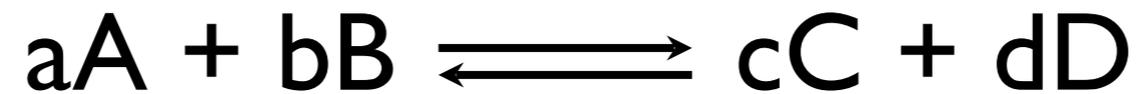


Relação entre ΔG da reação, e concentrações de reagentes e produtos



$$K_{eq} = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$$

$$\Delta G = \Delta G^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

No equilíbrio:

$\Delta G=0$, e portanto:

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

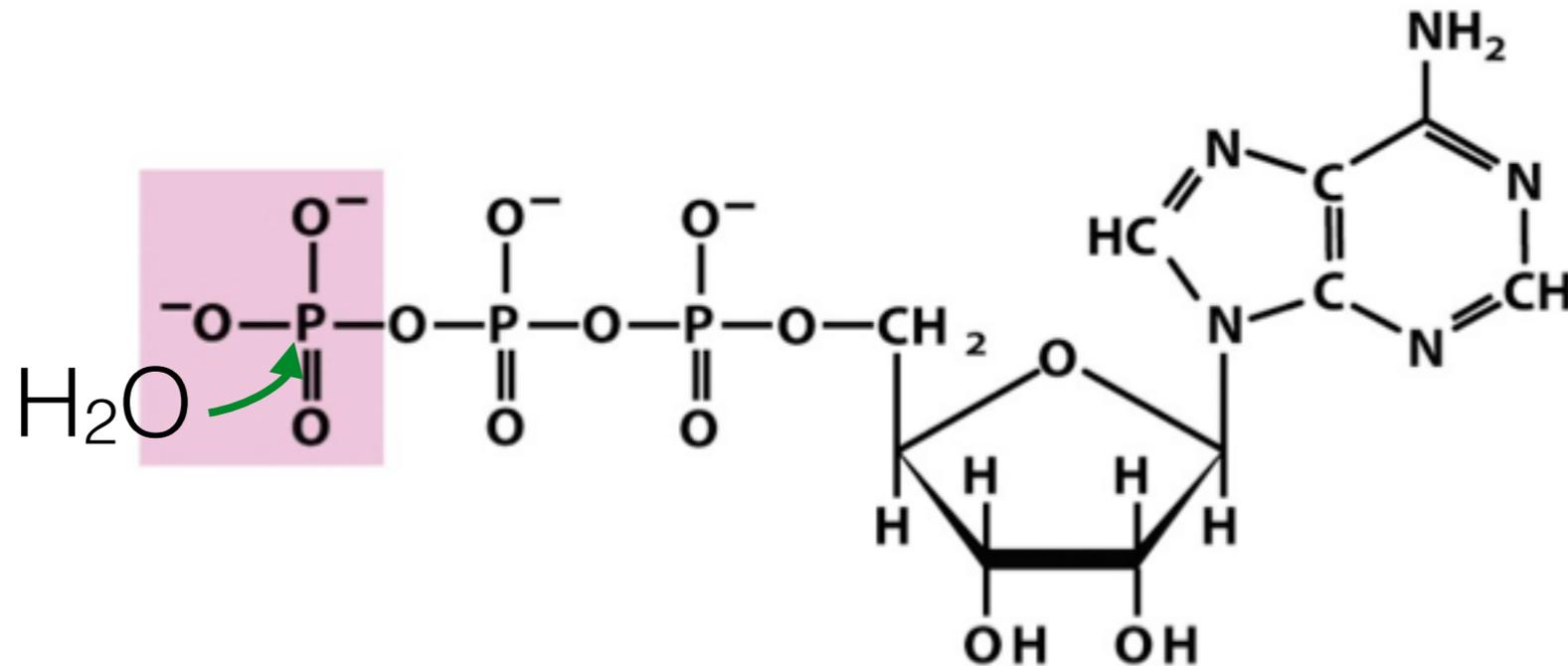
$$K_{eq} > 1 \longrightarrow \Delta G^0 < 0$$

$$K_{eq} < 1 \longrightarrow \Delta G^0 > 0$$

espontâneo

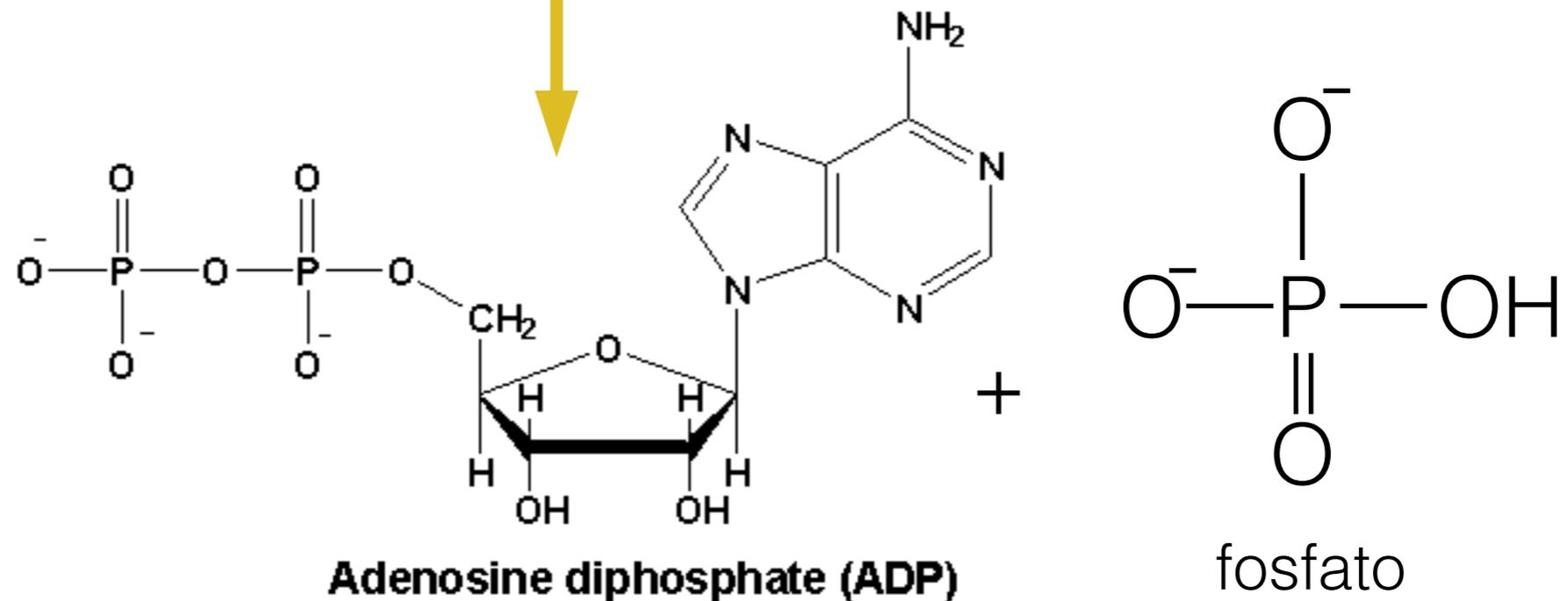
não
espontâneo

A energia necessária para promover os processos celulares é obtida a partir da hidrólise de ATP

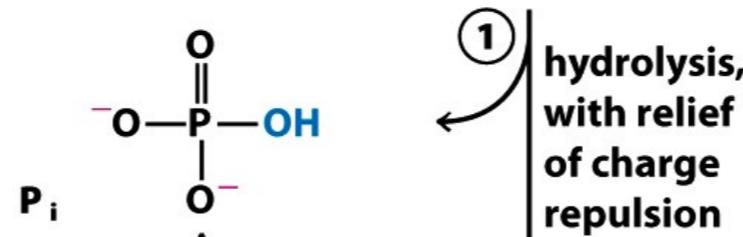
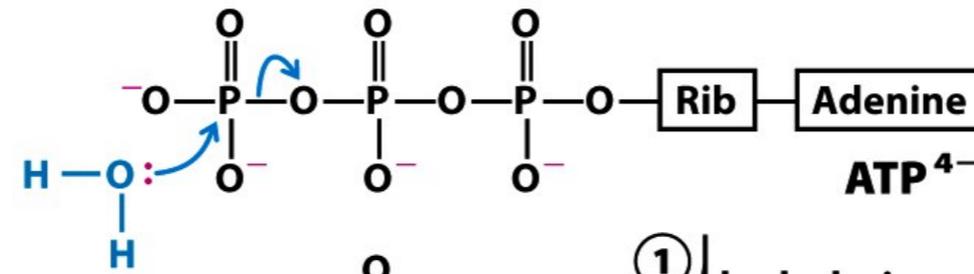


Adenosina trifosfato (ATP)

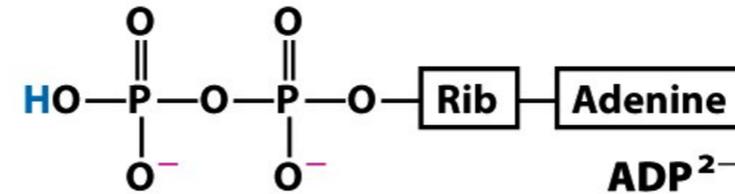
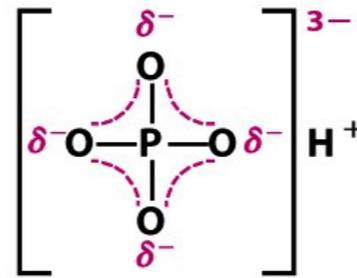
$$\Delta G^{0'} = -30.5 \text{ kJ mol}^{-1}$$



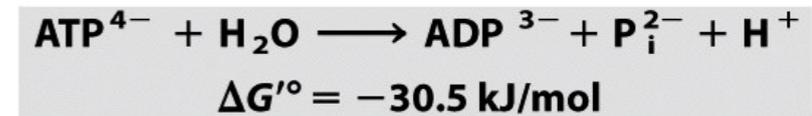
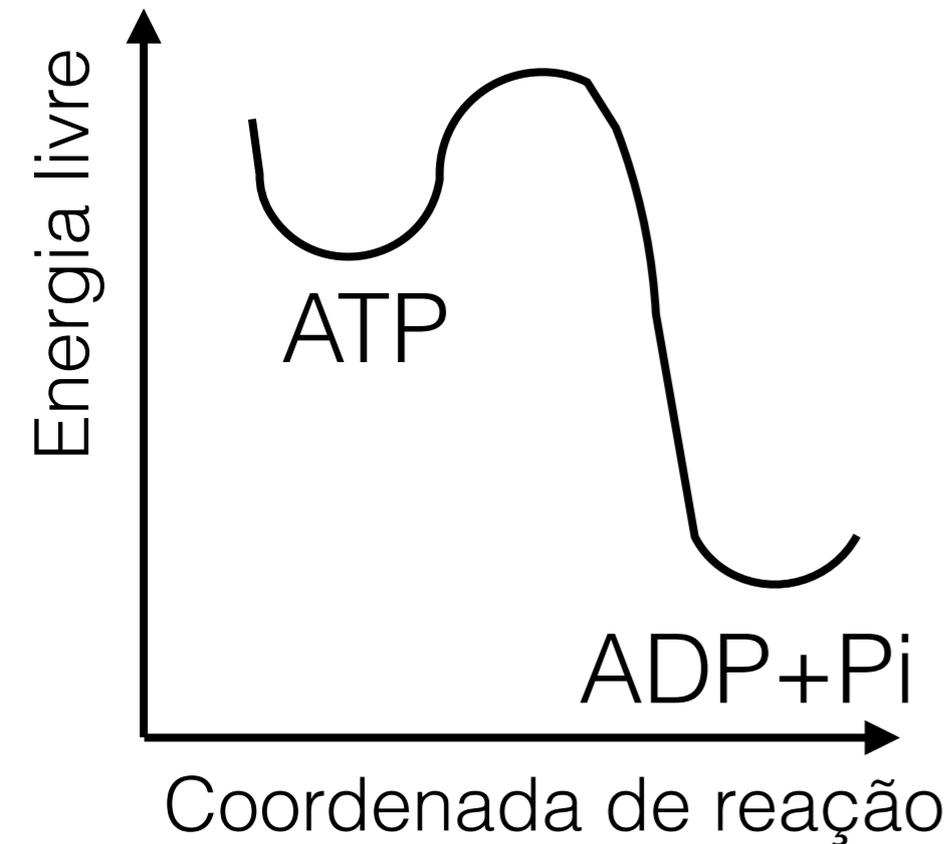
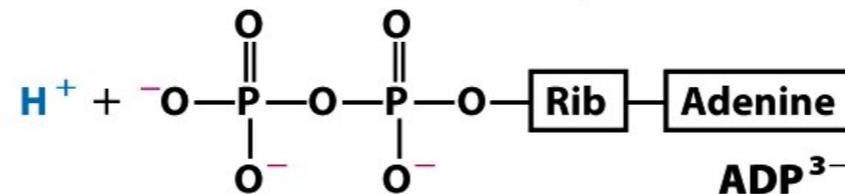
Por que a reação de hidrólise do ATP é tão exergônica?



② resonance stabilization



③ ionization



A reação de hidrólise do ATP libera de fato tanta energia?

Energia de hidrólise de ATP:

$$\Delta G^{0'} = -30.5 \text{ kJ mol}^{-1}$$

Energia de hidrólise de ATP
em células de eritrócitos:

$$\Delta G^{0'} = -52 \text{ kJ mol}^{-1}$$

Energia de hidrólise de ATP
em células musculares:

$$\Delta G^{0'} = -64 \text{ kJ mol}^{-1}$$

$$\Delta G = \Delta G^{0'} + RT \ln \frac{[\text{ADP}][\text{Pi}]}{[\text{ATP}]}$$

A energia livre nas condições celulares depende das concentrações de ATP, ADP e Pi

Energia de ligações covalentes

Ligação	E (kJ/mol)
H—C	337.23
C—C	411.29

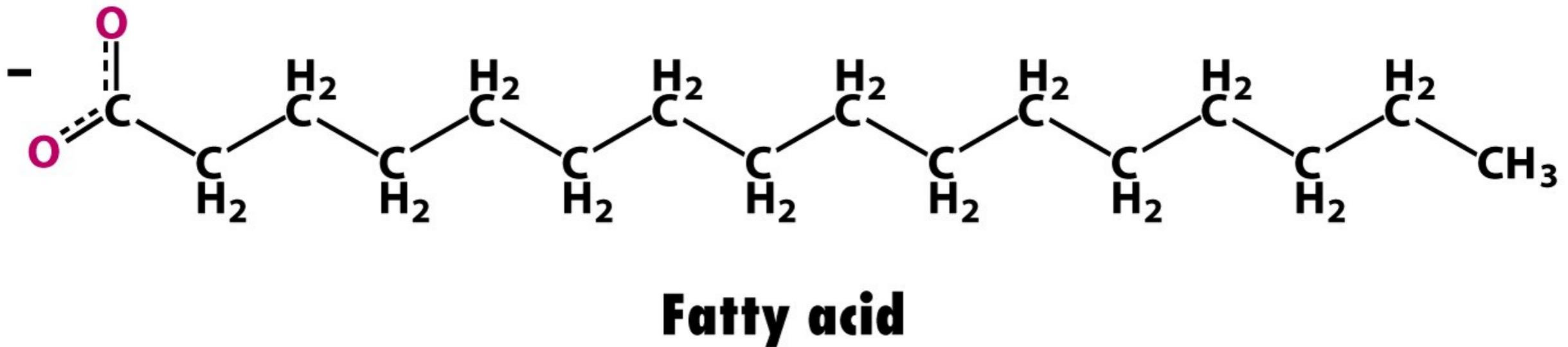
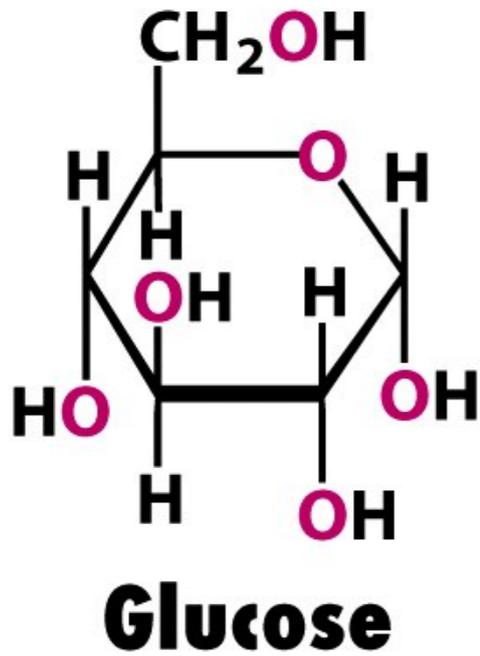
Ligação de hidrogênio:

Água/Água	23.01 kJ/mol
-----------	--------------

Dill, K. et al. Molecular Driving Forces, Garland Science, 1ª. ed., 2003, Madison

Moléculas de ATP são formadas durante a oxidação completa da glicose em CO_2 e H_2O

Ácidos graxos e moléculas de ATP são as principais fontes de energia das células



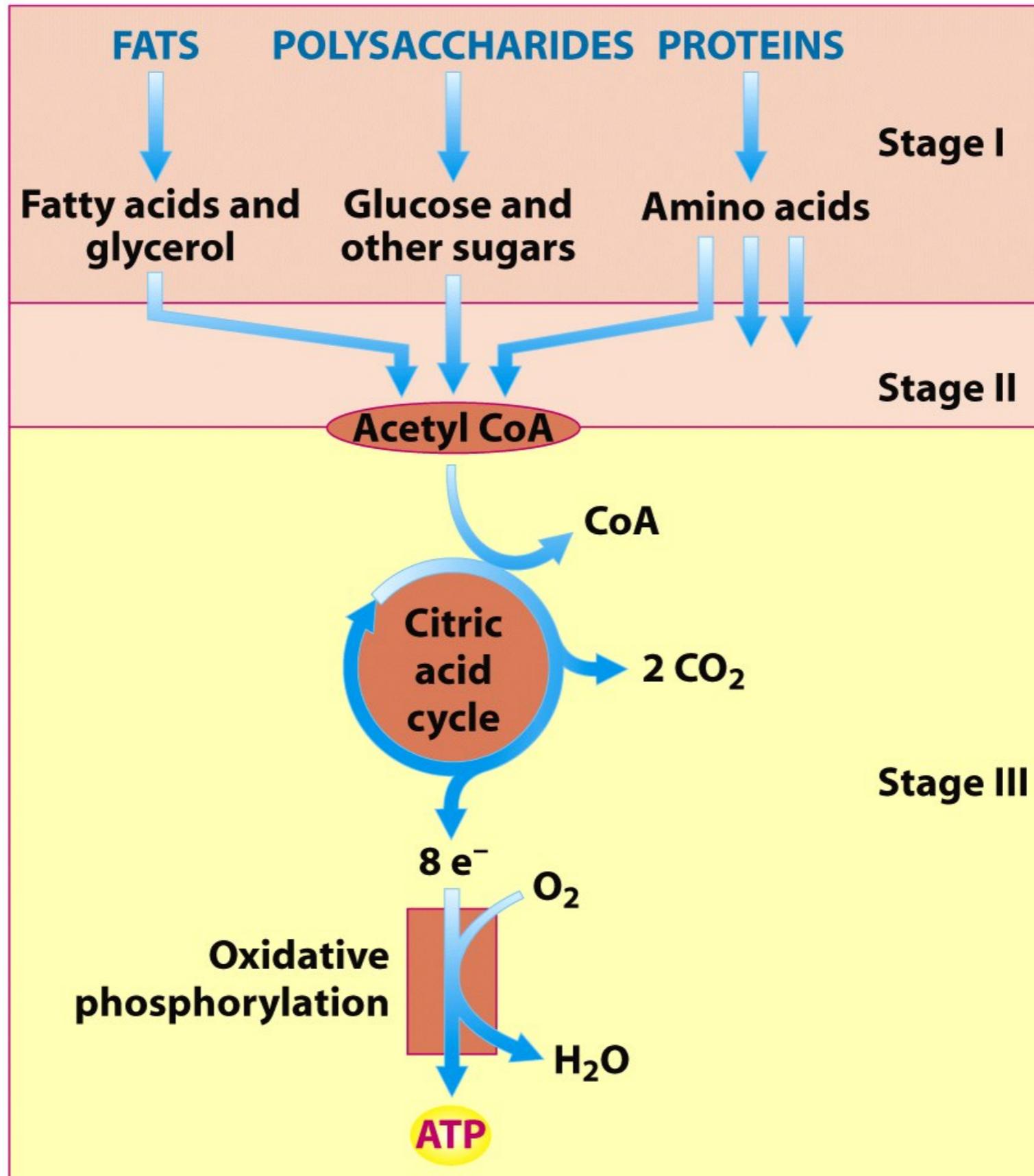
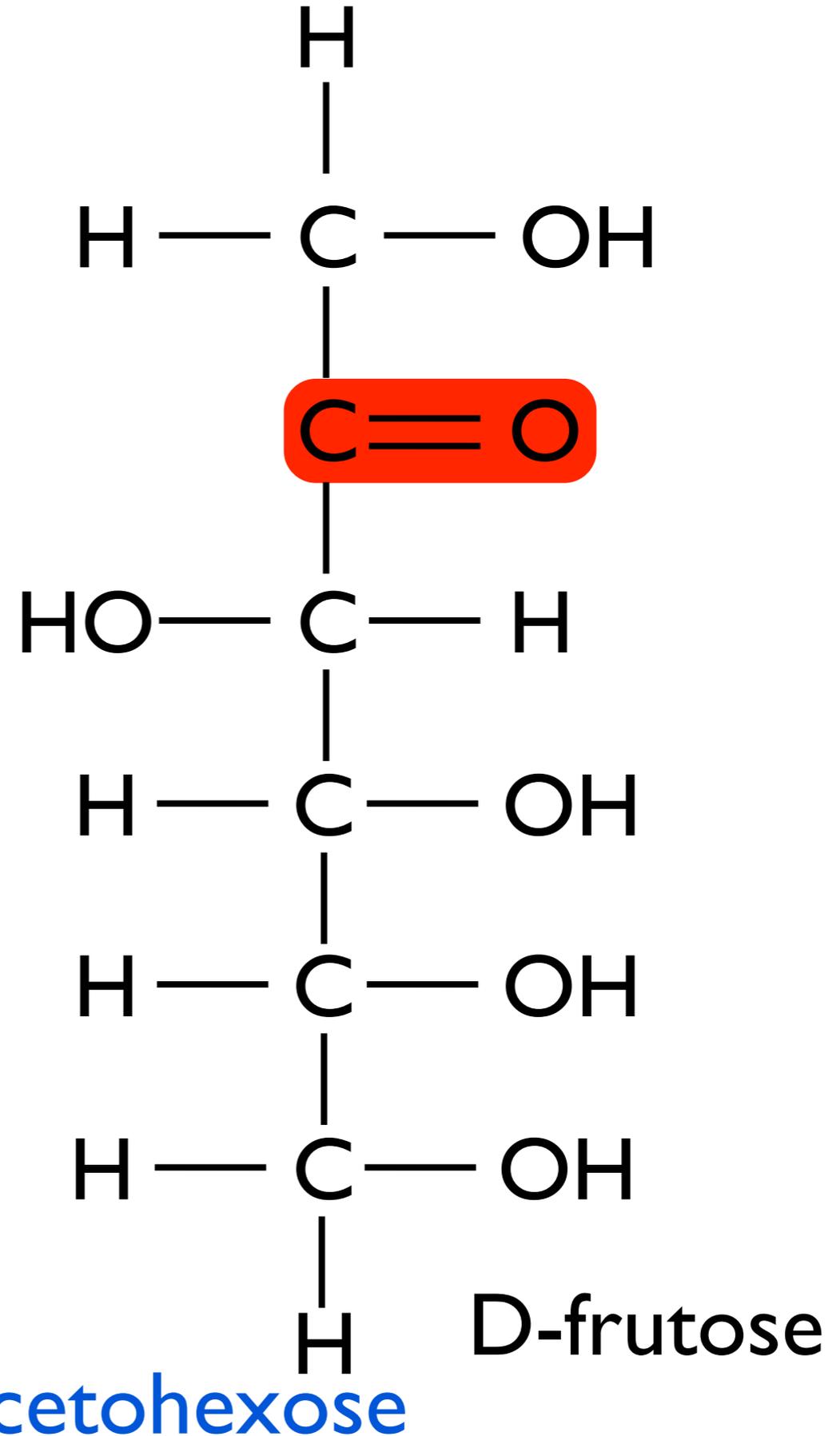
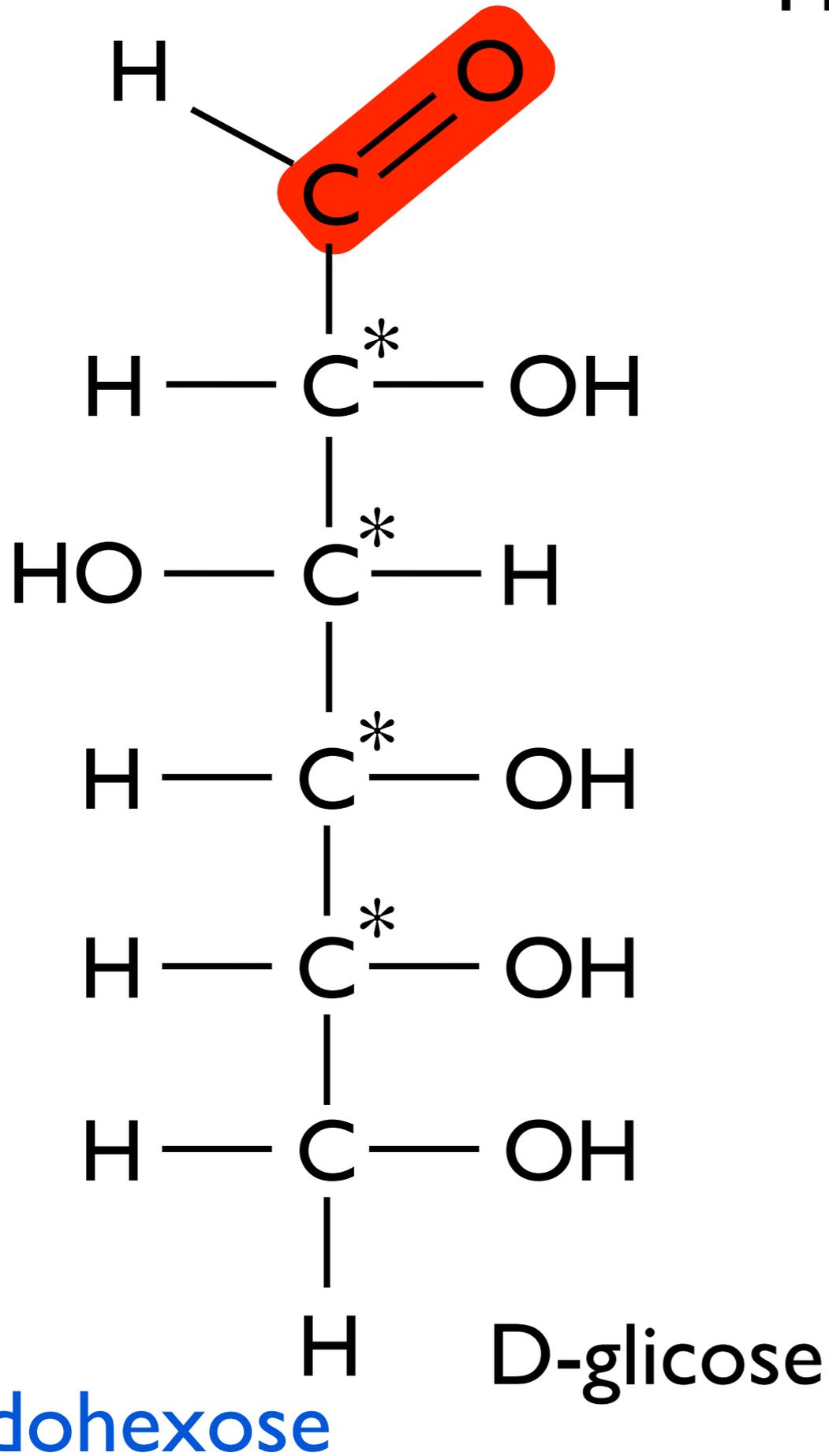
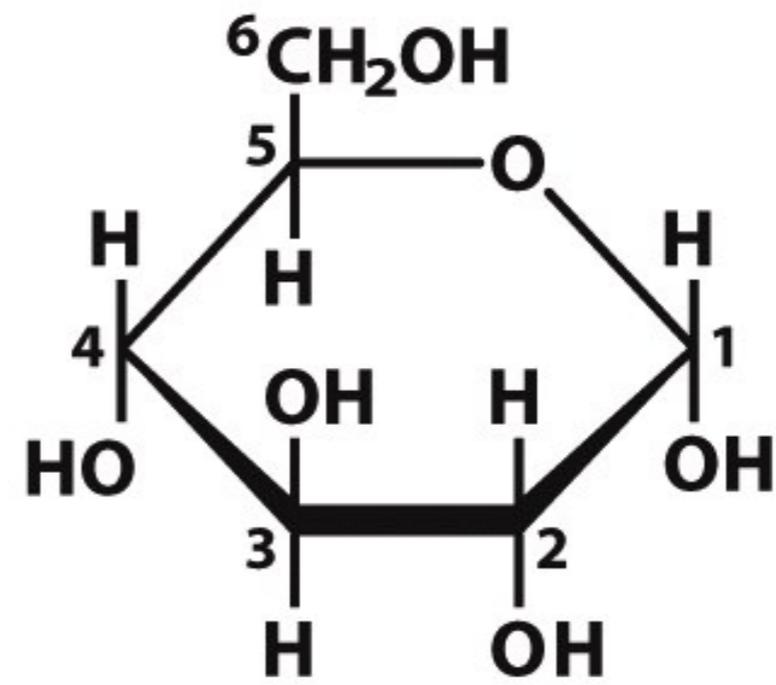
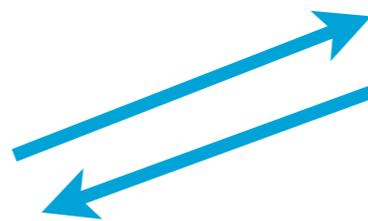
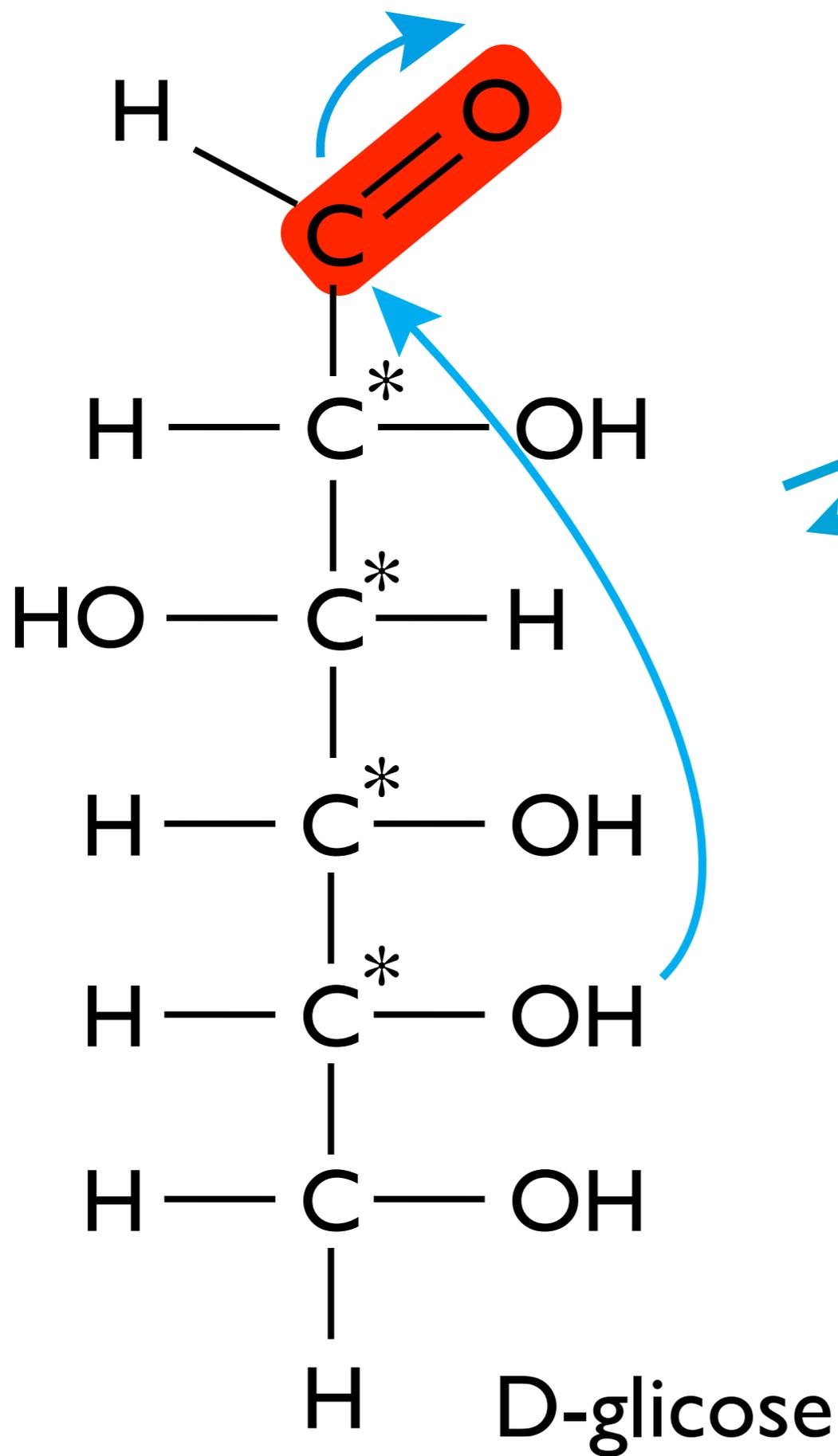


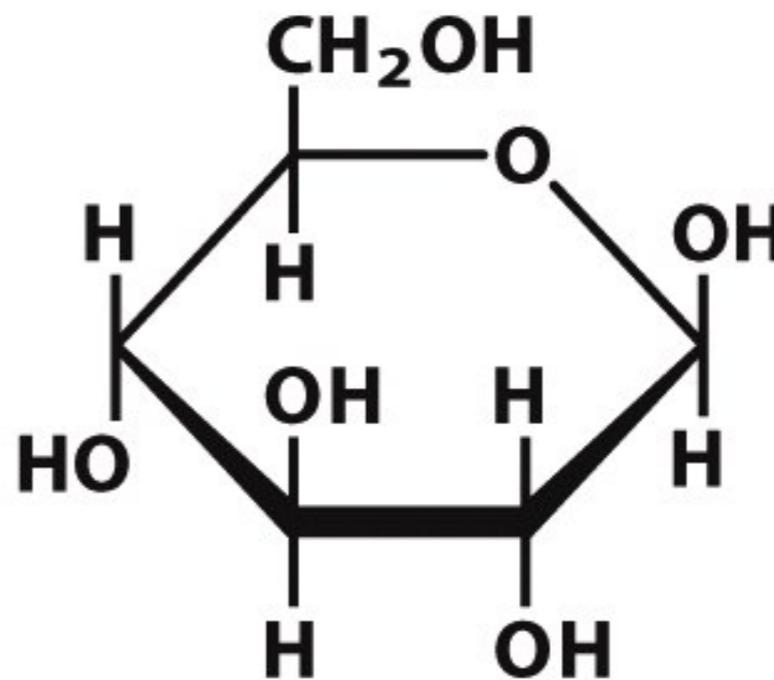
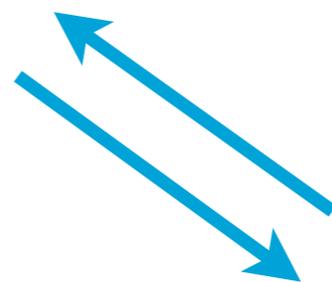
Figure 15-12
Biochemistry, Sixth Edition
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Hexoses





α -D-Glucopyranose



β -D-Glucopyranose

Lipídeos, membrana e transporte

cap. 10 e 11 - Lehninger 5a edição

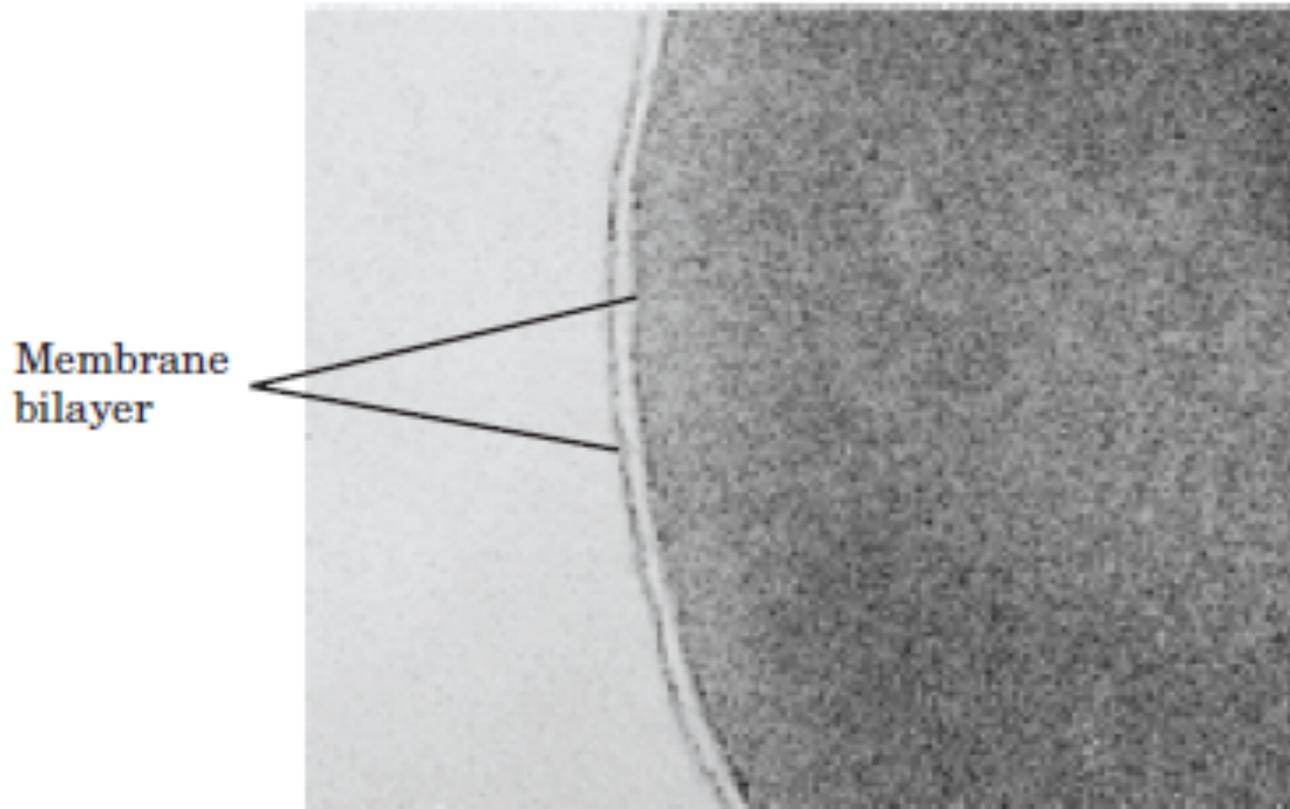
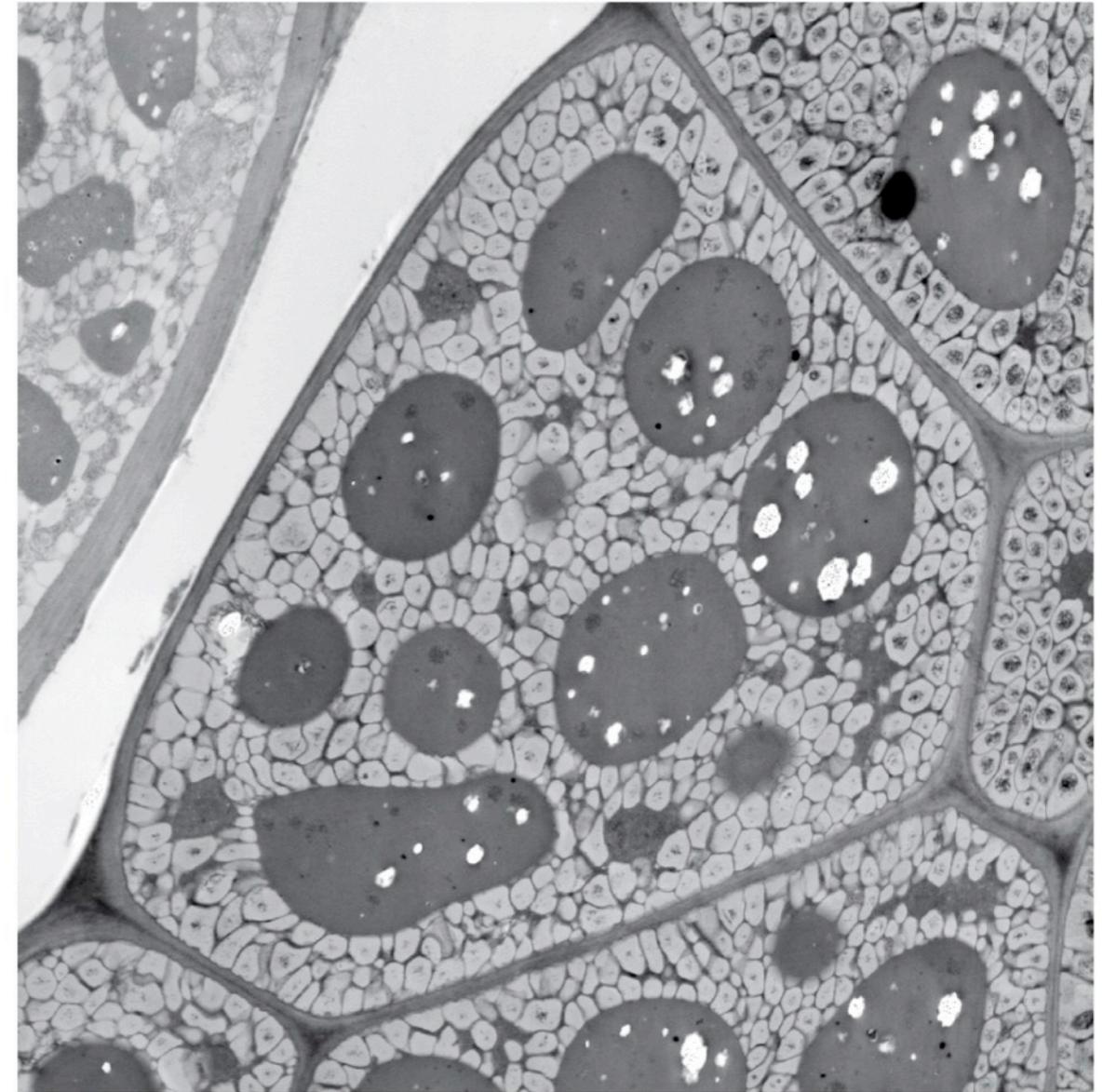


FIGURE 11-1 Biological membranes. Viewed in cross section, all cell membranes share a characteristic trilaminar appearance. When an erythrocyte is stained with osmium tetroxide and viewed with an electron microscope, the plasma membrane appears as a three-layer structure, 5 to 8 nm (50 to 80 Å) thick. The trilaminar image consists of two electron-dense layers (the osmium, bound to the inner and outer surfaces of the membrane) separated by a less dense central region.



3 μm

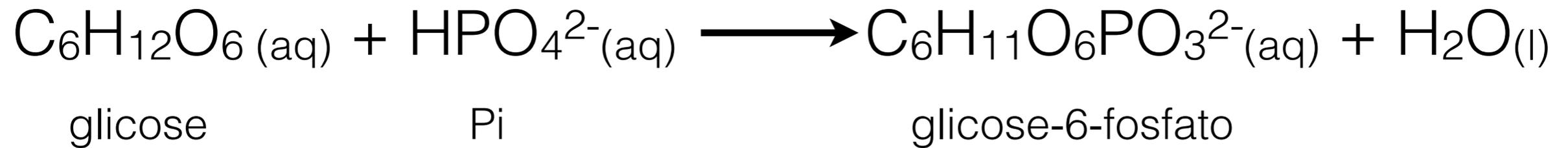
Figure 10-4b
Lehninger Principles of Biochemistry, Fifth Edition
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-Constituintes da membrana biológica

-Reserva de energia

A fosforilação d glicose não é termodinamicamente favorável

Primeira etapa da via glicolítica:



$\Delta G^{0'} = +13.4 \text{ kJmol}^{-1}$ a 37°C Não espontâneo

As reações acopladas:

Fosforilação da glicose $\Delta G^{0'} = +13.4 \text{ kJ mol}^{-1}$

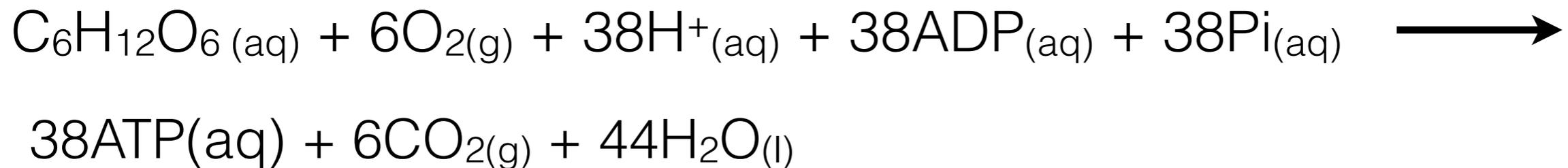
Hidrólise do ATP $\Delta G^{0'} = -30.5 \text{ kJ mol}^{-1}$

Reação global de oxidação da glicose:

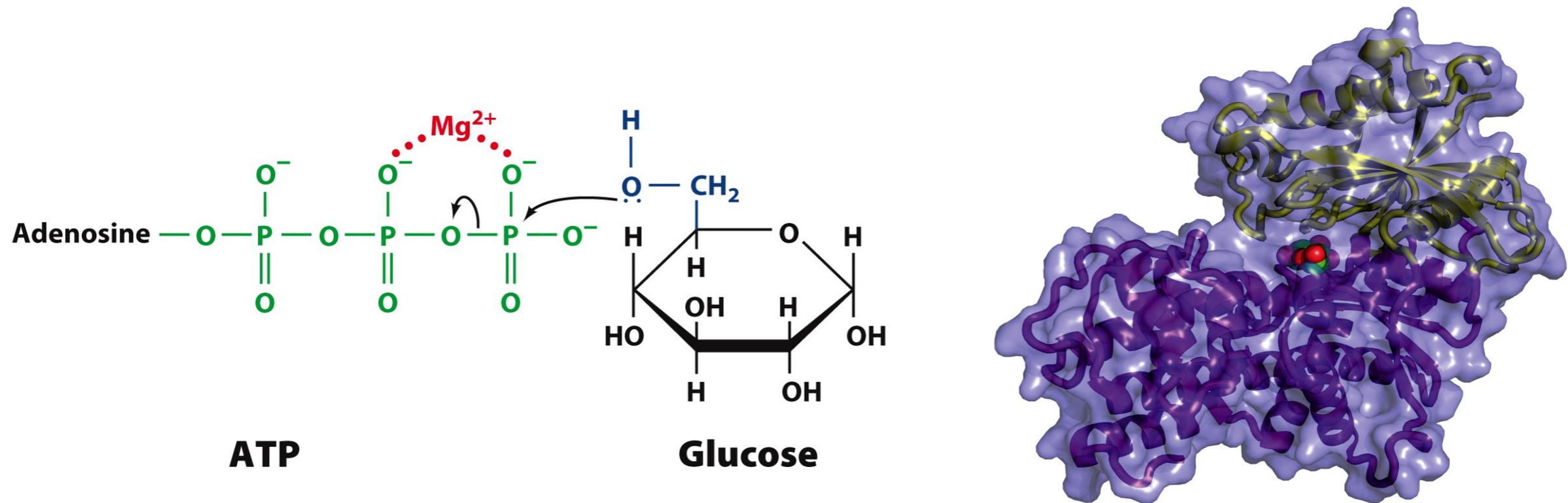


$$\Delta G^{0'} = -2872 \text{ kJ mol}^{-1} \text{ (a } 37^\circ\text{C)}$$

A oxidação global de glicose é suficiente para formar 38 moléculas de ATP



Dado o fato de que a hidrólise de ATP é altamente favorável, a mistura de glicose com ATP é suficiente para a reação de fosforilação ocorrer?

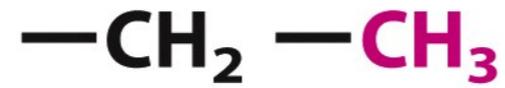


Quinase é uma enzima que transfere grupos fosforil entre ATP e um metabólito
Hexoquinase transfere grupos fosforil do ATP para hexoses

A reação de transferência do fosfato do ATP para a glicose é catalisada pela enzima hexoquinase

Reações de oxido-redução

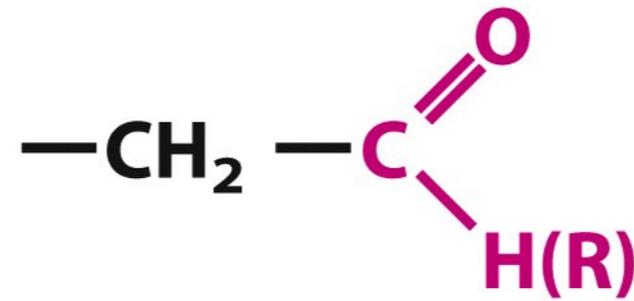
Oxidação



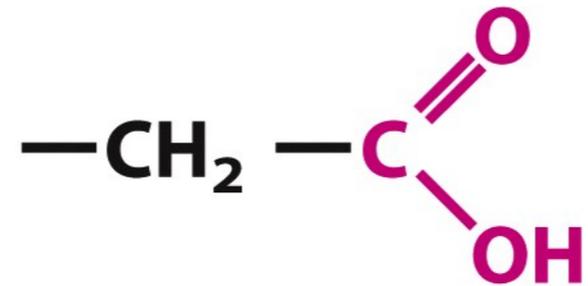
Alkane



Alcohol



Aldehyde (ketone)



Carboxylic acid



Carbon dioxide

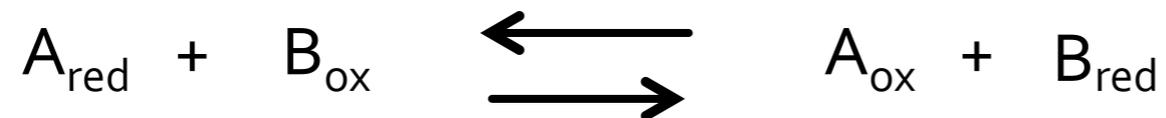
Figure 13-9
Lehninger Principles of Biochemistry, Fifth Edition
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Reações de oxido-redução

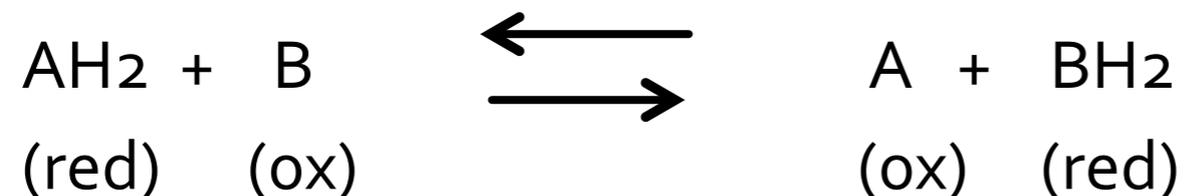
As formas oxidadas e reduzidas do composto (A_{ox}/A_{red}) são chamadas de par redox.



Redução e oxidação são processos acoplados, ou seja, um composto oxida-se reduzindo outra molécula.



Em sistemas biológicos, muitas das reações de óxido-redução envolvem a transferência de prótons (um átomo de Hidrogênio).



A energia livre da reação depende do potencial redutor (ΔE) do agente oxidante.

Potencial redutor de diversos sistemas biológicos

Assim como no caso da energia livre (G), o potencial redutor depende da concentração.

$$E' = E^{\circ'} + \frac{2,3RT}{nF} \cdot \log \frac{[A_{\text{oxi}}]}{[A_{\text{red}}]}$$

A energia livre também está relacionada com o potencial redutor do sistema:

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

F = constante de Faraday.

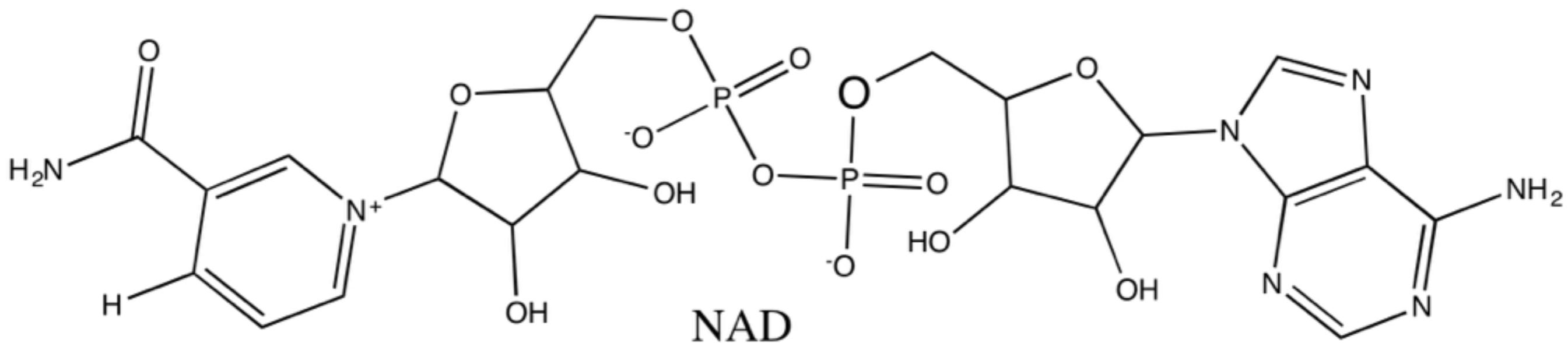
table 14-7

Standard Reduction Potentials of Some Biologically Important Half-Reactions, at 25 °C and pH 7

Half-reaction	E° (V)
$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \longrightarrow \text{H}_2\text{O}$	0.816
$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$	0.771
$\text{NO}_3^- + 2\text{H}^+ + 2e^- \longrightarrow \text{NO}_2^- + \text{H}_2\text{O}$	0.421
Cytochrome <i>f</i> (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>f</i> (Fe^{2+})	0.365
$\text{Fe}(\text{CN})_6^{3-}$ (ferricyanide) + $e^- \longrightarrow \text{Fe}(\text{CN})_6^{4-}$	0.36
Cytochrome <i>a</i> ₃ (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>a</i> ₃ (Fe^{2+})	0.35
$\text{O}_2 + 2\text{H}^+ + 2e^- \longrightarrow \text{H}_2\text{O}_2$	0.295
Cytochrome <i>a</i> (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>a</i> (Fe^{2+})	0.29
Cytochrome <i>c</i> (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>c</i> (Fe^{2+})	0.254
Cytochrome <i>c</i> ₁ (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>c</i> ₁ (Fe^{2+})	0.22
Cytochrome <i>b</i> (Fe^{3+}) + $e^- \longrightarrow$ cytochrome <i>b</i> (Fe^{2+})	0.077
Ubiquinone + $2\text{H}^+ + 2e^- \longrightarrow$ ubiquinol + H_2	0.045
Fumarate ²⁻ + $2\text{H}^+ + 2e^- \longrightarrow$ succinate ²⁻	0.031
$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$ (at standard conditions, pH 0)	0.000
Crotonyl-CoA + $2\text{H}^+ + 2e^- \longrightarrow$ butyryl-CoA	-0.015
Oxaloacetate ²⁻ + $2\text{H}^+ + 2e^- \longrightarrow$ malate ²⁻	-0.166
Pyruvate ⁻ + $2\text{H}^+ + 2e^- \longrightarrow$ lactate ⁻	-0.185
Acetaldehyde + $2\text{H}^+ + 2e^- \longrightarrow$ ethanol	-0.197
$\text{FAD} + 2\text{H}^+ + 2e^- \longrightarrow \text{FADH}_2$	-0.219*
Glutathione + $2\text{H}^+ + 2e^- \longrightarrow$ 2 reduced glutathione	-0.23
$\text{S} + 2\text{H}^+ + 2e^- \longrightarrow \text{H}_2\text{S}$	-0.243
Lipoic acid + $2\text{H}^+ + 2e^- \longrightarrow$ dihydrolipoic acid	-0.29
$\text{NAD}^+ + \text{H}^+ + 2e^- \longrightarrow \text{NADH}$	-0.320
$\text{NADP}^+ + \text{H}^+ + 2e^- \longrightarrow \text{NADPH}$	-0.324
Acetoacetate + $2\text{H}^+ + 2e^- \longrightarrow$ β -hydroxybutyrate	-0.346
α -Ketoglutarate + $\text{CO}_2 + 2\text{H}^+ + 2e^- \longrightarrow$ isocitrate	-0.38
$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$ (at pH 7)	-0.414
Ferredoxin (Fe^{3+}) + $e^- \longrightarrow$ ferredoxin (Fe^{2+})	-0.432

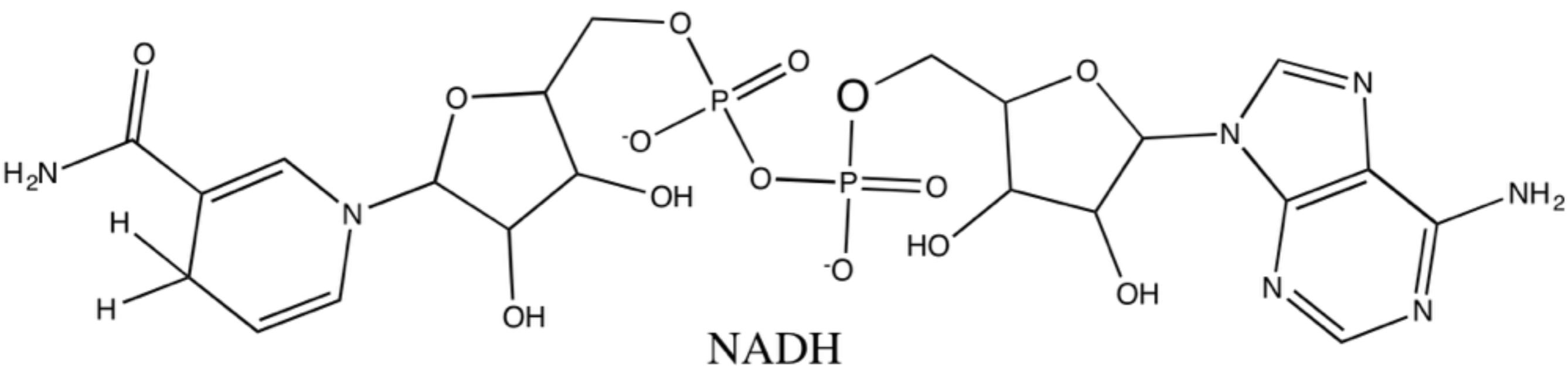
Data mostly from Loach, P.A. (1976) in *Handbook of Biochemistry and Molecular Biology*, 3rd edn (Fasman, G.D., ed.), *Physical and Chemical Data*, Vol. 1, pp. 122-130, CRC Press, Boca Raton, FL.

*This is the value for free FAD; FAD bound to a specific flavoprotein (for example succinate dehydrogenase) has a different E° .



nucleotideo de nicotinamida (oxidado)

nucleotideo de adenina



nucleotideo de nicotinamida (reduzido)

nucleotideo de adenina

