Bioenergetics

Laws of Thermodynamics

Bioenergetics is the field of biochemistry concerned with the transformation and use of energy by living cells. The chemical reactions occurring in living organisms are associated with the release of energy as the reacting system moves from a higher to lower energy level. Mostly the energy is released in the form of heat.

Thermodynamics is not only a discipline of physical chemistry; it is applicable in living system also. According to thermodynamics, a system is a matter with a defined region. The matter in the rest of universe is called as surroundings. In living organisms, the unit structure, cell or its organelle, may act as a system which acts as an open system permitting passage of both, the matter and the energy. All the biochemical reactions are guided by the flow of energy from the outside of the system .Flow of energy begins from the sun, passes to autotrophs and travels through different levels of consumers. The energy gets transformed into different forms at the end of the chain. Therefore, in living systems, there is flow and transformation of energy at different levels. This is explained in Bioenergetics.

Following are the universal laws of thermodynamics:

The first law:
This law is also referred to as the law of conservation of energy..This law was first given by V.Mayer (1841). In the inanimate systems, but it is applicable in the living system too. The first law of thermodynamics states that the total amount of energy in the universe is constant. It says that the energy neither be created nor destroyed. Thus, whenever energy is used to do any work or is converted to other forms, the total amount of energy remains unchanged. This is applicable and helpful in energy audit during the biochemical reactions.

The mathematical expression of this law can be given as below-

Let, the energy of a system at the beginning of the reaction= ΔE_A

The energy of that system at the end of the reaction = ΔE_B

Heat absorbed by the system= Q

Work done by the system = W

Then, according to the law, $\Delta E = E_B - E_A = Q - W$

The Second law -

The second law expresses the condition of feasibility of a reaction. The first law cannot explain whether the reaction can take place spontaneously, although the energy change (ΔE) is positive. In

such case, the system absorbs heat from its surroundings so that the sum of energy of system and its surroundings remains the constant. It is evident that a a function other than ΔE is required. That function is entropy, denoted by a symbol "S ". Entropy can be explained as the quantitative measurement of energy in a state of randomness or disorder. It is unavailable useless enegy.The entropy of a system increases (ΔS is positive) when it becomes more disordered. Entropy becomes maximum in a system as it approaches equilibrium. When equilibrium is attained, no further change can occur spontaneously unless additional energy from outside is added to it. This can be understood with the example that when a quantity of water is kept in a kettle, the water molecules are in a state of ordered arrangement, this will have lower entropy, but if we heat the water, the water molecules will be in a state of randomness. Heat is absorbed by the water molecules and as a result its entropy gets increased. Now if we continue on heating the water will change its physical state and it starts to be converted into steam. In such condition the entropy will increase to maximum level for that system.

The second law of thermodynamics gives the quantitative measurement of energy transformation. According to this, a process can occur spontaneously only if the sum total of the entropies of the system and its surroundings increases.

This can be expressed as-

$(\Delta S_{System} + \Delta S_{urroundings}) > 0$ for a spontaneous reaction

Since the entropy changes cannot be easily measurable, the entropy is not used as a criterion whether a biochemical reaction can occur spontaneously or not. To solve the limitations ,an another function "free energy" was created by Gibbs(1878) by combining both the laws of thermodynamics and following derivation was made-

$\Delta G = \Delta H – T\Delta S$, where, ΔG =change in free energy of a reacting system

ΔH =change in the enthalpy/heat content of the system

T = the absolute temperature at which the reaction is taking place

And ΔS = the change in entropy of this system

Units of ΔG and ΔH are Joules/mole or calories/mole (1 cal.=4.184 J)

Here TΔS is the fraction of ΔH which cannot be put to useful work. ΔG, which indicates the Gibbs' free energy. Here it indicates the change in free energy which is available for useful work. But in most of the systems it is not fully available as calculated theoretically.

Further, the enthalpy change $\Delta H = \Delta E + P\Delta V$

Where, ΔE= the change in internal energy of a reaction, and

ΔV = the change in volume in this reaction. As the volume change ΔV is small for nearly all biochemical reactions, hence ΔH is nearly equal to the change in internal energy, ΔE.

Therefore, the reaction can be expressed as

$$\Delta G \cong \Delta E - T\Delta S$$

Thus, the change in free energy of a reaction system, ΔG depends both on the change in enthalpy and on the change in entropy of the system. ΔG is an important criterion by which we can judge whether the reaction can take place spontaneously or not. This can be expressed as given below-

1. If energy of the reactant (E_R) is more than that of the product (E_P), in such condition ΔG is negative, here $E_P < E_R$ then $E_P - E_R$ will be negative, the energy will be released and the reaction is exergonic

2. If ΔG is positive, it means $E_P > E_R$ .this will require energy from outside (surroundings) and the reaction will be endergonic because heat is absorbed from the outside. Further, in a condition of high magnitude of ΔG, there will be no tendency of the reaction to occur.

3. If $\Delta G = 0$, then the reaction system is at equilibrium and no reaction will take place.

Free energy and Standard free energy

Free energy (G) and Standard free energy ($\Delta G^{0'}$) are two terms which are used in the thermodynamics.

Free energy change (ΔG)
The amount of energy available to do work in a system is called free energy and denoted by the symbol 'G'.This is always less than the theoretical value because some energy is dissipated as heat. Chemical reactions in closed system proceed spontaneously until equilibrium is reached. When a system is at equilibrium, the rate of product formation exactly equals the rate at which product is converted to reactant. Thus there is no net change in the concentration of reactants and products, a steady state is achieved. The energy change as the system moves from its initial state to the equilibrium with no change in temperature in temperature or pressure, is given by the expression ΔG, the free-energy change. The magnitude of ΔG depends on the specific reaction and on how far from equilibrium the system is initially.

Standard free energy change (ΔG^0) is the expression of free energy change (ΔG) under ideal conditions, which is quite different from biological conditions. Under standard conditions ($25C0C/298K$),when reactants and products are initially present at 1M concentration or ,for gases at partial pressure of 101.3 kPa or 1 atm,the force driving the system towards equilibrium is defined as Standard free energy change, denoted by ΔG^0. By this definition the standard state of reaction that involve hydrogen ions is $[H^+]=1M$ or pH 0. Most of biochemical reactions occur in buffered aq.solution s near pH 7; both pH and the concentration of water (55.5M) are essentially constant. For convenience it is defined a different state, in which the concentration of H^+ is $10^{-7}M$ (pH7) and that of water is 55.5 M ; for reactions that involve Mg^{++} (including most reactions for which ATP is substrate),its concentration is taken to be constant at 1 mM. Physical constants based on this biochemical standard state are called **standard transformed constants** and are written with a prime (e.g., $\Delta G^{'0}$ and K'_{eq}) to distinguish them from untransformed constants used by physicists and chemists. Usually at many places $\Delta G^{'0}$ is also written as $\Delta G^{0'}$.

The mathematical expression of the equilibrium constant (K_{eq}) is as below :

K_{eq} = [C][D]/[A][B]

Just as K'^{eq} is a physical constant characteristic for each reaction, so too is $\Delta G'^0$ a constant.

$\Delta G'^0$ = –RT ln K'_{eq}

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

Application of thermodynamic principles in living system:

As we know that biochemical reactions are the lifeline in living system. All these reactions are guided by thermodynamics laws which include transformation of energy. In other words wherever reactions are involved, there is change in the energy level otherwise no reaction will occur. As mentioned above the difference in energy levels between a product and the reactant is important to drive a biochemical reaction. Negative value of free energy change is essential for spontaneity of any reaction leading to release of energy. This is well maintained in the cellular system. Beginning with the utilization of glucose in glycolysis, which involves phosphorylation of glucose by ATP and formation of glucose 6- phosphate by the enzyme hexokinase, is unidirectional; this cannot be reversed by the same process and enzyme because it is thermodynamically unfavourable. Same with the conversion of fructose 6-phosphate to fructose2,6-biphosphate.This reaction cannot be reversed by the same pathway due to thermodynamic limitations. Conversion of Phosphoenolpyruvate to Pyruvate is another example where PEP can transfer its phosphoryl group to ADP and Pyruvate is formed, but conversion of Pyruvate to PEP is not possible due to thermodynamic barrier.

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