Advanced Cell Biology. Lecture 8

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Outline

Questions and answers

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Energy and chemistry

- Free energy
- Activated carriers: ATP and similar
- Other activated carriers

Previous final question: the answer

How living organisms are working against the second law of thermodynamics?

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How living organisms are working against the second law of thermodynamics?

- They run catabolic reactions to make an energy for anabolic (synthetic) reactions

Catalysis movie

Enzyme terminology: catalysis and substrate

- Enzyme binds with **substrate**,
- then catalyze conversion of substrate into **product**,
- and returns untouched to the initial state

Catalysis terms

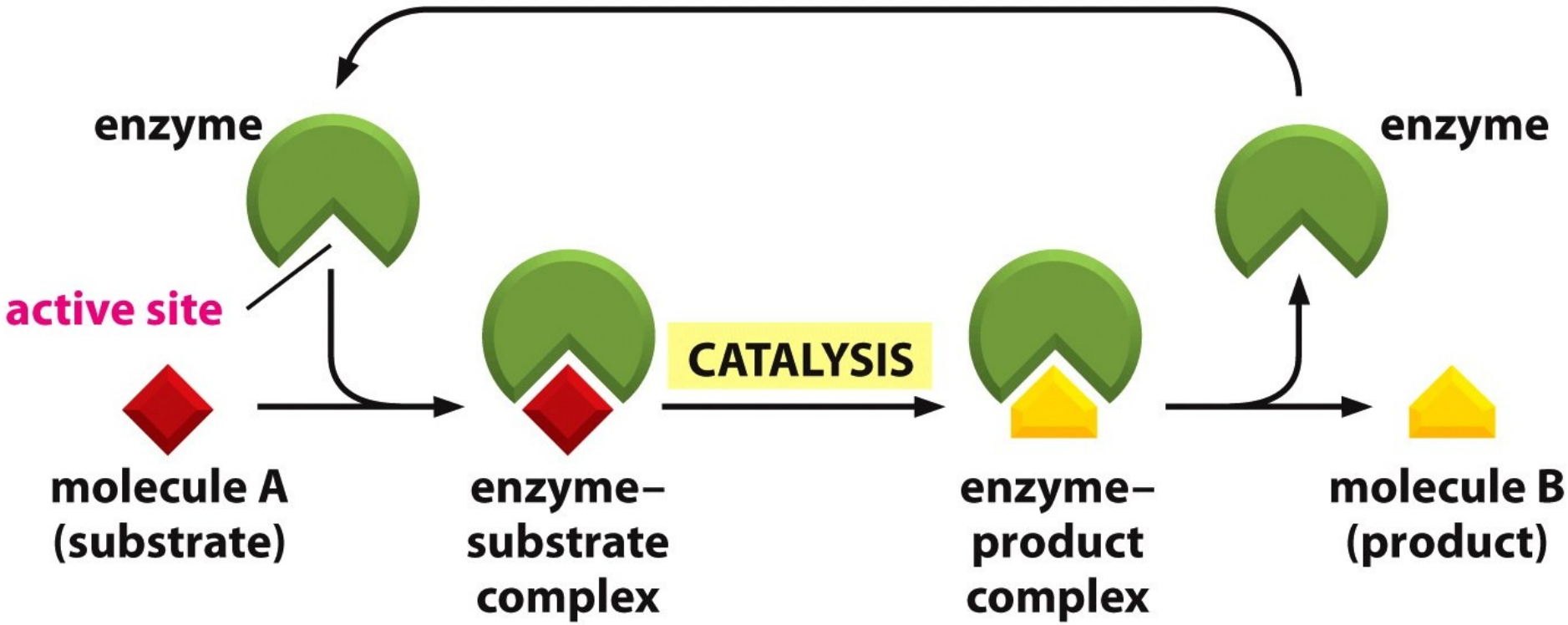
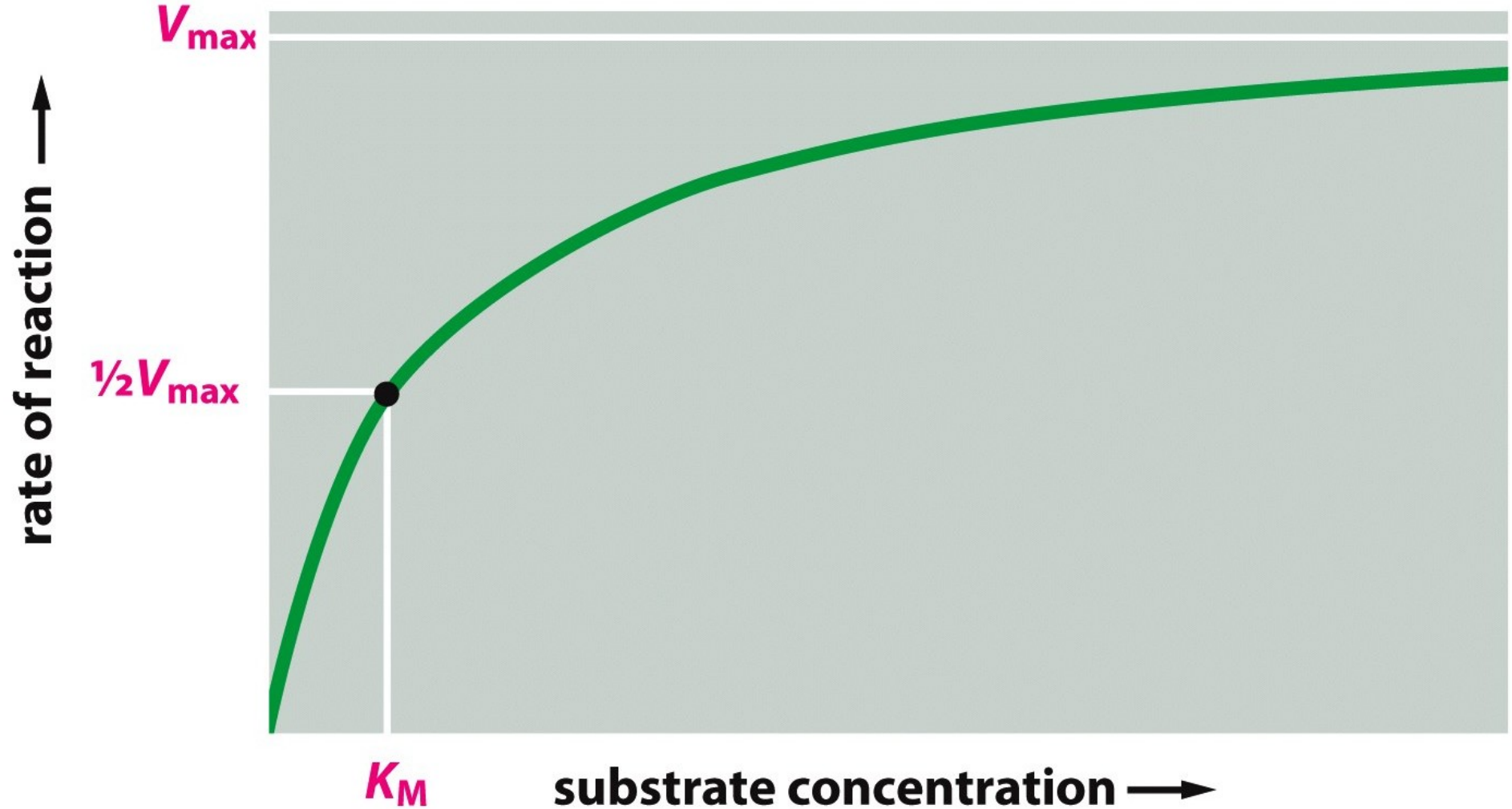


Figure 3-15 Essential Cell Biology 3/e (© Garland Science 2010)

Enzyme performance

- Two numbers are using for measuring enzyme performance: V_{max} and K_M
- V_{max} is maximal available reaction rate
- K_M is the concentration of substrate when the rate is $V_{max}/2$

Enzyme performance



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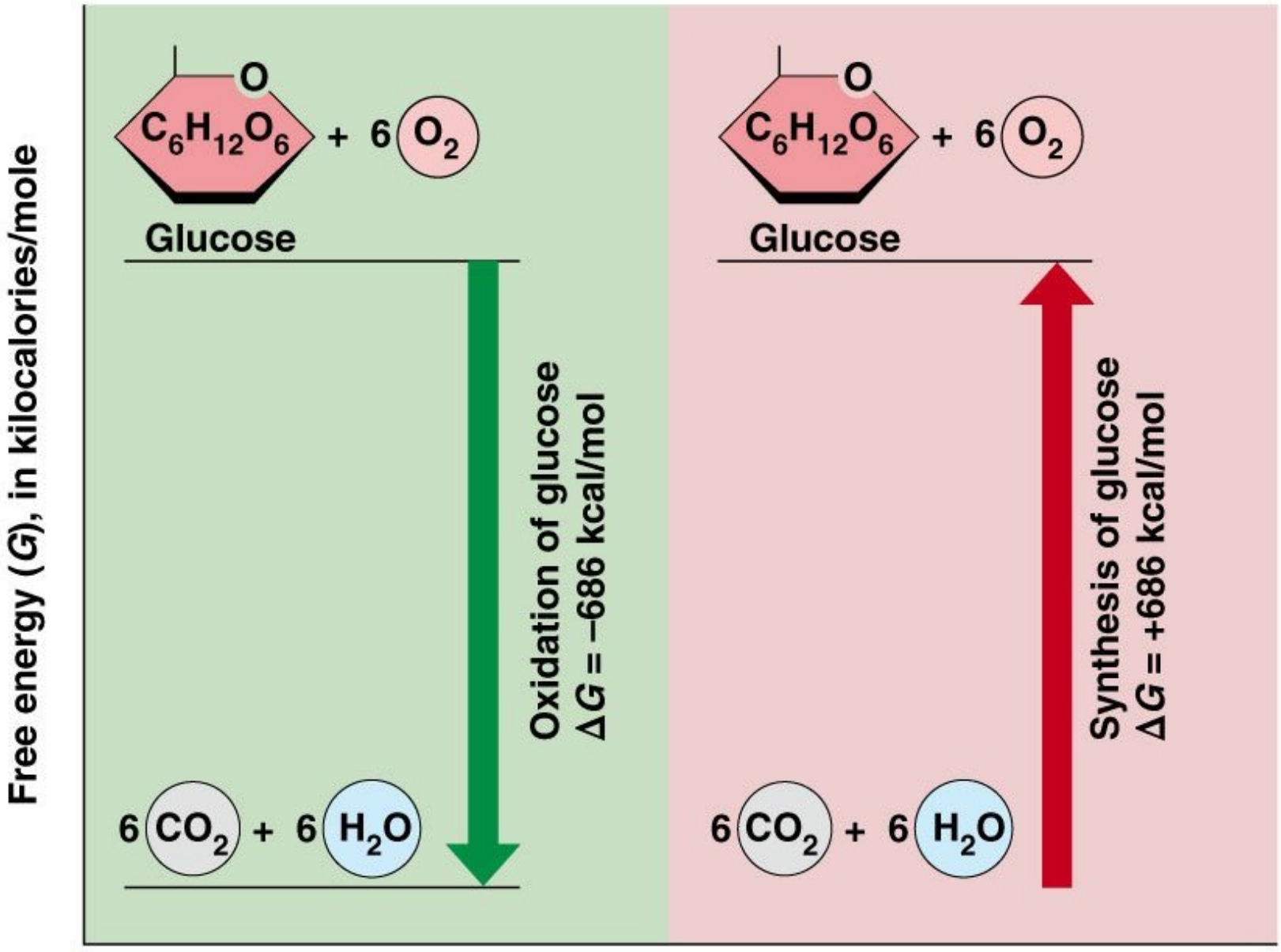
Energy and chemistry

Free energy

Free energy

- Gibbs energy, or G, is a chemical analog of potential energy
- If G increases ($\Delta G > 0$), the chemical reaction is non-favorable
- If G decreases ($\Delta G < 0$), chemical reaction is favorable

Delta G


Free energy (G), in kilocalories/mole
O
C6H12O6 + 6 O2
Glucose
Oxidation of glucose
ΔG = –686 kcal/mol
6 CO2 + 6 H2O
O
C6H12O6 + 6 O2
Glucose
Synthesis of glucose
ΔG = +686 kcal/mol
6 CO2 + 6 H2O

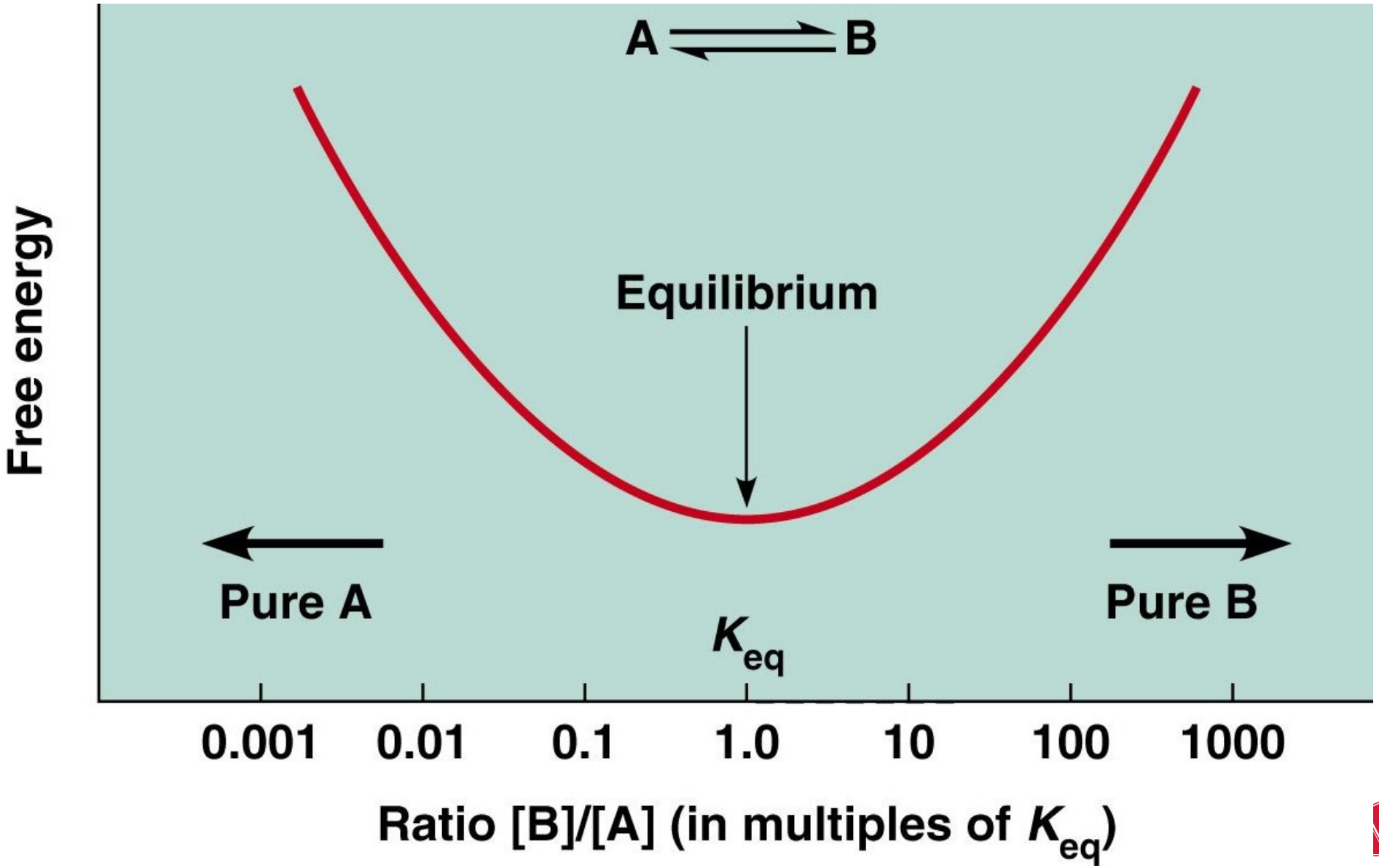
Standard free-energy change

- Simple chemical reaction like $X \rightarrow Y$ depends on reagent concentrations, $[X]$ and $[Y]$
- Free energy (Gibbs energy) will also depend on concentration
- To standardize G, we are using $\Delta G^{\circ} = \Delta G - RT \ln \frac{[X]}{[Y]}$, where R (gas constant) and T (absolute temperature) are constants

Chemical equilibrium

- Chemical reactions are going on until they reach a state of **chemical equilibrium**
- In the equilibrium, reaction is going in both directions without changing concentration of participating chemicals: $X \rightleftharpoons Y$

Equilibrium



Equilibrium constant

- On the stage of equilibrium, **equilibrium constant** $K = \frac{[X]}{[Y]}$, and $\Delta G = 0$ (why?*)
- Consequently, standard free-energy on the stage of equilibrium is:

$$\Delta G^\circ = \Delta G - RT \ln \frac{[X]}{[Y]} =$$
$$-RT \ln K = -0.616 \ln K =$$
$$-1.42 \log K$$

Equilibrium constant

- On the stage of equilibrium,
  equilibrium constant $K = \frac{[X]}{[Y]}$,
  and $\Delta G = 0$ (why?*)

  *Because equilibrium reaction does not take of give any energy
- Consequently, standard free-energy on the stage of equilibrium is:

$$\Delta G^{\circ} = \Delta G - RT \ln \frac{[X]}{[Y]} =$$
$$-RT \ln K = -0.616 \ln K =$$
$$-1.42 \log K$$

Equilibrium constant in complex reactions

- In complex reactions, K depends on concentrations of all participants
- E.g., for $A + B \rightleftharpoons AB$: $K = \frac{[AB]}{[A][B]}$
- If reaction has several steps, all changes of free-energy are additive

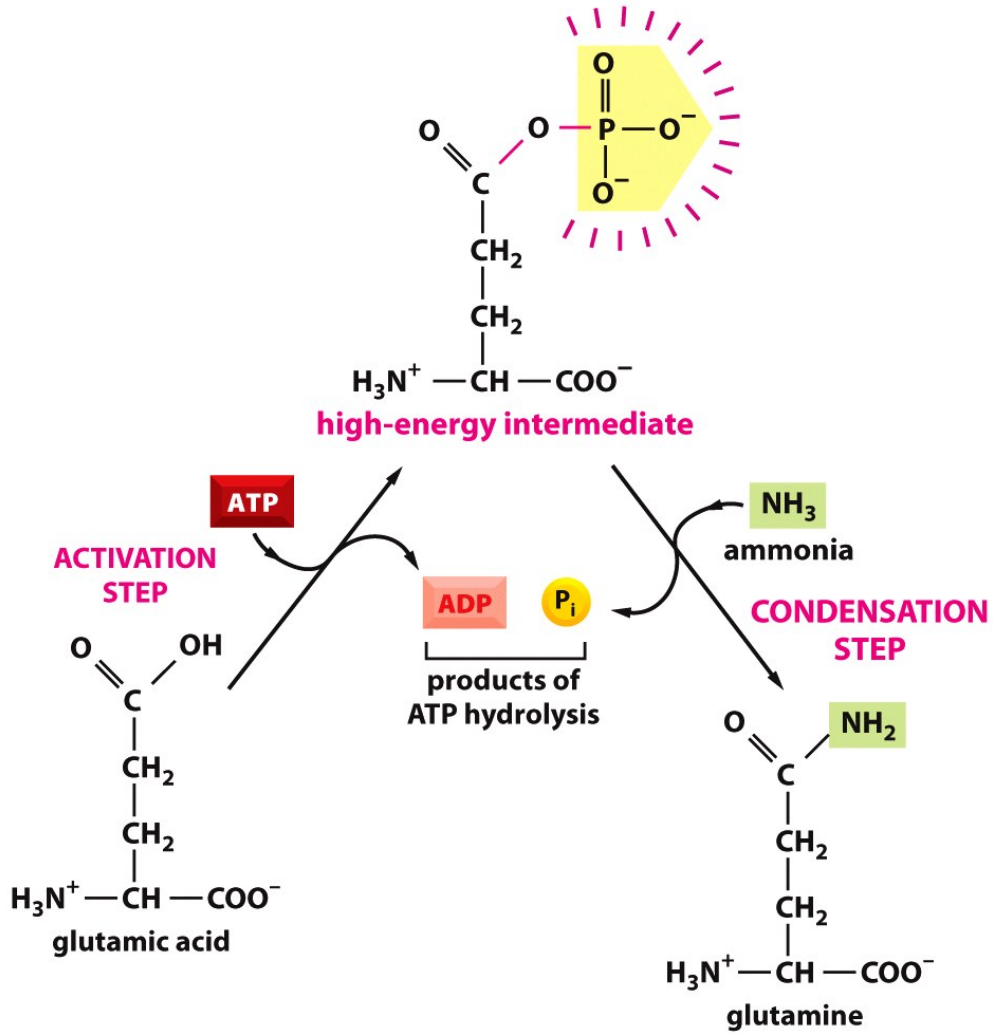
Energy and chemistry

Activated carriers: ATP and similar

Activated carrier molecules

- Carriers are used for temporarily storage of both energy and molecular pieces
- Carriers have high diffusion rates
- Carriers work in two steps: (a) activation and (b) condensation
- They are not enzymes!
- For example, ATP and GTP (guanosine triphosphate) store phosphate on the energetic bond

One component and the carrier



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ATP is a carrier of phosphate group, P_i

Two components and the carrier: coupled reactions

There are two variants of coupled reactions:

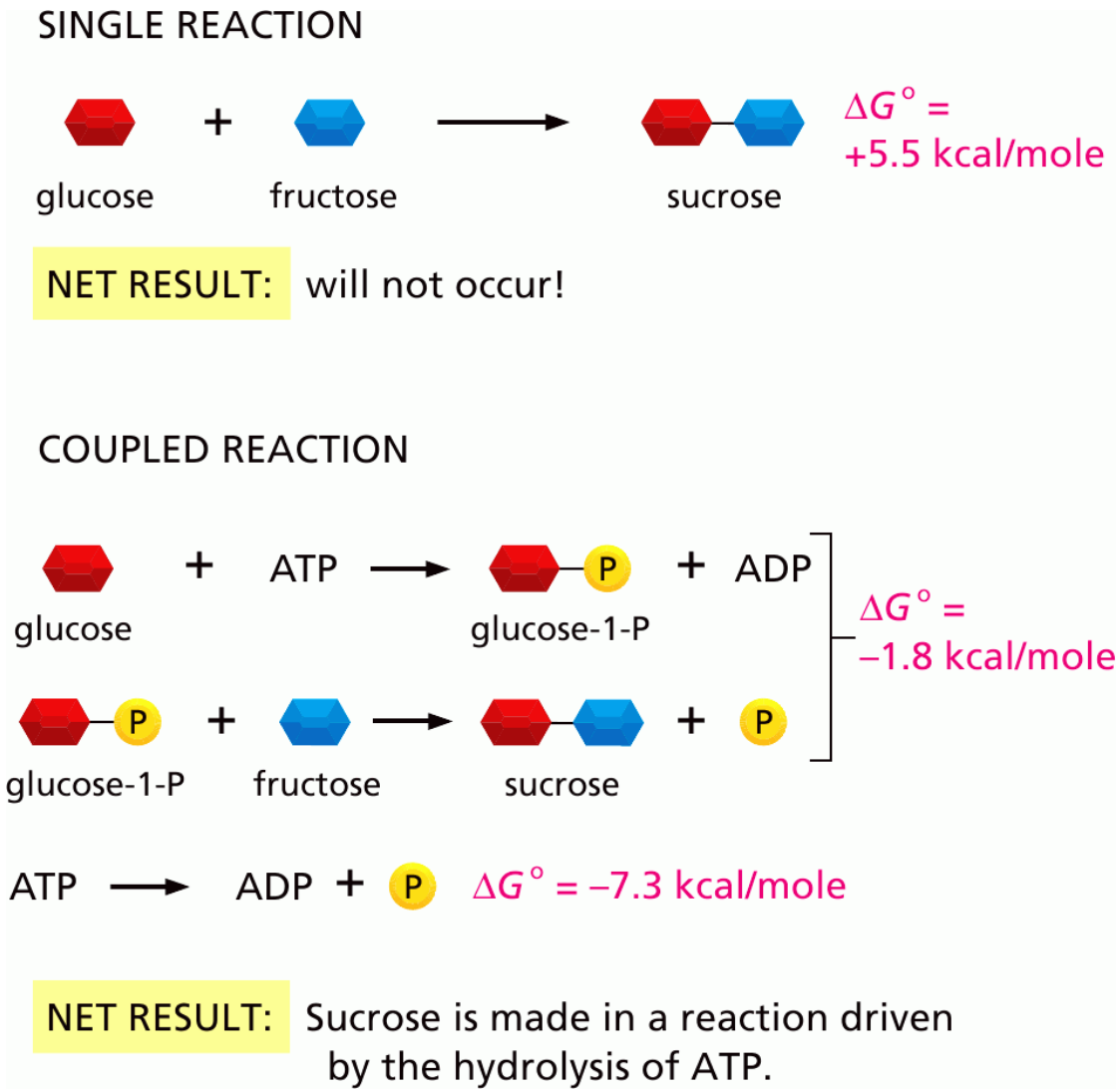
- Breaking (oxidizing) of something AND carrier synthesis
- Or carrier destruction AND synthesis of something (e.g., polymer from monomers)

ATP in coupled reactions

To join A and B, ATP usually acts as intermediate:

- $A + ATP \rightarrow A–0–P0_3 + ADP$
- $B–H + A–0–P0_3 \rightarrow A–B + P_i$

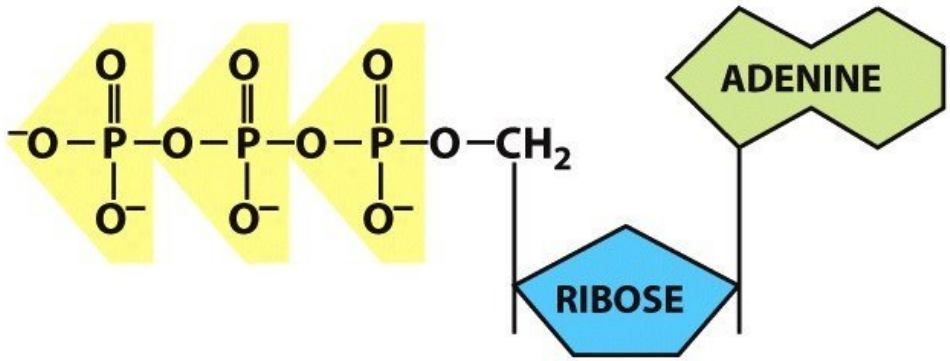
Two components, ATP and ΔG



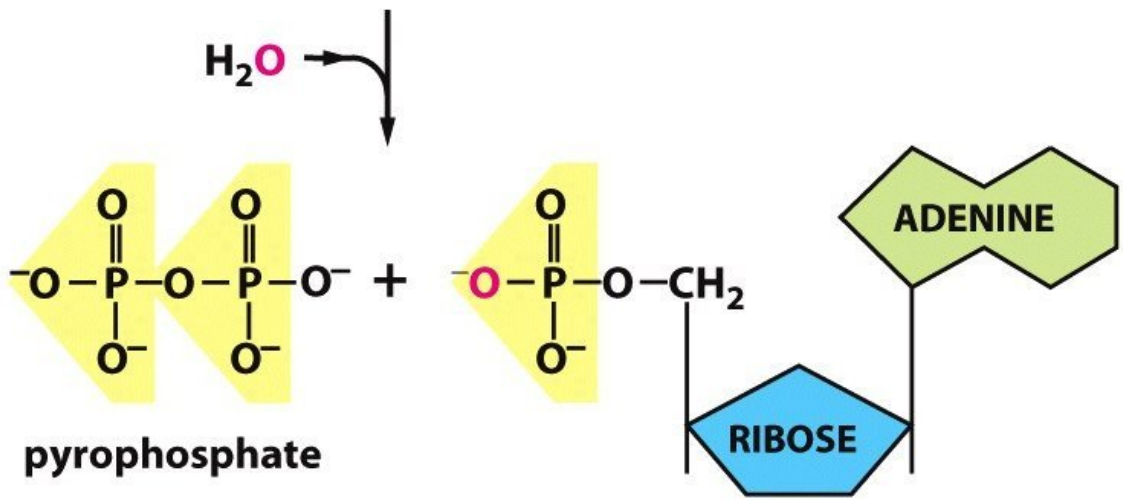
AMP and pyrophosphate

- Normally, ATP $\rightarrow$ ADP + P_i reaction has $\Delta G^\circ \approx -13$ kcal/mole
- However, some reactions (like synthesis of DNA from nucleotides) need more
- The alternative way: ATP $\rightarrow$ AMP + P_i–P_i (pyrophosphate) has $\Delta G^\circ \approx -26$ kcal/mole

How to make pyrophosphate



adenosine triphosphate (ATP)



pyrophosphate

adenosine monophosphate (AMP)

Energy and chemistry

Other activated carriers

Electron carriers: NAD/NADH, NADP/NADPH

- Both are derivatives of adenine transferring electrons with associated protons (or simply hydrogen, H)
- They are active redox molecules
- NADH typically works in catabolic reactions like cell respiration
- NADPH works mostly in anabolic reactions like synthesis of DNA or synthesis of cholesterol
- FAD belongs to the same group

NADPH gives H to make cholesterol

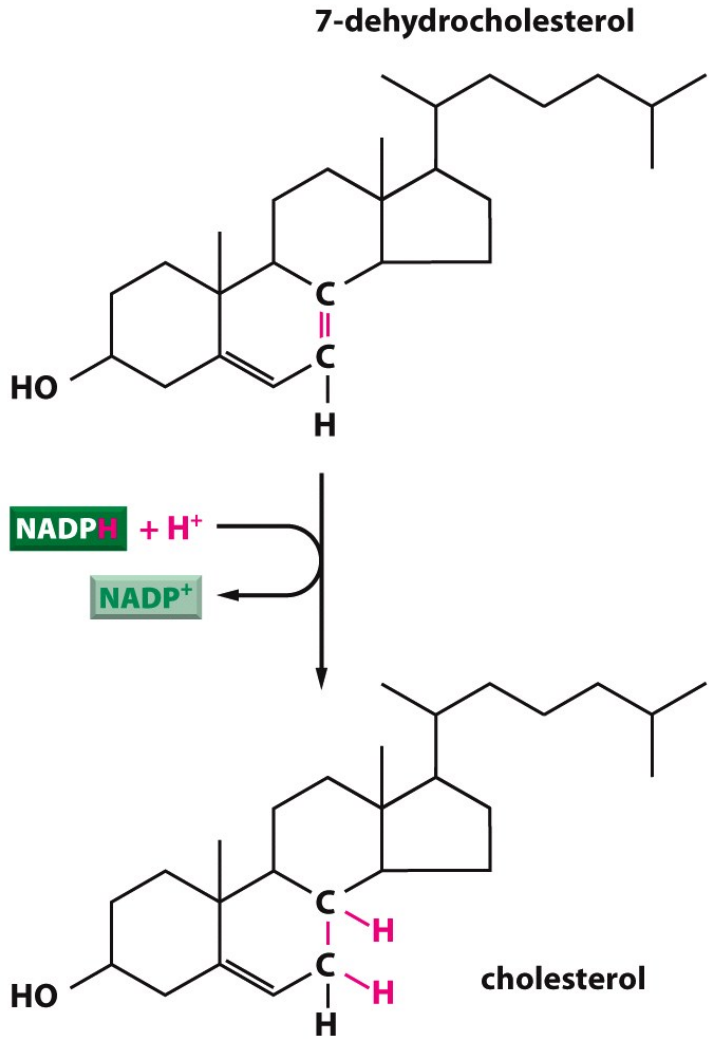


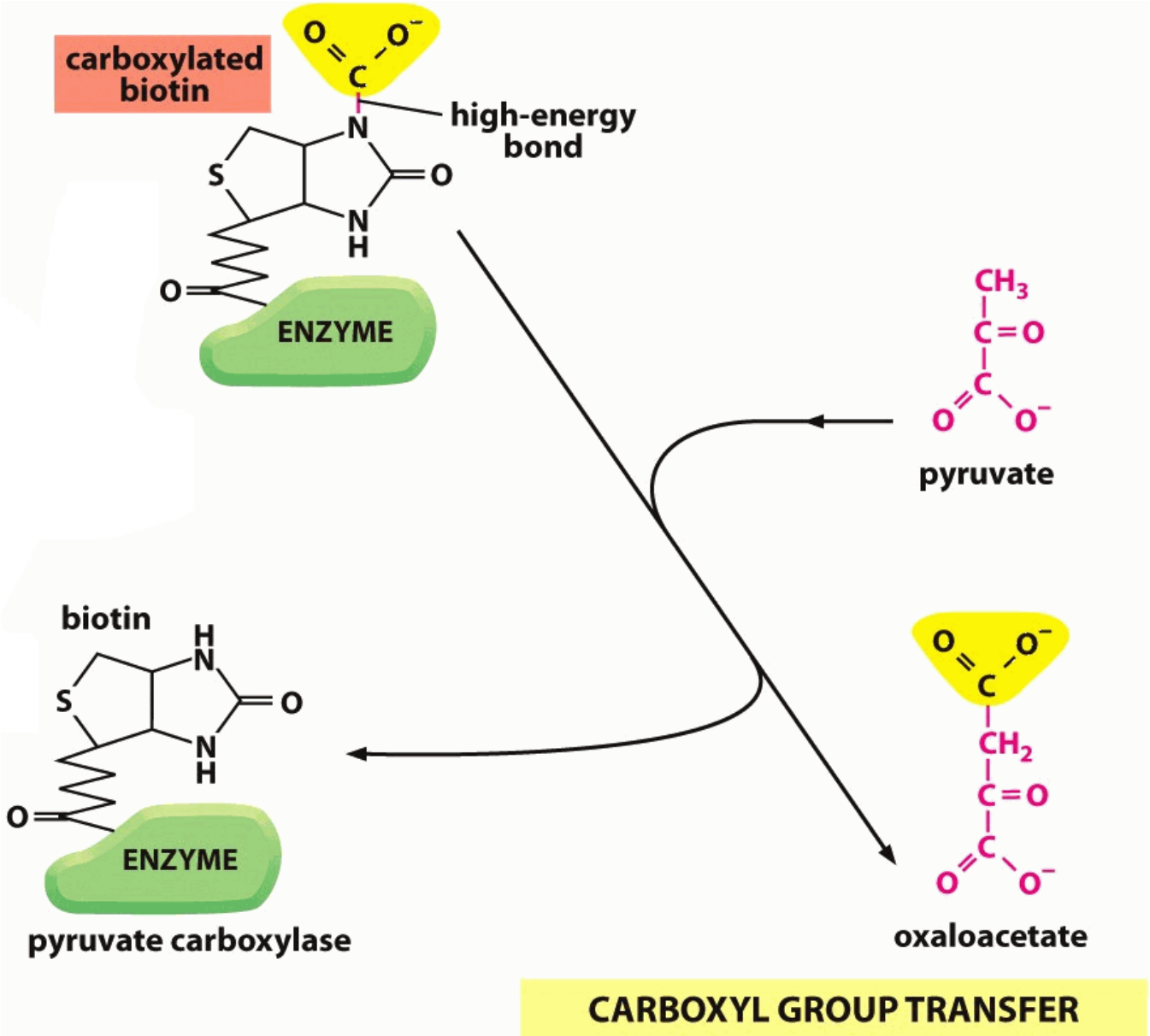
Figure 3-35 Essential Cell Biology 3/e (© Garland Science 2010)

Other carriers

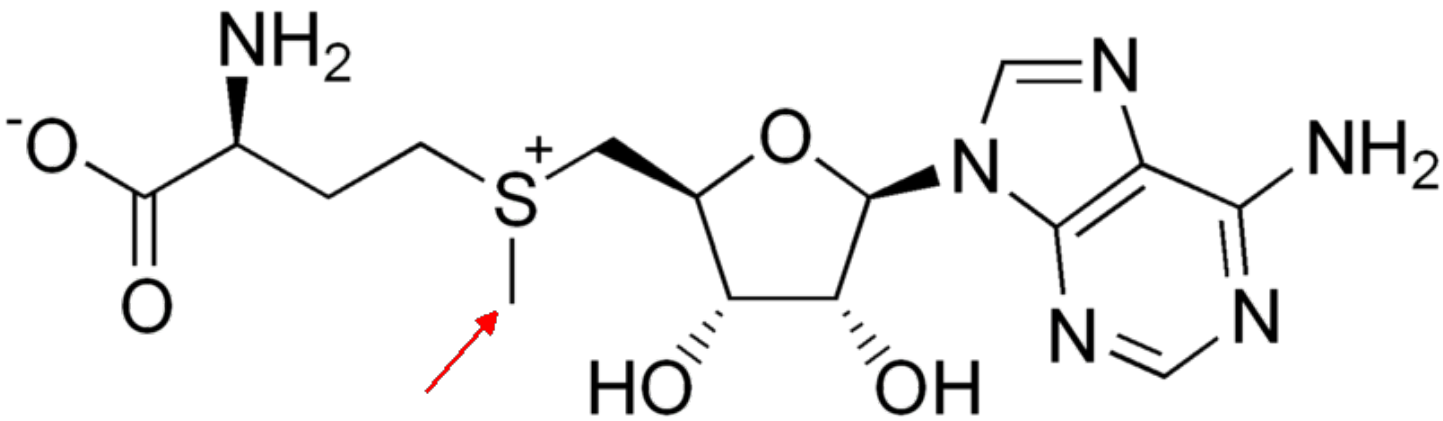
- CoA (or Acetyl–CoA): transfers acetyl group (CH_3–COOH)
- Biotin: carboxyl group (–COOH)
- S-Adenosyl methionine (SAM, SAMe): methyl group (–CH_3)
- Uridine diphosphate glucose (UDP-glucose): whole glucose molecules

The molecular piece which they transfer is attached to their molecules with high-energetic bond

Biotin, vitamin B_7 transfers –COOH



SAMe, S-Adenosyl methionine transfers –CH_3



Final question (2 points)

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What are enzymes?

Summary

- Some reactions are **endoenergetic** ($\Delta G > 0$, some are **exoenergetic** ($\Delta G < 0$)
- On the stage of equilibrium, all reactions at +37°C have $\Delta G^\circ = -1.42 \log K$
- Activated carriers are used in endoenergetic reactions
- Activated carriers may transfer phosphate or different organic groups

For Further Reading

A. Shipunov.
Advanced Cell Biology [Electronic resource].
2011—onwards.
Mode of access:
http://ashipunov.info/shipunov/school/biol_250

B. Alberts et al.
Essential Cell Biology. 3rd edition.
Garland Science, 2009.
Chapter 3.