Modern Biology - (Open + Free)

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Unit 5:: Metabolism

This course is not led by an instructor

Pathways   Energetics   Enzyme Nomenclature

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Specify the difference between standard energy and Gibbs free energy.	Explain the relationship between the equilibrium point of a system and the difference in standard energies.

Calculate the Gibbs free energy change, given the state of the system and the standard energy changes.

Determine the spontaneous direction of a reaction from the Gibbs free energy.

Free Energy and Spontaneity

Pathways accomplish the net conversion of the starting compounds to the final product of the pathway. During the normal operation of a pathway there is a constant flux of material through the pathway in one direction. Note that many pathways are reversible and operate in the forward or reverse direction, depending on the needs of the organism. The direction of a pathway depends on the energy difference between the starting compounds and final product of the pathway. The pathway will be spontaneous in the direction that causes a decrease in the **free energy** of the system. Reversing the direction of a pathway requires changing the relative energies of the reactants and products
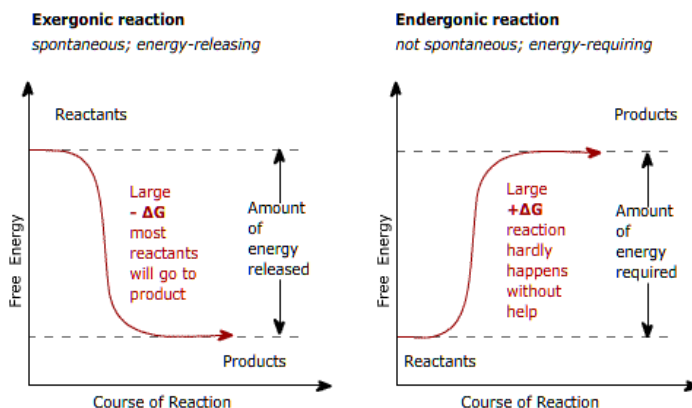
It is useful to have a quantitative way to predict the direction of a pathway given the current environment in the cell. A method of predicting the direction of a reaction was devised by J. Willard Gibbs in 1876 and the quantitative parameter that can be used to predict the direction of a reaction is called the **Gibbs free energy**. This method is particularly useful because it can be applied to reactions that are not at equilibrium, which is the situation encountered during metabolism. Before we can discuss the Gibbs free energy, we have to discuss standard energies and their relationship to equilibrium positions of reactions. Keep in mind that these discussions relate to the **thermodynamic** properties of pathways, more specifically the relative energy differences between reactants and products under cellular conditions. The presence of enzymes

simply increases the rate of conversion from reactants to products, the enzyme cannot alter the relative

simply increases the rate of conversion from reactants to products, the enzyme cannot alter the relative energies of these compounds.

Equilibria

Consider the simple reaction [A] to [B]. If we start with a system that is pure [A] it will spontaneously form some [B] until equilibrium is reached. When a system is at equilibrium, the concentration of products and reactants are constant and it is possible to write an equilibrium constant for the reaction:

where, K_{EQ} is:

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

Note that [A] and [B] are at their **equilibrium** concentrations in this formula.

Standard Energy

The standard energy change is the energy change when one mole of reactant is converted to one mole of product, it is the energy difference between reactants and products: $\Delta G^o = G_{products}{}^o - G_{reactants}{}^o$. The standard energy change defines the equilibrium position of a reaction through the following equation:

$$\Delta G^o = -RT \ln K_{EQ}$$

or

$$K_{EQ} = e^{-\Delta G^o / RT}$$

For the simple reaction of A to B, the fraction of the system in state [A] is:

$$f_A = \frac{[A]}{[A] + [B]} = \frac{1}{1 + K_{EQ}}$$

In a similar fashion, the fraction in state [B] is:

$$f_B = \frac{[B]}{[A] + [B]} = \frac{K_{EQ}}{1 + K_{EQ}}$$

You can see from the above equations that if the energy of the products are equal to the reactants, then the equilibrium concentration of [B] will be equal to [A]. Mathematically, this can be shown as follows:

If the energy of [B] is equal to [A], then ΔG^o = 0. Therefore

K_{EQ}=1, and

f_A=1/(1+1) = 0.5 and f_B=1/(1+1) = 0.5

> **Question:** What will happen to the relative concentrations of A and B if the energy of form A is lower than B, what will happen if the energy of form A is higher? Use the Learn-by-Doing tutorial below to find out.

Gibbs Free Energy

The formula for change in the Gibbs free energy in the reaction for the reaction direction [A] to [B] is:

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

Note that in this equation, the concentration of [A] and [B] are not necessarily at their equilibrium concentrations.

It can be shown that:

- If ΔG less than 0 then the reaction is not at equilibrium and will proceed spontaneously in the forward direction, A to B.
- If ΔG greater than 0 then the reaction is also not at equilibrium, but will proceed spontaneously in the reverse direction, B to A.
- If ΔG=0 the reaction is at equilibrium and the concentrations of reactants and products will not change.

You can explore these relationships in the following tutorial.

In addition to predicting the direction of the reaction, the absolute value of ΔG, |ΔG|, is the amount of energy released when the concentrations of reactants and products change from their non-equilibrium values to their equilibrium values.

> **Question:** What is the Gibbs free energy when the concentration of A is greater than its equilibrium value? In what direction will the reaction flow? From A to B or from B to A? Use the Learn-by-Doing tutorial below to find out.

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A reaction will be spontaneous in the reverse direction if the standard energy change is positive.

○ true

○ false

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