $Fe^{3+} + e^- \rightarrow Fe^{2+}$	−0.43
$2 H^+ + 2e^- \rightarrow H_2$ (at pH 7.0)	−0.42
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NAD^+ + 2 H^+ + $2e^-$ → NADH + H^+	−0.32
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FAD + 2 H^+ + $2e^-$ → $FADH_2$	−0.22
FMN + 2 H^+ + $2e^-$ → $FMNH_2$	−0.22
Acetaldehyde + 2 H^+ + $2e^-$ → Ethanol	−0.20
Pyruvate + 2 H^+ + $2e^-$ → Lactate	−0.18
Oxaloacetate + 2 H^+ + $2e^-$ → Malate	−0.17

Pr ... fr ... re ... re ... st ... n ... o′):

Reduced Coenzymes

Problem:

Determine the standard free energy change for the oxidation of NADH + H^+ by O_2.

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

$\Delta G^{\circ} = -n\mathscr{F}\Delta E^{\circ}$

- Like ΔG, the observed change in the reduction potential for a reaction, (ΔE), can be determined relative to the change in the standard reduction potential, ($\Delta E^{o\prime}$):

$$\Delta E = \Delta E^{o\prime} - \frac{RT}{n\mathscr{F}}\ln\left(\frac{[A_{ox}][B_{red}]}{[A_{red}][B_{ox}]}\right)$$

30-6

Reduced Coenzymes

- Like ΔG, the observed change in the reduction potential for a reaction, (ΔE), can be determined relative to the change in the standard reduction potential, ($\Delta E^{o\prime}$):

$$\Delta E = \Delta E^{o\prime} - \frac{RT}{n\mathscr{F}}\ln\left(\frac{[A_{ox}][B_{red}]}{[A_{red}][B_{ox}]}\right)$$

30-7

Reduced Coenzymes

Problem:

Determine the maximum number of ATP's that could be synthesized from ADP and P_i if coupled to the oxidation of NADH + H^+ by O_2.

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

$ADP + P_i \rightarrow ATP + H_2O$

$$\Delta E = \Delta E^{o\prime} - \frac{RT}{n\mathscr{F}}\ln\left(\frac{[A_{ox}][B_{red}]}{[A_{red}][B_{ox}]}\right)$$

31-1

Reduced Coenzymes

Problem:

Determine the max... d be synthesized from A... ation of NADH + H^+ by O_2.

$1/2\ O_2$ + N...

$\Delta E = \Delta$...

TABLE 10.3 Standard Gibbs free energies of hydrolysis for common metabolites

Metabolite	$\Delta G^{o\prime}_{hydrolysis}$ (kJ mol^{-1})
Phosphoenolpyruvate	−62
1,3-*Bis*phosphoglycerate	−49
ATP to AMP + PP_i	−45
Phosphocreatine	−43
Phosphoarginine	−32
Acetyl CoA	−32
ATP to ADP + P_i	−32
Pyrophosphate	−29
Glucose 1-phosphate	−21
Glucose 6-phosphate	−14
Glycerol 3-phosphate	−9

31-2

Reduced Coenzymes

Problem:

Determine the maximum number of ATP's that could be synthesized from ADP and P_i if coupled to the oxidation of NADH + H^+ by O_2.

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

$$ADP + P_i \rightarrow ATP + H_2O$$

$$\Delta E = \Delta E^{o'} - \frac{RT}{n\mathscr{F}} \ln\left(\frac{[A_{ox}][B_{red}]}{[A_{red}][B_{ox}]}\right)$$

31-3

Next Up

- Lecture 8 - Carbohydrate Metabolism
  - Part I: Glycolysis (Moran et al., Chapter 11)

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