Concept of Free Energy

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- Living things require energy. Movement, growth, synthesis of biomolecules, and the transport of ions and molecules across membranes all demand energy input.
- All organisms must acquire energy from their surroundings and must utilize that energy efficiently to carry out life processes.
- Many of these processes involve conversions of one kind of energy into another.
- To study such bioenergetic phenomena requires familiarity with **thermodynamics**.
- Thermodynamics also allows us to determine whether chemical processes and reactions occur spontaneously.

- In any consideration of thermodynamics, a distinction must be made between the system and the surroundings.
- The **system** is that portion of the *universe* with which we are concerned. It might be a mixture of chemicals in a test tube, or a single cell, or an entire organism.
- The **surroundings** include everything else in the universe.

- The nature of the system must also be specified. There are three basic kinds of systems: isolated, closed, and open.

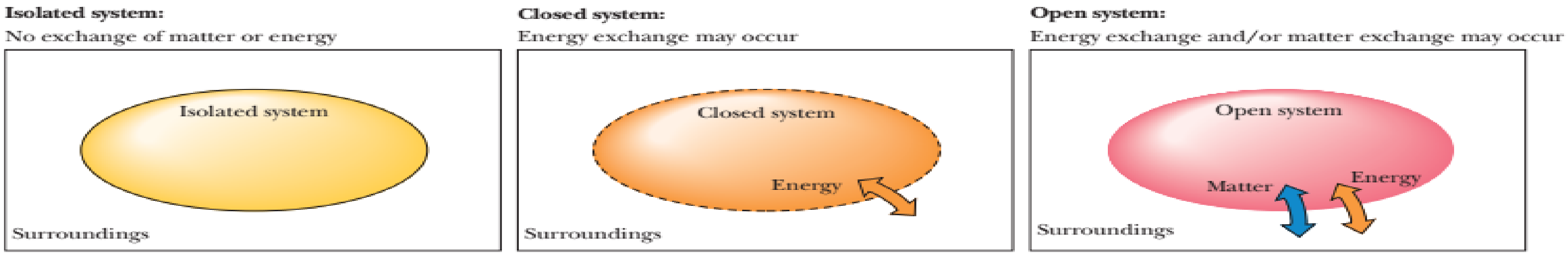


FIGURE 3.1 The characteristics of isolated, closed, and open systems. Isolated systems exchange neither matter nor energy with their surroundings. Closed systems may exchange energy, but not matter, with their surroundings. Open systems may exchange either matter or energy with the surroundings.

Living things are typically open systems that exchange matter (nutrients and waste products) and energy (heat from metabolism, for example) with their surroundings.

- The **first law** is the principle of the conservation of energy: *for any physical or chemical change, the total amount of energy in the universe remains constant; energy may change form or it may be transported from one region to another, but it cannot be created or destroyed.*
- The **second law** of thermodynamics, which can be stated in several forms, says that the universe always tends toward increasing disorder: *in all natural processes, the entropy of the universe increases.*

- Cells are isothermal systems, they function at essentially constant temperature (they also function at constant pressure).
- Heat flow is not a source of energy for cells, because heat can do work only as it passes to a zone or object at a lower temperature.
- The energy that cells can and must use is free energy, described by the Gibbs free-energy function *G*, which allows prediction of the direction of chemical reactions, their exact equilibrium position, and the amount of work they can in theory perform at constant temperature and pressure.
- Heterotrophic cells acquire free energy from nutrient molecules, and photosynthetic cells acquire it from absorbed solar radiation.
- Both kinds of cells transform this free energy into ATP and other energy-rich compounds capable of providing energy for biological work at constant temperature.

- **Gibbs free energy, *G,*** expresses the amount of energy capable of doing work during a reaction at constant temperature and pressure. When a reaction proceeds with the release of free energy (that is, when the system changes so as to possess less free energy), the free-energy change, *G,* has a negative value and the reaction is said to be exergonic. In endergonic reactions, the system gains free energy and *G* is positive.

- **Enthalpy, *H,*** is the heat content of the reacting system. It reflects the number and kinds of chemical bonds in the reactants and products. When a chemical reaction releases heat, it is said to be exothermic; the heat content of the products is less than that of the reactants and *H* has, by convention, a negative value. Reacting systems that take up heat from their surroundings are endothermic and have positive values of *H.*
- **Entropy, *S,*** is a quantitative expression for the randomness or disorder in a system.
  When the products of a reaction are less complex and more disordered than the reactants, the
  reaction is said to proceed with a gain in entropy.
- The units of *G* and *H* are joules/mole or calories/mole (recall that 1 cal 4.184 J); units of entropy are joules/mole Kelvin (J/mol K).

- Under the conditions existing in biological systems (including constant temperature and pressure), changes in free energy, enthalpy, and entropy are related to each other quantitatively by the equation.

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

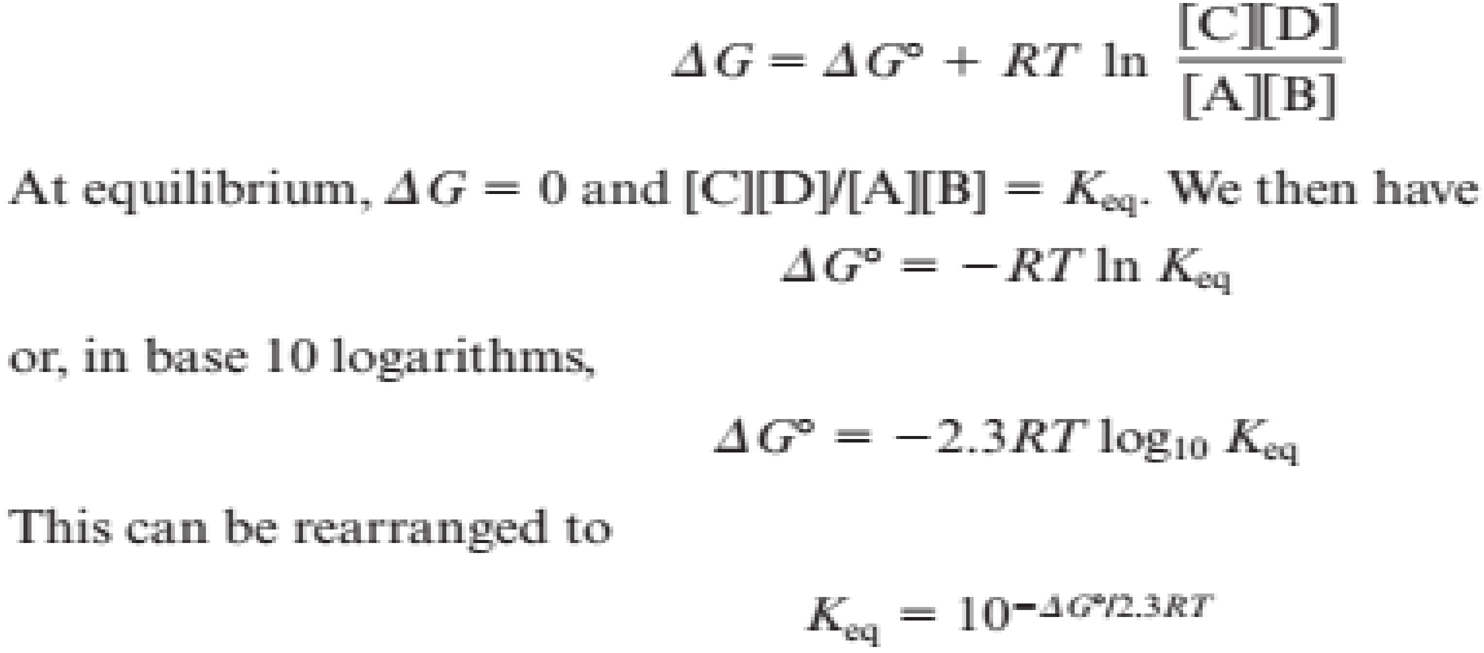
- **The Standard State** In order to compare the thermodynamic parameters of different eactions, it is convenient to define a *standard state*. For solutes in a solution, the standard state is normally unit activity (often simplified to 1 *M* concentration).
- Enthalpy, entropy, and other thermodynamic quantities are often given or determined for standard-state conditions and are then denoted by a superscript degree sign ("°"), as in $\Delta H°$, $\Delta S°$, and so on.

- **The Standard-State Free Energy Change** The free energy change, Δ*G*, for any reaction depends upon the nature of the reactants and products.
- It is also affected by the conditions of the reaction, including temperature, pressure, pH, and the concentrations of the reactants and products.

- If the free energy change for a reaction is sensitive to solution conditions, what is the particular significance of the standard-state free energy change?
- To answer this question, consider a reaction between two reactants A and B to produce the products C and D

$$A + B \rightleftharpoons C + D$$

- The free energy change for non–standard-state concentrations is given by



$$\Delta G = \Delta G^\circ + RT \ln \frac{[C][D]}{[A][B]}$$

At equilibrium, $\Delta G = 0$ and $[C][D]/[A][B] = K_{eq}$. We then have

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

or, in base 10 logarithms,

$$\Delta G^\circ = -2.3RT \log_{10} K_{eq}$$

This can be rearranged to

$$K_{eq} = 10^{-\Delta G^\circ/2.3RT}$$

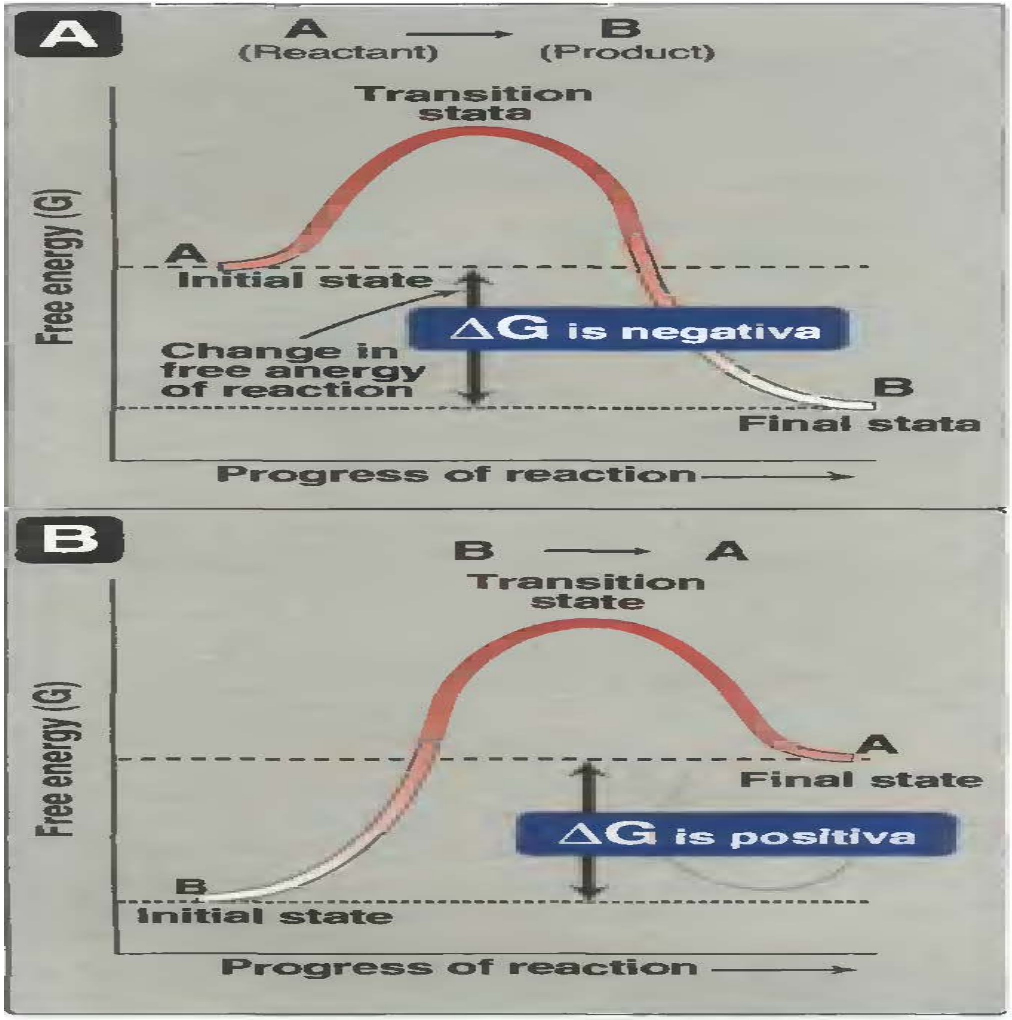


Figure 6.2
Change in free energy (ΔG) during a reaction. A. The product has a lower free energy (G) than the reactant. B. The product has a higher free energy than the reactant.

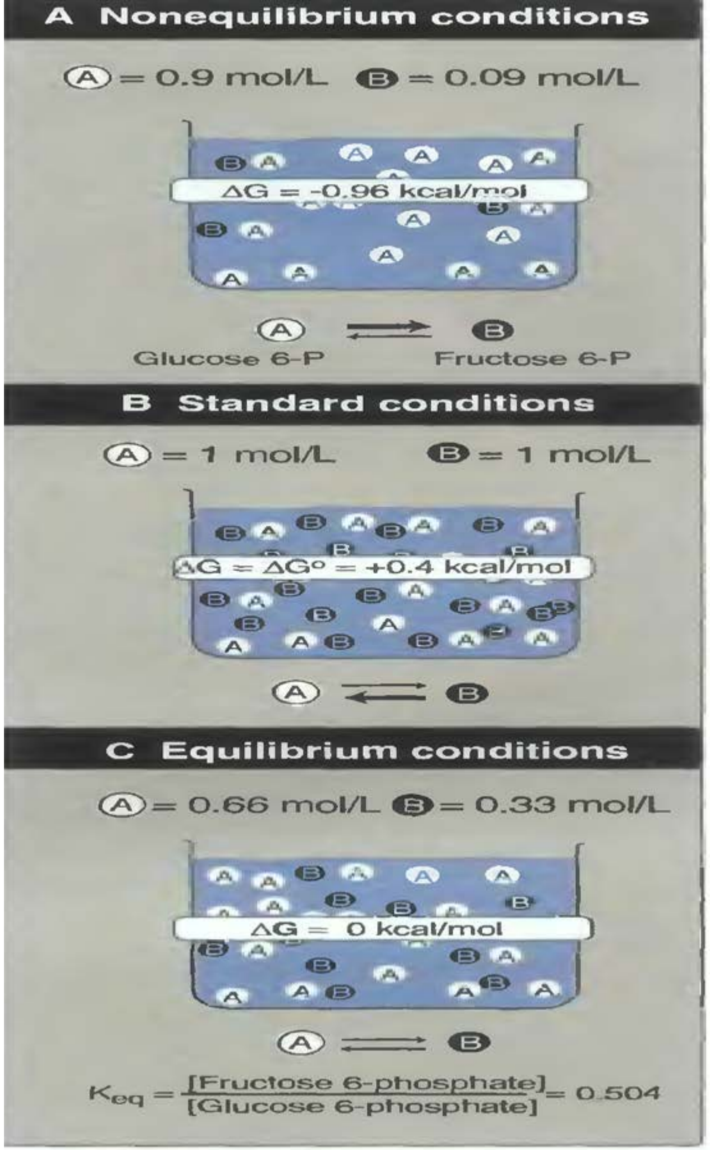


Figure 6.3
ΔG of a reaction depends on the concentration of reactant (A) and product (B). For the conversion of glucose 6-P to fructose 6-P, ΔG is negative when the ratio of reactant (A) to product (B) is large (top, panel A); is positive under standard conditions (middle, panel B); and is zero at equlibrium (bottom, panel C).

- For biochemical reactions in which hydrogen ions (H^+) are consumed or produced, the usual defnition of the standard state is awkward.
- Standard state for the H^+ ion is 1 *M*, which corresponds to pH 0. At this pH, nearly all enzymes would be denatured and biological reactions would not occur.
- It makes more sense to use free energies and equilibrium constants determined at pH 7.
- Biochemists have thus adopted a modifed standard state, designated with prime(′)symbols, as in **$\Delta G^{\circ\prime}$ $\Delta Keq^{\circ\prime}$ $\Delta H^{\circ\prime}$ ($\Delta G^{\prime\circ}$, $\Delta Keq^{\prime\circ}$ $\Delta H^{\prime\circ}$)** and so on.
- For values determined in this way, a standard state of 10^{-7} *M* H^+ and unit activity (1 *M* for solutions, 1 atm for gases and pure solids defned as unit activity) for all other components (in the ionic forms that exist at pH 7)

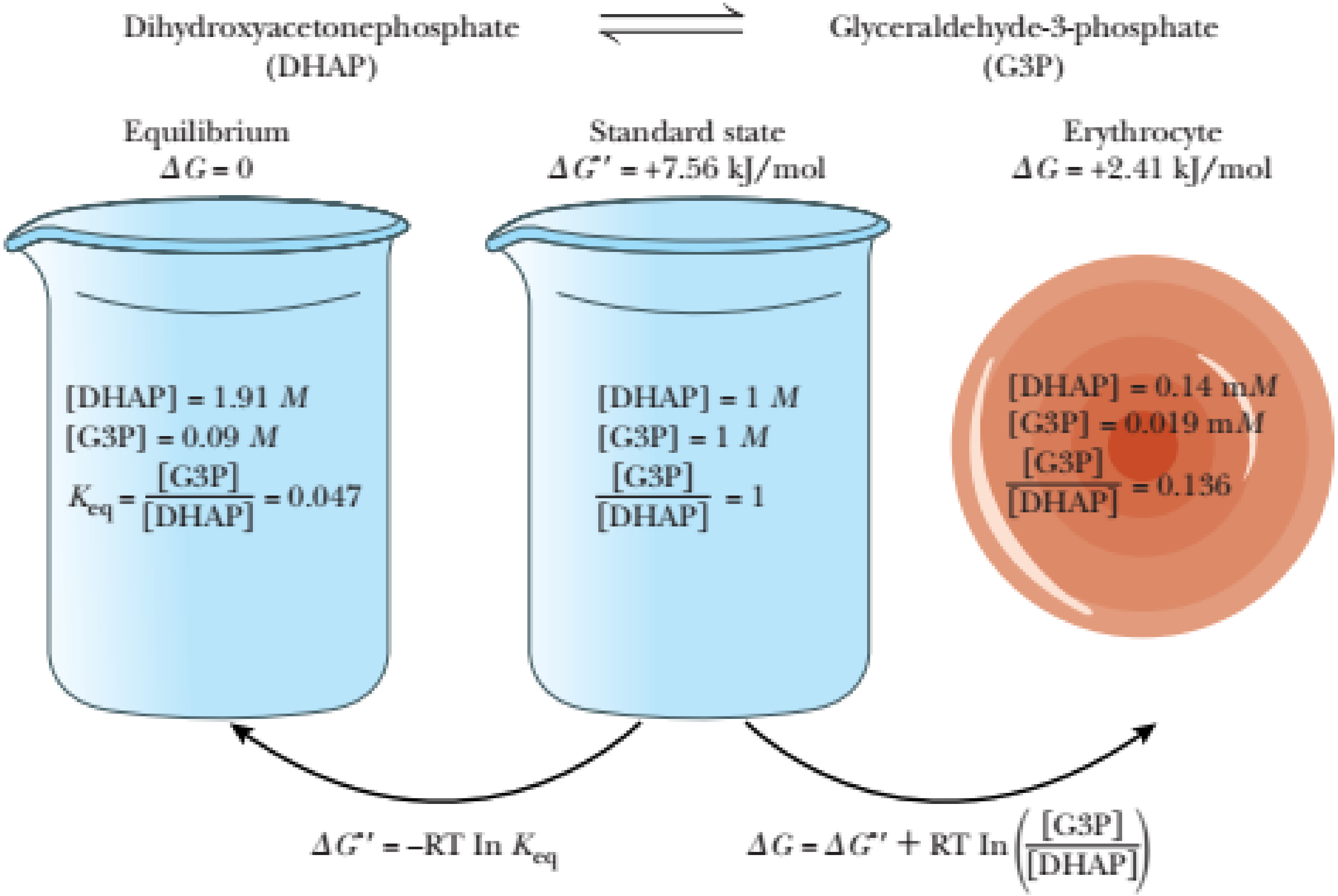
$$A \longrightarrow B^- + H^+$$

the relation of the equilibrium constants for the two standard states is

$$K_{eq} = \frac{[B^-][H^+]}{[A]} = K_{eq}'\,[H^+]$$

and $\Delta G^{\circ\prime}$ is given by

$$\Delta G^{\circ\prime} = \Delta G^{\circ} + RT \ln\,[H^+]$$


Dihydroxyacetonephosphate (DHAP)
$\rightleftharpoons$
Glyceraldehyde-3-phosphate (G3P)
Equilibrium
$\Delta G = 0$
Standard state
$\Delta G' = +7.56$ kJ/mol
Erythrocyte
$\Delta G = +2.41$ kJ/mol
$[\mathrm{DHAP}] = 1.91\ M$
$[\mathrm{G3P}] = 0.09\ M$
$K_{eq} = \frac{[\mathrm{G3P}]}{[\mathrm{DHAP}]} = 0.047$
$[\mathrm{DHAP}] = 1\ M$
$[\mathrm{G3P}] = 1\ M$
$\frac{[\mathrm{G3P}]}{[\mathrm{DHAP}]} = 1$
$[\mathrm{DHAP}] = 0.14\ \mathrm{m}M$
$[\mathrm{G3P}] = 0.019\ \mathrm{m}M$
$\frac{[\mathrm{G3P}]}{[\mathrm{DHAP}]} = 0.136$
$\Delta G' = -\mathrm{RT}\ \ln K_{eq}$
$\Delta G = \Delta G' + \mathrm{RT}\ \ln\left(\frac{[\mathrm{G3P}]}{[\mathrm{DHAP}]}\right)$

Standard Free-Energy Changes Are Additive

$$
\begin{array}{lll}
(1) & \mathrm{A} \longrightarrow \mathrm{B} & \Delta G_1'^{\circ} \\
(2) & \mathrm{B} \longrightarrow \mathrm{C} & \Delta G_2'^{\circ} \\
\hline
\textit{Sum:} & \mathrm{A} \longrightarrow \mathrm{C} & \Delta G_1'^{\circ} + \Delta G_2'^{\circ}
\end{array}
$$

$$\text{Glucose} + P_i \longrightarrow \text{glucose 6-phosphate} + H_2O \qquad \Delta G'^{\circ} = 13.8\ \text{kJ/mol}$$

$$\text{ATP} + H_2O \longrightarrow \text{ADP} + P_i \qquad \Delta G'^{\circ} = -30.5\ \text{kJ/mol}$$

$$\begin{array}{ll}
(1) & \text{Glucose} + P_i \longrightarrow \text{glucose 6-phosphate} + H_2O \\
(2) & \text{ATP} + H_2O \longrightarrow \text{ADP} + P_i \\
\hline
\textit{Sum:} & \text{ATP} + \text{glucose} \longrightarrow \text{ADP} + \text{glucose 6-phosphate}
\end{array}$$

The overall standard free-energy change is obtained by adding the $\Delta G'^{\circ}$ values for individual reactions:

$$\Delta G'^{\circ} = 13.8\ \text{kJ/mol} + (-30.5\ \text{kJ/mol}) = -16.7\ \text{kJ/mol}$$

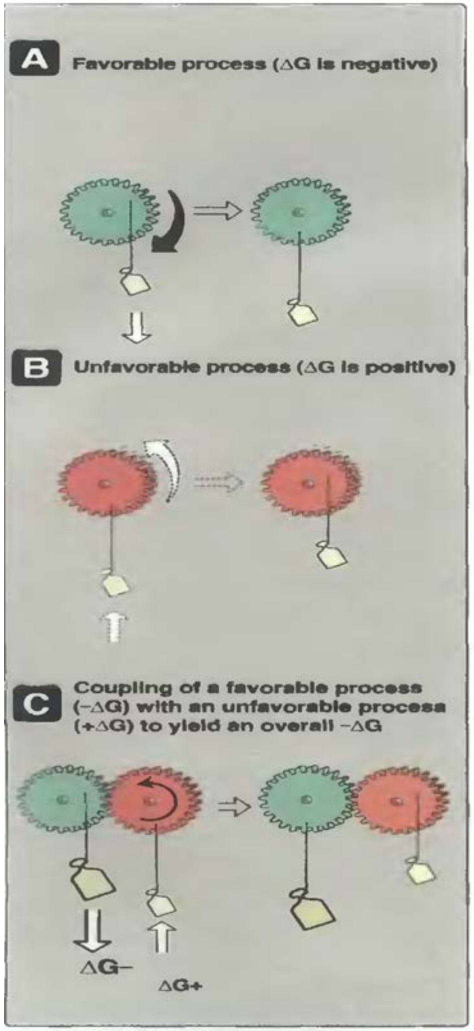


Figure 6.4
Mechanical model of coupling of favorable and unfavorable processes.

We have said that $\Delta G'^{\circ}$ is a way of expressing the equilibrium constant for a reaction. For reaction (1) above,

$$K'_{\mathrm{eq}_1} = \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}][\mathrm{P_i}]} = 3.9 \times 10^{-3}\ \text{M}^{-1}$$

Notice that H_2O is not included in this expression, as its concentration (55.5 M) is assumed to remain unchanged by the reaction. The equilibrium constant for the hydrolysis of ATP is

$$K'_{\mathrm{eq}_2} = \frac{[\text{ADP}][\mathrm{P_i}]}{[\text{ATP}]} = 2.0 \times 10^{5}\ \text{M}$$

The equilibrium constant for the two coupled reactions is

$$\begin{aligned} K'_{\mathrm{eq}_3} &= \frac{[\text{glucose 6-phosphate}][\text{ADP}][\mathrm{P_i}]}{[\text{glucose}][\mathrm{P_i}][\text{ATP}]} \\ &= (K'_{\mathrm{eq}_1})(K'_{\mathrm{eq}_2}) = (3.9 \times 10^{-3}\ \text{M}^{-1})\ (2.0 \times 10^{5}\ \text{M}) \\ &= 7.8 \times 10^{2} \end{aligned}$$

Summary

- *The free-energy change for a reaction is independent of the pathway by which the reaction occurs;* it depends only on the nature and concentration of the initial reactants and the final products.
- Enzymes cannot, therefore, change equilibrium constants; but they can and do increase the *rate* at which a reaction proceeds in the direction dictated by thermodynamics.

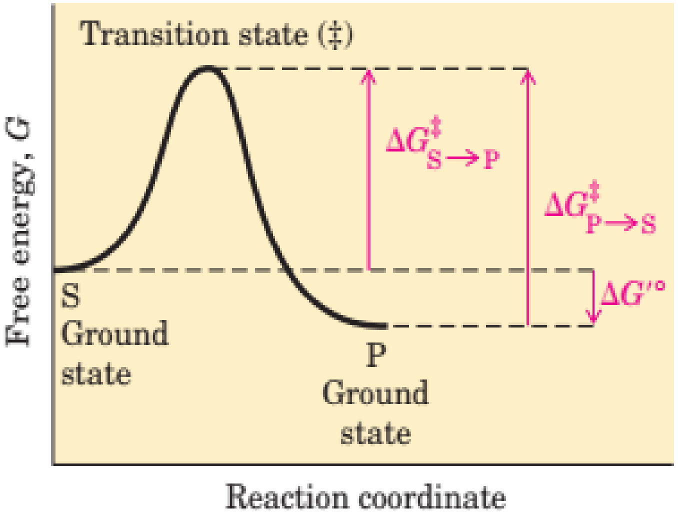


FIGURE 6–2 Reaction coordinate diagram for a chemical reaction. The free energy of the system is plotted against the progress of the reaction S ⟶ P. A diagram of this kind is a description of the energy changes during the reaction, and the horizontal axis (reaction coordinate) reflects the progressive chemical changes (e.g., bond breakage or formation) as S is converted to P. The activation energies, $\Delta G^{\ddagger}$, for the S ⟶ P and P ⟶ S reactions are indicated. $\Delta G'^{\circ}$ is the overall standard free-energy change in the direction S ⟶ P.

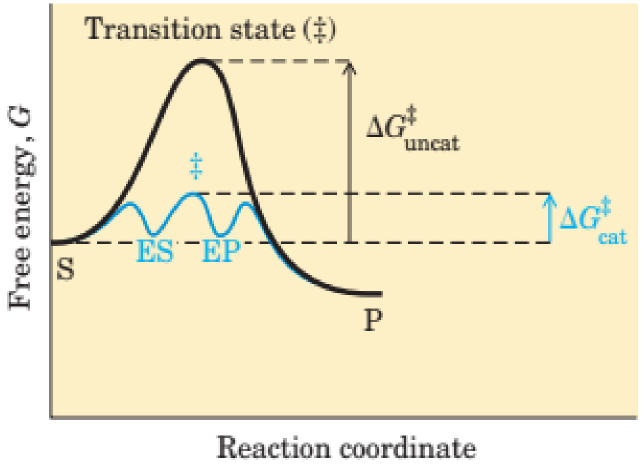


FIGURE 6–3 Reaction coordinate diagram comparing enzyme-catalyzed and uncatalyzed reactions. In the reaction S ⟶ P, the ES and EP intermediates occupy minima in the energy progress curve of the enzyme-catalyzed reaction. The terms $\Delta G^{\ddagger}_{\text{uncat}}$ and $\Delta G^{\ddagger}_{\text{cat}}$ correspond to the activation energy for the uncatalyzed reaction and the overall activation energy for the catalyzed reaction, respectively. The activation energy is lower when the enzyme catalyzes the reaction.

References

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