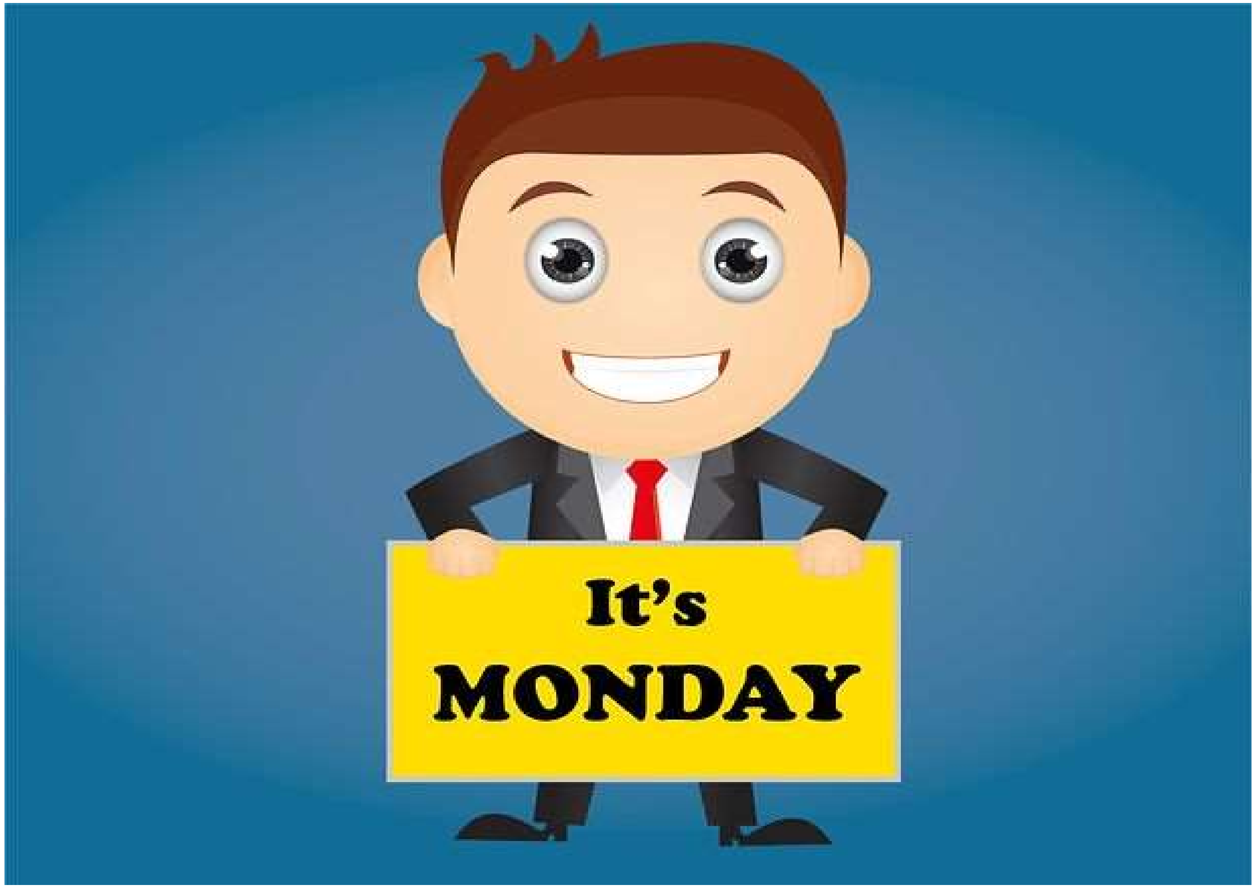
Last week



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- Living organisms (domains, kingdoms, definition?)
- Cellular foundation: Structure and function of the cell (2 types)
- Chemical foundation: Biomolecules and building blocks

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Typical Animal Cell

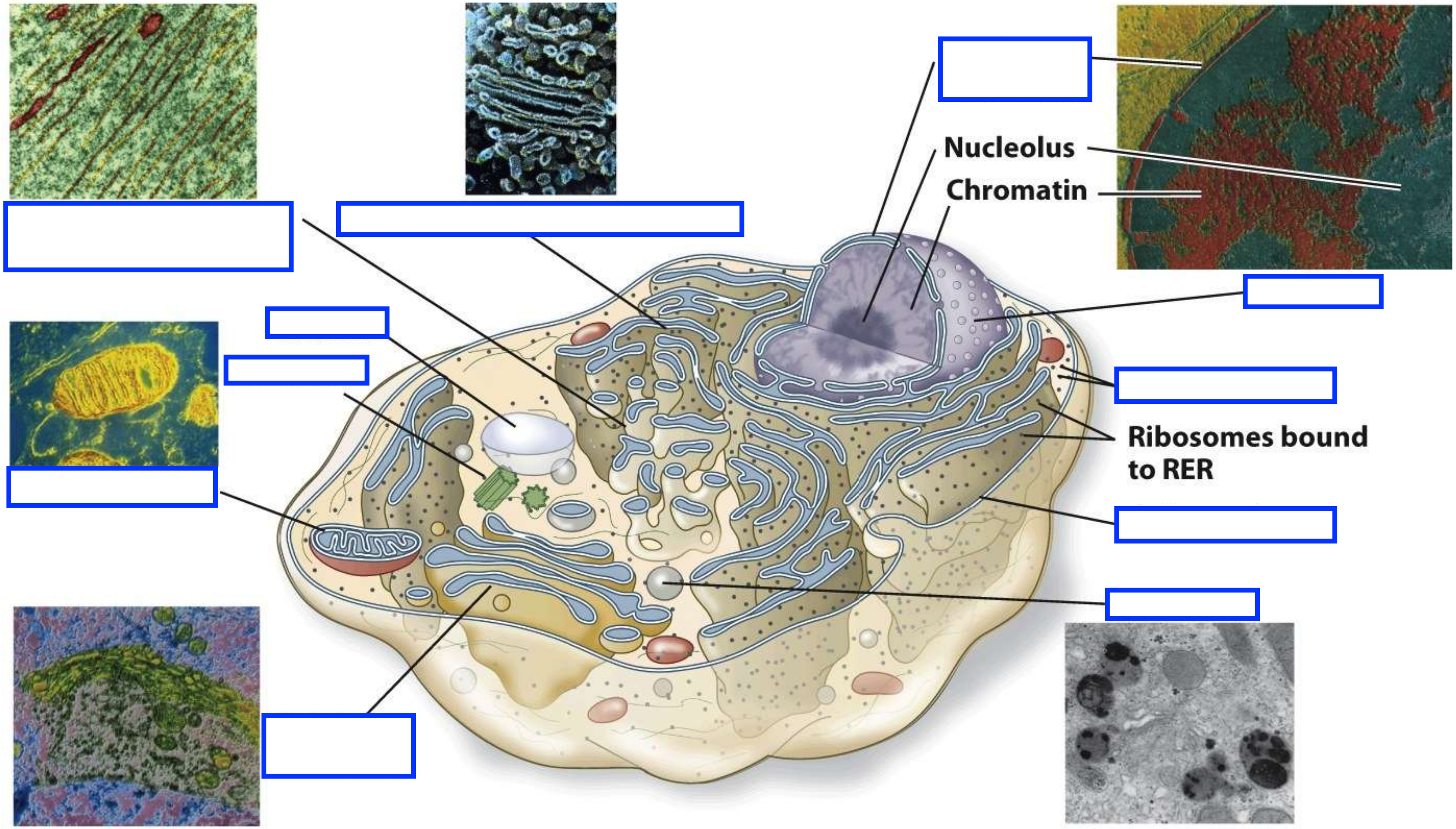
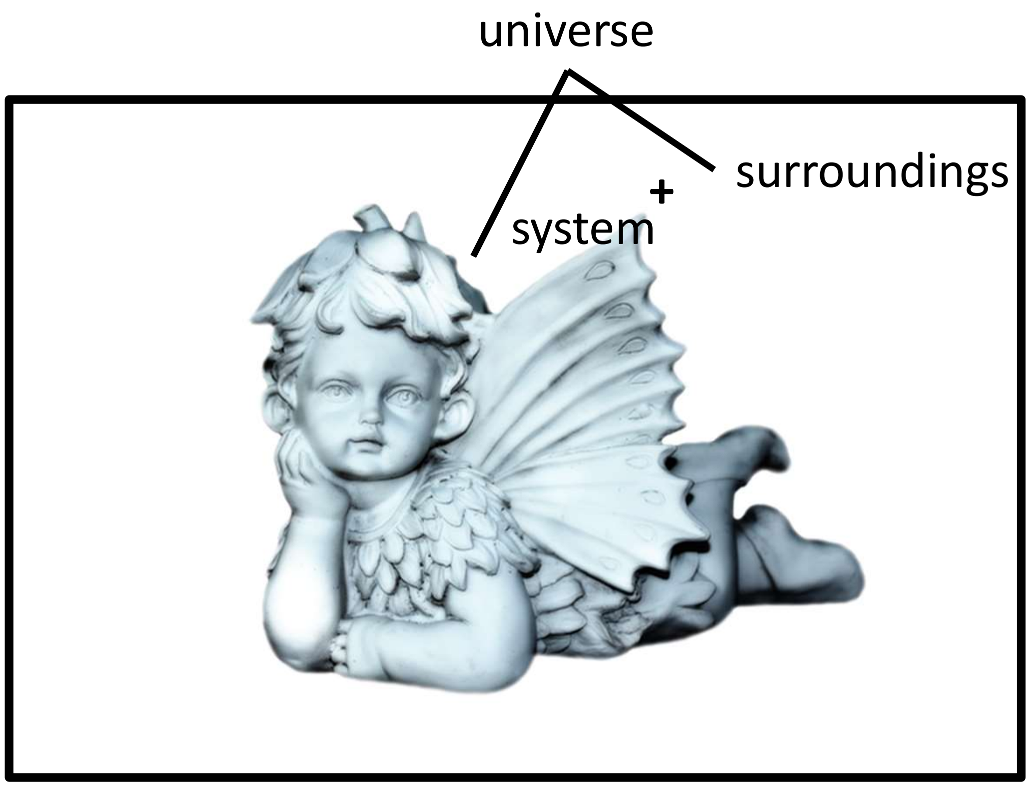


Figure 1-8

Physical Foundation: Thermodynamics

- Energy must be conserved, but it can take different forms.
- In most biochemical systems (under constant pressure), enthalpy is equivalent to heat (H).
- Entropy, a measure of a system's disorder, tends to increase (S).
- The free energy (G) change for a process is determined by the change in enthalpy (H) and the change in entropy (S).
- A spontaneous process occurs with a decrease in free energy.
- Organisms are nonequilibrium, open systems that constantly exchange matter and energy with their surroundings.
- Enzymes increase the rates of thermodynamically favorable reactions.

Thermodynamics:
System + Surroundings = Universe



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the system + surroundings = universe

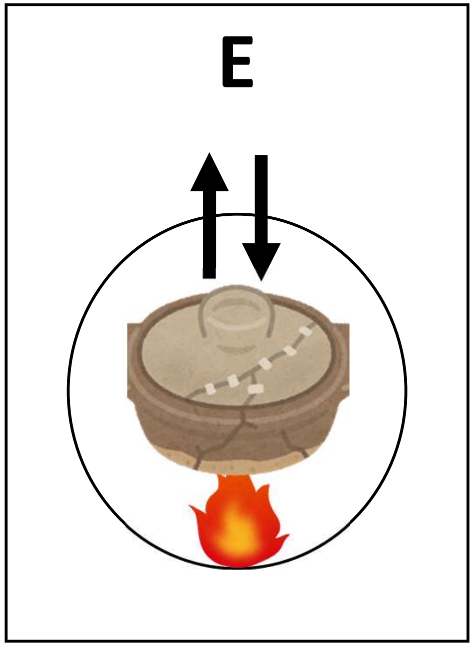
$E_{system} + E_{surroundings} = E_{universe}$

Systems: Isolated, Closed and Open

Isolated

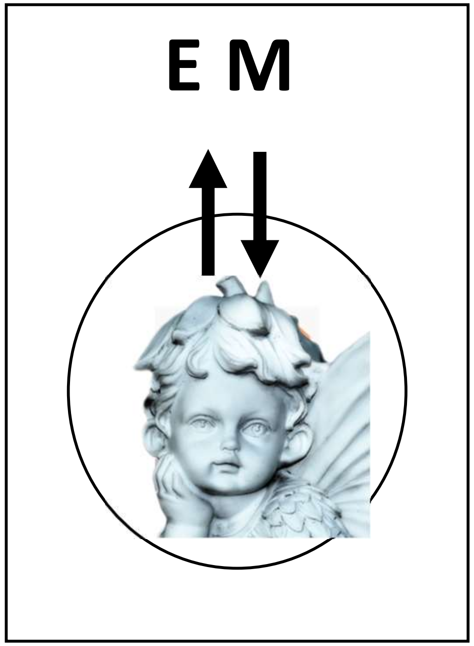
https://www.amazon.co.jp/dp/B008JC76X
A

Closed



https://www.irasutoya.com/

Open



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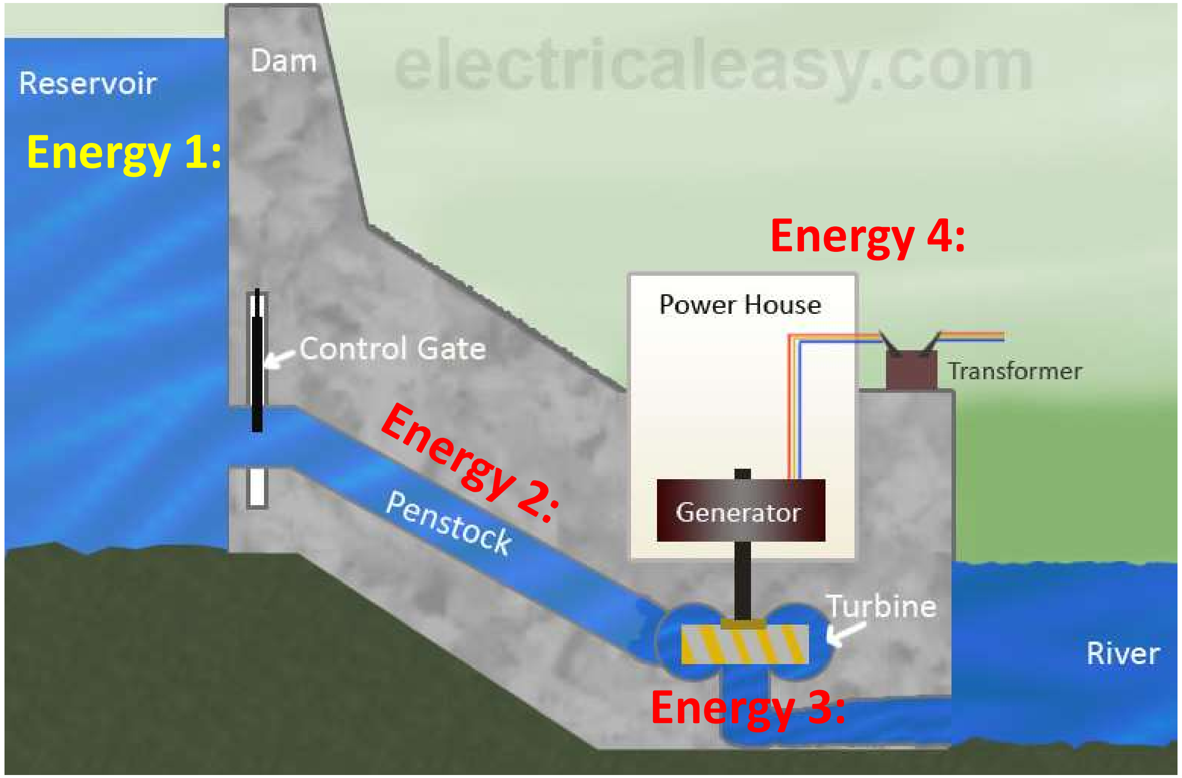
E: energy
M: matter

The three laws of thermodynamics
1. Energy is conserved

- Energy:
- SI unit: ***Joule*** (the work to move an object a distance of 1 m against a force of 1 newton)
- 1 newton is the force needed to **accelerate** 1 kg of mass at the rate of 1 m/sec^2 in the direction of the applied force.

https://www.electricaleasy.com/2019/02/how-solar-and-hydropower-drive-electricity.html 2019/06/03



different form of energy

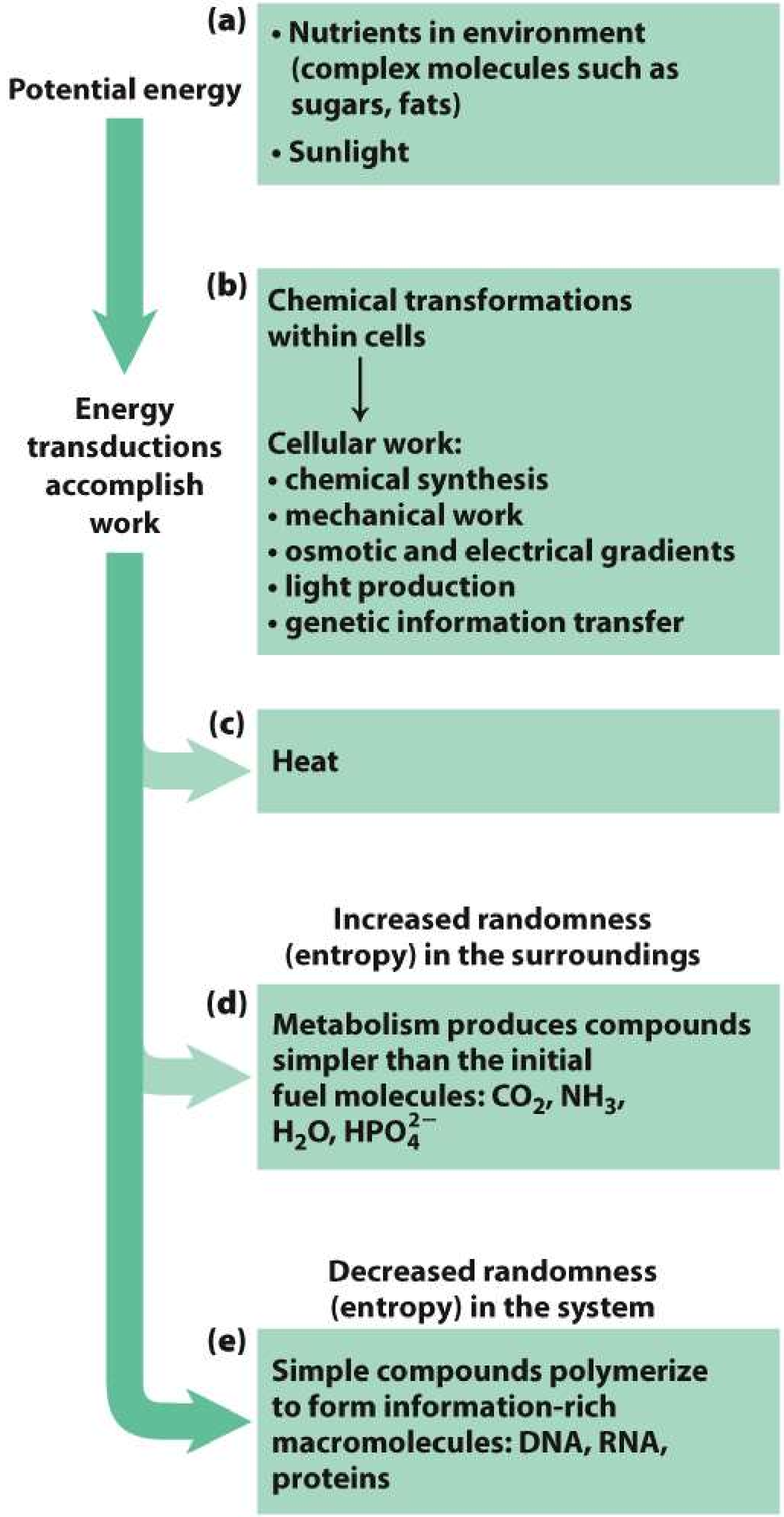
The three laws of thermodynamics:
2. Entropy increases

https://wordsandwires.wordpress.com/2012/06/17/the-three-great-laws-of-songwriting-2/ 2019/06/03

The three laws of thermodynamics:
3. At T= 0 °K, S = *C*

Metabolism and Energy

- Living organisms exist in a dynamic steady state and are **never at equilibrium** with their surroundings.
- **Energy coupling** allows living organisms to transform matter into energy.
- **Biological catalysts** reduce energy requirement for reactions while offering specificity.
- As the entropy of the universe increases, creating and maintaining order requires **work and energy**.



Spontaneity Depends on Enthalpy (H) & Entropy (S)

Before (H1) ***After (H2)***

hot coffee (70 ˚C) ⇄ cooled coffee (30 ˚C)

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Where did 40 go?

H2 - H1 > 0 ?

H2 - H1 < 0 ?

ΔH

ΔH < 0

Before (S1) ***After (S2)***

clean room (10) ⇄ dirty room (100)

S2 - S1 > 0 ?

S2 - S1 < 0 ?

ΔS

ΔS > 0

Spontaneity Depends on Enthalpy (H) & Entropy (S)

TABLE 1-4 Variation of Reaction Spontaneity (Sign of ΔG) with the Signs of ΔH and ΔS

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
−	+	The reaction is both enthalpically favored (exothermic) and entropically favored. It is spontaneous (exergonic) at all temperatures.
Always happens spontaneously		
−	−	The reaction is enthalpically favored but entropically opposed. It is spontaneous only at temperatures *below* $T = \Delta H/\Delta S$.
+	+	The reaction is enthalpically opposed (endothermic) but entropically favored. It is spontaneous only at temperatures *above* $T = \Delta H/\Delta S$.
Temp dependent		
+	−	The reaction is both enthalpically and entropically opposed. It is nonspontaneous (endergonic) at all temperatures.
Never happens spontaneously		

ΔG°
Measure Spontaneity of a Reaction

Gibbs free energy (G): Energy a system contains:

$$\mathbf{G = H - TS}$$

At constant temperature;

G1 = H1 – TS2 (before) G2 = H2 – TS2 (after)

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

To happen spontaneously $\Delta G < 0$

Sample Calculation 1-1

The enthalpy and entropy of the initial and final states of a reacting system are shown in the table.

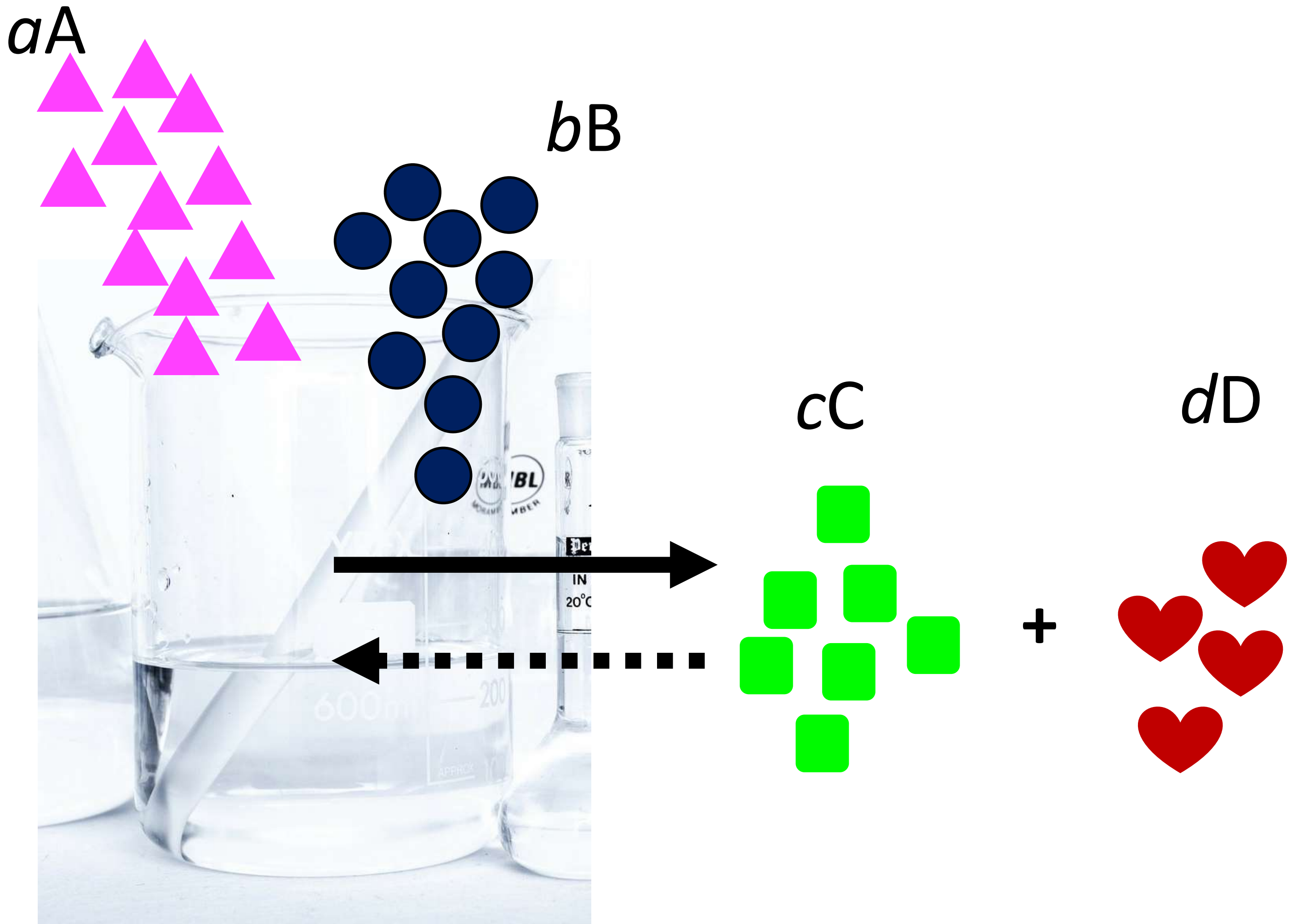
	H (J . mol^{-1})	**S (J . K^{-1} . mol^{-1})**
Initial state (before reaction)	54,000	22
Final state (after reaction)	60,000	43

Q1: Calculate the change in enthalpy and change in entropy for the reaction.

Q2: Calculate the change in free energy for the reaction when the temperature is 4 ˚C. Is the reaction spontaneous?

Q3: Is the reaction spontaneous at 37 ˚C?

Equilibrium Constant



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Equilibrium constants and *ΔG*

a moles of A react with *b* moles of B to produce *c* moles of C and *d* moles of D

$$aA + bB \rightleftharpoons cC + dD$$

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

$[A]_{eq}$: the concentration of A,
$[B]_{eq}$: the concentration of B,
$[C]_{eq}$: the concentration of C,
$[D]_{eq}$: the concentration of D,
When the system has reached equilibrium

Example 1-1

Are ATP and ADP at Equilibrium in Cells?

The equilibrium constant, K_{eq}, for the following reaction is 2×10^5 :

$$ATP \longrightarrow ADP + P_i$$

If the measured cellular concentrations are

[ATP] = 5 mM

[ADP] = 0.5 mM

[Pi] = 5 mM,

is this reaction at equilibrium in living cells?

Example 1-2

Is the Hexokinase reaction at Equilibrium in Cells?

The equilibrium constant, K_{eq}, for the following reaction is 7.8×10^2 :

$$\text{Glucose} + \text{ATP} \longrightarrow \text{glucose-6-P} + \text{ADP}$$

In living *E. coli* cells,
[ATP] = 5 mM
[ADP] = 0.5 mM
[glucose] = 2 mM
[glucose 6-P] =1 mM
is this reaction at equilibrium in *E. coli*?

Equilibrium and ΔG°

R = gas constant
T = absolute Temp

Equilibrium constant: the reactants and products are at equilibrium – experimentally measurable

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

ΔG°:

- Standard free energy change
- Thermodynamic constant characteristic of each reaction

The relationship between ΔG° and K_{eq}

When $K_{eq} \gg 1$ (=ln > 0), ΔG° is large and negative.
When $K_{eq} \ll 1$ (=ln < 0), ΔG° is large and positive.

How to Speed Reactions Up

Higher temperatures

− stability of macromolecules is limiting

Higher concentration of reactants

− costly, as more valuable starting material is needed

Changing the reaction by coupling to a fast one

− universally used by living organisms

Lower activation barrier by catalysis

− universally used by living organisms

Unfavorable and Favorable Reactions

- Synthesis of complex molecules and many other metabolic reactions requires energy (endergonic).
  - A reaction might be thermodynamically unfavorable ($\Delta G^\circ > 0$).
    - Creating order requires work and energy.
  - A metabolic reaction might have too high an energy barrier ($\Delta G^\ddagger > 0$).
    - Metabolite is kinetically stable.
- The breakdown of some metabolites releases a significant amount of energy (exergonic).
  - Such metabolites (ATP, NADH, NADPH) can be synthesized using the energy from sunlight and fuels.
  - Their cellular concentration is far higher than their equilibrium concentration.

Energy Coupling

- Chemical coupling of exergonic and endergonic reactions allows otherwise unfavorable reactions.
- The “high-energy” molecule (ATP) reacts directly with the metabolite that needs “activation.”

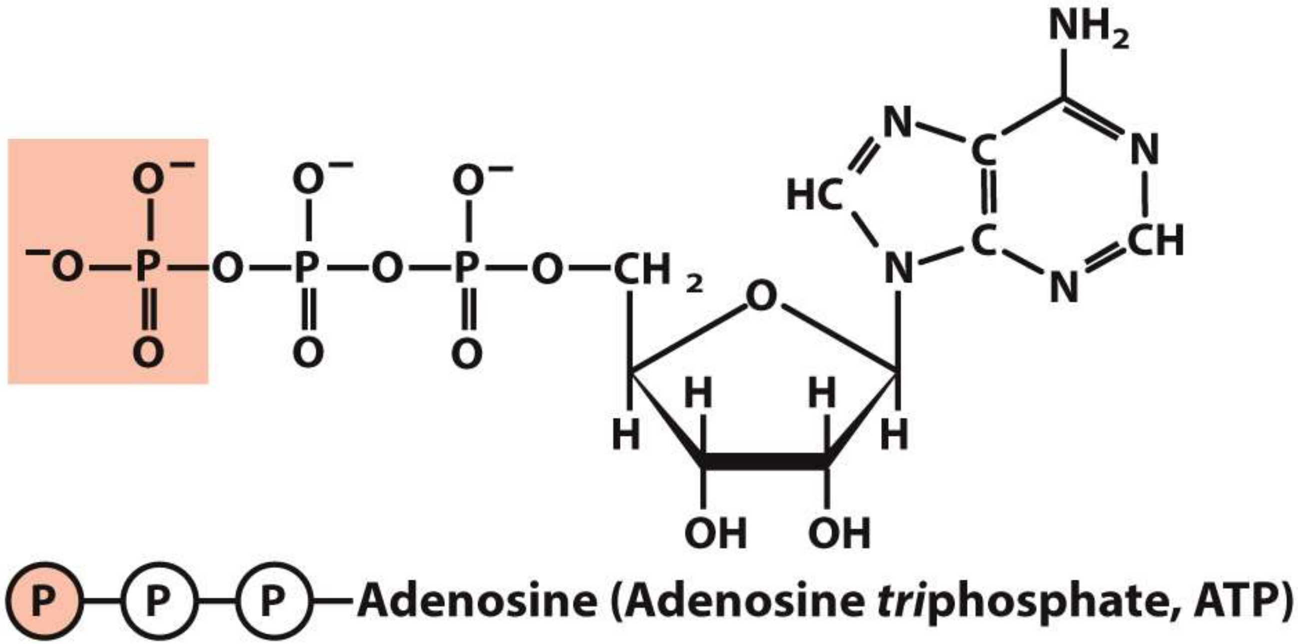


Figure 1-27
Lehninger Principles of Biochemistry, Seventh Edition

Chemical example

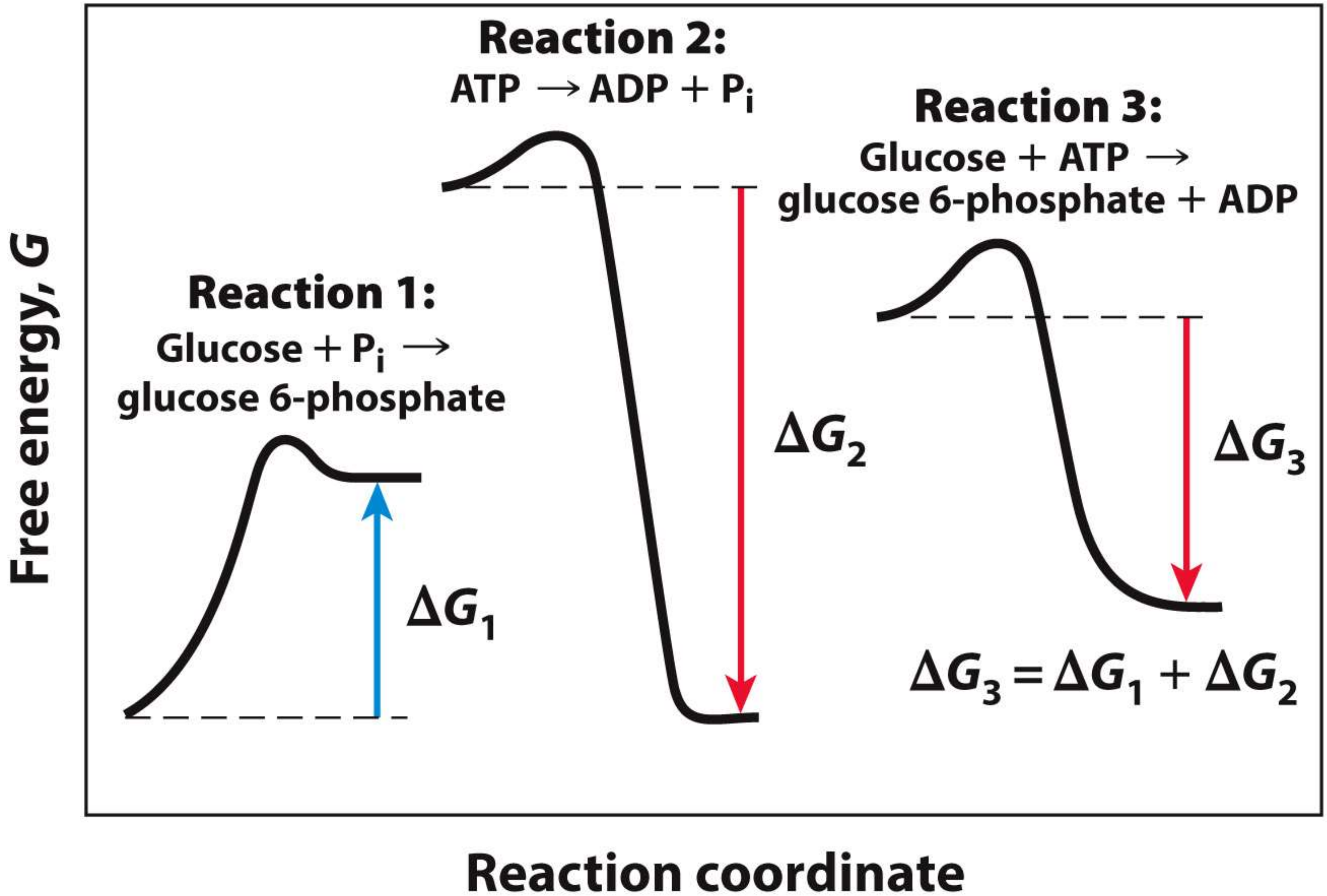


Figure 1-28b
Lehninger Principles of Biochemistry, Seventh Edition

Catalysis

- A catalyst is a compound that increases the rate of a chemical reaction.
- Catalysts lower the activation free energy $\Delta G^{\ddagger}$.
- Catalysts do not alter $\Delta G°$.
- Enzymatic catalysis offers:
  - acceleration under mild conditions
  - high specificity
  - possibility for regulation

Enzymes Lower the Activation Energy to Increase the Reaction Rate

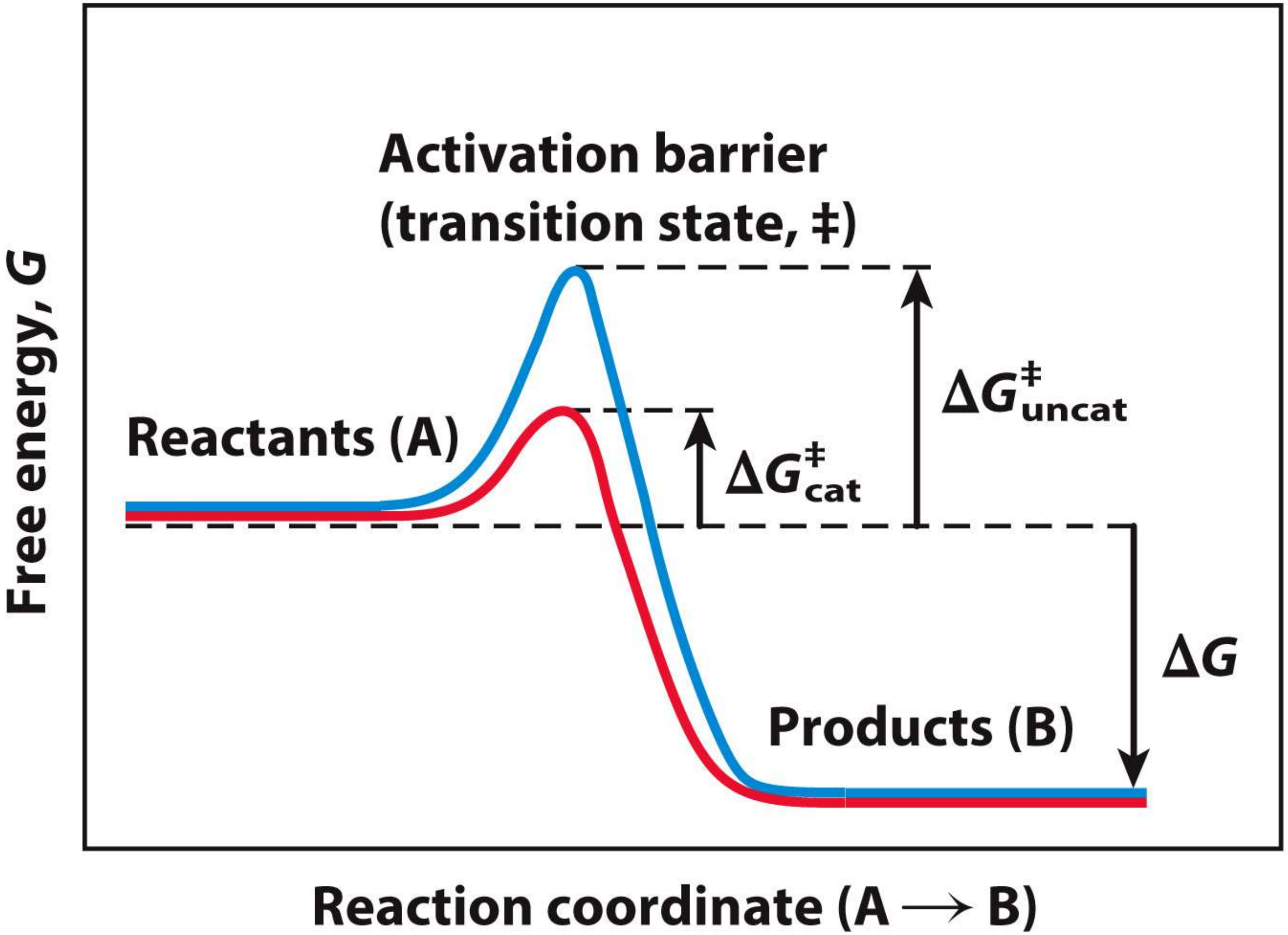


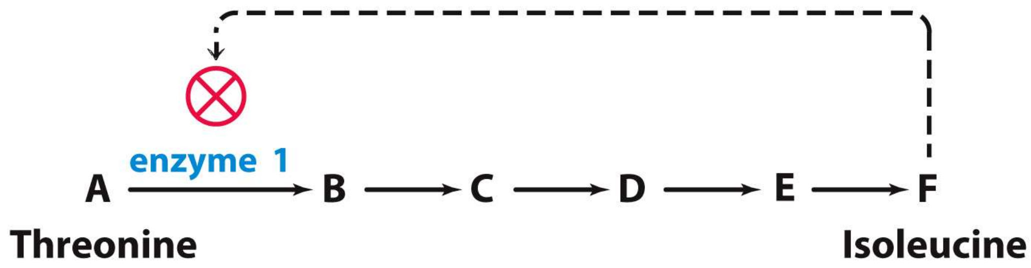
Figure 1-29
Lehninger Principles of Biochemistry, Seventh Edition

Series of Related Enzymatically Catalyzed Reactions Forms a Pathway

$$A \xrightarrow{\text{enzyme 1}} B \xrightarrow{\text{enzyme 2}} C \xrightarrow{\text{enzyme 3}} D \xrightarrow{\text{enzyme 4}} E \xrightarrow{\text{enzyme 5}} F$$

Metabolic pathway: produces energy or valuable materials
Signal transduction pathway: transmits information

Pathways Are Controlled in Order to Regulate Levels of Metabolites



Unnumbered 1 p29
Lehninger Principles of Biochemistry, Seventh Edition

Example of a negative regulation: Product of enzyme 5 inhibits enzyme 1 to prevent wasteful excess products.

Summary

- Three laws of thermodynamics (1, 2)
- Why is this important?
- Is a living organism at equilibrium with surrounding?
- What is ΔG?
- What is an equilibrium constant?
- What is ΔG°?
- What is chemical coupling?
- Enzymes function as catalysts. How?