4

Biochemistry

carbohydratesisomersketone starchlipidproteinamine

Doctor 2017 | Medicine | JU

● Sheet ○ Slides

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A QUICK RECAP

We have discussed earlier the definition of bioenergetics and the concept of free energy, now let's continue what we were talking about.

As mentioned earlier free energy change (**ΔG**) is the total energy change in a system with respect to its temperature. It's also the portion of a system's energy that can perform work when temperature and pressure are uniform through the system.

The change in free energy (**ΔG**) can be calculated for a certain reaction by applying the following equation:

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{[P_1]^a[P_2]^b \ldots}{[R_1]^c[R_2]^d \ldots} \quad \text{......... (EQ1)}$$

Where: **ΔG°** symbolizes the change in free energy under what are called "**standard conditions**" (1 M of each reactant and product, 25°C, pH 7)
R is the gas constant
T is the absolute temperature (K)
$[P_1]$, $[P_2]$,$[R_1]$, $[R_2]$ are the concentrations of the products and reactants
In represents the natural logarithm

- Once we know the value of **ΔG** for a process, we can use it to predict whether the process will be spontaneous, i.e., whether it is **energetically favorable** and will occur **without** being driven by an outside source of energy).
- the magnitude of **ΔG** for any reaction represents the maximum amount of **work** the reaction can perform. The sign of **ΔG** tells us whether the reaction is energetically favorable or not, in other words, whether it will go spontaneously or not.
- **e.g.:** Assume that a reaction has a **ΔG** of -40 kcal/mol, then we can tell that the reaction is energetically favorable as the sign of **ΔG** is negative and the reaction proceeds with a net release of 40 kcal/mol as a free energy.

Only processes with a negative **ΔG** are spontaneous, in other words, every spontaneous process decreases the system's free energy, and processes that have a positive **ΔG** are never spontaneous.

We can think of free energy as a measure of system's instability (its tendency to change to a more stable state). Unstable systems (higher **G**) tend to change in such a way that they become more stable (lower **G**). for example, a glucose molecule is less stable than the simpler molecule into which it can be split (more likely to break down). Unless something prevents it (activation energy), this system will move toward the greater stability, so the glucose molecule is broken down into smaller molecules.

Equilibrium

Recall that most chemical reaction are reversible and proceeds to a point at which the forward and backward reactions occur at the same rate. The reaction is then said to be at equilibrium and there is no further **net change** in the relative concentrations of products and reactants.

NOTE **For a reaction to be at equilibrium it's not necessary that the concentrations of products and reactants are equal. The reaction is said to be at equilibrium ONLY if the rate of forward Rxn = rate of backward Rxn.**

There is an important relationship between free energy and equilibrium since it describes a state of maximum stability. As a reaction proceeds towards equilibrium, the free energy of the mixture of **(P & R)** decreases. Free energy increases when a reaction is somewhat pushed away from equilibrium, perhaps removing some of the reactants and thus changing the P/R ratio.

for a system at equilibrium, **G (not ΔG!!!)** is at its lowest possible value in that system. So that any change from equilibrium will have a **+ΔG** and will not be spontaneous. For this reason, systems never spontaneously move away from equilibrium (the driving force at equilibrium is zero).

Based on free-energy changes, chemical reactions can be classified as either **exergonic** or **endergonic**.

- exergonic: proceeds with a net release of energy, **G** decreases, **ΔG** is negative, occurs spontaneously
- endergonic: absorbs free energy from surrounding, **G** increases, **ΔG** is positive, doesn't occur spontaneously

NOTE **(energetically favorable) doesn't mean that reactions occur rapidly, ΔG has nothing to do with the rate of reaction.**

At equilibrium:

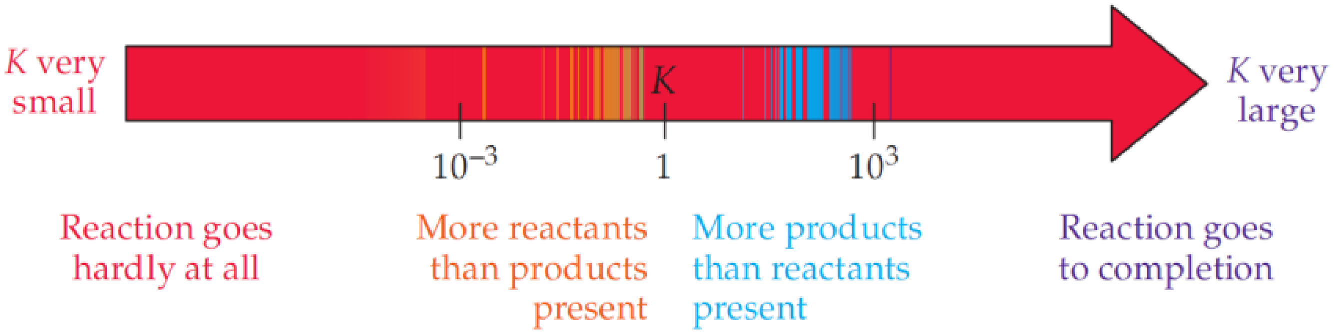
ΔG=0 *(since the driving force of any reaction at equilibrium is zero)*

substitute **ΔG=0** into (EQ1), we get;

$$\Delta G^\circ = -RT \ln \frac{[P_1]^a[P_2]^b \ldots}{[R_1]^c[R_2]^d \ldots} \rightarrow \frac{[P_1]^a[P_2]^b \ldots}{[R_1]^c[R_2]^d \ldots} = K_{eq}$$

where K_{eq} is the equilibrium constant. So, once we know the K_{eq} for a reaction we can tell the ratio between products and reactants when the reaction reaches equilibrium.

e.g. if the K_{eq}=100 that means at equilibrium [P]=100*[R]



If **K$_{eq}$** is high (>1000) then we conclude that at equilibrium the reaction mixture is mostly composed of products and a small proportion of reactants, thus we can say that the reaction is almost *completed*.
while when **K$_{eq}$** is low (<0.001) we can say that the reaction is hardly going.

The effect of changing Concentrations:

when changing the concentrations, if we know **K$_{eq}$,** we can predict whether the reaction proceeds towards producing more reactants or producing more products.
An endergonic reaction under standard conditions can be exergonic under physiological conditions. [check slides for further details]

NOTE **Metabolic reactions can take advantage of this effect.** **Important!!**

Effect of Temperature:

ΔH: ENTHALPY (Heat content) for a reaction.
Based on enthalpy changes, chemical reactions can be classified as either exothermic or endothermic.

NOTE ***An exothermic reaction isn't necessary an exergonic reaction and vice versa***

when changing the temperature of a reaction, the reaction either proceeds forward or backward.
If the reaction is exothermic then heat is being released during the reaction and thus heat content is considered to be a part of the **products**, so increasing T is the same as increasing products concentration therefore the reaction shifts toward making more reactants.

Effect of Catalysts:

ΔG and equilibrium **don't** change when using catalysts, as **ΔG** represents the difference in free energy between products and reactants. As mentioned earlier **ΔG** has nothing to do with the rate of reactions. (we are talking about dynamics not kinetics)

Effect of Stress:

When a stress is applied to a system at equilibrium, the equilibrium shifts to relieve the stress.

Stress: any change that disturbs the original equilibrium.

Energy machinery in the cell

Mitochondria “powerhouses” of the cell are *unusual* organelles that have their own small genome (DNA).

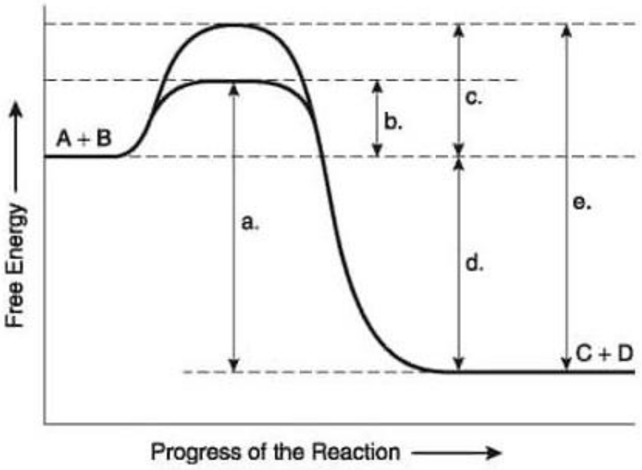
- mitochondria produce 90% of the body’s energy ATP. The remaining 10% are produced anaerobically in the cytosol in a process called 'glycolysis'. This is so important in cells that don’t have (mitochondria) such as RBCs.
- The number of mitochondria is greatest in eye, brain, heart, & muscle, where the need for energy is the most.
- mitochondria have the ability to reproduce, which means that mitochondria can increase in number upon need of energy by training (athletes)
- Maternal inheritance, mitochondria are normally inherited exclusively from the mother; the mitochondria in sperm are usually destroyed by the egg cell after fertilization so the paternal genetic material only gets transmitted.
  Nuclear DNA has two copies per cell (except for sperm and egg cells), one copy being inherited from the father and the other from the mother. Mitochondrial DNA, however, is strictly inherited from the mother. During cell division the mitochondria segregate randomly between the two new cells. As DNA is copied when mitochondria proliferate, they can accumulate random mutations, a phenomenon called **heteroplasmy**.
- Most of mitochondrial membrane proteins are made from mRNA that gets translated by ribosomes and a little amount is produced from mitochondrial DNA. Inner membrane is almost entirely made of proteins while the outer membrane has a mixture of proteins and lipids.
- Mitochondria can divide by **binary fission** and since they require mitochondrial DNA for their function, fission is coordinated with DNA replication.

Key difference between nuclear DNA and mitochondrial DNA	
Nu DNA	**Mt DNA**
linear	**circular**
Inherited from both parents	**Inherited from mother only**
Mutations appear in all body cells	**Mutations appear only in cells that have the defective mitochondria (heteroplasmy)**
Mitosis	**Binary fission**

QUIZ

1. A chemical reaction that has a positive ΔG is correctly described as
    a) Endergonic.
    b) Endothermic
    c) Enthalpic
    d) Spontaneous
    e) Exothermic

the questions 2-7 are based on the reaction A+B → C+D shown in this figure



2. which of the following terms best describes this reaction?
    a) Endergonic
    b) Exergonic
    c) Anabolic
    d) Allosteric
    e) Nonspontaneous

3. Which of the following represents the ΔG of the reaction?
    a) A
    b) B
    c) C
    d) D
    e) E

4. which of the following would be the same in an enzyme-catalyzed or noncatalyzed reaction?
    a) A
    b) B
    c) C
    d) D
    e) E

5. Which of the following best describes the reaction?
    a) Negative **ΔG**, spontaneous
    b) Positive **ΔG**, nonspontaneous
    c) Positive **ΔG**, exergonic
    d) Negative **ΔG**, endergonic
    e) **ΔG** of zero, chemical equilibrium

6. Which of the following represents the difference between the free-energy content of the reaction and the free-energy content of the products?
   a) A
   b) B
   c) C
   d) D
   e) E

7. Which best describes the reaction?
   a) The amount of free energy initially present in the reactants is indicated by “a.”
   b) The amount of free energy present in the products is indicated by “e.”
   c) The amount of free energy released as a result of the noncatalyzed reaction is indicated by “c.”
   d) The amount of free energy released as a result of the catalyzed reaction is indicated by “d.”
   e) The difference between “b.” and “c.” is the activation energy added by the presence of the enzyme.

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