



**DC-1, Semester-2**

**Paper IV: Fundamentals of Plant Biochemistry**

**Lesson: Bioenergetics**

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## Introduction

Energy makes the living systems go round. They are continually in the process of acquiring energy which primarily starts at the level of plants which attain energy from sun through photosynthesis and pass it further on as carbohydrates and other organic substances and utilizing this energy for a variety of activities like synthesis of biomolecules, maintaining concentration gradients and performing muscular activities. Transformation or transduction of energy in physical and biological systems is the classic concept behind understanding thermodynamics. Even though the subject originated to understand several key theories behind the physical and chemical processes it has extended itself towards biology where it tries to quantitate the levels and assess the feasibility of energy expenditure towards the development of an organism at large. The branch of bioenergetics is mainly attributed to the application of thermodynamics to the biochemical reactions. Hans Krebs and Hans Kornberg are credited for introducing the application of thermodynamics to calculate and determine the free energy for the feasible biochemical reactions.

Thermodynamics is known to have an intimate alliance with the subject of bioenergetics which performs the fundamental study of protocols of energy production primarily through catabolic metabolism. Four fundamental laws of thermodynamics have been defined for justifying a variety of physical and chemical concepts like energy, entropy, enthalpy and temperature at macroscopic as well as microscopic level.

## Terms related to thermodynamics

Universe- the reacting system and its surroundings

System- Portion of universe under consideration; could be a reaction tube, an organism, a cell or a biochemical component of a metabolic pathway. Depending upon its ability to exchange matter and energy with the surroundings a system could be classified as an open system which can exchange both matter and energy or closed which exchanges only energy or an isolated system which can exchange neither of the two components. A living organism is an example of an open system which can take up nutrients as food excrete the wastes and generate work and heat in the process.

Surroundings- Rest of the universe; environment of the system  
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## Laws of thermodynamics

The four laws are defined as:

Zeroth law: If two systems have thermal equilibrium with a third system, they are thermally equilibrated with each other.

First Law: Heat is a form of energy and energy is conserved in nature. Thus one can see an alteration in internal energy values if there is a movement of heat in the system.

Second Law: When there is no thermal equilibrium in a closed system, there is a gradual increase in the randomness or entropy until thermal equilibrium or a state of maximum entropy is achieved.

Third law: When the temperature approaches zero, the entropy of a pure substance also touches zero.

Even though all the four laws are applicable to biology, the first and the second laws are more vital with respect to the biological perspective particularly in terms of their role in understanding the rate of a reaction and the attainment of subsequent equilibrium in terms of energy. They are especially significant owing to their applicability in

- Spontaneity in the biological reactions and understanding of the metabolism
- Energy released/acquired during metabolism especially biosynthesis
- Folding of the biomolecules in their native conformation
- Enzyme activity, muscle activity, membrane transport

### The first law

Illustrates the law of conservation of energy i.e. the energy can neither be created nor destroyed and just can be changed from one place or form to another place or form. Heat and work (measured in joules) are two synonymous forms of this inter convertible energy

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = q + w$$

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Wherein  $\Delta U$  is the change in the internal energy,  $q$  is the heat absorbed by the system from the surroundings, while  $w$  is the work done and could be either positive or negative in nature depending upon whether the work is done by the system on the surroundings (Negative) or down upon the system by the surroundings (Positive). In exothermic processes heat is released and  $q$  is negative in nature while in endothermic reactions system gains heat and hence  $q$  is positive in nature.

In terms of molecular motion heat is more random in nature than work which is more organized and represents the force times the distance being moved by the organism. Work could be of varied types like gravitation, gaseous expansion, muscular contraction, electrical force or it could even be a contradictory dissipative force of friction and viscosity.

The law also discusses the theory of internal energy and how it is related to temperature. Heat can't be contained in a system and hence flows from the higher temperature to lower temperature thereby leading to a change in the internal energy of the system. Internal energy can further be altered by the variation in a range of parameters including an establishment of a particular temperature, flow of heat and thus work which is composed of three energy elements i.e. kinetic energy, potential energy and internal energy is an amalgamation of the kinetic energy and potential energy interactions of the movements of its atoms for a given matter.

$$E_{total} = KE + PE + U_{system}$$

$$Q_{in} - Q_{out} = \Delta U_{system}$$

$$W_{net} = \Delta KE + \Delta PE + \Delta U_{system}$$

Hess law being an extension of the first law attributes the flow of heat in terms of evolution and absorption to be invariable and autonomous of the type of reaction. The henceforth change from one state to another is a cumulative effect of state variables like pressure, volume and  $n$  (number of moles). The specificity of the state is attributed to particular values of these state variables and another state is established if these values change. The so called change from first state to another is path independent ( $\Delta E$ ) even though  $q$  and  $w$  are path dependent.

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In the biological systems, the organisms have to perform a dual act of not only acquiring energy from their physical environment but also to convert or assimilate it into an utilizable form for their survival. Thus a cell with the help of its metabolic machinery converts the chemical energy of carbohydrates and lipids into its energy currency ATP which in turn is used to perform a variety of work like biosynthesis, transport, locomotion and reproduction.

Joule is the SI unit of energy and is correlative with the amount of work being done by a force of 1 newton over a distance of 1meter with its unit being  $\text{kg}\cdot\text{m}^2/\text{s}^2$ . Another unit associated with the heat facet of energy and is represented by calorie and expressed as the amount of energy which is used to increase the temperature of 1g of water by  $1^\circ\text{C}$ .

4.18 Joules = 1 calorie

Complete metabolic breakdown of food so as to release its energy content is represented as food calorie or Calorie.

1Calorie = 1000 calorie

### Enthalpy

A measurable slightly different alternative to internal energy is enthalpy. Usually an expansion work is a product of pressure and volume and is equivalent to

$w = -\Delta(PV) = -P\Delta V - V\Delta P$  ( A negative sign is indicative of work being done by the system on the surroundings)

Under constant P condition,

$$w = -P\Delta V$$

Also,

$$\Delta E = q_p - P\Delta V \text{ or } q_p = \Delta E + P\Delta V \text{ which is path independent}$$

$q_p$  is the heat content or  $\Delta H$  which represents enthalpy. Therefore

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$$\Delta H = \Delta E + P\Delta V$$

The value of  $\Delta H$  is indicative of the nature of the reaction (Exothermic  $\Delta H < 0$  or endothermic  $\Delta H > 0$ ) with respect to its surroundings. As is usually seen in most biological reactions there is little or no change in the value thereby implying that there is a negligible difference between  $H$  and  $E$ .

Usually the bond energy comprised of translation, vibration and rotation contribute additively to the extrinsic state function of  $\Delta H$ .  $\Delta H$  can't really determine the direction of the reaction as one can see that even in a single process of dissolving salts different kinds of reactions exist wherein the  $\Delta H$  value for these reactions could be either  $>$ ,  $=$  or  $<$  than 0.

### The second law

Entropy is the principal concept behind the second law which is an evaluation of the degree of randomness or disorder and the second law describes that any process in the universe proceeds with  $\Delta S$  being greater than zero. While introspecting on the feasibility and direction of a process it also emphasizes on the concept of entropy as being applied to the irretrievable nature of life and also on physical processes especially with respect to thermal conditions. Thus according to an efficient Carnot engine,

$$\Delta S = q_{\text{rev}}/T = > 0$$

Where  $q_{\text{rev}}$  is the maximum reversible heat change that can be transferred between bodies and  $T$  is the temperature.

Thus Entropy is the ratio of heat and temperature. At lower temperature, a greater heat change produces a greater entropy change. Therefore

$$\Delta q_{\text{rev}}/T = \Delta S_{\text{univ}} > 0$$

Ludwig Boltzmann analyzed entropy statistically and said that even though the distribution of energies of molecules in a system is graphically bell shaped in nature, whenever there is an increase in the number of possible states there is an increase in entropy. He gave a calculation to estimate entropy which is

$S = k \ln W$  (Wherein  $S$  is the entropy,  $k$  is the Boltzmann constant ( $R/N_A$  and is the ratio of gas constant  $R$  and Avogadro's number  $N_A$  and  $W$  is the number of ways a system can be arranged). The product should have a greater degree of freedom to have a positive entropy value. Usually a disorganized molecule has more possible states than an organized molecule.

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Usually with the consequent loss of energy to the surroundings primarily as heat, there is an increase in the randomness or entropy. Besides the loss of energy due to friction, attainment of equilibrium as well as diffusion of molecules from a concentration gradient is known to increase the entropy of the system.

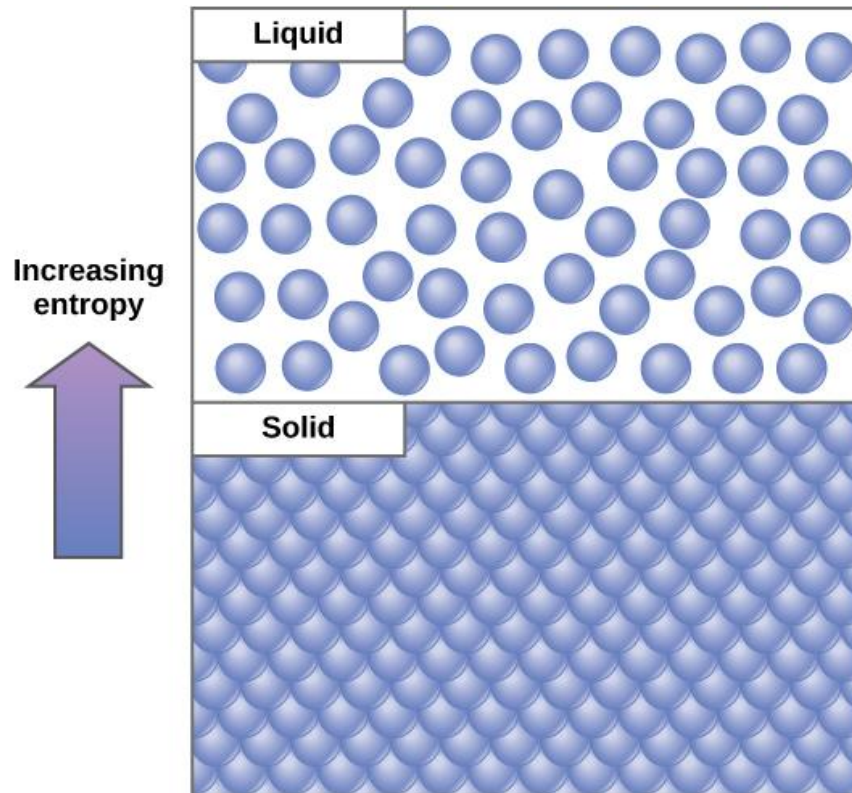


Figure: Entropy

Source: [https://www.boundless.com/image/fig-ch06\\_03\\_02](https://www.boundless.com/image/fig-ch06_03_02)

Thus two individual isolated molecular events with varied thermodynamic equilibrium would acquire communal thermodynamic equilibrium. An experimental entropy value is attributed to every probable status or condition which in turn defines the direction of work to be done by the system such that either there should be no or a positive change in its value. At absolute zero temperatures the entropy of a system achieves a steady value.

$$\delta Q = T dS .$$

The primary reason behind difficulties of performing a task by the living cell is being attributed to the second law. The inefficient energy transfers leads to loss of energy usually



in the form of heat as well as waste and byproducts especially in metabolic reactions thereby wasting a portion of energy. The increasing organized hierarchical organization of the living systems tends to reflect a disobedience of the second law. This misconception could be cleared by considering a living organism as an open system which can easily barter matter and energy with the surroundings thus increasing the overall entropy of the environment. This continuous process of inept energy exchange leads to continuous increase in the universal entropy thereby leading to a persistent efforts being done by the living organisms to regulate it.

### Concept of free energy

|   |
|---|
| <u>Thermodynamics</u>   |
| <u>Potentials</u>   |
| Free energy   |
| <ul style="list-style-type: none"><li>• <u>Free entropy</u></li><li>• <u>Internal energy</u><br/><math>U(S, V)</math></li><li>• <u>Enthalpy</u><br/><math>H(S, p) = U + pV</math></li><li>• <u>Helmholtz free energy</u><br/><math>A(T, V) = U - TS</math></li><li>• <u>Gibbs free energy</u><br/><math>G(T, p) = H - TS</math></li></ul> |

Free energy is the quantified energy which is available during chemical reactions for performing work after accounting for the loss of energy due to entropy. Josiah Willard Gibbs is credited with the measurement of this energy and since then it is also called Gibbs free

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energy (G). Unlike the second law of thermodynamics which is applicable to the universe Free energy also called Gibbs free energy is the competent energy content of a chemically reactive system through which a given work can be performed and gives us a fairly good idea about the preferential likes of the system towards a given reaction. This potential gets diminished when a system achieves equilibrium under constant conditions of temperature and pressure. The term is better expressed as  $\Delta G$  for an undergoing chemical reaction at a given temperature and is calculated by subtracting energy loss due to entropy  $\Delta S$  from the total energy change or enthalpy  $\Delta H$ .

$\Delta G < 0$  Preferential, spontaneous reaction

$\Delta G = 0$  Equilibrium with no favor to forward or reverse step of the reaction

$\Delta G > 0$  Non preferential, non-spontaneous reaction

Alfred Lotka is appreciated for the attempt for the understanding of the evolutionary with the free energy perspective. Gibbs free energy or G is a state function which correlates energy with entropy and is an important parameter which establishes spontaneity of a chemical reaction even in biological systems.

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

Where:

- $H$  is the enthalpy (SI unit: joule)
- $T$  is the temperature (SI unit: Kelvin)
- $S$  is the entropy (SI unit: joule per Kelvin)

While entropy has been described earlier, Enthalpy or H is the heat content of the system. It represents the number and kind of chemical bonds in the reactants and the products of the chemical reaction system.

$$\Delta H = \Delta E + P\Delta V$$

Where E is the internal energy of the system

P is the pressure and V is the volume of the system

A beautiful correlation exists between Gibbs free energy, the second law of thermodynamics and metabolism. While the spontaneity of a reaction depends on the negative values of free energy and increased or positive entropy, several endergonic biological reactions in

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metabolism of a living cells like photosynthesis and DNA synthesis are able to proceed in nature as they are coupled with exergonic reactions with a high negative  $\Delta G$  value such that the laws of thermodynamics are not defied.

### Standard and non standard free energy changes

Standard free energy change ( $\Delta G^\circ$ ) is measured as kJ/mol or kcal/mol under routine standard conditions for biological reactions of pH 7.0, 25°C and 1 atm pressure but may vary also in terms of free energy change a particular reaction ( $\Delta G$ ).

For a given equation,



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

Under equilibrium conditions when  $\Delta G$  is zero

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

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

Under steady state conditions as is seen in the cells where equilibrium is never reached,

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

$$\text{Or, } \Delta G = - RT \ln K_{eq} + RT \ln \frac{[C][D]}{[A][B]}$$

Or  $\Delta G = - RT \ln K_{eq} + RT \ln Q$  where  $Q$  is the mass action ratio and is represented as the ratio of product to substrate i.e.  $\frac{[C][D]}{[A][B]}$

Metabolic systems or pathways usually proceed as a linear string of reactions which have nearly the same rate of reaction and are usually exergonic in nature with  $Q < K_{eq}$ . Comprised of two types the first of this occurs in majority with abundant enzyme content in the cell and are very little displaced from equilibrium and hence are said to be in a state of near equilibrium with  $Q$  very close to  $K_{eq}$ . As a result these reactions become very sensitive to

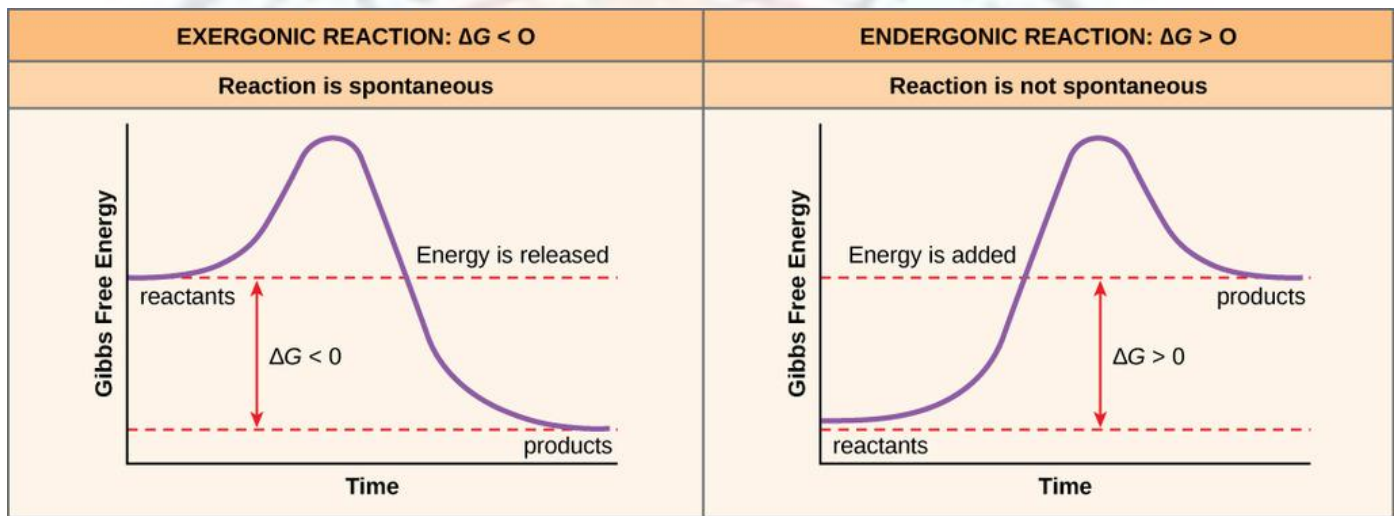
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the concentration of the substrate and product. Also these reactions are rarely under regulatory control.

The second type of reactions are rate limiting and irreversible in nature with stringent regulatory control and are lesser in number also their Q value is quite less than  $K_{eq}$ .

Thus a comparative analysis of the values of Q values with  $K_{eq}$  helps in determining the type of reactions.

### Endergonic and Exergonic Reactions



Source: <https://www.boundless.com/image/exergonic-and-endergonic-reactions>

#### Exergonic reaction

Exergonic implies the release of energy from a spontaneous chemical reaction without any concomitant utilization of energy. The reactions are significant in terms of biology as these reactions have an ability to perform work and include most of the catabolic reactions in cellular respiration. Most of these reactions involve the breaking of bonds during the formation of reaction intermediates as is evidently observed during respiratory pathways. The bonds that are created during the formation of metabolites are stronger than the cleaved bonds of the substrate.

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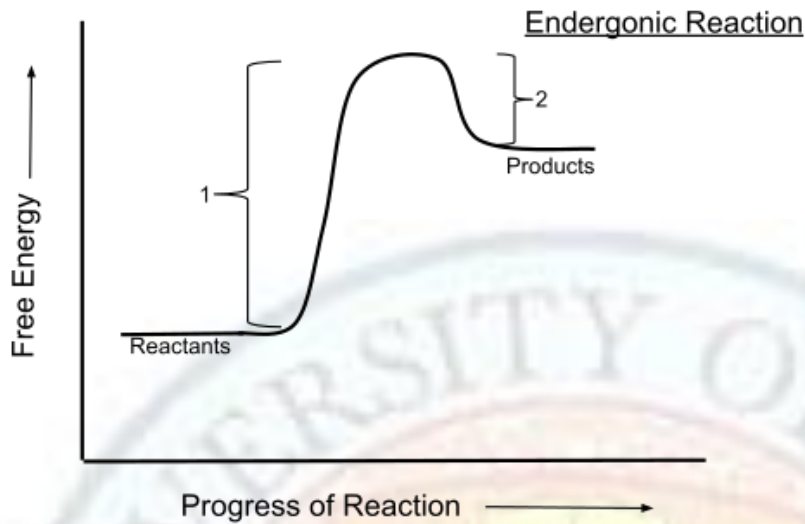


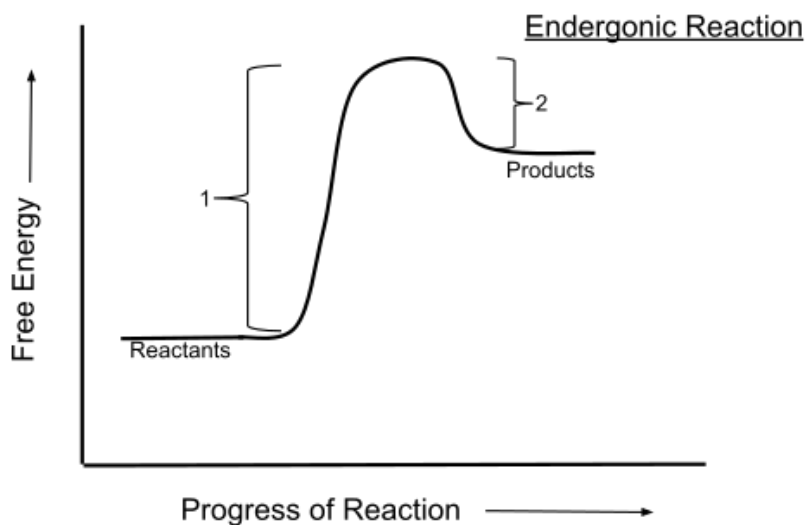
Figure: Exergonic Reactions

Source: [http://en.wikipedia.org/wiki/File:Endergonic\\_Reaction.svg](http://en.wikipedia.org/wiki/File:Endergonic_Reaction.svg)

$\Delta G = G_{\text{products}} - G_{\text{reactants}} < 0$ . In this case  $Q < K_{\text{eq}}$

### Endergonic reactions

Endergonic in turn is the opposite of exergonic in being non-spontaneous and requires an input of free energy. Most of the anabolic reactions like photosynthesis and DNA and protein synthesis are endergonic in nature.



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Source: [http://en.wikipedia.org/wiki/File:Endergonic\\_Reaction.svg](http://en.wikipedia.org/wiki/File:Endergonic_Reaction.svg)

$\Delta G = G_{\text{products}} - G_{\text{reactants}} > 0$ . In this case  $Q > K_{\text{eq}}$

Endergonic reactions are able to proceed in nature only when they are either dragged or shoved using an exergonic reaction such that the thermodynamic criteria of the feasibility of reaction ( $\Delta G$  negative and  $\Delta S$  positive) are achieved. The reaction is pulled or dragged when there is a brisk utilization of the products of the endergonic reactions by an ensuing exergonic reaction thereby ensuring that the concentration of the products of the endergonic reaction is always low.

The reaction can also be shoved or pushed by coupling them to strong exergonic reactions like ATP hydrolysis through mutual intermediates which provide the excess free energy required for the transition to occur. The relative strength of the bonds being formed due to endergonic reaction are generally weaker than the bonds that were originally present in the substrate.

| Category of Reaction | Spontaneity of Reaction | Variation in Free Energy ( $\Delta G$ ) | Variation in Entropy ( $T \Delta S$ ) | Variation in Enthalpy ( $\Delta H$ )                                     |
|----------------------|-------------------------|---|---------------------------------------|--|
| Exergonic            | Yes                     | Negative and $< 0$                      | Positive, increasing, Equal to 0      | Absorb/ release heat, so $\Delta H > / < 0$ with $\Delta H < T \Delta S$ |
| Exergonic            | Yes                     | Negative, $< 0$ .                       | Negative, decreasing, $< 0$ .         | Release heat, so $\Delta H < 0$ , and $ \Delta H  >  T \Delta S $        |
| Endergonic           | No                      | Positive, and $> 0$ .                   | Positive, increasing, and $> 0$ .     | Absorb heat, so $\Delta H > 0$ , and $\Delta H > T \Delta S$             |

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|            |    |                       |                                   |    |  |
|------------|----|-----------------------|-----------------------------------|----|--|
| Endergonic | No | Positive, and $> 0$ . | Negative, decreasing, and $< 0$ . | or | Absorb/release heat, so $\Delta H >/< 0$ with $ \Delta H  <  T\Delta S $ |
|------------|----|-----------------------|-----------------------------------|----|--|

Table: Properties of various reactions

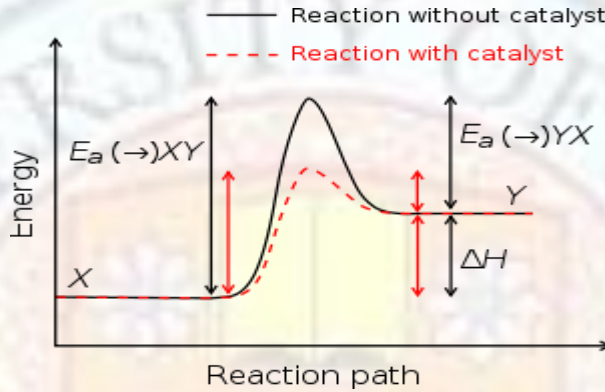


Figure: Activation energy

Source: [http://upload.wikimedia.org/wikipedia/commons/thumb/2/24/Activation\\_energy.svg/300px-Activation\\_energy.svg.png](http://upload.wikimedia.org/wikipedia/commons/thumb/2/24/Activation_energy.svg/300px-Activation_energy.svg.png)

### Activation Energy

This is the minimal amount of energy even required by the exergonic reactions to commence the energy-releasing reactions. Generally called activation energy ( $E_A$ ), this energy (usually provided as heat from the surroundings) brings about the much needed transition state before the downhill reaction is initiated. These values determine the rate of a given reaction and higher the value of  $E_A$  the slower the rate of the reaction.  $E_A$  are greatly lowered during catalysis especially by enzymes.

This is indeed interesting that  $E_A$  is required even for the reactions which have a negative  $\Delta G$  value. This is explained by the fact for the covalent bonds to break and release energy in catabolic exergonic reactions it is necessary that they should be contorted with a little energy. With respect to the reactants and products this contortion is highly transient and

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highest energy requiring in nature. Thus  $E_A$  is always positive in value. The fate of the reaction in terms of being exergonic or endergonic in nature is determined by the energy levels of the reactants and the products. The cumulative bond energy of the reactants and the products in the form of heat/temperature or pressure is known to accelerate the collision of molecules so that the activation energy barrier is crossed and transition state is reached. In biological system the presence of activation energy barrier especially for exergonic catabolic reactions of essential components of the cell protects them from self disintegration at room temperature.

### **Coupled reactions**

As discussed earlier chemical reactions can be explained with help of variations in free energy values i.e.  $\Delta G$ . In a given biochemical reaction under constant conditions, changes in enthalpy values  $\Delta H$  is the difference in the heat changes in the form of absorption or emission of heat in the initial and final state. In endothermic reactions this value is positive while in exothermic reactions this value is negative. For a reaction to be spontaneous in nature,  $\Delta G$  value has to be negative as this is the energy available for work.

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

Therefore a negative  $\Delta G$  and positive  $\Delta S$  reflects the spontaneity of the reaction as well as increased disorder and is thermodynamically favorable in nature and are called downhill reaction. The reaction emits heat and is exergonic in nature.  $\Delta G$  value of zero indicates equilibrium in the reaction. The reactions with a positive  $\Delta G$  are thermodynamically unfeasible and thus require an energy source for the reaction to proceed and are generally endergonic in nature and are called uphill reaction. Usually the endergonic uphill reactions have to be supported or coupled with an exergonic reaction so that the energy released by the second downhill reaction should be able to pull the first reaction to its culmination. The process is called coupling and the reactions are coupled reactions. It should be ensured however that the summative  $\Delta G$  should be negative in value. Usually ATP hydrolysis an exergonic reaction is coupled with endergonic reactions which exploit the energy released from the phosphate linkages of ATP.

Coupled reactions have an ability to share intermediates. Usually coupled reactions are described in terms of a cumulative  $\Delta G$  values from each reaction. Several times a non spontaneous unfavorable reaction with a positive  $\Delta G$  is clubbed with a second spontaneous highly favorable reaction having a negative  $\Delta G$  such that both the reactions can proceed



provided their additive  $\Delta G$  is negative in value. Several examples of such coupled reactions involve hydrolysis of ATP with other reactions which have a positive free energy value so that a negative  $\Delta G$  value could be attained. This coupling of reactions so that free energy values of the given reaction could be altered is the underlying basis of enzyme based reactions.

### Redox reactions

A variety of biochemical reactions are an outcome of energy transitions from one substrate to another and are classified as redox reactions. Redox reaction is comprised of two coupled reactions namely oxidation and reduction in which there is a gain of an electron in reduction and there is a loss of an electron in oxidation. The reactions have an analogy to acid base reactions and these transfers could be in the form of hydrogen or electrons at varying energy states. The transfers are simultaneous in nature and the reaction is split into two halves. There is a critical role of oxidation number (total charge exchanged) as this decides the number of electrons which are to be exchanged and is indicative of the strength of the redox reaction. These reactions are comprised of reducing equivalents or electron carrier intermediates which can donate and gain electrons thereby driving the reaction to proceed in a particular direction. NADH, FAD, NADPH are some of the examples of such carrier intermediates. The reactions are generally reversible in nature and usually work towards gaining equilibrium. Several metabolic process are comprised of redox reactions namely glycolysis, citric acid cycle and oxidative phosphorylation.

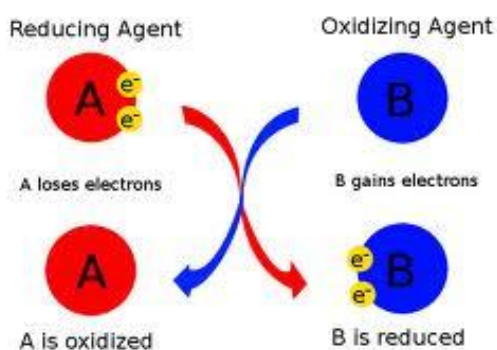
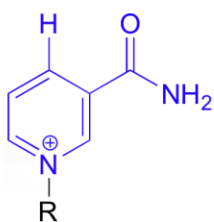


Figure: Redox reaction

Source: <http://chemwiki.ucdavis.edu/%40api/deki/files/140/reducingoxidizingdiagram.png>

hydride acceptor  
(oxidizing agent)



NAD<sup>+</sup>  
NADP<sup>+</sup>

hydride donor  
(reducing agent)



NADH  
NADPH

Figure: Role of NAD/NADP in redox reactions

Source: <http://chemwiki.ucdavis.edu/%40api/deki/files/3956/image037.png%3Frevision%3D1>

### ATP: structure, its role as a energy currency molecule

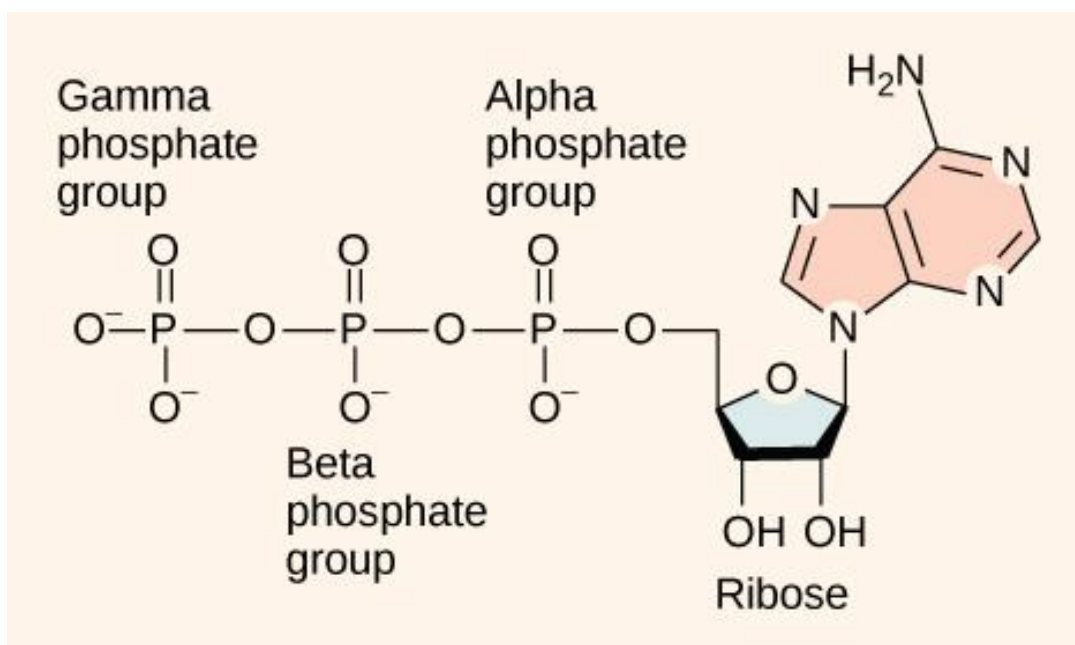


Figure: Structure of ATP

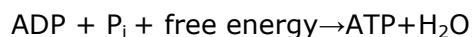
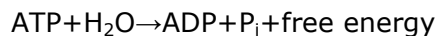
Source: <https://www.boundless.com/image/adenosine-triphosphate>

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Biological processes have tremendous amount of free energy which if left unchecked would create wasteful thermal movements and could even harm or demolish the cell. Also this energy is subsequently required for cellular processes. ATP or Adenosine triphosphate (ATP) is the nature's way of storing its excess free energy vital for ensuing metabolism. Therefore ATP is considered as the principle energy currency, the powerhouse or a rechargeable battery of the living cell. Karl Lohmann, Fiske and Y. Subbarao are credited with the discovery of ATP in 1929 while its role as an energy currency was discovered by Fritz Albert Lipmann in 1941.

The structure is comprised of a nucleoside adenosine (Adenine linked to a ribose sugar) to which three phosphate moieties are attached leading to the formation of three alternative forms AMP, ADP and ATP after every phosphate residue addition using enzymes like ATP synthase. The molecule generally is found complexed with magnesium ions in a living cell with a concentration of 1 to 10 mM. Owing to the strong repulsion between the phosphate moieties the ATP molecule is inherently unstable and can effortlessly be hydrolyzed into ADP to yield free energy exergonically. The  $\Delta G$  value of the reaction is  $-57 \text{ kJ/ mol}$ . The reaction is reversible in nature however free energy is required to regenerate ATP back from ADP as the three negatively charged phosphate residue require energy to contravene their repelling forces. The tremendous amount of free energy released by ATP drives several key exergonic and endergonic reactions in the living cell and is an integral part of cellular metabolism. Examples include its use in DNA replication, protein synthesis, muscle contraction, membrane transport etc.

Each of the three phosphate linkage (phosphor anhydride bonds) labeled as  $\alpha$ ,  $\beta$  and  $\gamma$  have tremendous potential energy when broken yields a very high amount of energy which is used either as energy to perform work or to phosphorylate a given substrate which in turn alters the native conformation so that the reaction can proceed further. Each cleavage is associated with release of an inorganic phosphate group along with ADP/AMP.



However ATP as a molecule is degenerative in nature and has to be swiftly utilized to perform work or its hydrolysis will lose the free energy as heat. It is also observed there is a

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lesser difference in  $\Delta G^\circ$  for the breakdown of AMP to adenosine than from the hydrolysis of ATP to ADP or AMP. This is due to increased entropy owing to the splitting. Also the negative repulsive forces functional in the phosphoryl groups are relieved and their resonance possibility is increased.

It is important that ATP should be coupled to key reactions by energy coupling. Several examples of such energy coupling exist in metabolism in which the exergonic process of ATP hydrolysis is used to gear up several endergonic reactions. A typical example is seen during glycolysis where glucose moiety is phosphorylated using hydrolysis such that the high energy unstable intermediate glucose-6-phosphate is readily converted to phosphorylated fructose using enzymes and thus provides the necessary product required for the glycolysis to proceed. Similarly in the case of sodium potassium pumps in the nerve cells the energy required to create the action potential which conveys the nerve impulse is created using ATP hydrolysis. This action potential is characteristically an outcome of the movement of the sodium and potassium ions across the membrane. The breaking of the high energy phosphate bond of ATP provides the requisite energy to this pump through phosphorylation which in turn undergoes a conformational change so that the two ions of sodium can move out of the cell. The process is completed by the influx of three potassium ions which again assist in altering the conformation of the pump so that it can be dephosphorylated and hence regain its natural shape.

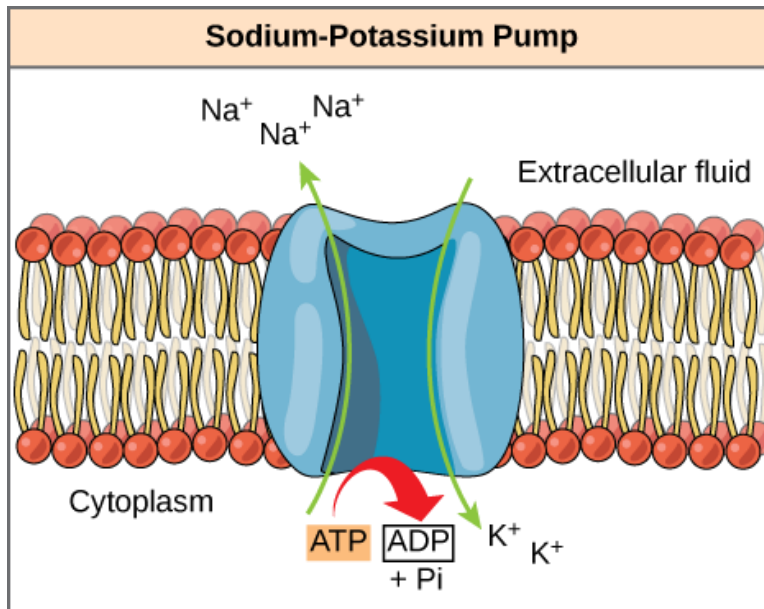


Figure: Sodium potassium pump

Source: <https://www.boundless.com/image/energy-coupling>

### Uses of ATP

Besides being the energy currency of the cell as is seen in energy coupling, ATP can also be used in energy maintenance. The process of energy maintenance is performed with help of three enzymes namely Creatine phosphokinase, adenylate kinase and NDP kinase. Creatine phosphokinase is a predominant muscle enzyme which converts creatine into creatine kinase using ATP and the reaction is near equilibrium in nature. During muscle contraction the reaction reverses and shifts its direction into the formation of creatine thereby leading to the replenishment of ATP which is intensely required at that time. Similarly both NDP kinase and adenylate kinase by having an equilibrium constant of 1 or by being in a near equilibrium state help in the maintenance of ATP levels in the cell.

ATP is also used as a coenzyme. The ATP molecule is produced during several metabolic processes which include substrate level, oxidative or photo phosphorylation, respiration, fermentation etc and predominantly found in the mitochondria and chloroplast. It is consumed in processes like biosynthesis of DNA and proteins, mobility, transport and cellular division. ATP also has a critical role to play in signal transduction process where several kinases involved use ATP for phosphorylation and adenylyl cyclase use it for the production of cyclic AMP, the second messenger. ATP is also integrated during transcription into nucleic acids.

### Summary

- Four fundamental laws of thermodynamics have been defined for justifying a variety of physical and chemical concepts like energy, entropy, enthalpy and temperature at macroscopic as well as microscopic level.
- Zeroth law: If two systems have thermal equilibrium with a third system, they are thermally equilibrated with each other.
- First Law: Law of conservation of energy.
- Second Law: When there is no thermal equilibrium in a closed system, there is a gradual increase in the randomness or entropy until thermal equilibrium or a state of maximum entropy is achieved.
- Third law: When the temperature approaches zero, the entropy of a pure substance also touches zero.

## Bioenergetics

- Gibbs free energy or  $G$  is a state function which correlates energy with entropy and is an important parameter which establishes spontaneity of a chemical reaction even in biological systems.
- Exergonic implies the release of energy from a spontaneous chemical reaction without any concomitant utilization of energy.
- Endergonic in turn is the opposite of exergonic in being non-spontaneous and requires an input of free energy. Most of the anabolic reactions like photosynthesis and DNA and protein synthesis are endergonic in nature.
- Activation Energy is the minimal amount of energy even required by the exergonic reactions to commence the energy-releasing reactions.
- In coupled reactions usually the endergonic uphill reactions have to be supported or coupled with an exergonic reaction so that the energy released by the second downhill reaction should be able to pull the first reaction to its culmination.
- Redox reaction is comprised of two coupled reactions namely oxidation and reduction in which there is a gain of an electron in reduction and there is a loss of an electron in oxidation.
- ATP or Adenosine triphosphate (ATP) is the nature's way of storing its excess free energy vital for ensuing metabolism.
- The tremendous amount of free energy released by ATP drives several key exergonic and endergonic reactions in the living cell and is an integral part of cellular metabolism. Examples include its use in DNA replication, protein synthesis, muscle contraction, membrane transport etc.

### Exercise/ Practice

- **Fill in the blanks**

1. ----- are credited for introducing the application of thermodynamics to calculate and determine the free energy for the biochemical reactions. Hans Krebs and Hans Kornberg
2. In exothermic processes heat is released and  $q$  is ---- in nature while in endothermic reactions system gains heat and hence  $q$  is ---- in nature. Negative, positive

## Bioenergetics

3. Work is composed of ----, ----- and ----- . Kinetic energy, potential energy and internal energy
4. Besides the ----- due to friction, attainment of equilibrium as well as diffusion of molecules from a concentration gradient is known to increase the entropy of the system. loss of energy
5. This potential gets diminished when a system achieves ----- under constant conditions of temperature and pressure. Equilibrium
6. -----brings about the much needed transition state before the downhill reaction is initiated. Activation energy ( $E_A$ )
7. The fate of the reaction in terms of being exergonic or endergonic in nature is determined by the ----- of the reactants and the products. Energy levels
8. Role of ATP as an energy currency was discovered by ----- . Fritz Albert Lipmann.

### ▪ State True or False

1. Enthalpy or H is the heat content of the system. True
2. The bonds that are created during the formation of metabolites in exergonic reactions are weaker than the cleaved bonds of the substrate. False
3.  $E_A$  are greatly increased during catalysis especially by enzymes. False
4. Several examples of redox reactions involve hydrolysis of ATP with other reactions which have a positive free energy value so that a negative  $\Delta G$  value could be attained. False
5. Redox reactions have an analogy to acid base reactions and these transfers could be in the form of hydrogen or electrons at varying energy states. True
6. Karl Lohmann, Fiske and Y. Subbarao are credited with the discovery of Activation energy. False
7.  $\Delta G$  value of the ATP hydrolysis reaction is -257 kJ/ mol. False
8. ATP generally is found complexed with magnesium ions in a living cell with a concentration of 1 to 10 mM. True

### ▪ Short answer questions

1. The first and the second laws are more vital with respect to the biological perspective. Justify.

## Bioenergetics

2. Define the four laws of thermodynamics
3. Why is activation energy required even for the reactions which have a negative  $\Delta G$  value?
4. The ATP hydrolysis reaction is reversible in nature however free energy is required to regenerate ATP back from ADP. Explain.
5. ATP hydrolysis is coupled to endergonic reactions. Explain the significance with the help of an example.
6. List some uses of ATP
7. How are entropy and enthalpy correlated with each other?

### Glossary

- ATP: Adenosine triphosphate, a nucleotide which is the energy currency of the cell
- Gibbs free energy: energy content of a chemically reactive system through which a given work can be performed
- Potential energy: The inherent energy of a molecule owing to its position or condition
- Endothermic: Reactions which absorb energy from the environment
- Endergonic: a reaction which absorbs (heat) energy from its environment to proceed further into products.
- Exothermic: Reaction that releases energy in the form of heat
- Hydrolysis: Breakdown of the molecule in the presence of water.
- Exergonic: a reaction which releases energy (especially as heat).
- Enthalpy: Total energy of a thermodynamic system.
- Entropy: Tendency of a system to randomness
- First law of thermodynamics: law of the conservation of energy
- Second law of thermodynamics: Describes the role of entropy in the universe
- Activation energy: Energy which initiates a reaction
- Transition state: An intermediate with higher energy than both the reactants and the products.
- Equilibrium: A balanced state with no net change.
- Heat: Energy transition from one system to another by thermal interaction
- Metabolism: an array of chemical reactions that happen in living cells



## References/ Bibliography/ Further Reading

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