Energy and catalysis

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Second law of thermodynamics

- The Second law of thermodynamics expresses the universal tendency of things to become disordered. This law states that, in the universe or in any isolated system (a collection of matter that is completely isolated from the rest of the universe), the degree of disorder can only increase.

- Or, systems will change spontaneously toward those arrangements that have the greatest probability.

- Example:

(i)   Consider a box of 100 coins all lying heads up. A series of events that disturbs the box will tend to move the arrangement toward a mixture of 50 heads and 50 tails facing up.
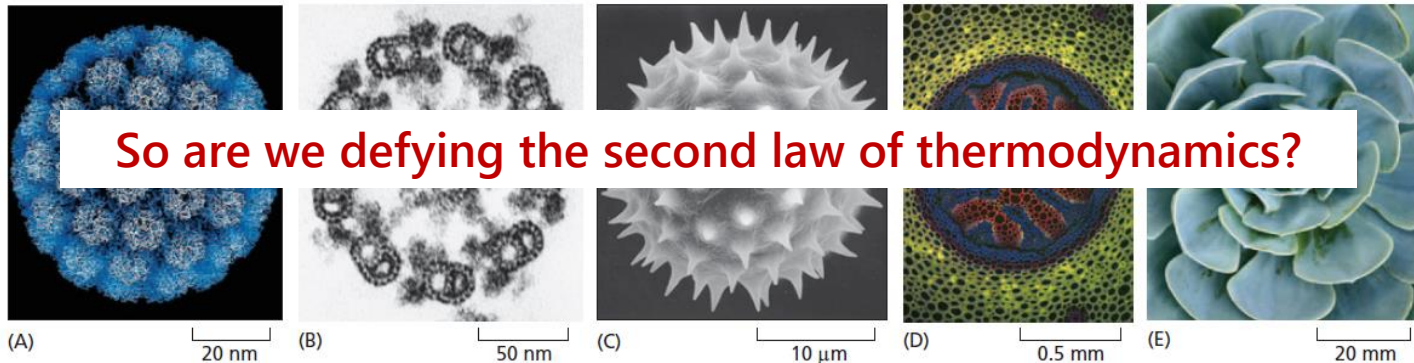
Second law of thermodynamics

- One's living space becomes increasingly disordered without an intentional effort to keep it organized.

- Movement toward disorder is a spontaneous process, requiring a periodic input of energy to reverse it.

ORGANIZED EFFORT REQUIRING ENERGY INPUT

"SPONTANEOUS" REACTION
as time elapses

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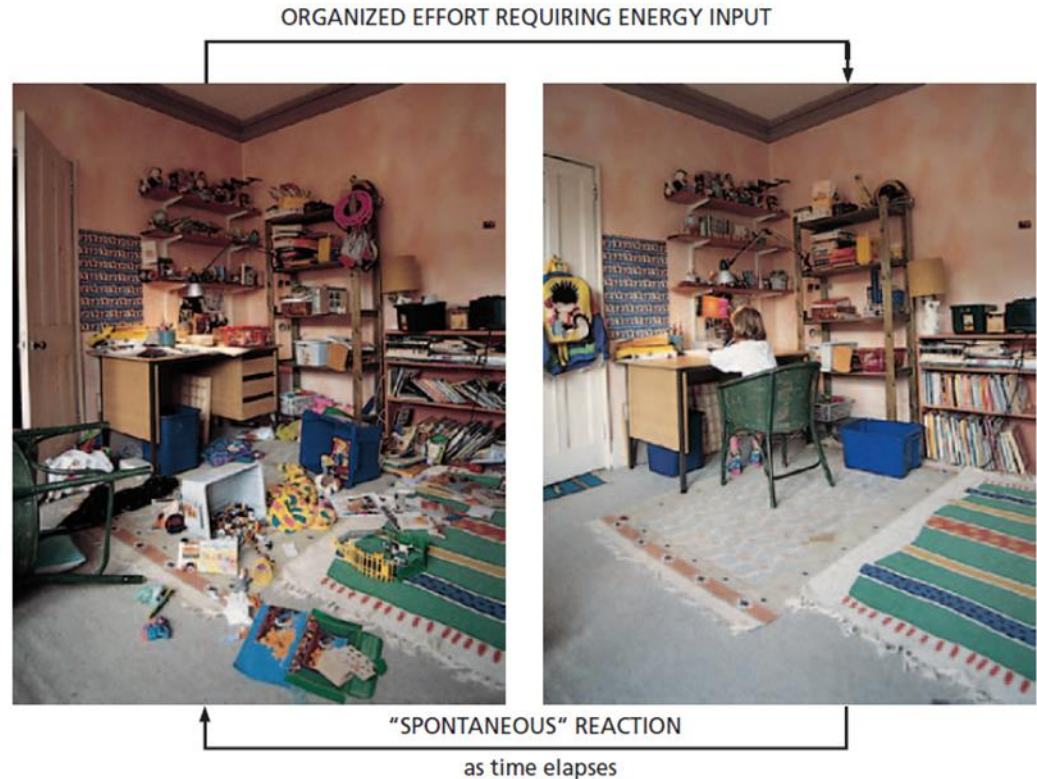
Entropy

- The measure of a system's disorder is called the entropy of the system, and the greater the disorder, the greater the entropy. Therefore systems will change spontaneously toward arrangements with greater entropy.

- Living cells - by surviving, growing, and forming complex communities and even whole organisms - generate order.

So are we defying the second law of thermodynamics?

(A) 20 nm   (B) 50 nm   (C) 10 μm   (D) 0.5 mm   (E) 20 mm

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Living cells do not defy the second law of thermodynamics

- A living cell takes in energy from its environment and it then uses this energy to generate order within itself.

- While performing the chemical reactions that generate order, some energy is lost in the form of heat.

- Heat is energy in its most disordered form.

- The heat energy generated is quickly dispersed into the cell's surroundings which increases the intensity of the thermal motions of nearby molecules, thereby increasing the entropy of the environment. The total entropy of the system - that of the cell plus its environment - increases as a result of the chemical reactions inside the cell.
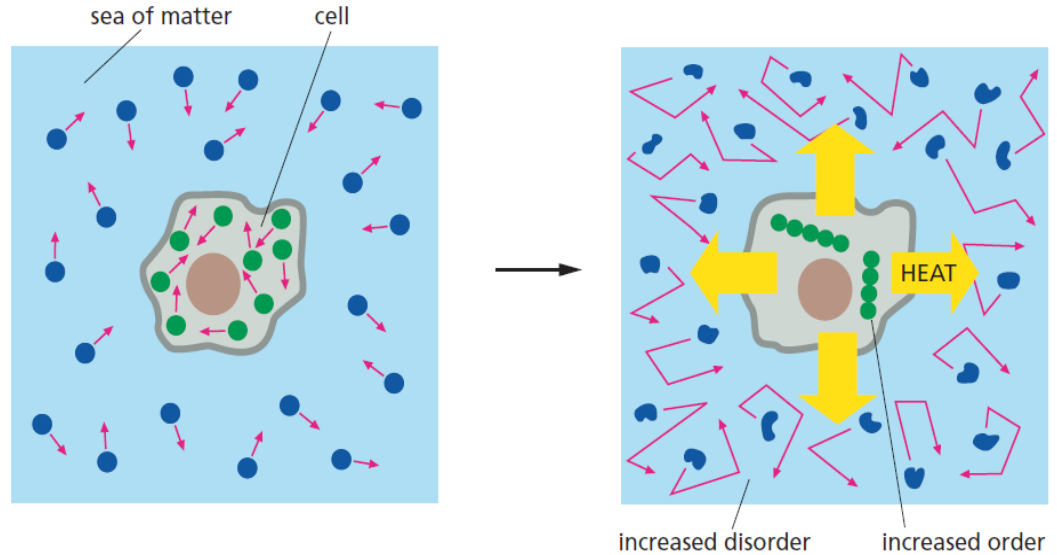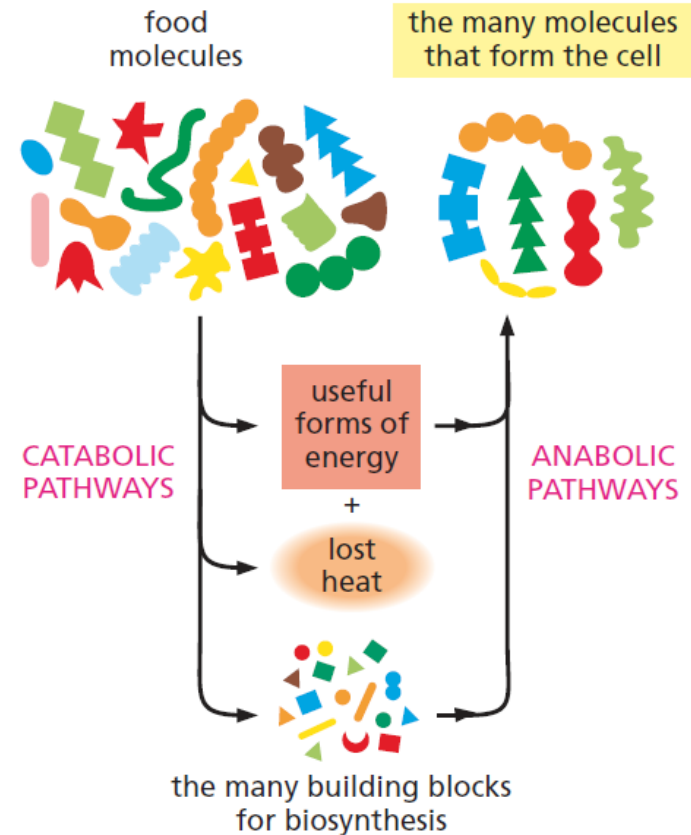
Cells obey the first law of thermodynamics as well

- According to the first law of thermodynamics, energy cannot be created or destroyed - but it can be converted from one form to another.

- Cells convert the energy from sunlight into the energy in the chemical bonds of sugars and other small organic molecules during photosynthesis.

- These cell when breaks down foodstuffs, some of the energy in the chemical bonds in the food molecules (chemical-bond energy) is converted into the thermal motion of molecules (heat energy).

- This conversion of chemical energy into heat energy causes the universe as a whole to become more disordered - as required by the second law of thermodynamics.

- Cells efficiently couple the heat-generating reactions to processes that maintain molecular order inside the cell.
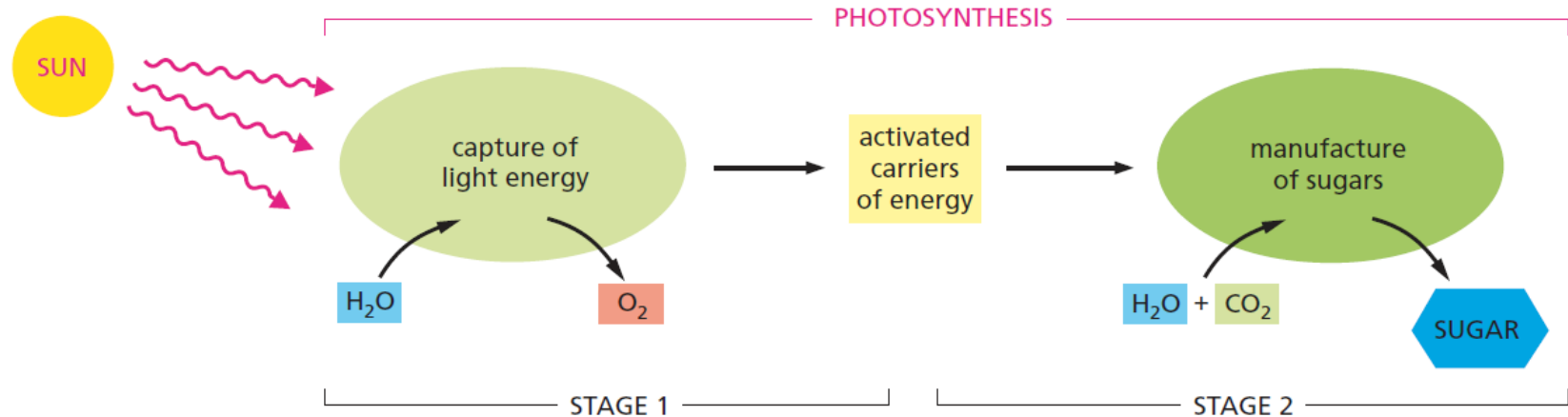
Cell metabolism

- To create and maintain order in a universe that is tending always toward greater disorder cells need to carry out a never-ending stream of chemical reactions.

- Each cell can be viewed as a tiny chemical factory, performing many millions of these reactions every second.

- These reactions are usually connected in series, so that the product of one reaction becomes the starting material for the next, and the long linear reaction pathways are called metabolic pathways.

food molecules

the many molecules that form the cell

CATABOLIC PATHWAYS

useful forms of energy

+

lost heat

ANABOLIC PATHWAYS

the many building blocks for biosynthesis

Radiant energy of sunlight sustains all life

- All animals live on energy stored in the chemical bonds of organic molecules, which they take in as food. Some animals obtain their food by eating other animals, others by eating plants. Plants, by contrast, obtain their energy directly from sunlight (process called photosynthesis). Thus, the energy animals obtain ultimately comes from the sun.
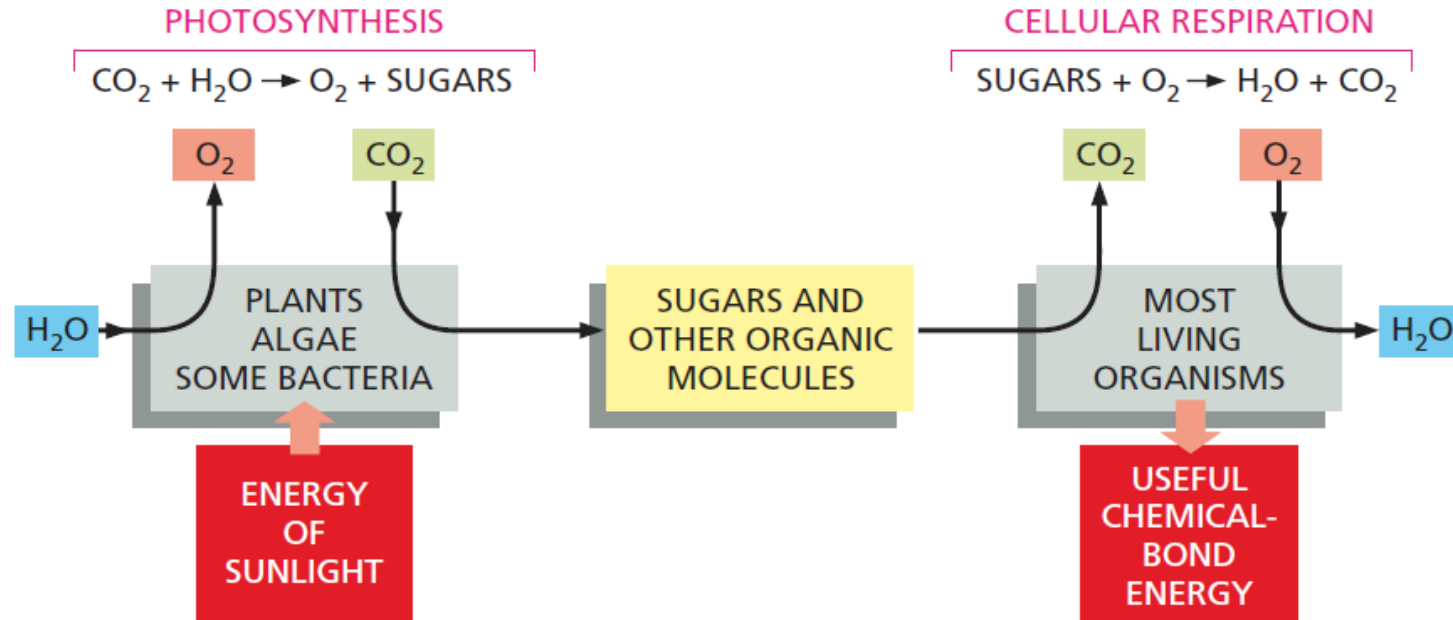

PHOTOSYNTHESIS

SUN

capture of light energy

H_2O

O_2

activated carriers of energy

manufacture of sugars

H_2O + CO_2

SUGAR

STAGE 1

STAGE 2

Cells obtain energy by the oxidation of organic molecules

- In both plants and animals, energy is extracted from food molecules by a process of gradual oxidation, or controlled burning.

- In the presence of oxygen, the most energetically stable form of carbon is CO_2 and that of hydrogen is H_2O. A cell is therefore able to obtain energy from sugars or other organic molecules by allowing the carbon and hydrogen atoms in these molecules to combine with oxygen—that is, become oxidized—to produce CO_2 and H_2O, respectively—a process known as cellular respiration.

Cells obtain energy by the oxidation of organic molecules

Photosynthesis and cellular respiration are complementary processes in the living world.

PHOTOSYNTHESIS
$$CO_2 + H_2O \rightarrow O_2 + SUGARS$$

CELLULAR RESPIRATION
$$SUGARS + O_2 \rightarrow H_2O + CO_2$$

O_2 | CO_2

H_2O

PLANTS ALGAE SOME BACTERIA

ENERGY OF SUNLIGHT

SUGARS AND OTHER ORGANIC MOLECULES

CO_2 | O_2

MOST LIVING ORGANISMS

H_2O

USEFUL CHEMICAL-BOND ENERGY

Oxidation and reduction in living cells

- The cell does not oxidize organic molecules in one step, as occurs when organic material is burned in a fire [organic compound + oxygen → water + carbon dioxide]

- Metabolism directs the molecules through a large number of reactions, few of which actually involve the direct addition of oxygen.

- The term oxidation literally means the addition of oxygen atoms to a molecule. More generally, oxidation is said to occur in any reaction in which electrons are transferred from one atom to another.

- Oxidation = removal of electrons from an atom; Reduction = addition of electrons to an atom.

- The number of electrons stay conserved in a chemical reaction (there is no net loss or gain), therefore oxidation and reduction always occur simultaneously.

# Oxidation and reduction in living cells

- The terms oxidation and reduction apply even when there is only a partial shift of electrons between atoms linked by a covalent bond.

- A simple reduced carbon compound, such as methane, can be oxidized in a stepwise fashion by the successive replacement of its covalently bonded hydrogen atoms with oxygen atoms. With each step, electrons are shifted away from the carbon, and the carbon atom becomes progressively more oxidized. Moving in the opposite direction, carbon dioxide becomes progressively more reduced as its oxygen atoms are replaced by hydrogens to yield methane.
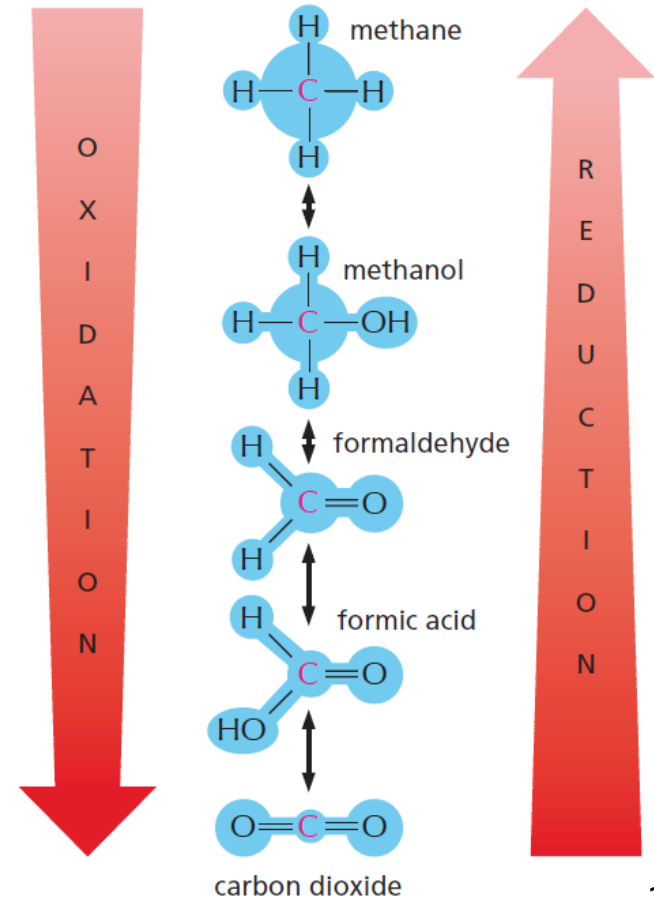
Oxidation and reduction in living cells

- When a molecule in a cell picks up an electron (e^-), it often picks up a proton (H^+) at the same time (protons being freely available in water). The net effect in this case is to add a hydrogen atom to the molecule:

$$A + e^- + H^+ \rightarrow AH$$
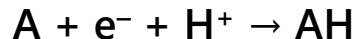
- Even though a proton plus an electron is involved (instead of just an electron), such **hydrogenation** reactions are reductions, and the reverse, **dehydrogenation**, reactions are oxidations.

- An easy way to tell whether an organic molecule is being oxidized or reduced is to count its C–H bonds: reduction occurs when the number of C–H bonds increases, whereas oxidation occurs when the number of C–H bonds decreases.

Free Energy

- Paper burning process:

    Paper + O_2 → smoke + ashes + heat + CO_2 + H_2O (Irreversible reaction)
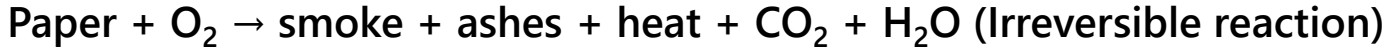
- When paper burns, much of its chemical energy is dissipated as heat in the chaotic random thermal motions of molecules. At the same time, the atoms and molecules of the paper become dispersed and disordered.

- There has been a release of free energy - that is, energy that can be harnessed to do work or drive chemical reactions.

- Chemical reactions proceed only in the direction that leads to a loss of free energy. In other words, the spontaneous direction for any reaction is the direction that goes "downhill." A "downhill" reaction in this sense is said to be energetically favorable.

Free energy and catalysis

- Most of the chemical reactions that cells perform would normally occur only at temperatures that are much higher than those inside a cell.

- Each reaction therefore requires a major boost in chemical reactivity to enable it to proceed rapidly within the cell. **Enzymes** speed up (boost) energetically favorable reactions -those that produce disorder in the universe.

- Enzymes lower the activation energy needed to initiate reactions in the cell.
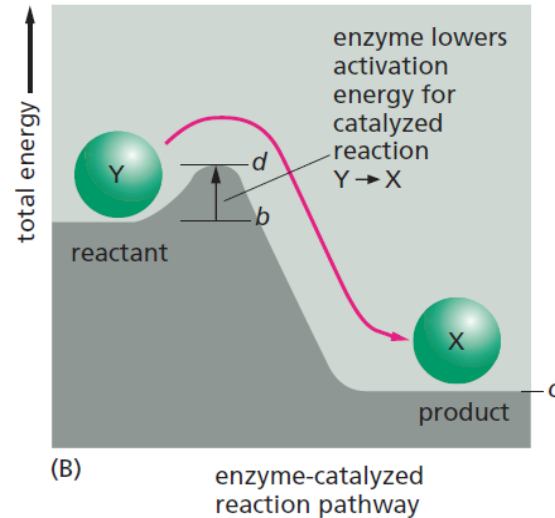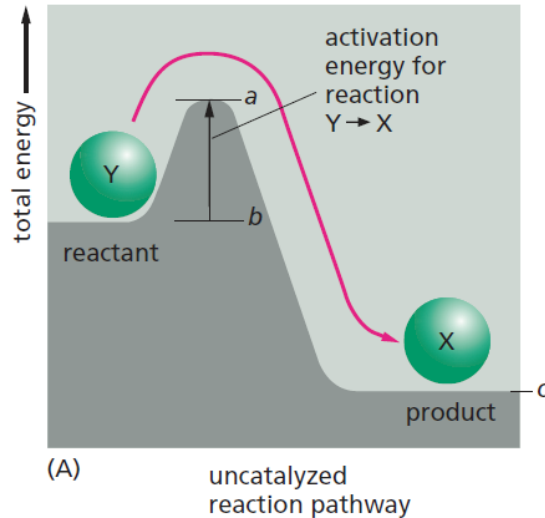
Activation energy

- Even energetically favorable reactions require activation energy to get them started.

- The molecules in both the living organism or non-living things like a book are in a relatively stable state, and they cannot be changed to lower-energy states without an initial input of energy.

- In other words, a molecule requires a boost over an energy barrier before it can undergo a chemical reaction that moves it to a lower energy (more stable) state. This boost is known as the activation energy.

- In the case of a burning book, the activation energy is provided by the heat of a lighted match.


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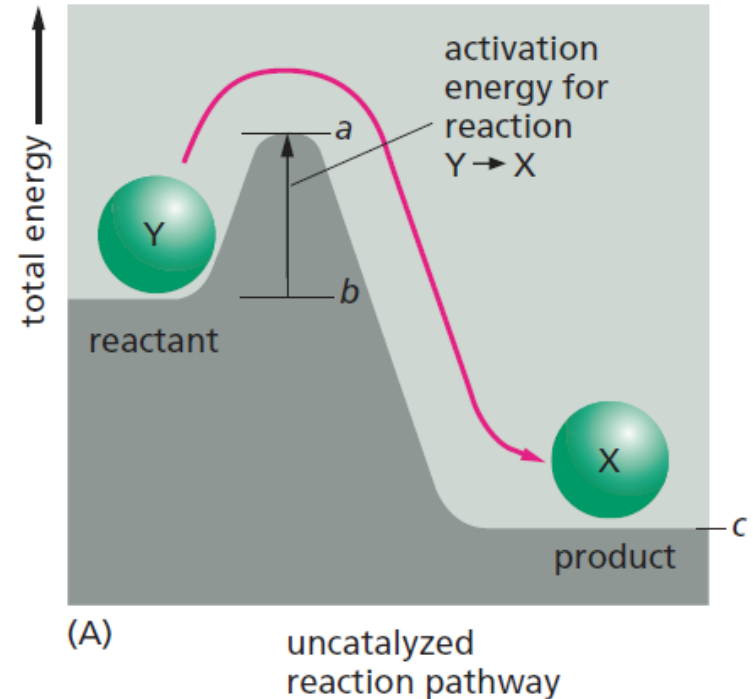
Enzymes reduce the activation energy

- Cells can't raise their temperature to drive biological reactions. Inside cells, the push over the energy barrier is aided by specialized proteins called enzymes.

- Each enzyme binds tightly to one or two molecules, called substrates, and holds them in a way that greatly reduces the activation energy needed to facilitate a specific chemical interaction between them. They can speed up reactions by a factor of as much as 10^{14}.
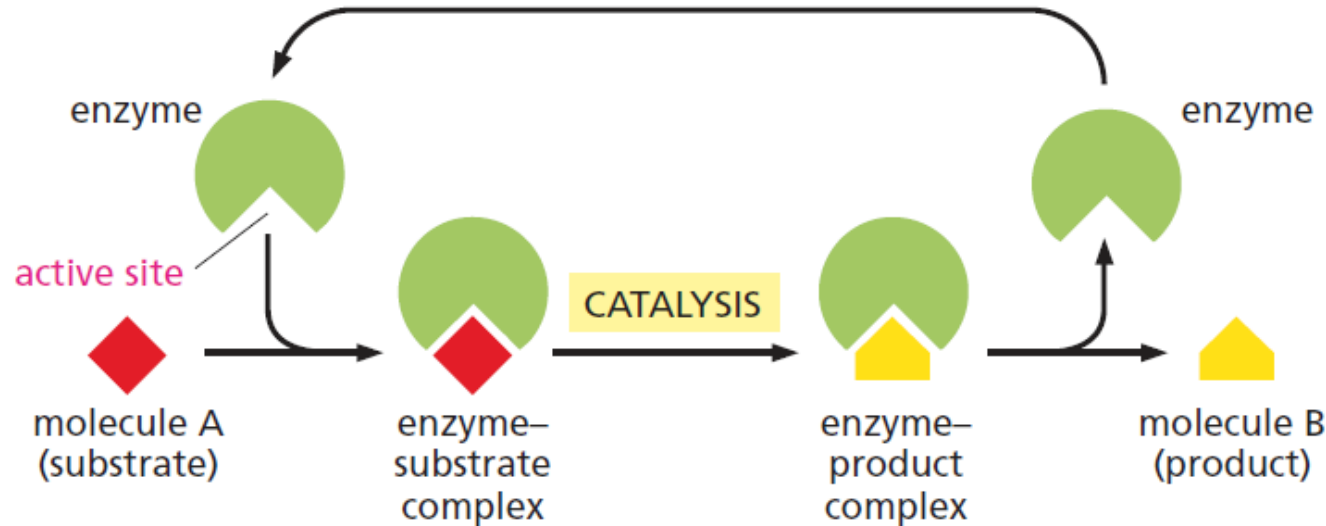
Activation energy

Lowering the activation energy greatly increases the probability that a reaction will occur.
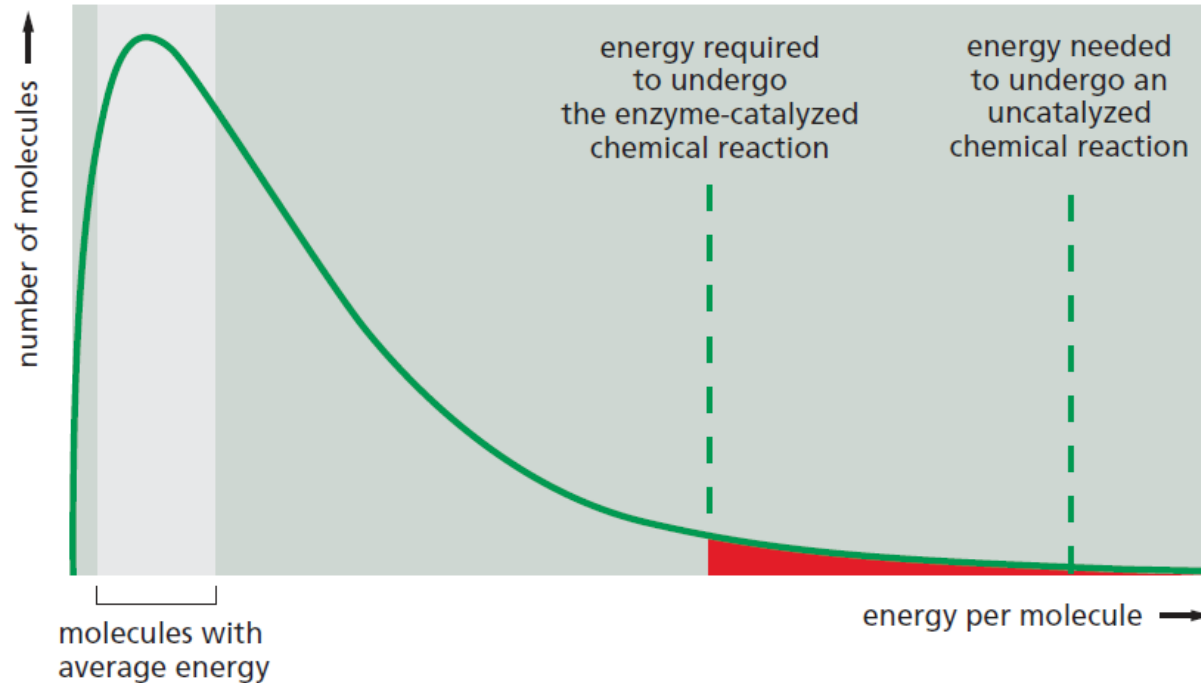
Enzymes are highly selective

- Unlike the effects of temperature, enzymes are highly selective. Each enzyme usually speeds up only one particular reaction out of the several possible reactions that its substrate molecules could undergo.

Coupling of reactions

- But cells do carry out a number of energetically unfavorable reactions in order to grow and divide - or just to survive. They build highly ordered and energy-rich molecules from small and simple ones - a process that requires an input of energy.

- So, do enzymes catalyze these energetically unfavorable reactions?

- Enzymes can exploit differences in the free-energy changes of different reactions to drive the energetically unfavorable reactions that produce biological order. Such enzyme-assisted catalysis is crucial for cells: without it, life could not exist.

Creating and maintaining order requires work and energy

- Macromolecules present in a cell (DNA, RNA, protein, complex organic molecules) are highly ordered.

- Chemical energy is used to form the covalent bonds between the subunits in these polymers. Energy is also required to maintain the correct sequence of the monomers.

- There are three thermodynamic quantities that describe the energy changes occurring in a chemical reaction: Free energy, Enthalpy, Entropy

Enthalpy and Entropy

Enthalpy, H, is the heat content of the reacting system. It reflects the number and kinds of chemical bonds in the reactants and products.

Exothermic reactions: Reaction proceeding with release of heat.

The heat content of the products is less than that of the reactants.

ΔH has a negative value.

Endothermic reactions: Reacting systems that take up heat from their surroundings.

The heat content of the products is more than that of the reactants .

ΔH has a positive value.

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.

Gibbs free energy

Gibbs free energy, G, expresses the amount of energy capable of doing work during a reaction at constant temperature and pressure

$$G = H - TS$$

The units of G and H are joules/mole or calories/mole (1 cal = 4.184 J)
The units of entropy are joules/mole.Kelvin (J/mol.K)

When a chemical reaction occurs at constant temperature, we get free energy change, ΔG, determined by the enthalpy change, ΔH, reflecting the kinds and numbers of chemical bonds and non-covalent interactions broken and formed, and the entropy change, ΔS, describing the change in the system's randomness.

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

Gibbs free energy

- **Exergonic reactions: 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, ΔG, has a negative value.**

- **Endergonic reactions: The system gains free energy and ΔG is positive.**

- **A process tends to occur spontaneously only if ΔG is negative.**

Energy Coupling Links Reactions in Biology

- Cell function depends largely on molecules, such as proteins and nucleic acids, for which the free energy of formation is positive: the molecules are less stable and more highly ordered than a mixture of their monomeric components.

- To carry out these thermodynamically unfavorable, energy-requiring (endergonic) reactions, cells couple them to other reactions that liberate free energy (exergonic reactions), so that the overall process is exergonic: the sum of the free energy changes is negative.

$$\text{Amino acids} \longrightarrow \text{polymer} \qquad \Delta G_1 \text{ is positive (endergonic)}$$

$$\text{—P—P} \longrightarrow \text{—P} + \text{P} \qquad \Delta G_2 \text{ is negative (exergonic)}$$

- When these reactions are coupled, the sum of ΔG_1 and ΔG_2 is negative—the overall process is exergonic.

State of equilibrium

- The composition of a reacting system (a mixture of chemical reactants and products) tends to continue changing until equilibrium is reached.

- At the equilibrium concentration of reactants and products, the rates of the forward and reverse reactions are exactly equal and no further net change occurs in the system.

- The concentrations of reactants and products at equilibrium define the equilibrium constant, K_{eq}

$$aA + bB \rightleftharpoons cC + dD \qquad K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where,

a, b, c, and d are the number of molecules of A, B, C, and D

[A], [B], [C], and [D] are the molar concentrations of the reaction components at the point of equilibrium

Standard free-energy change

- When a reacting system is not at equilibrium, the tendency to move toward equilibrium represents a driving force, the magnitude of which can be expressed as the free-energy change for the reaction, ΔG.

- Under standard conditions (298 K = 25°C), when reactants and products are initially present at 1 M concentrations or, for gases, at partial pressures of 101.3 kilopascals (kPa), or 1 atm, the force driving the system toward equilibrium is defined as the standard free-energy change, ΔG'°.

- Just as K'$_{eq}$ is a physical constant characteristic for each reaction, ΔG'° is also a constant.

$$\Delta G'° = -RT \ln K'_{eq}$$

Gas constant, R = 8.315 J/mol.K (1.987 cal/mol .K)

Standard free-energy change

- The standard free-energy change of a chemical reaction is simply an alternative mathematical way of expressing its equilibrium constant.

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

Relationship between the Equilibrium Constants and Standard Free-Energy Changes of Chemical Reactions

K'_{eq}	$\Delta G'^\circ$ (kJ/mol)	(kcal/mol)*
10^3	−17.1	−4.1
10^2	−11.4	−2.7
10^1	−5.7	−1.4
1	0.0	0.0
10^{-1}	5.7	1.4
10^{-2}	11.4	2.7
10^{-3}	17.1	4.1
10^{-4}	22.8	5.5
10^{-5}	28.5	6.8
10^{-6}	34.2	8.2

- Because the relationship between $\Delta G'^\circ$ and K'_{eq} is exponential, relatively small changes in $\Delta G'^\circ$ correspond to large changes in K'_{eq}.

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Standard free-energy change

- $\Delta G'^o$ is the difference between the free-energy content of the products and the free-energy content of the reactants, under standard conditions.

- When $\Delta G'^o$ is negative, the products contain less free energy than the reactants and the reaction will proceed spontaneously under standard conditions; all chemical reactions tend to go in the direction that results in a decrease in the free energy of the system.

- A positive value of $\Delta G'^o$ means that the products of the reaction contain more free energy than the reactants, and this reaction will tend to go in the reverse direction if we start with 1.0 M concentrations of all components (standard conditions).

Actual free-energy change

- The actual free-energy change, ΔG, is a function of reactant and product concentrations and of the temperature prevailing during the reaction. ΔG of any reaction proceeding spontaneously toward its equilibrium is always negative, becomes less negative as the reaction proceeds, and is zero at the point of equilibrium, indicating that no more work can be done by the reaction.

$$\text{So, for reaction} \quad A + B \rightleftharpoons C + D, \quad \Delta G = \Delta G'^{\circ} + RT \ln \frac{[C][D]}{[A][B]}$$

- The criterion for spontaneity of a reaction is the value of ΔG, not ΔG'º.

- A reaction with a positive ΔG'º can go in the forward direction *if* ΔG *is negative.* This is possible if the term *RT* ln([products]/[reactants]) is negative and has a larger absolute value than ΔG'º. For example, the immediate removal of the products of a reaction can keep the ratio [products]/[reactants] well below 1, such that the term *RT* ln([products]/[reactants]) has a large, negative value.