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Topic: Bioenergetics and Thermodynamics

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Bioenergetics and Thermodynamics

Bioenergetics

Energy is defined as a measure to do work. The various forms of energy (potential, kinetic, chemical, heat, electrical etc.) are interconvertible to each other. Bioenergetics is the quantitative study of energy transductions (flow of energy) in living organisms. This is also the study of the nature and function of the chemical processes underlying these transductions. Nearly all living organisms derive their energy, directly or indirectly from the radiant energy of sunlight. This radiant energy arises from the thermonuclear fusion reactions carried out in the Sun.

Thermodynamics (Greek: *therme* = heat; *dynamis* = power)

Thermodynamics is the science that deals with flow of heat and other forms of energy into or out of a **system**. There are two fundamental laws of thermodynamics. However, to understand the laws of thermodynamics, we need to be familiar with some concepts. These are:

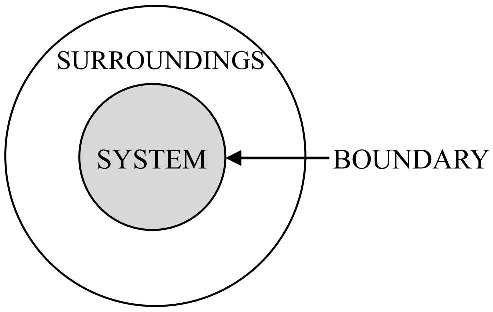
System: A system is defined as a part or place of the universe chosen for observation. In other words system is "everything within a defined region of space". A system may be a molecule, a cell, an organism, a solution, our earth or a whole galaxy.

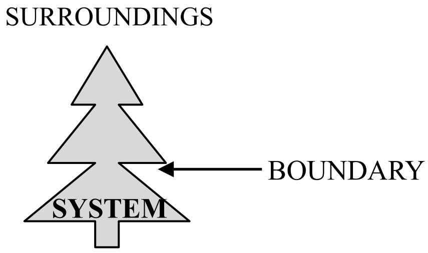
Boundary: The system is separated from its surroundings by a boundary which may be real (definite) or imaginary. The boundary of a system may be of two types:

Diathermal: permit the transmission of heat through them (eg. A liquid contained in a glass vessel)

Adiabetic: do not allow any heat to enter into or to come out of the system (eg. A liquid contained in a silver-mirrored double walled Dewar flask).

Surroundings: All other parts of the universe outside the boundary of the system are called the surroundings.





Example

System is of three types. These are

Isolated system: A system is said to be an isolated system when it is incapable of exchanging either energy or matter with the surroundings.

Change of energy $\Delta E = 0$; change of mass $\Delta M = 0$

Closed system: A closed system is one in which energy exchange with the surroundings is possible but no mass transfer across the boundary is permitted.

Change of energy $\Delta E \neq 0$; change of mass $\Delta M = 0$

Open system: An open system is one in which the transfer of both mass and energy across the boundary is possible.

Change of energy $\Delta E \neq 0$; change of mass $\Delta M \neq 0$

Zeroth law of thermodynamics: if two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other. Let there are three systems: A, B and C. If A is in thermodynamic equilibrium with system B and B is in thermodynamic equilibrium with system C, the A is also in thermodynamic equilibrium with C.

First law of thermodynamics: For any physical or chemical change, the total amount of energy in the universe remains constant; energy may change form or it may be transported from one region to another but it cannot be created or destroyed.

$\Delta U = U_{\text{final}} - U_{\text{initial}} = q - w$ [where U is energy, q represent the heat absorbed by the system from the surroundings and w is the work done by the system on the surroundings.]

Enthalpy

Enthalpy is the heat content of a reacting system. It is symbolized by H.

$H = U + PV$ [where U = Total internal energy of a system, P = Pressure, V = Volume]

So, change in Enthalpy is - $\Delta H = \Delta U + \Delta V$ (under constant pressure)

Second law of thermodynamics: In all natural processes, the entropy of the universe increase. In other words, the universe always tends toward increasing disorder.

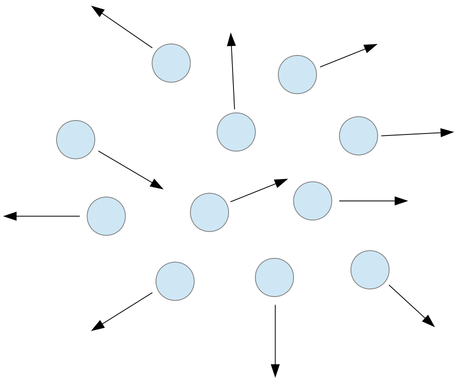
$\Delta S > 0$ [where ΔS is change in entropy]

Entropy

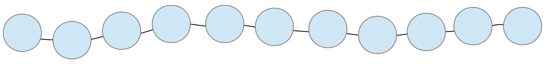
Entropy, symbolized by S, is a measure of the degree of randomness or disorder of a system. A change in entropy is denoted by ΔS. Entropy increases as a system becomes more disordered, and is decreased as it becomes more structured. According to the second law of thermodynamics, a reaction tends to occur spontaneously when the total entropy of the system and its surroundings increases.

Example:

One example is the reaction that links amino acids together to form a protein. A solution of unlinked amino acids has greater entropy because the amino acid molecules move randomly in the solution. They are thus unorganized. But, a solution of protein molecules made up of those same amino acids has lower entropy because now the amino acid molecules are organized into a protein molecule and their movement is restricted by its being bound in a long chain.



Unlinked amino acids: high entropy



A peptide: Low entropy

Third law of thermodynamics: The entropy of a substance approaches zero as its temperature approaches absolute zero. Physically, the law implies that it is impossible for any procedure to bring a system to the absolute zero of temperature in a finite number of steps.

Free energy

One thermodynamic concept, particularly useful in biochemistry, is free energy (G). The thermodynamic measure of the maximum energy available for conversion of work (at constant temperature and pressure), is called the **Gibbs free energy** symbolized as 'G', after John Williard Gibbs drew attention to its significance in systems maintained at constant pressure.

If A is converted to B in a chemical reaction, the reaction can be written as-

$$A \rightleftharpoons B$$

Change of free energy is-

$$\Delta G = G_B - G_A$$

This is the maximum amount of energy made available as A is converted to B. If, the free energy content of the product B (G_B) is less than the free-energy content of the reactant A (G_A) [$G_A > G_B$], the ΔG will be a negative quantity.

Relation of free energy with enthalpy and entropy

Gibbs showed that free energy (G) can be defined as $G = H - TS$

Where H is the heat energy or enthalpy of the system, T is its temperature in Kelvins and S is its entropy. In an exothermic reaction, ΔH (change in enthalpy) is negative as heat is given off. In an endothermic reaction, ΔH is positive as the reaction system absorbs energy from the surroundings. These energy release and absorbance is related to their bond formation or breakage. Also, as bond formation and breakage is related to the organization and disorganization of a molecule, entropy is important here. So, free energy is related both to enthalpy and entropy.

In constant pressure, $\Delta G = \Delta H - T\Delta S$ (T = temperature)

In any closed system (T and P constant), which is not at equilibrium, only exergonic reactions ($-\Delta G$) can occur spontaneously.

Standard free energy changes

It is necessary to refer these differences to some standard state in order to compare the free energies of different substances. Normally, the free energy change is influenced by several factors like temperature, pressure, initial concentration o the reactants and products and pH. The standard free energy change, denoted by $\Delta G^{\circ\prime}$, is the free energy change of a reaction under certain standard conditions namely a temperature of 298 K (25°C), a pressure f 1 atm, a pH of 7.0 and initial concentration of 1M of both reactants and products. The sign (+ or -) of $\Delta G^{\circ\prime}$ depends on the direction of the reaction; i.e., if the reaction $A \longrightarrow B$ has a $\Delta G^{\circ\prime}$ of –a Kcal/mol, then the reaction $B \longrightarrow A$ has a $\Delta G^{\circ\prime}$ of +a Kcal/mol.

However, the conditions of most biological systems differ from the standard conditions, particularly the concentrations of reactants. However, we can estimate free energy changes for different temperatures and beginning concentrations by using the following equation-

$$\Delta G = \Delta G^{\circ\prime} + RT \ln \frac{[\text{products }]}{[\text{reactants }]}$$

Where $\Delta G^{\circ\prime}$ = standard free energy change in Joules (J) or calories (Cal).

R = Universal gas constant
T = Absolute temp. (K)
Ln = natural logarithm

It is possible to evaluate $\Delta G^{\circ\prime}$ if we consider the ΔG at equilibrium. At equilibrium, there is no conversion of the reactants to products, and hence the change in free energy ΔG is 0. Similarly, the ratio of [products] to [reactants] is the ratio at equilibrium or the **equilibrium constant K_{eq}**.

We know that

$$\Delta G = \Delta G^{\circ\prime} + RT \ln \frac{[\text{products }]}{[\text{reactants }]}$$

So, at equilibrium,

$$0 = \Delta G^{\circ\prime} + RT \ln \frac{[\text{products }]}{[\text{reactants }]}$$

$$0 = \Delta G^{\circ\prime} + RT \ln K_{eq}$$

or

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

If we express this equation in base 10 logarithms, it becomes-

$$\boldsymbol{\Delta G^{\circ\prime} = - 2.3\ RT \log K_{eq}}$$

Now,

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

or

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

At standard conditions, $\Delta G^{\circ\prime} = \Delta H^{\circ} - T\Delta S^{\circ}$ [where H° and S° are the enthalpy and entropy at standard conditions]

So, $\ln K_{eq} = \frac{-\Delta H^{\circ} + T\Delta S^{\circ}}{RT}$

or, $\ln K_{eq} = \frac{-\Delta H^{\circ}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^{\circ}}{R}$

As ΔH°, R and ΔS° is constant, so the equation has the form y = mx + c, the equation for a straight line.

A plot of $\ln K_{eq}$ versus $\frac{1}{T}$ is known as **Vant Hoff plot**. From the measurement of K_{eq}, at different temperatures, the values of ΔH°, ΔS° and ΔG° can be determined more easily than measuring by calorimetry.

In biochemistry, standard free energy change is symbolized by ΔG°′, in physical chemistry it is ΔG°. If a reaction includes neither H_2O or H^+, nor an ionizable species, then ΔG°′ = ΔG°.

Thus, relationship between K_{eq} and ΔG°′ is like the following

When K_{eq} is >1.0, ΔG°′ is negative and the reaction proceeds forward,

When K_{eq} is <1.0, ΔG°′ is posative and the reaction proceeds in reverse, and

When K_{eq} is =1.0, ΔG°′ is zero and the reaction is at equilibrium.

Coupling of reactions

In the cell, the energy made available in an exergonic reaction is often utilized to drive a related endergonic reaction. This is called coupling of reactions.

We know that the free energy change (ΔG) for the formation of products C and D from substrate A and B is given by

$\Delta G = \Delta G^{\circ\prime} + RT \ln\frac{[C][D]}{[A][B]}$

Thus, the ΔG of a reaction depends on-

1) The standard free energy change and
2) The concentration of the reactants and products.

The overall free energy change for a chemically coupled series of reactions is equal to the sum of the free energy changes of the individual steps. Consider the following reactions

$$\begin{array}{lll} A \rightleftharpoons B + C & & \Delta G^{\circ\prime} = +5\text{Kcal/mol} \\ B \rightleftharpoons D & & \Delta G^{\circ\prime} = -8\text{Kcal/mol} \\ \hline A \rightleftharpoons C + D & & \Delta G^{\circ\prime} = -3\text{Kcal/mol} \end{array}$$

Under standard conditions, A can not be spontaneously converted to B and C, because $\Delta G^{\circ\prime}$ is positive. But as this reaction is coupled with another reaction ($B \rightleftharpoons D$), which is spontaneous ($\Delta G^{\circ\prime}$ is negative), the overall reaction is feasible.

Also, as any B that is formed from A, is readily converted into D, the equilibrium concentration of B will be lowered, and thus more and more B will be produced from A.

In the cell, many endergonic reactions are coupled to the hydrolysis of ATP which is an exergonic reaction. Likewise, ATP formation (which itself is an endergonic reaction), is coupled with some exergonic reactions like oxidation of glucose etc.

Example:

During the conversion of glucose to lactic acid (or alcohol), the phosphorylated triose i.e. glyceraldehydes 3-phosphate is oxidized to 3-phosphoglyceric acid.

Glyceraldehyde 3-phosphate + $H_2O \longrightarrow$ [intermediate] $\longrightarrow$ 3-bisphosphoglyceric acid

$$\Delta G = -12 \text{ Kcal}$$

So, it is a spontaneous and exergonic reaction.

The energy liberated in this reaction might be lost as heat. But the living cell evolved an elegant mechanism for coupling this reaction to the generation of ATP, a process that has a ΔG of about +7.3 Kcal/mol at 37°C at pH 7.

$$\text{ADP} + H_3PO_4 \longrightarrow \text{ATP} + H_2O \qquad \Delta G' \ +7.3 \text{ Kcal (pH 7.0, 37°C)}$$

Coupling of these two reactions is done through the participation of a common intermediate called 1, 3-bisphosphoglyceric acid. The actual reaction in which 1, 3-bisphosphoglyceric acid is formed is a combined oxidation-reduction and phosphorylation reaction.

Glyceraldehyde 3-phosphate + NAD^+ + H_3PO_4 $\longrightarrow$ 1, 3-bisphosphoglyceric acid + $NADH^+$ + H^+

ΔG′of this reaction is +1.5 Kcal

The acyl phosphate (1, 3-bisphosphoglyceric acid), in a subsequent reaction, is then utilized to convert ADP to ATP.

1, 3-bisphosphoglyceric acid + ADP $\longrightarrow$ 3-bisphosphoglyceric acid + ATP.

ΔG′of this reaction is - 4.5 Kcal

Now, combining these two reactions-

$$\begin{array}{ll} GAP + NAD^+ + H_3PO_4 \longrightarrow 1,3\text{-BPGA} + NADH^+ + H^+ & \Delta G^{\circ\prime} = +1.5\ \text{Kcal/mol} \\ 1,3\text{-BPGA} + ADP \longrightarrow 3\text{-PGA} + ATP & \Delta G^{\circ\prime} = -4.5\ \text{Kcal/mol} \\ \hline GAP + NAD^+ + H_3PO_4 + ADP \longrightarrow 3\text{-PGA} + NADH^+ + H^+ + ATP & \Delta G^{\circ\prime} = -3.0\ \text{Kcal/mol} \end{array}$$

So, a significant amount of energy which is made available in the oxidation of an aldehyde to a carboxylic acid has been utilized to drive the formation of ATP rather than simply being lost to the environment as heat.

High energy bonds

Cell is a very complicated system and it requires large amount of free energy for all important activities like synthesis of biomolecules, performance of mechanical work, cellular movements etc. Cell uses free energy to maintain these activities and this maintains an organism in a state far from equilibrium. All these processes mentioned above are energetically very demanding. Cells use chemical energy to maintain these processes. There are some compounds which give large amount of energy upon hydrolysis of some group which is bonded to the compound by high energy bonds. For example, ATP is hydrolysed to ADP and Pi. The ΔG°′ is −30.5 kJ/mol (−7.3 kcal/mol) at pH 7.0. There is nothing special about the bonds themselves. They are high energy bonds in the sense that a high amount of free energy is released when they are hydrolysed.

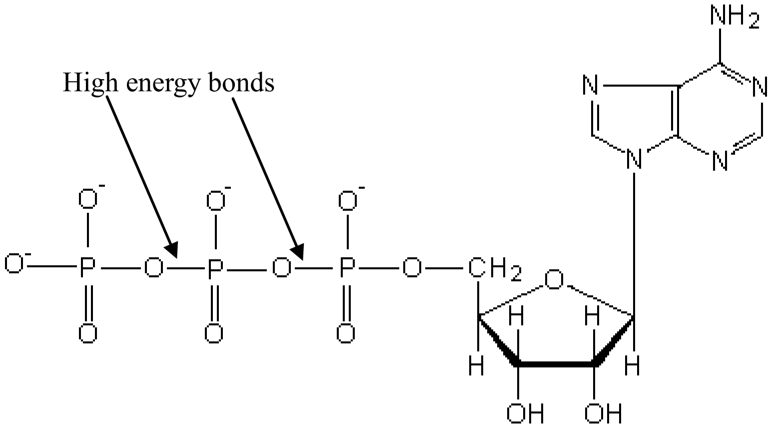
Most of the chemical bonds in compounds of organism as ester, peptide and glycoside bonds are not high energy and in hydrolysis, they liberate about 10-15 kJ/mol of energy. If high energy bond is hydrolysed from a compound, much more free energy is liberated (30-60 kJ/mol).

Energy rich molecules are formed by the oxidation of substrates which cell obtains from the environment.

The creation of energy-rich compounds in cells is carried out by three main ways:

1. During oxidation of substrates (for instance glucose) are formed intermediates with high energy phosphate group.
2. ATP-the most important high energy phosphate compound and its phosphoanhydride bonds are referred to as high-energy bonds and are created by oxidative phosphorylation in mitochondria.
3. Some energy-rich compounds are produced so that phosphate is transferred from ATP to another molecule in the reaction which is catalysed by kinase and highenergy bond is preserved.
4. In cells, there are five kinds of high energy bonds: phosphoanhydride, acyl phosphate, enolphosphate, guanidine phosphate and thioester bond.

ATP: ATP is regarded as a universal source of energy occurring in all cell types. It is produced mainly during the oxidation of energy-rich (reduced) compounds processed in the respiratory chain and in photosynthesis. ATP is needed.



The phosphates are linked anhydrously (phosphoanhydride bonds between two molecules of phosphoric acid i.e. H_3PO_4); the innermost phosphate residue and the sugar residue are linked by an ester bond which is not energy rich. Hydrolysis of two phosphoanhydride bonds gives rise the following products

$ATP + H_2O \rightarrow ADP + P_i$

$ATP + H_2O \rightarrow AMP + PP_i$

$ADP + H_2O \rightarrow AMP + P_i$

Since the delta $\Delta G^{\circ\prime}$ for the breakdown of a pyrophosphate (PPi) and for that of one phosphate residue (Pi) are roughly the same, ATP, ADP and AMP can rather easily be converted into each other:

$ATP + AMP \rightleftharpoons 2\ ADP$

As the $\Delta G^{\circ\prime}$ of breaking down of the phosphate bonds is high [$\Delta G^{\circ\prime} = -30.5$ kJ/mol (-7.3 kcal/mol) at pH 7.0 and $\Delta G^{\circ\prime} = -45.6$ kJ/mol (-10.9 kcal/mol) at pH 9.0], thus breakdown of ATP to ADP and to AMP release high energy. Thus, these bonds are called high energy bonds. This energy is used by the cell for the following

a) as a source of energy for biochemical syntheses
b) for transport processes (active transport) and
c) for mechanical work like movements (ciliar movements, plasma currents etc.).

Besides the adenosine nucleotide phosphates, uracil, cytosine and guanine phosphates occur, too: UMP, UDP, UTP, CMP, CDP, CTP, GMP, GDP, and GTP.

Redox potential

Oxidation-reduction

Oxidation-reduction reactions are those in which there is transfer of electrons from an electron donor to an electron acceptor. The **electron donor** is the **reducing agent** or **reductant**, the **electron acceptor** is the **oxidizing agent** or **oxidant**. These two processes are simultaneous, i.e., there will be no oxidation without concomitant reduction.

Example 1:

$$Fe^{2+} \xrightarrow{\text{oxidized}} Fe^{3+} + 1 \text{ electron}$$

So, Fe^{3+} is an oxidizing agent because it can an electron and be reduced to Fe^{2+}.

$$Fe^{3+} \xrightarrow{\text{reduced}} Fe^{2+} + 1 \text{ electron}$$

Half-reactions

$$H^+ + 1\ \text{electron} \xrightarrow{\text{reduced}} \tfrac{1}{2}\,H_2$$

These reactions in which electrons are indicated as being consumed or produced, but in which we have not indicated the donor or acceptor, are called **half-reactions**.

The reduced and oxidized forms of the compound constitute a conjugate pair which is called the **oxidation-reduction couple** or **redox couple**. Thus,

$$\text{Reductant} \rightleftharpoons \text{Conjugate oxidant}^{\,n+} + ne^-$$

Where n is the number of electrons (e) liberated from one molecule of the reductant.

A reduction of an oxidant produces its conjugate reductant.

$$.\qquad \text{oxidant}^{\,n+} + ne^- \rightleftharpoons \text{Conjugate reductant.}$$

Any oxidation-reduction reaction must involve two redox couples that differ in their affinity for electrons. The couple that shows the greated electron affinity assumes for oxidizing role, and the oxidant will be reduced. The couple with laser affinity for electrons is the oxidizing couple. The overall reaction can be considered to be the resultant of two half-reactions as follows:

Oxidation: $\text{red}_a \rightleftharpoons \text{conjugate ox}_a + e^-$

Reduction: $\text{ox}_b + e^- \rightleftharpoons \text{conjugate red}_b$

Overall oxidation-reduction: $\text{red}_a + \text{ox}_b \rightleftharpoons \text{conjugate ox}_a + \text{conjugate red}_b$

Now, if, by the isothermal transfer of electrons from red_a to ox_b, the Gibbs free energy of the system is decreased, the overall reaction is thermodynamically spontaneous from left to right. When the Gibbs free energy content of the system reaches its maximum value, net reaction ceases and the system is in equilibrium. Since, the oxidation and reduction involves electron transfer from red_a to ox_b, the reaction could perform electrical work. This would be equal to its $-\Delta G$ (change in free energy), if the reaction could be carried out at constant temperature and pressure in a thermodynamically reversible manner.

Different reducing agents differ in their tendency to lose electrons. The intensity of the tendency of a reducing agent to lose electrons or an oxidizing agent to accept electrons is measured as the **standard oxidation-reduction potential** or **Redox potential**. The Redox potential is defined as the **electromotive force (e.m.f.)** in volts given by a half-cell having both oxidant and reductant at 1.0 Molar concentration, at 25°C and pH 7.0, at equilibrium. The half-cell possesses an electrode which can reversibly accept electrons from the reductant.

The standard oxidation-reduction potential of the hydrogen electrode reaction ($2H^+ + 2e^- \rightleftharpoons H_2$) is used as the reference potential. The standard hydrogen electrode consists of H_2 gas in equilibrium with H^+ ions (1.0 M) in solution, at 1.0 atm pressure and 25°C. The electrons are transmitted to the redox couple via an inert platinum electrode. The reference potential is set at 0.0V. **The standard reduction potential is denoted by E_0.** The standard oxidation-reduction potential of the hydrogen electrode becomes -0.42V. With this as a standard, it is possible to determine the reduction potential of any other compound capable of oxidation-reduction with reference to hydrogen.

A negative reduction potential means that the reduced form of a substance has lower affinity for electrons than H_2. A positive reduction potential means that the reduced form of a substance has higher affinity for electrons than does H_2. Thus, a strong reducing agent (such as NADH) is poised to denote electrons and has a negative reduction potential, whereas a strong oxidizing agent (such as O_2) is ready to accept electrons and has a positive reduction potential.

Lists of Redox potential of some biologically significant reactions are given below.

Half reaction (written as a reduction)	Redox potential at pH 7.0
$\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$	+0.82
$\text{CytC} - Fe^{3+} + 1e^- \longrightarrow \text{CytC} - Fe^{2+}$	+0.29
Fumerate + $2H^+ + 2e^- \longrightarrow$ Succinate	+0.03
Oxaloacetate + $2H^+ + 2e^- \longrightarrow$ Malate	-0.10
$NAD^+ + 2H^+ + 2e^- \longrightarrow NADH + H^+$	-0.32
$H^+ + 1e^- \longrightarrow \frac{1}{2} H_2$	-0.42
Acetate + $2H^+ + 2e^- \longrightarrow$ Acetaldehyde + H_2O	-0.47

Relationship between standard free-energy change and redox potential

Change in Standard reduction potential is denoted by $\Delta E_0'$. The standard free-energy change $\Delta G^{\circ\prime}$ is related to the change in Redox potential $\Delta E_0'$ by the following formula

$$\Delta G^{\circ\prime} = -nF\Delta E_0'$$

Where n = no. of electrons transferred,

F = proportionality constant called the Faraday [23.06 Kcal/mol/volt]

$\Delta E_0'$ is in volt,

$\Delta G^{\circ\prime}$ is in Kilocalories per mole.

Criteria for a spontaneous reaction

By calculating $\Delta E_0'$ or by calculating $\Delta G^{\circ\prime}$, we can determine whether a reaction will occur spontaneously or not. If $\Delta E_0'$ has a positive value (and thus, $\Delta G^{\circ\prime}$ has a negative value), the reaction will be spontaneous.

Example:

$$\text{Pyruvate} + \text{NADH} + H^+ \rightleftharpoons \text{Lactate} + \text{NAD}^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ 1$$

We are to calculate the redox potential and free energy change.

The redox potential of the NAD^+:NADH couple is -0.32 V, whereas that of the pyruvate:Lactate couple is -0.19 V.

$$\text{Pyruvate} + 2H^+ + 2e^- \longrightarrow \text{Lactate} \qquad E_0' = -0.19\text{ V} \ldots\ldots\ldots\ldots\ldots\ 2$$

$$\text{NAD}^+ + H^+ + 2e^- \longrightarrow \text{NADH} \qquad E_0' = -0.32\text{ V} \ldots\ldots\ldots\ldots\ldots\ 3$$

Reversing the equation, we get

$$\text{NADH} \longrightarrow \text{NAD}^+ + H^+ + 2e^- \qquad E_0' = +0.32\text{ V} \ldots\ldots\ldots\ldots\ldots\ 4$$

Reaction 2 and 4 can be added to get reaction 1

$$\text{Pyruvate} + 2H^+ + 2e^- \longrightarrow \text{Lactate}$$

$$\text{NADH} \longrightarrow NAD^+ + H^+ + 2e^-$$

$$\text{Pyruvate} + \text{NADH} + H^+ \longrightarrow \text{Lactate} + NAD^+$$

$\Delta E_0' = (-0.19 + 0.32)\ V = +0.13\ V$.

The free energy change will be

$\Delta G^{\circ\prime} = -nF\Delta E_0'$

$= -2 \times 23.06 \times 0.13 = -6$ Kcal/mol

A positive $\Delta E_0'$ (but a negative $\Delta G^{\circ\prime}$) indicates an exergonic (and spontaneous) reaction under standard condition.

Significance of redox potential in oxidative phosphorylation

The driving force of oxidative phosphorylation is the electron transfer potential of NADH or $FADH_2$ relative to that of O_2.

The half reactions are

$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$ $E_0' = +0.82$ V ……………..………..1

$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$ $E_0' = -0.32$ V ………………………..2

Or

$NADH \rightleftharpoons NAD^+ + H^+ + 2e^-$ $E_0' = +0.32$ V ……………………….3

Adding 1 and 3, we get

$\frac{1}{2} O_2 + NADH + H^+ \rightleftharpoons H_2O + NAD^+$ $\Delta E_0' = (+0.82 + 0.32)\ V = +1.14\ V$….4

The free energy change of this reaction is

$\Delta G^{\circ\prime} = -nF\Delta E_0' = -2 \times 23.06 \times 1.14 = -52.6$ Kcal/mol.

Now, we know $ADP + H_3PO_4 \rightleftharpoons ATP + H_2O$

$\Delta G^{\circ\prime}$ of this reaction is +7.5 kcal. So, this is not spontaneous.

The energy released by the reaction 4 is used initially to generate a proton gradient that is then used to synthesis of ATP and the transport of metabolites across the mitochondrial membrane.

Further reading:

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