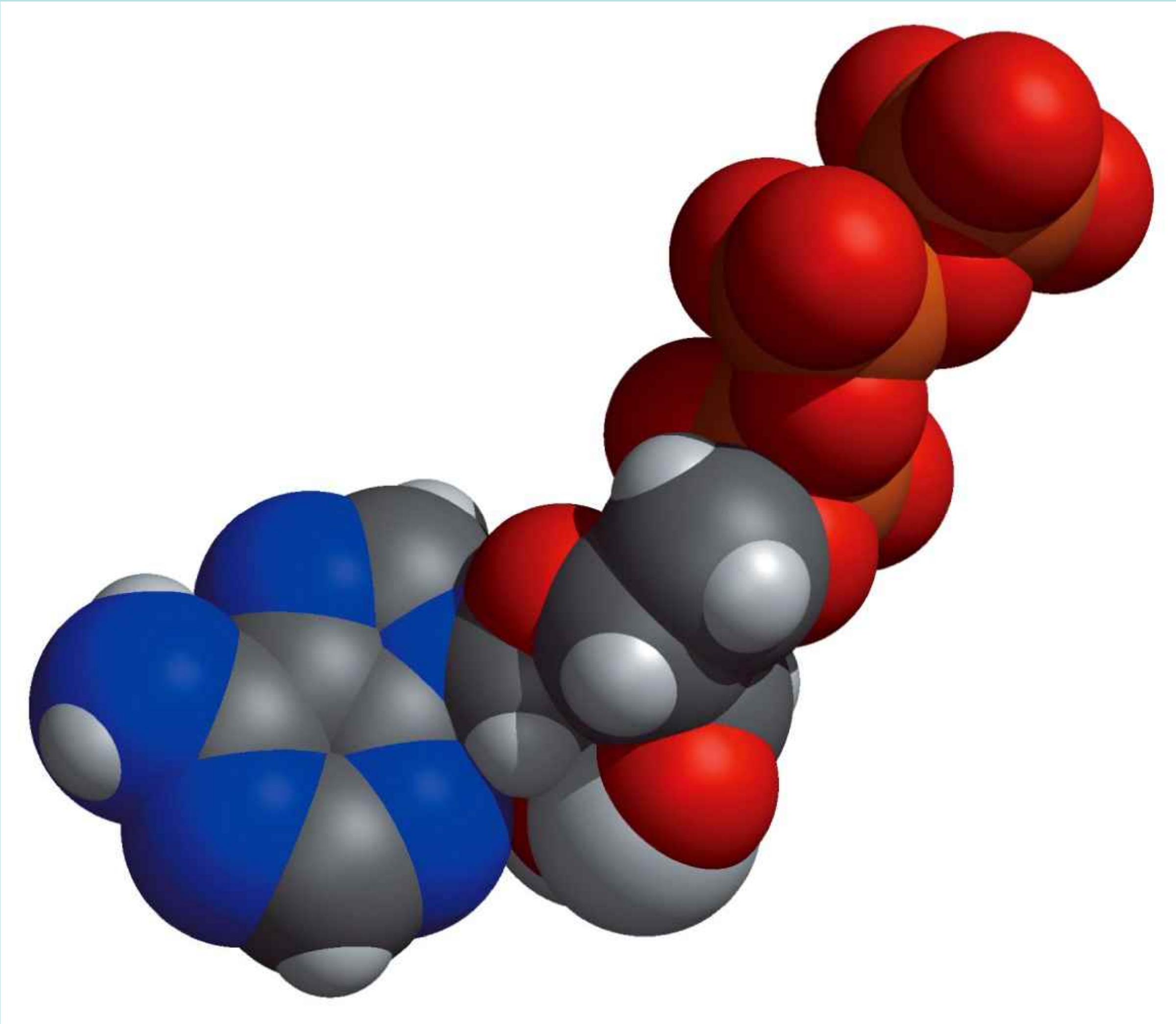
Chapter 13:

Bioenergetics and Biochemical Reaction Types



Three Thermodynamic Quantities

Reactants $\longrightarrow$ **Products**

Gibbs free energy, *G*

(the amount of energy capable of doing work during a reaction)

ΔG : (-) exergonic

(+) endergonic

Enthalpy, *H*

(the heat content of the reacting system)

ΔH : - exothermic

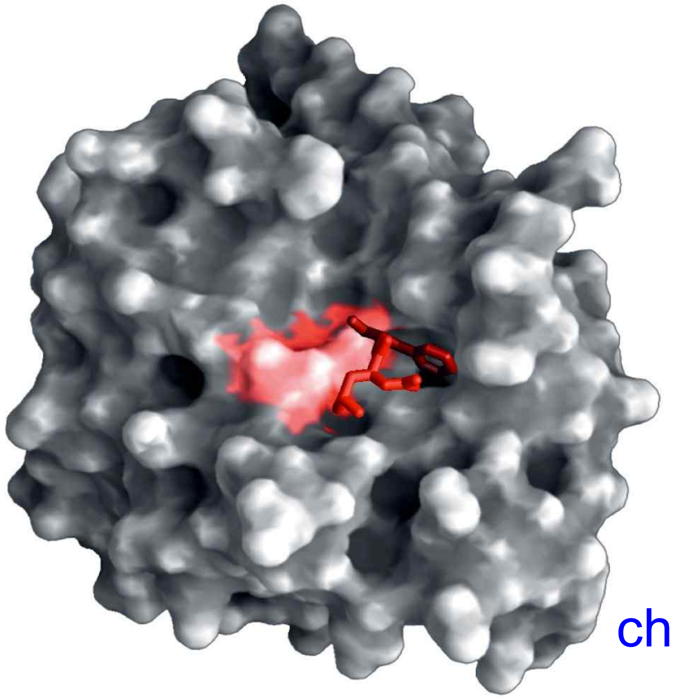
\+ endothermic

Entrophy, *S*

(the randomness or disorder in a system)

How enzymes work ?

$$E + S \rightleftharpoons \boxed{ES \rightleftharpoons EP} \rightleftharpoons E + P$$

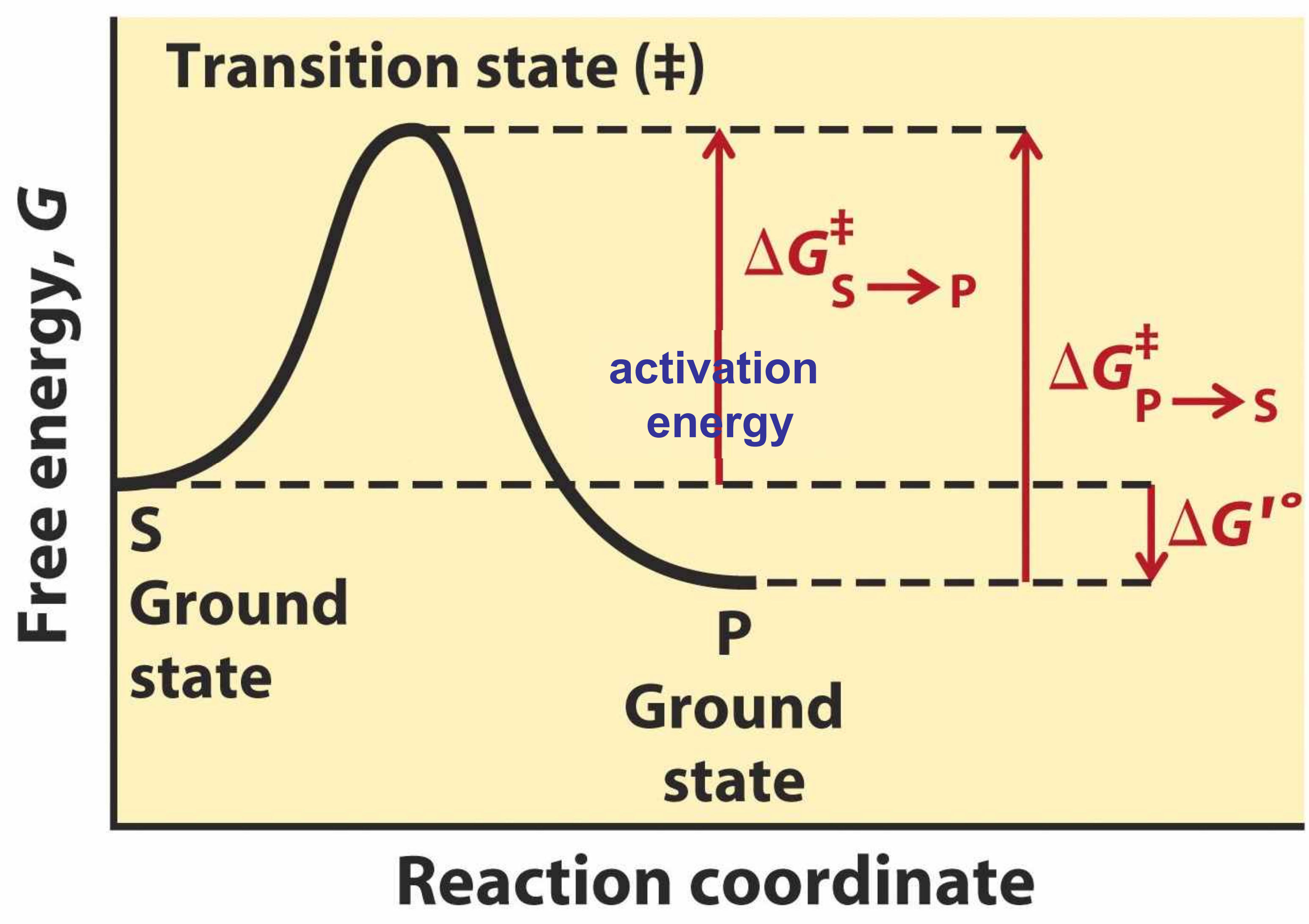


chymotrypsin

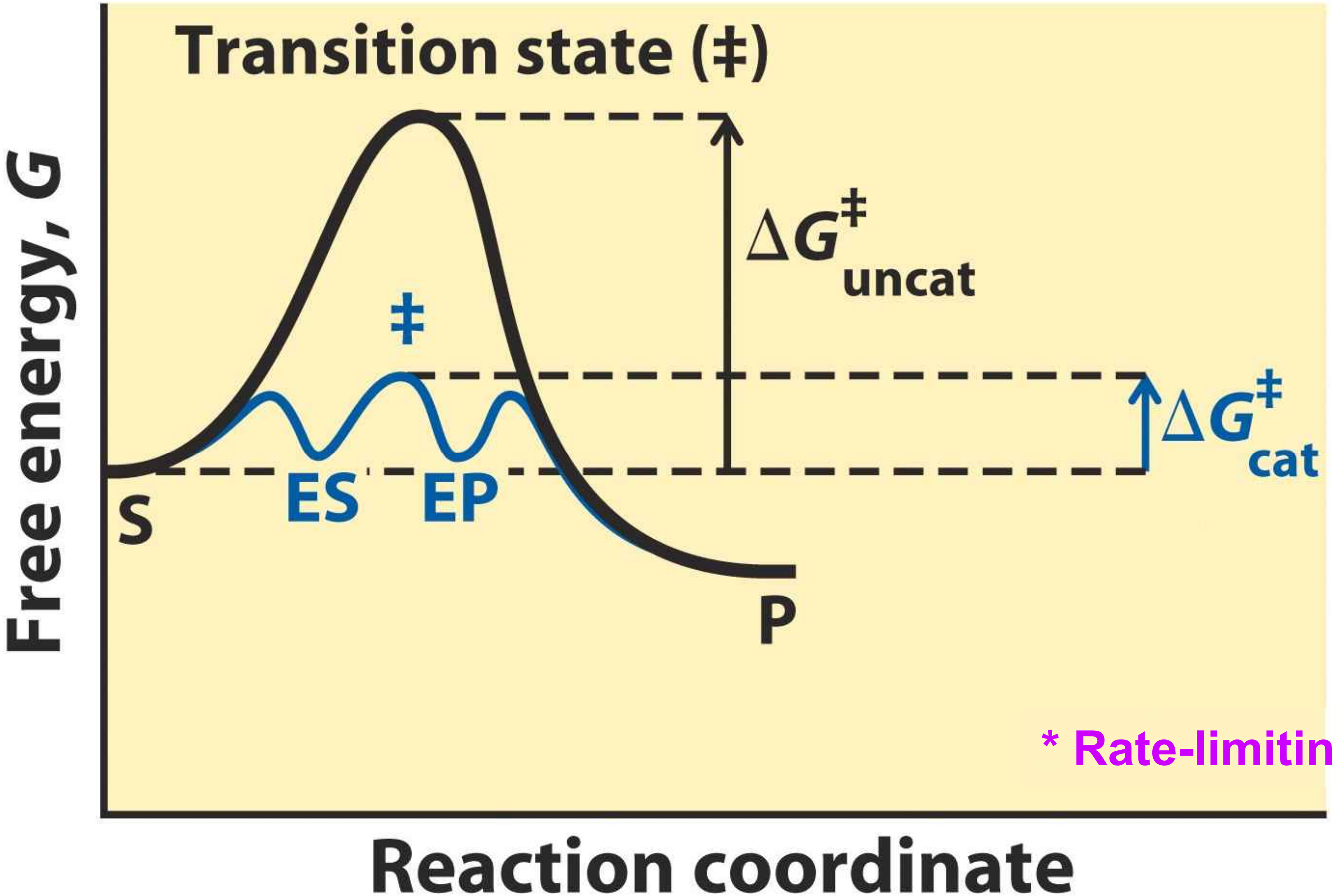
The function of a catalyst is to increase the **rate** of a reaction

(Catalysts do not affect reaction equilibria)

Reaction coordinate diagram for a chemical reaction



Reaction coordinate diagram comparing enzyme-catalyzed and uncatalyzed reactions



* Rate-limiting step

Catalysts enhance reaction rates by lowering activation E.

Reaction rates and Equilibria have precise thermodynamic definitions

$$S \rightleftharpoons P$$

$$K_{eq} = \frac{[P]}{[S]}$$ (K_{eq} : equilibrium constant)

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

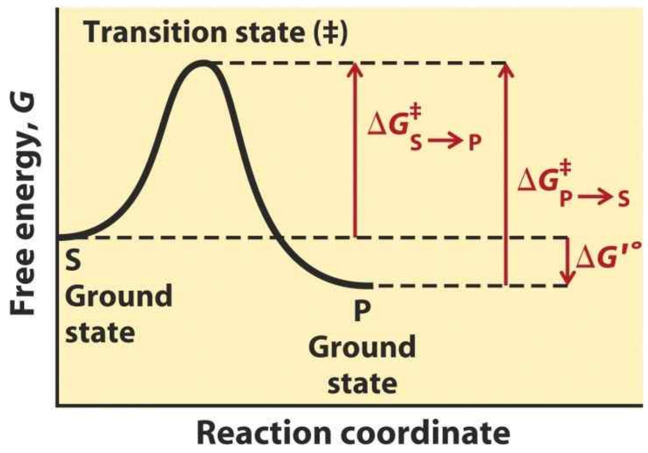


TABLE 6–4 Relationship between K'_{eq} and $\Delta G'^{\circ}$

K'_{eq}	$\Delta G'^{\circ}$ (kJ/mol)
10^{-6}	34.2
10^{-5}	28.5
10^{-4}	22.8
10^{-3}	17.1
10^{-2}	11.4
10^{-1}	5.7
1	0.0
10^{1}	−5.7
10^{2}	−11.4
10^{3}	−17.1

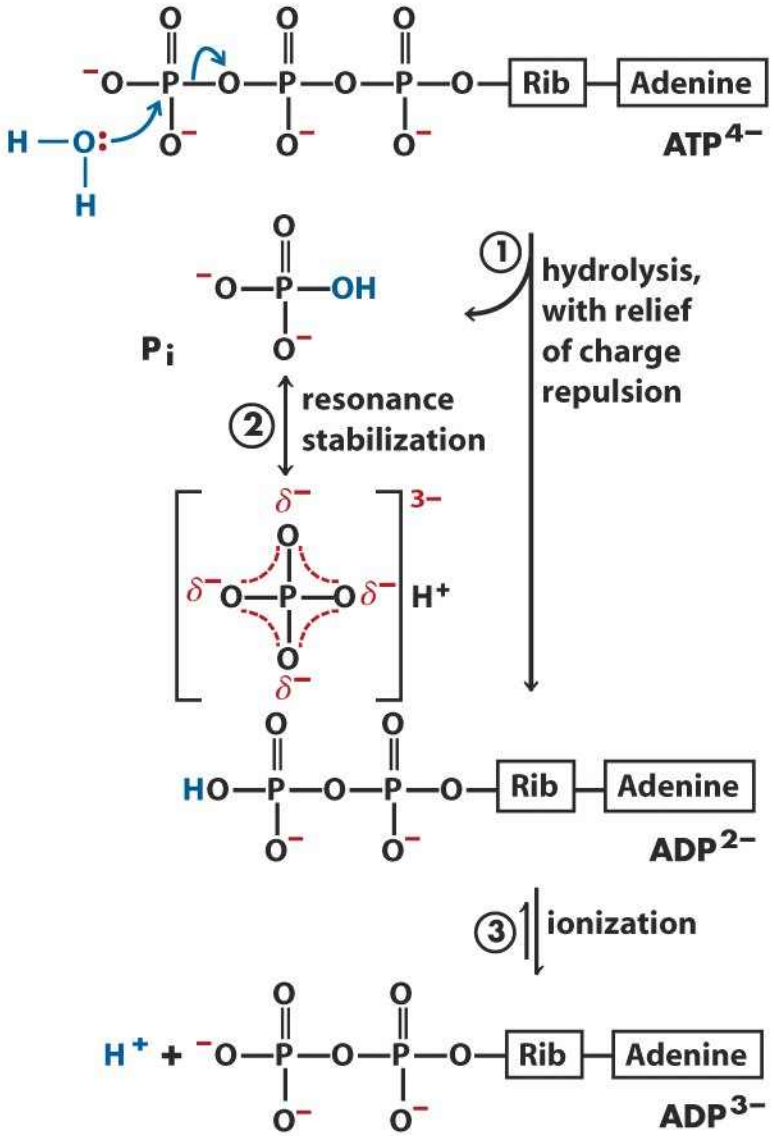
Note: The relationship is calculated from $\Delta G'^{\circ} = -RT \ln K'_{eq}$ (Eqn 6–3).

TABLE 13–3 **Relationships among K'_{eq}, $\Delta G'^{\circ}$, and the Direction of Chemical Reactions under Standard Conditions**

When K'_{eq} is . . .	$\Delta G'^{\circ}$ is . . .	Starting with all components at 1 M, the reaction . . .
>1.0	negative	proceeds forward
1.0	zero	is at equilibrium
<1.0	positive	proceeds in reverse

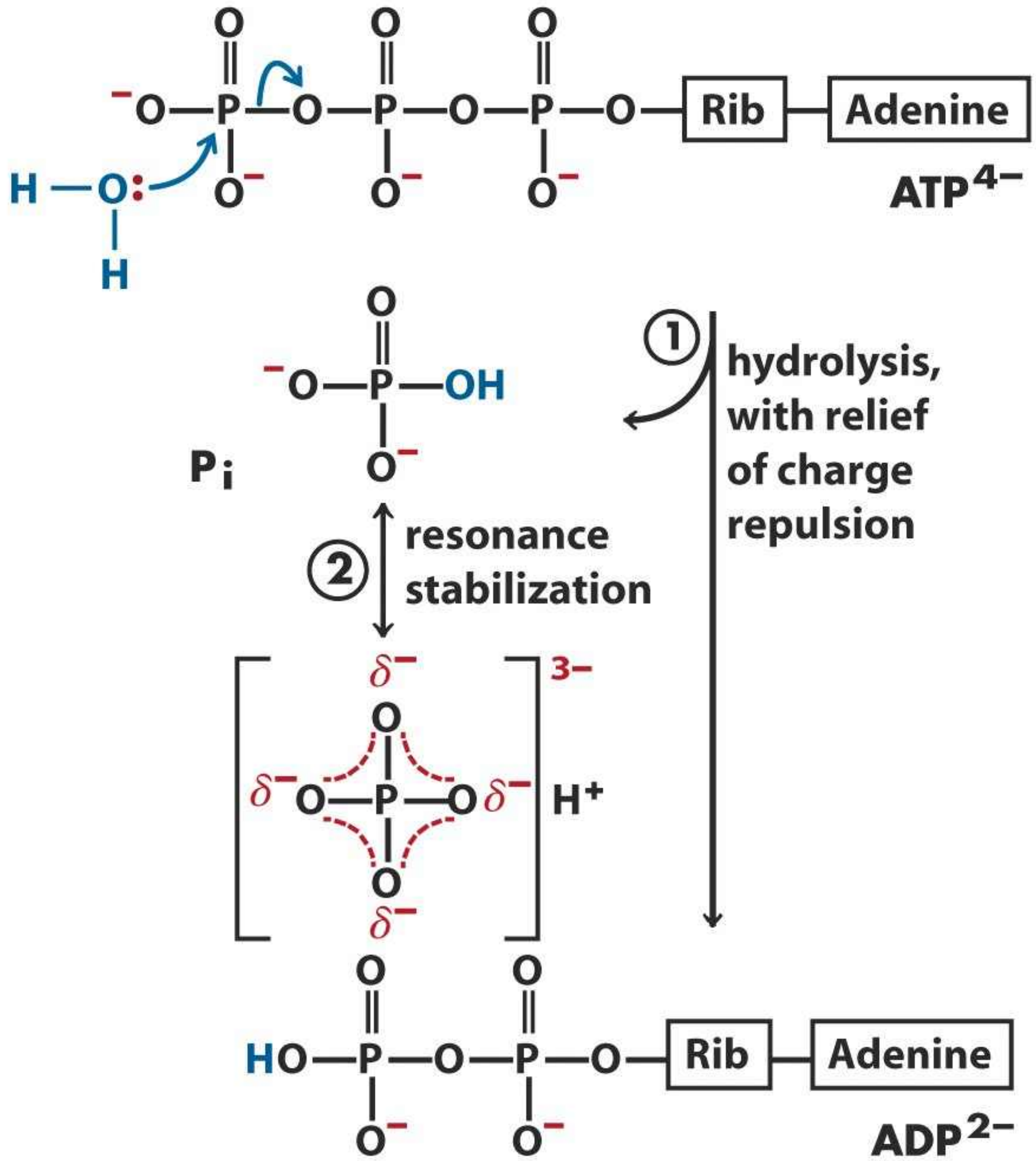
TABLE 13–4 **Standard Free-Energy Changes of Some Chemical Reactions at pH 7.0 and 25 °C (298 K)**

Reaction type	$\Delta G'^{\circ}$ (kJ/mol)	$\Delta G'^{\circ}$ (kcal/mol)
Hydrolysis reactions		
Acid anhydrides		
Acetic anhydride + $H_2O \longrightarrow$ 2 acetate	−91.1	−21.8
ATP + $H_2O \longrightarrow$ ADP + P_i	−30.5	−7.3
ATP + $H_2O \longrightarrow$ AMP + PP_i	−45.6	−10.9
PP_i + $H_2O \longrightarrow$ $2P_i$	−19.2	−4.6
UDP-glucose + $H_2O \longrightarrow$ UMP + glucose 1-phosphate	−43.0	−10.3
Esters		
Ethyl acetate + $H_2O \longrightarrow$ ethanol + acetate	−19.6	−4.7
Glucose 6-phosphate + $H_2O \longrightarrow$ glucose + P_i	−13.8	−3.3
Amides and peptides		
Glutamine + $H_2O \longrightarrow$ glutamate + NH_4^+	−14.2	−3.4
Glycylglycine + $H_2O \longrightarrow$ 2 glycine	−9.2	−2.2

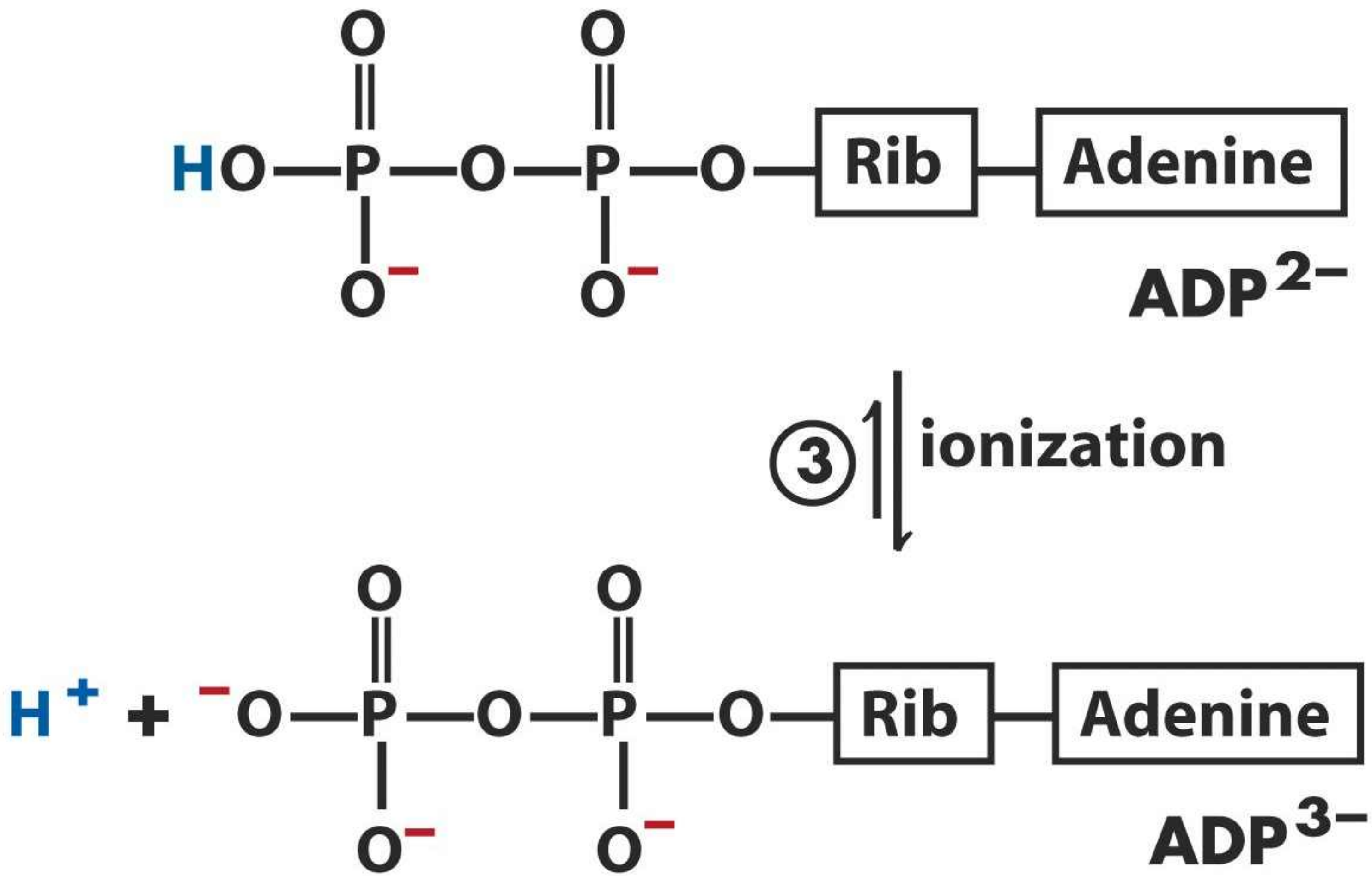


$$ATP^{4-} + H_2O \longrightarrow ADP^{3-} + P_i^{2-} + H^+$$

$$\Delta G'^{\circ} = -30.5\ \text{kJ/mol}$$

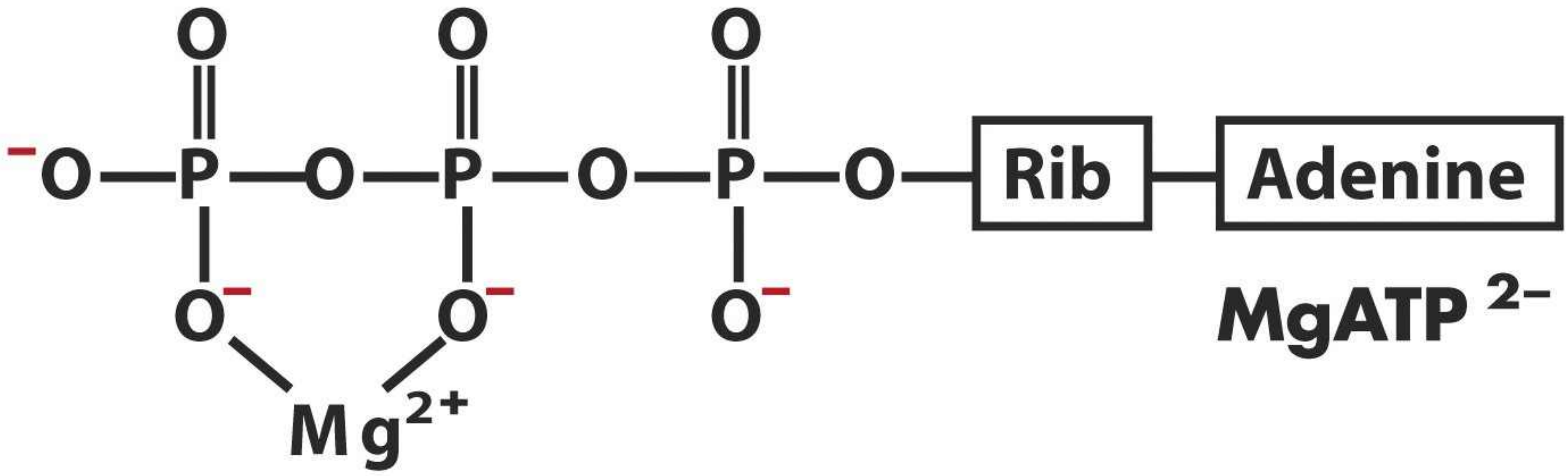


Rib
Adenine
ATP4−
Pi
OH
① hydrolysis, with relief of charge repulsion
② resonance stabilization
3−
H+
HO
Rib
Adenine
ADP2−

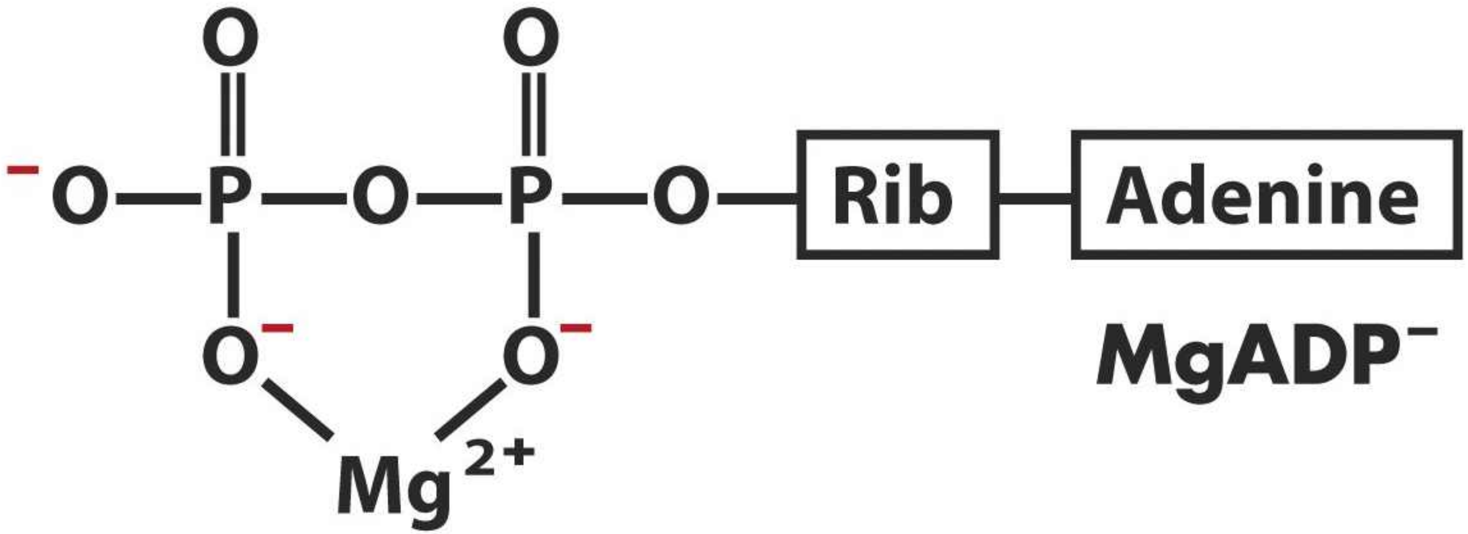


$$ATP^{4-} + H_2O \longrightarrow ADP^{3-} + P_i^{2-} + H^+$$

$$\Delta G'^{\circ} = -30.5\ \text{kJ/mol}$$



$MgATP^{2-}$



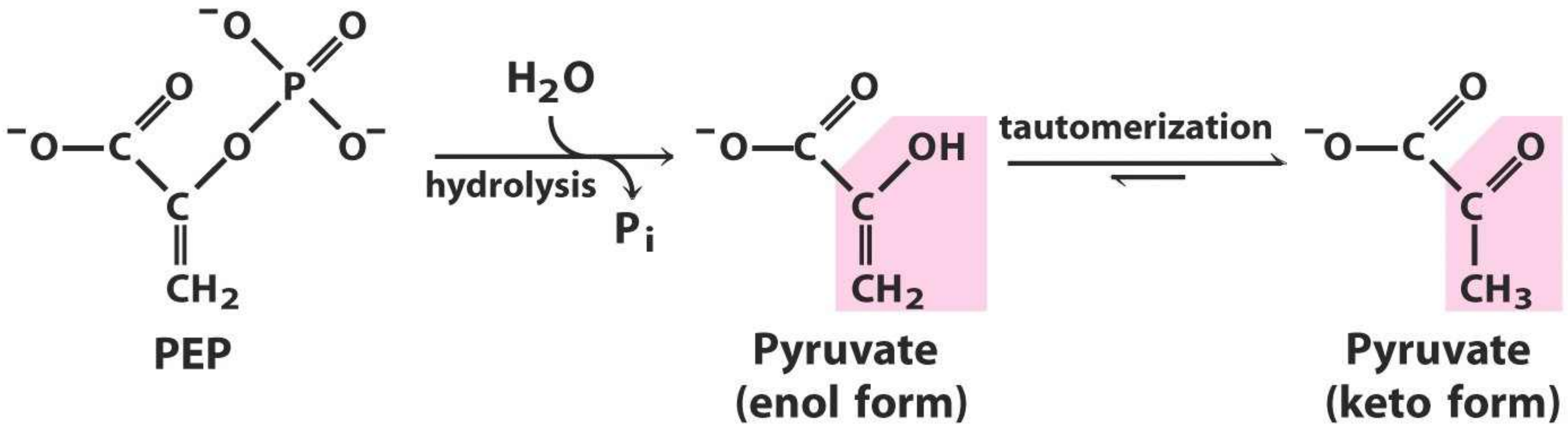
$MgADP^{-}$

TABLE 13–5 Adenine Nucleotide, Inorganic Phosphate, and Phosphocreatine Concentrations in Some Cells

	Concentration (mM)*				
	ATP	*ADP*†	*AMP*	P_i	*PCr*
Rat hepatocyte	3.38	1.32	0.29	4.8	0
Rat myocyte	8.05	0.93	0.04	8.05	28
Rat neuron	2.59	0.73	0.06	2.72	4.7
Human erythrocyte	2.25	0.25	0.02	1.65	0
E. coli cell	7.90	1.04	0.82	7.9	0

*For erythrocytes the concentrations are those of the cytosol (human erythrocytes lack a nucleus and mitochondria). In the other types of cells the data are for the entire cell contents, although the cytosol and the mitochondria have very different concentrations of ADP. PCr is phosphocreatine, discussed on p. 505.

†This value reflects total concentration; the true value for free ADP may be much lower (see Box 13–1).



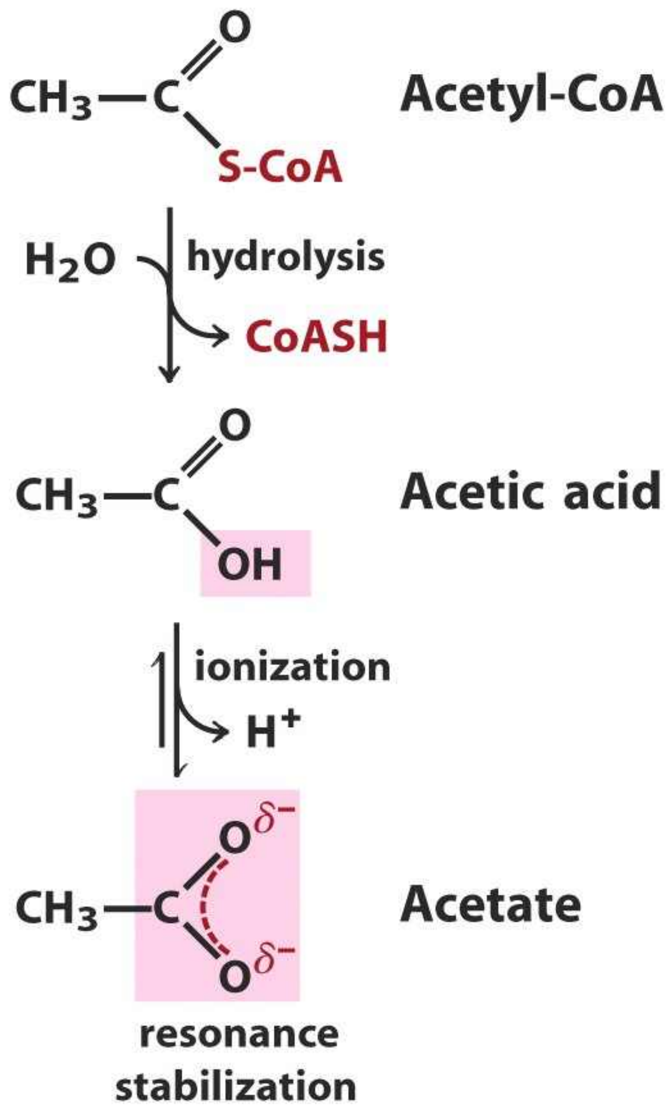
$$PEP^{3-} + H_2O \longrightarrow pyruvate^{-} + P_i^{2-}$$

$$\Delta G'^{\circ} = -61.9\ \text{kJ/mol}$$

TABLE 13–6 Standard Free Energies of Hydrolysis of Some Phosphorylated Compounds and Acetyl-CoA (a Thioester)

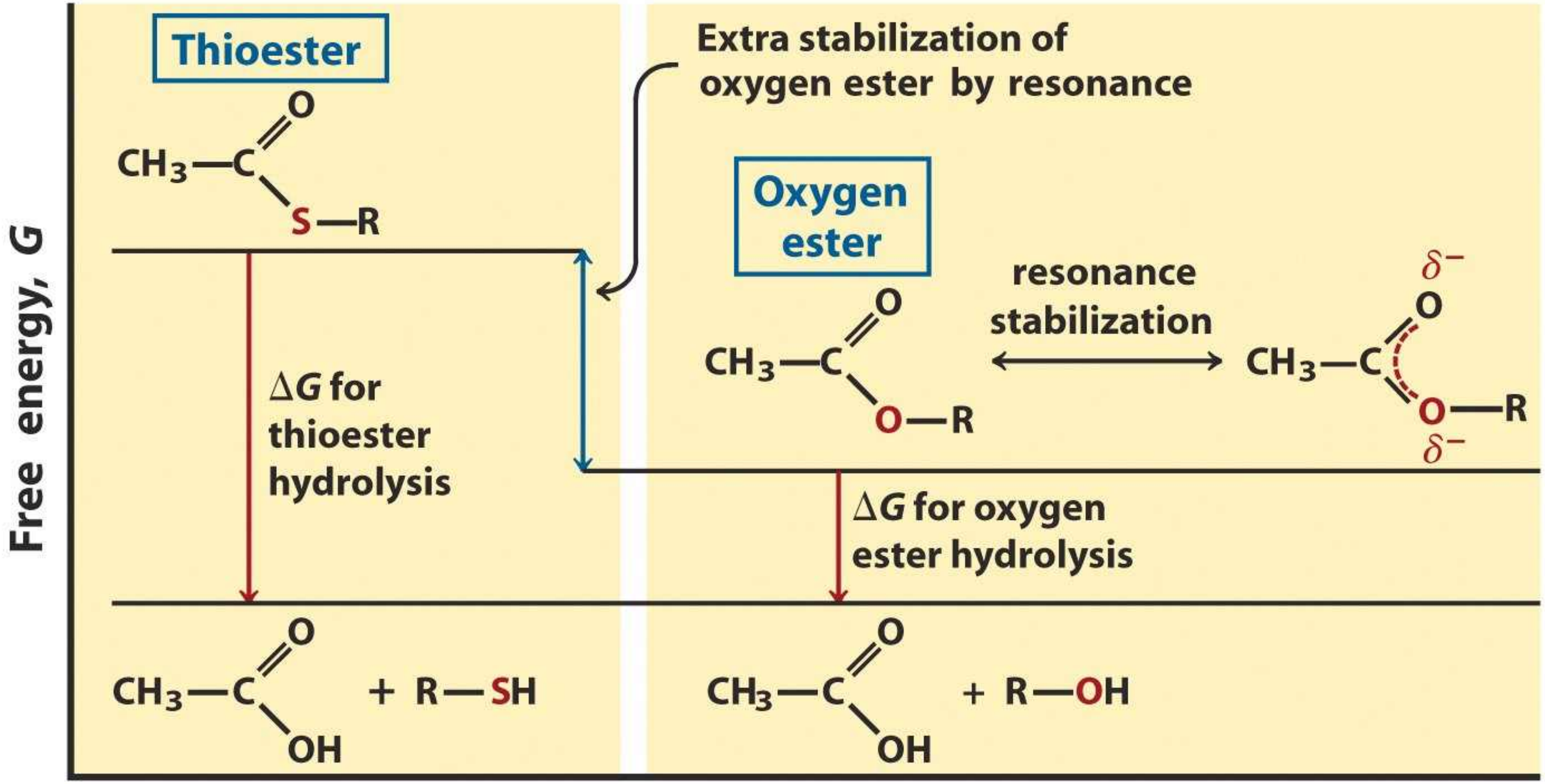
	$\Delta G'^{\circ}$ (kJ/mol)	$\Delta G'^{\circ}$ (kcal/mol)
Phosphoenolpyruvate	−61.9	−14.8
1,3-bisphosphoglycerate ($\rightarrow$ 3-phosphoglycerate + P_i)	−49.3	−11.8
Phosphocreatine	−43.0	−10.3
ADP ($\rightarrow$ AMP + P_i)	−32.8	−7.8
ATP ($\rightarrow$ ADP + P_i)	−30.5	−7.3
ATP ($\rightarrow$ AMP + PP_i)	−45.6	−10.9
AMP ($\rightarrow$ adenosine + P_i)	−14.2	−3.4
PP_i ($\rightarrow$ 2P_i)	−19.2	−4.0
Glucose 1-phosphate	−20.9	−5.0
Fructose 6-phosphate	−15.9	−3.8
Glucose 6-phosphate	−13.8	−3.3
Glycerol 1-phosphate	−9.2	−2.2
Acetyl-CoA	−31.4	−7.5

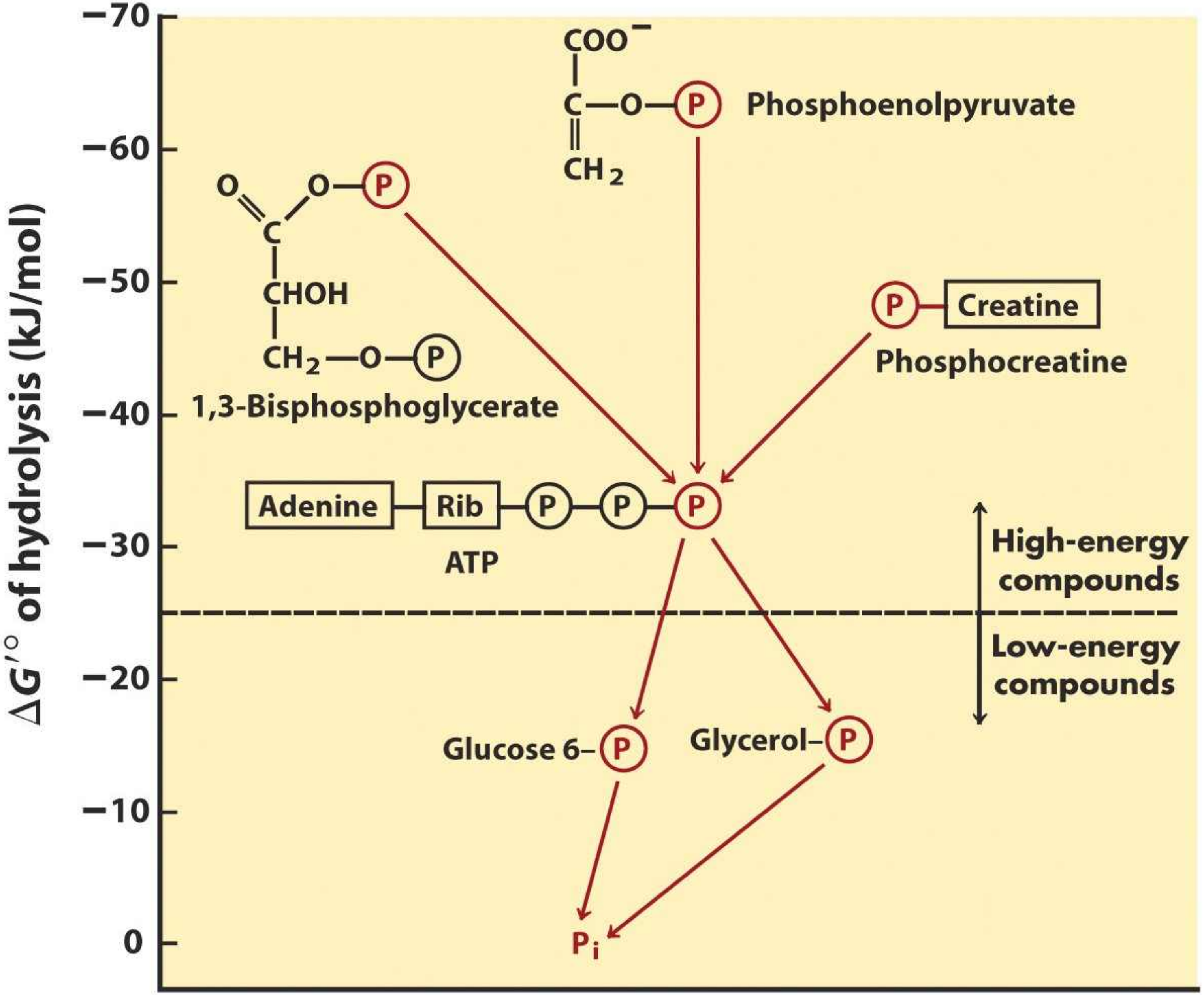
Source: Data mostly from Jencks, W.P. (1976) in *Handbook of Biochemistry and Molecular Biology,* 3rd edn (Fasman, G.D., ed.), *Physical and Chemical Data,* Vol. I, pp. 296–304, CRC Press, Boca Raton, FL. The value for the free energy of hydrolysis of PP_i is from Frey, P.A. & Arabshahi, A. (1995) Standard free-energy change for the hydrolysis of the α–β-phosphoanhydride bridge in ATP. *Biochemistry* **34,** 11,307–11,310.



$$\text{Acetyl-CoA} + H_2O \longrightarrow \text{acetate}^- + \text{CoA} + H^+$$

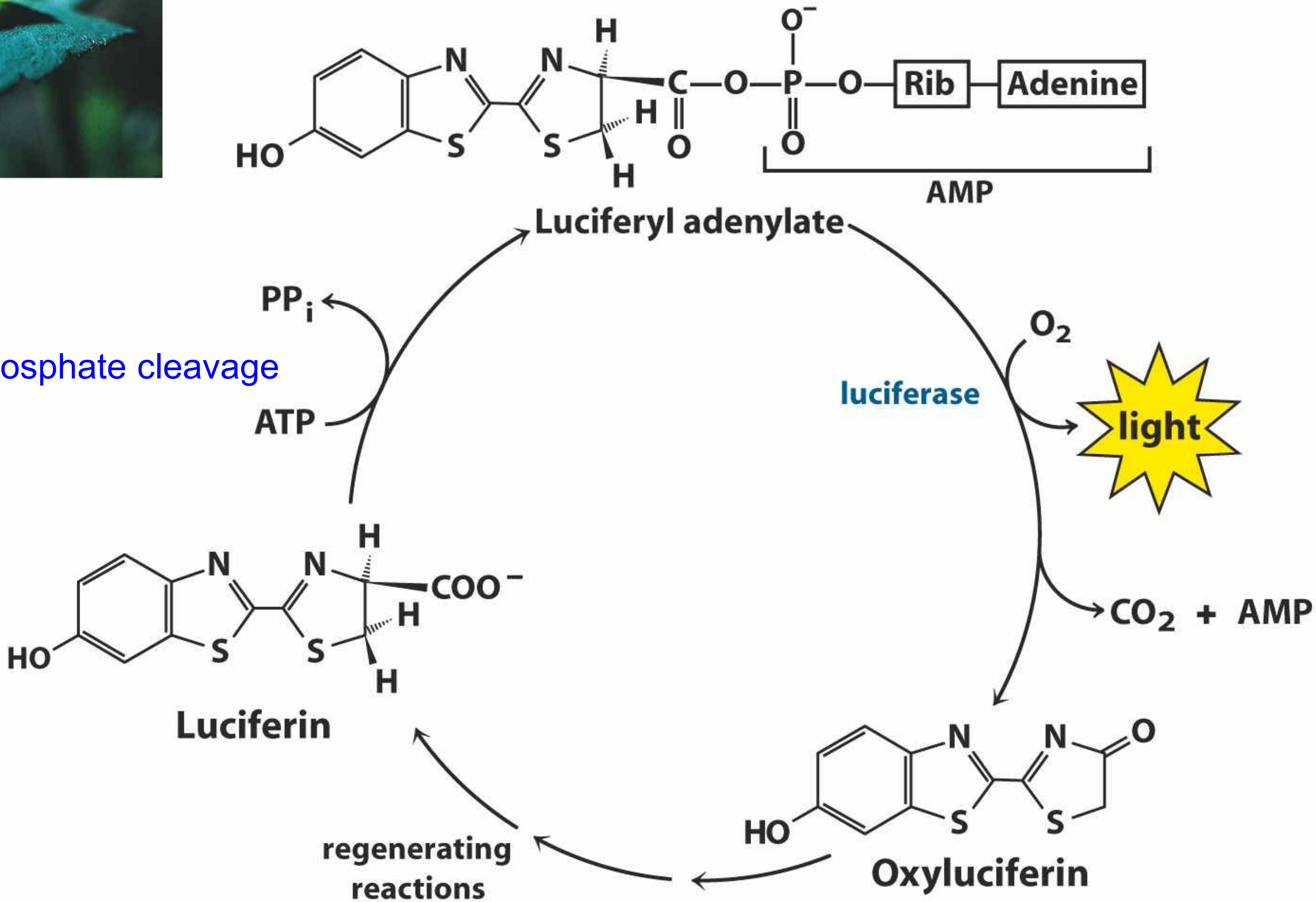
$$\Delta G'^\circ = -31.4 \text{ kJ/mol}$$

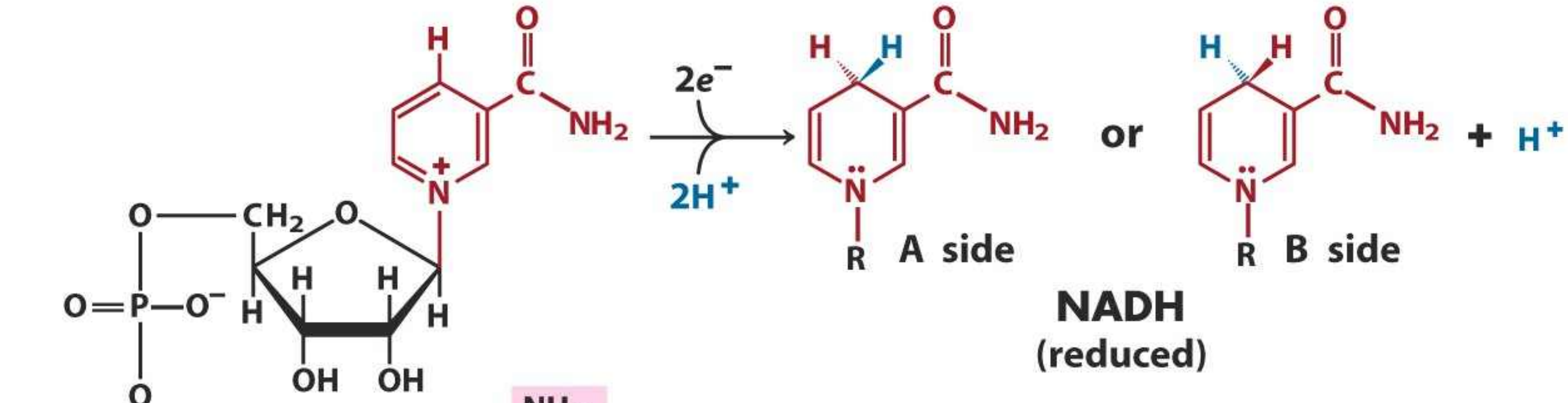

Thioester
Extra stabilization of oxygen ester by resonance
Oxygen ester
resonance stabilization
Free energy, G
ΔG for thioester hydrolysis
ΔG for oxygen ester hydrolysis
δ−
δ−

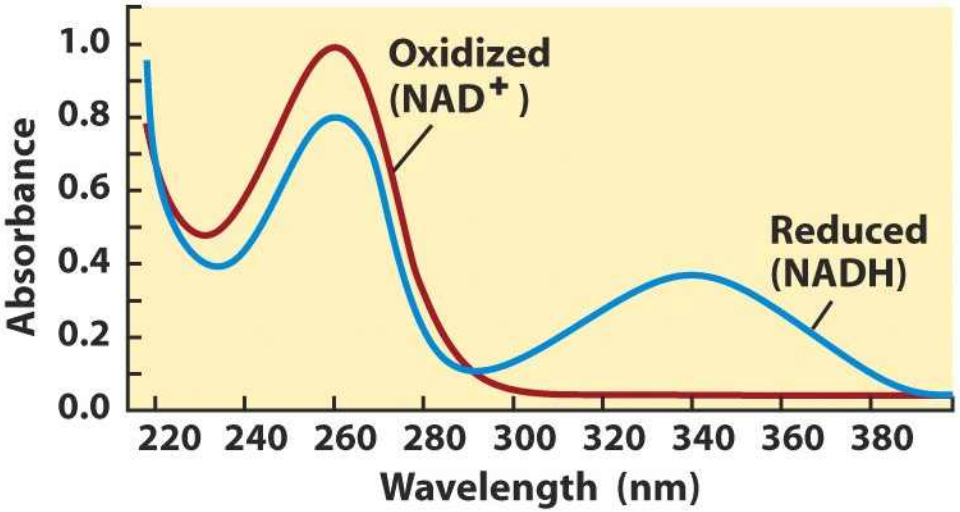


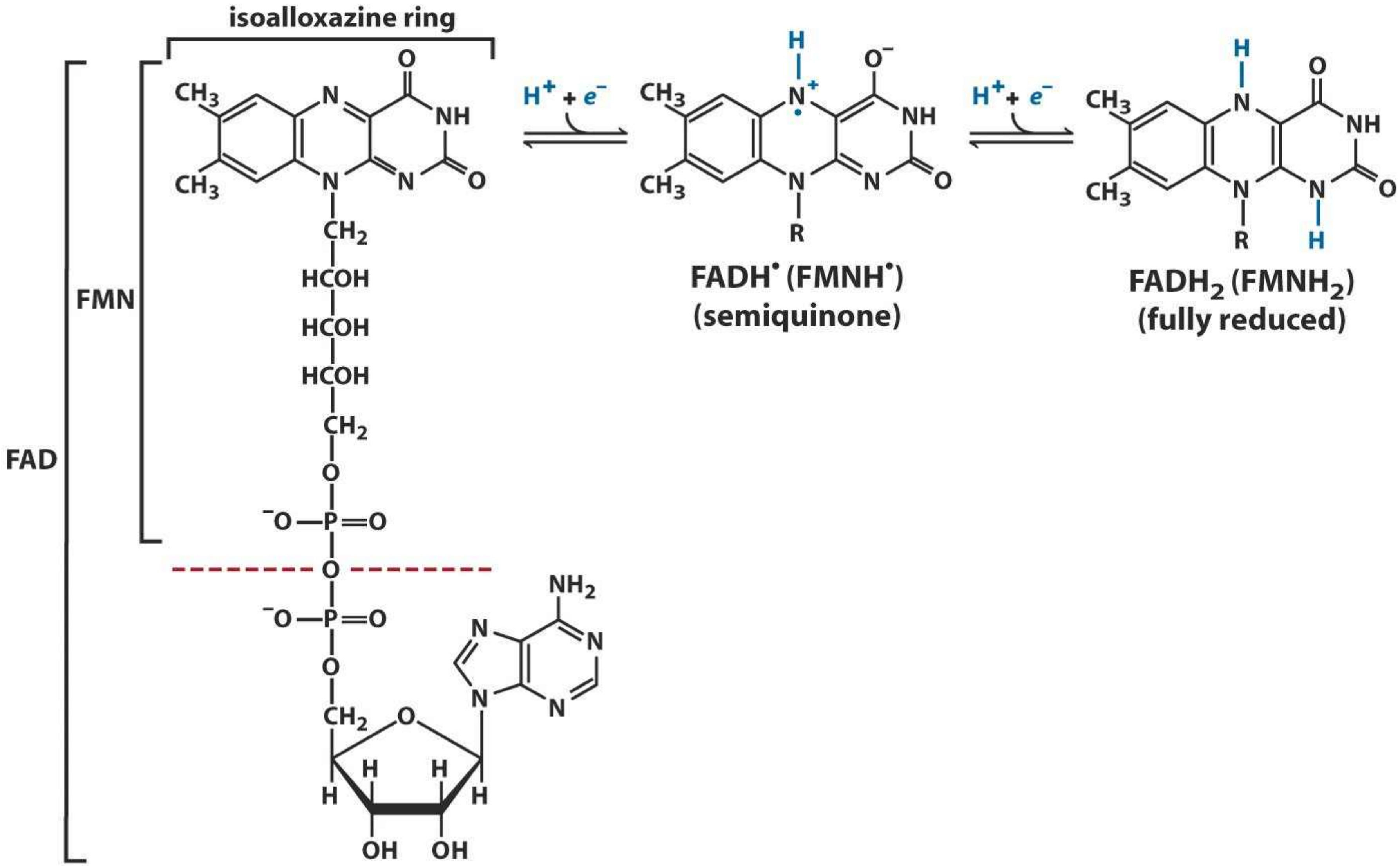
ΔG′° of hydrolysis (kJ/mol)
−70
−60
−50
−40
−30
−20
−10
0
COO⁻
C—O—P
CH2
Phosphoenolpyruvate
O
O—P
C
CHOH
CH2—O—P
1,3-Bisphosphoglycerate
P
Creatine
Phosphocreatine
Adenine
Rib
P
P
P
ATP
High-energy compounds
Low-energy compounds
Glucose 6–P
Glycerol–P
Pi

Pyrophosphate cleavage




2e⁻
2H⁺
A side
B side
or
+ H⁺
NADH
(reduced)
Adenine
NAD⁺
(oxidized)
In NADP⁺ this hydroxyl group is esterified with phosphate.


Absorbance
Wavelength (nm)
Oxidized (NAD⁺)
Reduced (NADH)
1.0
0.8
0.6
0.4
0.2
0.0
220
240
260
280
300
320
340
360
380



Flavin adenine dinucleotide (FAD) and flavin mononucleotide (FMN)