

## CH. 6

## Energy & life

universe = system + surroundings  
Gibbs defined a very useful function called Gibbs free energy of system without considering its surroundings.

free energy is the portion of energy that can perform work when temperature & pressure are uniform throughout the system.  
(measure of a system's stability)

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

change in entropy ( $S_f - S_i$ )

Free energy change

change in enthalpy

$K = ^\circ C + 273$   
(Total energy)

depends on

pH, temperature, concentration of reactants & products

$\Delta G \rightarrow$  negative  $\rightarrow$  spontaneous  $\rightarrow \Delta H$  must be negative

the system gives up Enthalpy and H decreases  
or  $T \Delta S$  must be positive

the system gives up order and S increase)

process involves loss of energy  
more stable because it has less free energy

The released free energy can be harnessed to do work

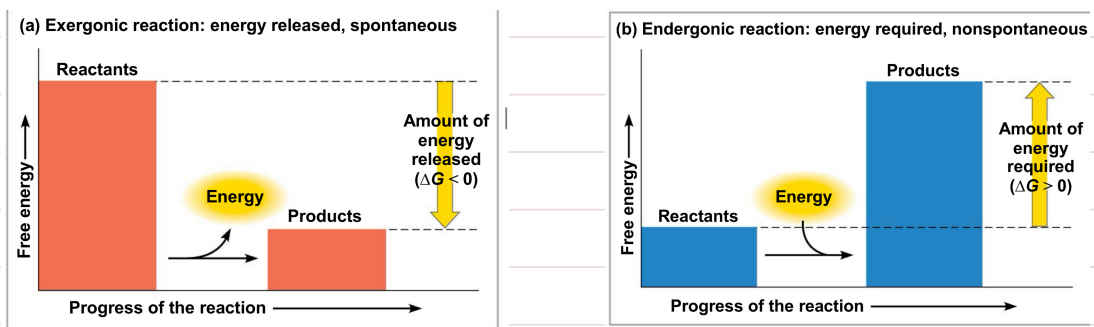
**chemical Equilibrium** → the most chemical reactions are reversible and proceed to a point at which the forward and backward reactions on the same rate

As a reaction proceeds toward equilibrium the mixture of reactants and products decreases

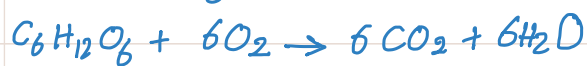
G is at its lowest possible value

A cell that has reached metabolic equilibrium is dead

Chemical reactions (based on their free energy changes) classified into exergonic reaction (energy outward) occur spontaneously endergonic (energy inward),



ex. for exergonic reaction



$$\Delta G = -686 \text{ kcal/mol}$$

$$= -2870 \text{ kJ/mol}$$

The reverse of process of cellular respiration must be endergonic with

$$\Delta G = +686 \text{ kcal/mol}$$

## Concept 6.3

A cell does three main kinds of work:-

**Chemical work**: The pushing of endergonic reactions that would not occur spontaneously such as synthesis polymers from monomers

**Transport work**: the pumping of substances across membranes against the direction of spontaneous movement

**Mechanical work**: such as beating in cilia, the contraction of muscle cells, the movement of chromosomes during cellular reproduction.

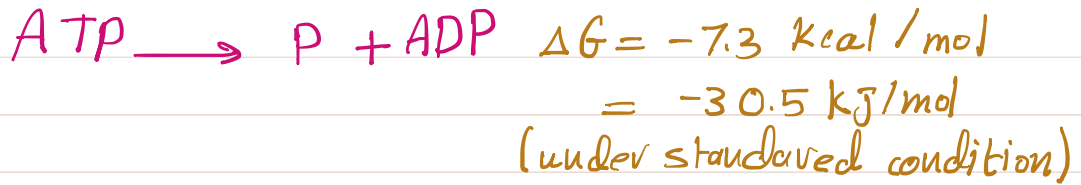
**Energy coupling** → • The use of an exergonic process to drive an endergonic one.

- It is the key feature in the way cells manage their energy resources to do this work
- ATP is responsible for mediating most energy coupling in cells.

**ATP** → contains sugar ribose, nitrogenous base (adenine) and chain of phosphate groups (the triphosphate group)

the bond between groups ATP can be broken by hydrolysis

ATP one of the nucleoside triphosphates used to make RNA

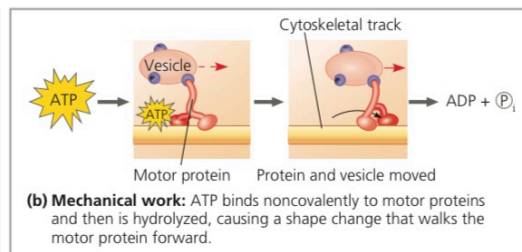
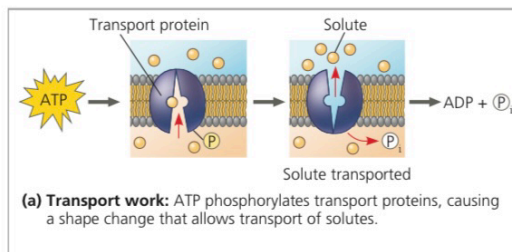
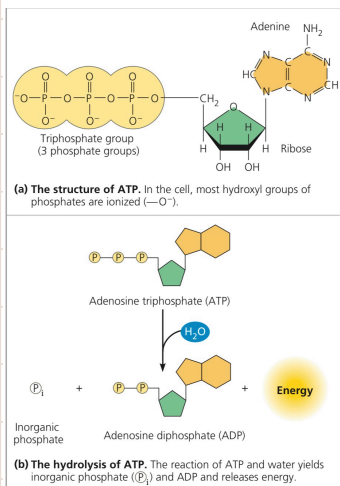


when ATP hydrolysis occurs under cellular conditions the actual  $\Delta G$  is about  $-13 \text{ kcal/mol}$ .

= 78% greater than ...

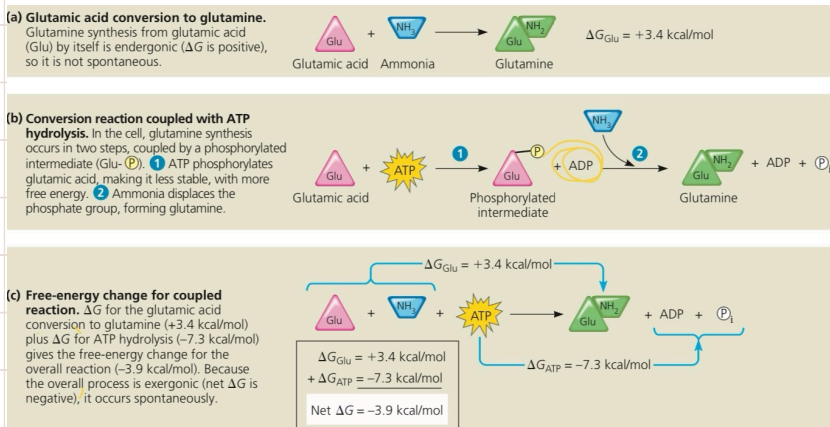
P: abbreviation for inorganic phosphate ( $\text{HPO}_4^{2-}$ )

the release of energy during the hydrolysis of ATP comes from the chemical change of the system to a state lower free energy (ADP+P) not from the phosphate bonds themselves.

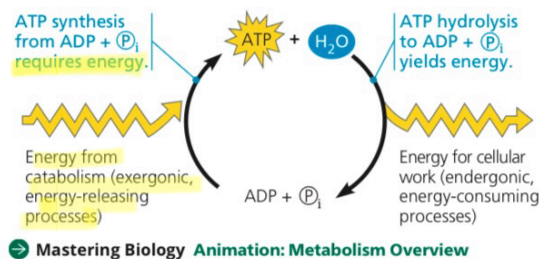


phosphorylation: The transfer of phosphate group from ATP to some other molecule such as reactant.

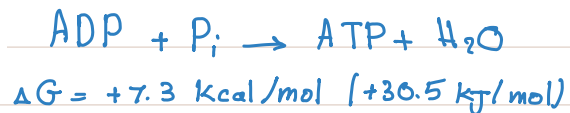
The ' molecule recipient with the phosphate group covalently bonded to it is then called phosphorylated intermediate which is the key for coupling exergonic & endergonic reactions



**▼ Figure 6.12 The ATP cycle.** Energy released by breakdown reactions (catabolism) in the cell is used to phosphorylate ADP, regenerating ATP. Chemical potential energy stored in ATP drives most cellular work.



IF ATP could not be regenerated by the phosphorylation of ADP humans would use up nearly their body weight in ATP each day



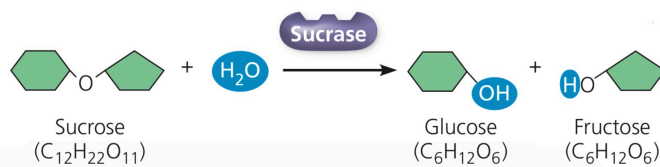
cellular respiration provide the energy for the endergonic process of making ATP

The release of Energy during the hydrolysis of ATP comes from the chemical change of the system to a state of lower free energy, not from the phosphate

## Concept 6.4

Enzymes speed up metabolic reactions by lowering energy barriers.

Hydrolysis of sucrose is exergonic occurring spontaneously with a release of free energy  $\Delta G = -7 \text{ kcal/mol}$ .



enzyme is a macromolecule that acts as a catalyst most of enzymes are proteins (some RNA molecules called ribozymes)

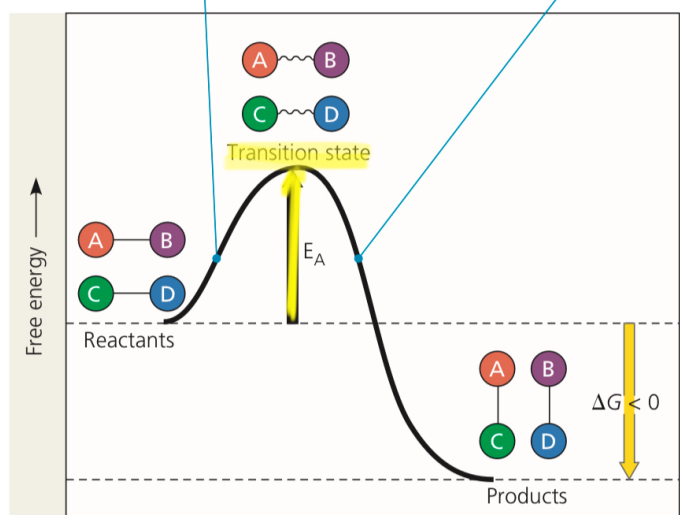
changing one molecule into another generally involves contorting the starting molecule into a highly unstable state before the reaction can proceed [transition state]

the initial investment of energy for starting a reaction the energy required to contort the reactant molecules so the bonds can be broken is known as the free energy of activation or activation energy  $E_A$

The amount of energy needed to push the reactants to the top of an energy barrier

The reactants AB and CD must absorb enough energy from the surroundings to reach the unstable transition state, where bonds can break.

After bonds have broken, new bonds form, releasing energy to the surroundings.

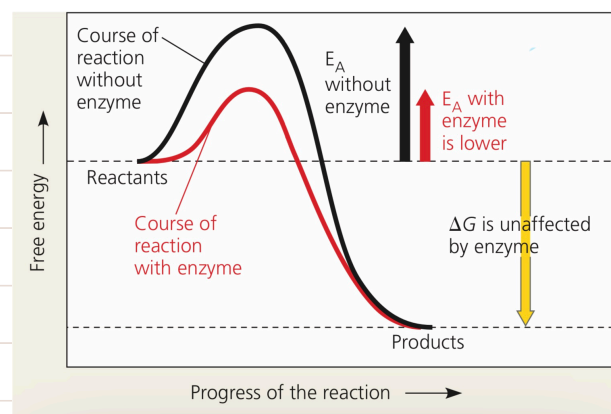


Heat can increase the rate of reaction, but this would not work well in biological systems

**Because :** 1) high temperature denatures proteins & kill cells  
2) heat would speed up all reactions not just those that are needed

Instead of heat, organisms carry out catalysis by lowering the  $E_A$  barrier

An Enzymes can not change the  $\Delta G$ , it can not make an endergonic reaction exergonic, they can only hasten reactions that would eventually occur anyway



substrate; The reactant an enzyme acts on

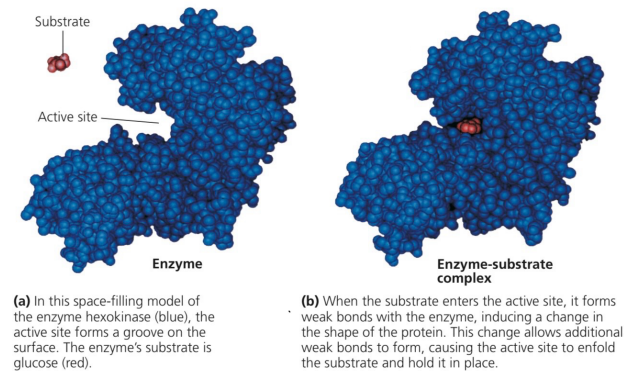
substrate complex: The enzyme binds to its substrates

The reaction catalyzed by each Enzyme is very specific

The specificity of an enzyme results from its shape which is a result of amino acids

active site is typically a pocket or groove on the surface of the enzyme where catalysis occurs

▼ Figure 6.15 Induced fit between an enzyme and its substrate.



The substrate is held in the active site by weak interactions such as hydrogen bonds and ionic bond.

Most metabolic reactions are reversible and an enzyme can catalyze either the forward or the reverse reactions.

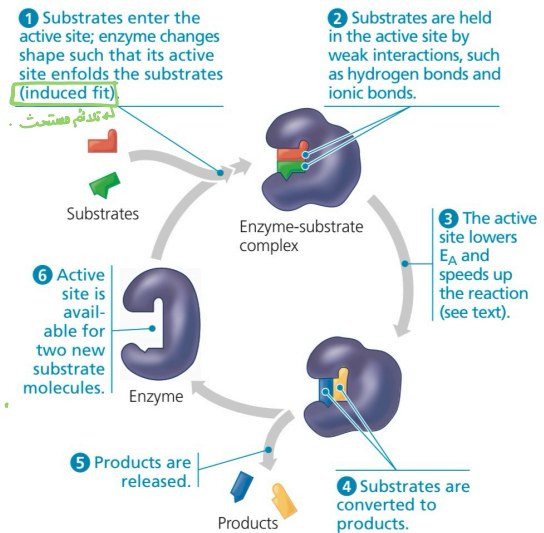
Enzymes use variety of mechanisms that lower activation energy and speed up a reaction.

- proper orientation
- stretch the substrate molecules toward their transition state form
- provide a microenvironment that is more conducive to a certain reaction
- Amino acids in the active site participate in the chemical reaction

The rate in which a particular amount of enzyme converts substrate to product is partly a function of the initial concentration of substrate but there is a limit to how fast reaction can be

when it reach saturation state the only way to increase the speed is to increase the number of enzymes.





## Effects of local conditions on Enzyme's Activity

- temperature
- PH
- chemicals

- Most human enzymes have optimal temperatures of about 35-40 (close to human body temperature)
- the thermophilic bacteria that live in hot springs contain enzymes with optimal temperatures of 70C to or higher
- The optimal pH values for most enzymes fall in the range of pt 6-8 but there are exceptions
  1. pepsin, a digestive enzyme in the human stomach work best in a very low pH

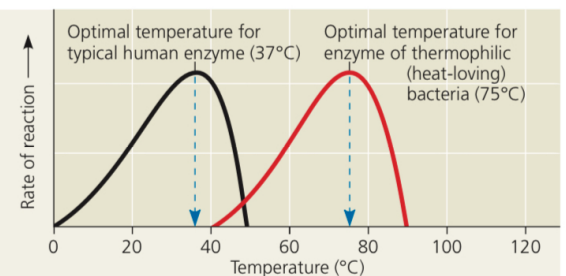
2-Trypsin, a digestive enzyme residing in the more alkaline environment of the human intestine

## cofactors

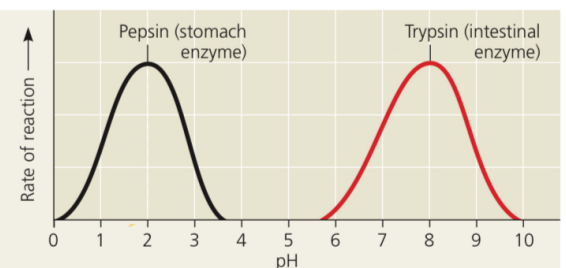
non-protein helpers for catalytic activity often to chemical process like electron transfers that can not easily be carried out by the amino acid

Maybe bond tightly to the enzyme as permanent residents or may bind loosely and reversible along with the substrate

- inorganic such as metal atoms zinc iron and copper in ionic form
- organic molecule coenzyme-Most vitamins are important in nutrition



(a) The photo shows thermophilic cyanobacteria (green) thriving in the hot water of a Nevada geyser. The graph compares the optimal temperatures for an enzyme from the thermophilic bacterium *Thermus oshimai* (75°C) and human enzymes (37°C, body temperature).



(b) This graph shows the rate of reaction for two digestive enzymes over a range of pH values.

## Enzyme Inhibitors

- The inhibitor attaches to the enzyme by covalent bonds in which case the inhibition is usually irreversible
- Many inhibitors bind to the enzyme by weak interactions the inhibition is reversible

### Enzyme Inhibitors

#### competitive

they resemble the shape of the normal substrate.. they compete with the normal substrate for the active site

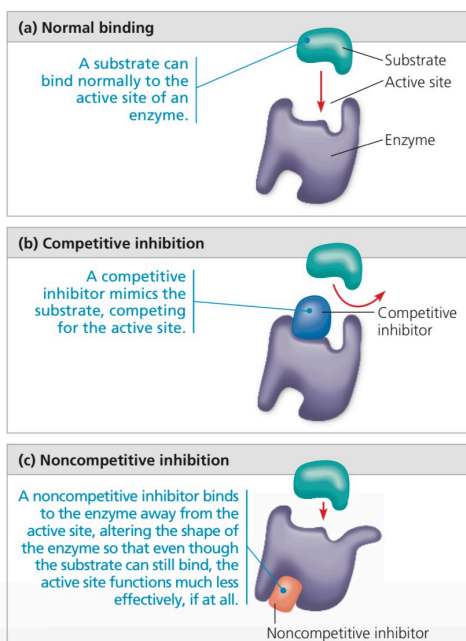
#### non-competitive

the shape does not matter, they don't bind to the active site instead, they bind to another sites on the enzyme (change in 3D structure.)

### Example

- Toxins & poisons, Irreversible enzyme Inhibitors.

▼ Figure 6.18 Inhibition of enzyme activity.



- sarin (nerve gas) binds covalently to the R group on the amino acid serine which found in the active site the (acetylcholinesterase)
- pesticides DDT & parathion
- Antibiotics (inhibitors of specific ienzymes in bacteria)
- penicillin blocks the active site of an enzyme that many bacteria use to make cell wall

Enzyme Inhibitors are not always abnormal & harmful molecules often regulate enzyme's activity by acting as inhibitors like cellular metabolism

### Concept 6.5

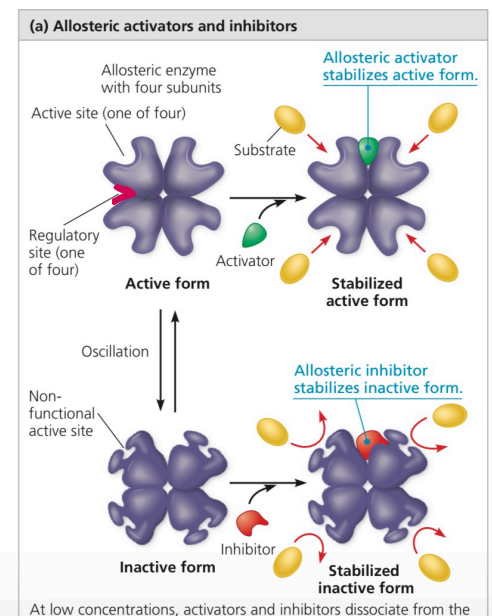
Controlling when & where its various enzymes are active by  
1) switching on and off the genes that encode specific enzymes  
2) regulating the activity of enzymes once they are made

o molecules that regulate enzyme activity behaves like reversible non-competitive inhibitors.

Allosteric regulation: describe any case in which a protein's function at one site is affected by the binding of a regulatory molecule to separate site. It may result in either inhibition or stimulation of enzyme activity

Ex. ATP binds to several catabolic enzymes allosterically lowering their affinity for substrate and thus inhibiting their activity  
ADP (function as activator)

▼ Figure 6.20 Allosteric regulation of enzyme activity.



**Cooperativity** : this mechanism amplifies response of enzymes to substrates . one substrate molecule primes an enzyme to act on additional substrates molecules more rapidly

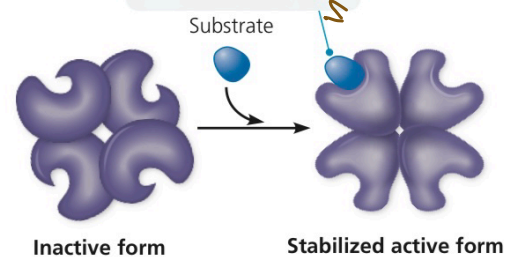
**Ex. Hemoglobin**

have elucidated the principle of cooperativity. Hemoglobin is made up of four subunits, each with an O<sub>2</sub>-binding site (see Figure 5.18). The binding of an O<sub>2</sub> to one binding site increases the affinity for O<sub>2</sub> of the remaining binding sites. Thus, where O<sub>2</sub> is at a high level, such as in the lungs or gills, hemoglobin's affinity for O<sub>2</sub> increases as more binding sites are filled. In O<sub>2</sub>-deprived tissues, however, the release of each O<sub>2</sub> molecule decreases the O<sub>2</sub> affinity of the other binding sites, resulting in the release of O<sub>2</sub> where it is most needed. Cooperativity works similarly in multisubunit enzymes that have been studied.

(b) Cooperativity: another type of allosteric activation

Binding of one substrate molecule to active site of one subunit locks all rmination.

Saving PDF

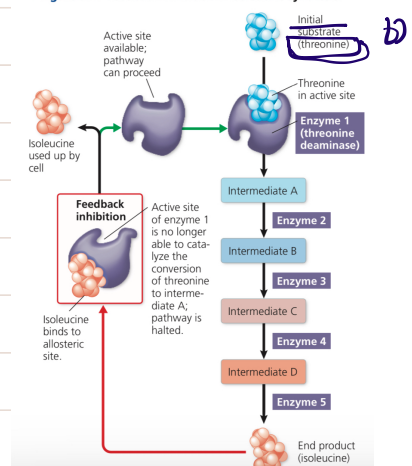


The inactive form shown on the left oscillates with the active form when the active form is not stabilized by substrate.

**Feedback inhibition.**

A metabolic pathway is halted by the inhibitory binding of the product to an enzyme that acts early in the pathway

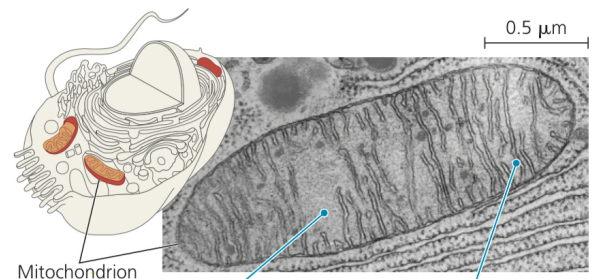
Figure 6.21 Feedback inhibition in isoleucine synthesis.



- localization of Enzymes within the cell is not random because the cell is compartmentalized
- product from the first enzyme becoming the substrate for an adjacent enzyme in the complex.....
- some enzymes have fixed locations acts like structural components of particular membranes
- others in solution within particular membrane enclosed eukaryotic organelles.n
- organisms are open systems, energy and matters can be transferred between the system and it's surroundings

▼ **Figure 6.22 Organelles and structural order in metabolism.**

Organelles such as the mitochondrion (TEM) contain enzymes that carry out specific functions, in this case the second and third stages of cellular respiration. (See also Figure 7.32b, lower left.)



The matrix contains enzymes in solution that are involved in the second stage of cellular respiration.

Enzymes for the third stage of cellular respiration are embedded in the inner membrane.



Good luck 🍀

دعوة حلوة منك يا حلوه