




BIOENERGETICS






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BIOENERGETICS

- **Bioenergetics or biological thermodynamics** is the quantitative study of energy transductions (changes of one form of energy into another) that occur in living cells, and of the nature and function of the chemical processes underlying these transductions.
 - ie. Bioenergetics deals with the **study of energy changes** (transfer and utilization) in biochemical reactions
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BIOENERGETICS

- Bioenergetics concerns only the initial and final energy states of reaction components, not the mechanism or how much time is needed for the chemical change to take place (the rate).
 - It predicts if a process is possible
 - The goal of bioenergetics is to describe how living organisms acquire and transform energy in order to perform biological work.
 - The reactions are classified as **exergonic** (energy releasing) and **endergonic** (energy consuming)
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- Biological energy transformations obey the **Laws of Thermodynamics.**

- [Note : Thermodynamics is concerned with the flow of heat and it deals with the relationship between heat and work.]

- **First Law of Thermodynamics**

- The total energy of a system, including its surroundings, remains constant.
- This is also called the law of conservation of energy.


- **Second Law of Thermodynamics**

- The total entropy of a system must increase if a process is to occur spontaneously.
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GIBB'S FREE ENERGY(G)

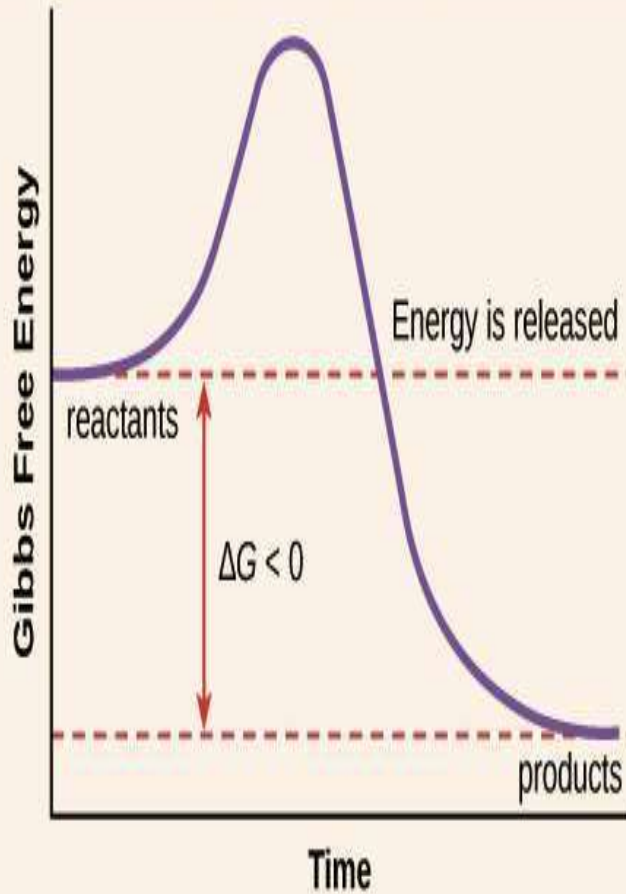
- **Gibbs free energy (G)** expresses the amount of an energy capable of doing work during a reaction at constant temperature and pressure.
- The direction and extent to which a chemical reaction proceeds is determined by the degree to which two factors (enthalpy and entropy) change during the reaction.

1. **Free energy** is a measure of the energy available to perform useful work.
2. ΔG can predict the direction of a chemical reaction.
3. Chemical reactions can be **coupled** which allows an energetically unfavorable reaction to proceed to conclusion.
4. ΔG measured under physiological conditions may be different from that at a standard state.

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- **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 ΔH has a negative value.
 - Reacting systems that take up heat from their surroundings are endothermic and have positive values of ΔH .
 - **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.

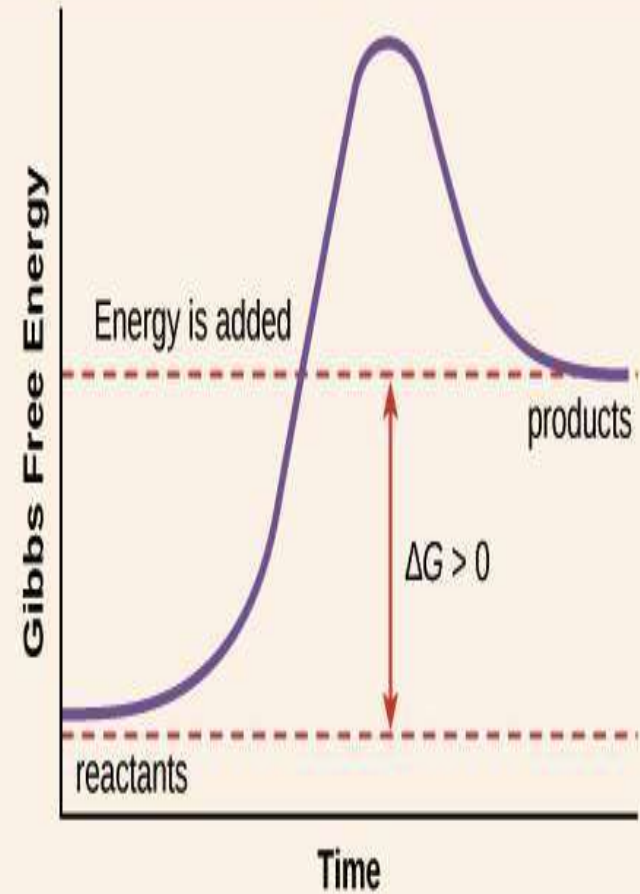
EXERGONIC REACTION: $\Delta G < 0$

Reaction is spontaneous



ENDERGONIC REACTION: $\Delta G > 0$

Reaction is not spontaneous

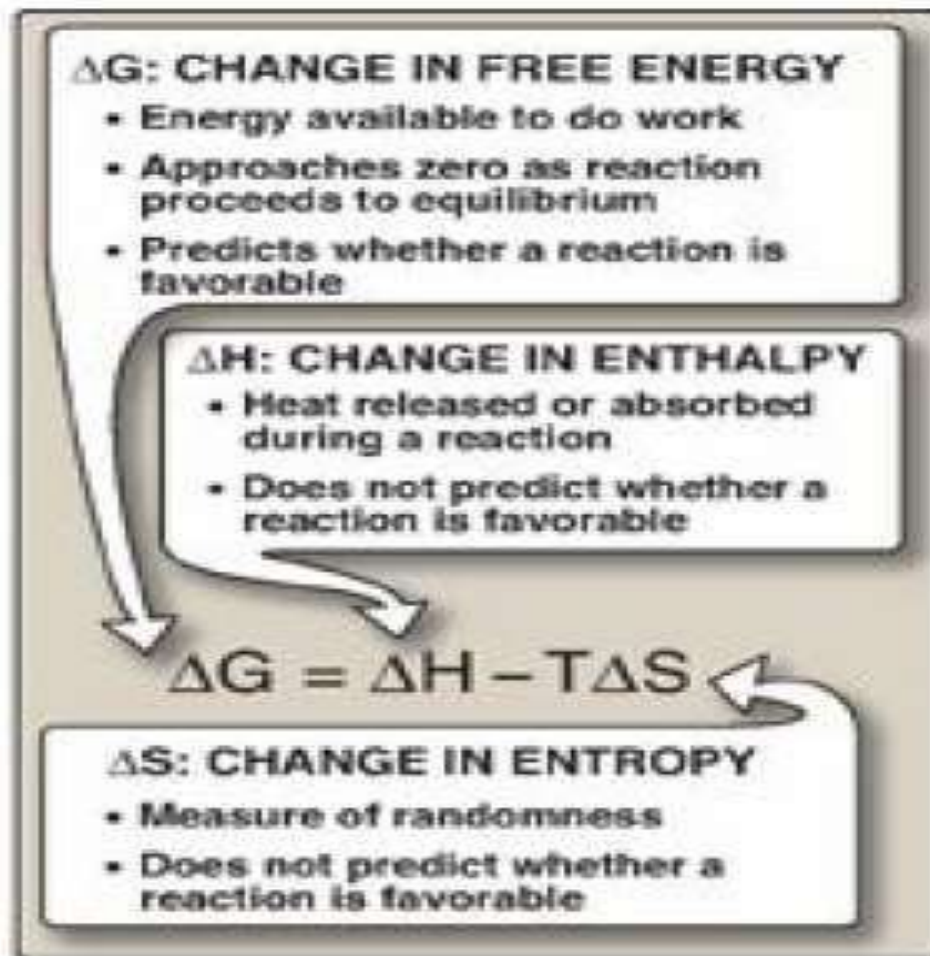


- The units of ΔG and ΔH are joules/mole or calories/mole
- Units of entropy are joules/mole x Kelvin (J/mol *K)
- Under the conditions existing in biological systems (including constant temperature and pressure), changes in free energy, enthalpy, and entropy are related to each other quantitatively by the equation

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

- ΔG is the change in Gibbs free energy of the reacting system
- ΔH is the change in enthalpy of the system
- T is the absolute temperature
- ΔS is the change in entropy of the system.

ΔS has a positive sign when entropy increases and ΔH has a negative sign when heat is released by the system to its surroundings.



- Relationship between changes in free energy (G), enthalpy (H), and entropy (S)
- T is the absolute temperature in Kelvin (K)

- The change in free energy is represented in two ways, ΔG and ΔG° .
- ΔG represents the change in free energy and, thus, the direction of a reaction at any specified concentration of products and reactants. ΔG , then, is a variable.
- ΔG° is the energy change when reactants and products are at a concentration of 1 mol/l. [Note: The concentration of protons is assumed to be 10^{-7} mol/l (that is, pH = 7).
- Although ΔG° , a constant, represents energy changes at these non physiologic concentrations of reactants and products, it is nonetheless useful in comparing the energy changes of different reactions.

(A) Sign of ΔG and the direction of a reaction:

- ΔG can be used to predict the direction of a reaction at constant temperature and pressure.
- **Negative ΔG :** If ΔG is negative, there is a net loss of energy and the reaction is said to be exergonic.
- **Positive ΔG :** If ΔG is positive, there is a net gain of energy, and the reaction is said to be endergonic.
- **ΔG is zero:** If $\Delta G = 0$, the reactants are in equilibrium. [Note: When a reaction is proceeding spontaneously (that is, free energy is being lost) then the reaction continues until ΔG reaches zero and equilibrium is established.]


(B) ΔG of the forward and back reactions:

- The free energy of the forward reaction ($A \rightarrow B$) is equal in magnitude but opposite in sign to that of the back reaction ($B \rightarrow A$).
- For example, if ΔG of the forward reaction is -5 kcal/mol, then that of the back reaction is $+5$ kcal/mol.

(C) ΔG and the concentration of reactants and products:

- The ΔG of the reaction $A \rightarrow B$ depends on the concentration of the reactant and product.
- At constant temperature and pressure,

$$\Delta G = \Delta G_o + RT \ln \frac{[B]}{[A]}$$

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- where ,
 - ΔG° is the standard free energy change
 - R is the gas constant (1.987 cal/mol K)
 - T is the absolute temperature (K)
 - $[A]$ and $[B]$ are the actual concentrations of the reactant and product
 - \ln represents the natural logarithm.
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- A reaction with a positive ΔG° can proceed in the forward direction (have a negative overall ΔG) if the ratio of products to reactants ($[B]/[A]$) is sufficiently small (that is, the ratio of reactants to products is large).

- For example, consider the reaction:



- Concentration of Glucose 6-phosphate, is high compared with the concentration of product, fructose 6-phosphate.
- This means that the ratio of the product to reactant is small, and $RT \ln([\text{fructose 6-phosphate}]/[\text{glucose 6-phosphate}])$ is large and negative, causing ΔG to be negative despite ΔG° being positive.
- Thus, the reaction can proceed in the forward direction.

(D) Standard free energy change

- The standard free energy change, ΔG° , is the free energy change, ΔG , under standard conditions (ie, when reactants and products are at 1 mol/l concentrations or at PH 7).
- Under these conditions, the natural logarithm of the ratio of products to reactants is zero ($\ln 1 = 0$), and, therefore, the equation becomes:

$$\Delta G = \Delta G^\circ + 0$$

(i) ΔG° and the direction of a reaction:

- Under standard conditions, ΔG° can be used to predict the direction a reaction proceeds because, under these conditions, $\Delta G^\circ = \Delta G$.
- However, ΔG° cannot predict the direction of a reaction under physiologic conditions, because it is composed solely of constants (R, T, and Keq and is not, therefore, altered by changes in product or substrate concentrations).

(ii) Relationship between ΔG° and K_{eq} (equilibrium constant)

- In a reaction $A \rightleftharpoons B$, a point of equilibrium is reached at which no further net chemical change takes place (that is, when A is being converted to B as fast as B is being converted to A).
- In this state, the ratio of [B] to [A] is constant, regardless of the actual concentrations of the two compounds:

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$$

- where K_{eq} is the equilibrium constant, and $[A]_{eq}$ and $[B]_{eq}$ are the concentrations of A and B at equilibrium.
- If the reaction $A \rightleftharpoons B$ is allowed to go to equilibrium at constant temperature and pressure, then, at equilibrium, the overall ΔG is zero.
- Therefore,

$$\Delta G = 0 = \Delta G^\circ + RT \ln \frac{[B]_{eq}}{[A]_{eq}}$$

- where the actual concentrations of A and B are equal to the equilibrium concentrations of reactant and product $[A]_{eq}$ and $[B]_{eq}$, and their ratio is equal to the K_{eq} .
- Thus,

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

- This equation allows some simple predictions:

If $K_{eq} = 1$, then $\Delta G^{\circ} = 0$



If $K_{eq} > 1$, then $\Delta G^{\circ} < 0$

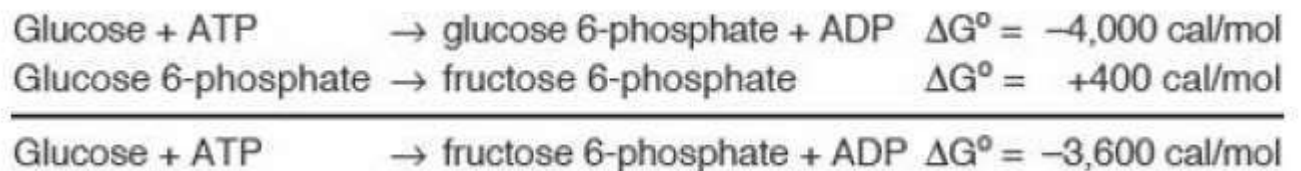


If $K_{eq} < 1$, then $\Delta G^{\circ} > 0$



(iii) ΔG° of two consecutive reactions:

- The ΔG° s are additive in any sequence of consecutive reactions, as are the ΔG -s.
- For eg:



(iv) ΔG s of a pathway:

- The additive property of free energy changes is very important in biochemical pathways through which substrates must pass in a particular direction ($A \rightarrow B \rightarrow C \dots$)
- As long as the sum of the ΔG s of the individual reactions is negative, the pathway can potentially proceed, even if some of the individual reactions of the pathway have a positive ΔG .
- The actual rate of the reactions depend on the lowering of activation energies by the enzymes that catalyze the reactions