# Bioenergetics-The Principles of thermodynamics in living World

**R. K. Prajapati**

Associate Professor

Department of Chemistry

D J College Baraut, Baghpat,

U.P., India

_____

**Introduction**

Bioenergetics or biochemical thermodynamics involves the study of free energy changes accompanied during the biochemical reactions. It has been established that these reactions are accompanied by release of energy from substrates or a system when it moves from a higher to a lower energy level of products. Most frequently, the excess energy is liberated as heat or light. In material systems, heat energy is transformed into thermal or electrical energy. As it is clear that biological systems are exclusively isothermic, no direct use can be made of heat liberated in biological reactions to continue the vital process where input of energy is required. A continuous input of free energy is utmost required in living organisms for performing three major biological processes which are as follows

1.    To perform mechanical work in body tissues, for locomotion.

2.   In transport of molecules and ions by active transport Mechanism and in other cellular functions.

3.   For biosynthesis  of biomolecules (Proteins, nucleic acids and carbohydrates) from its simple monomers precursors and also in synthesis of other important macromolecules (ATP, NADPH etc).

The required change in free energy for such processes are directly derived from the environment by oxidation reactions, chemical linkage  or coupling and in such a way an organism maintains a state which is away from equilibrium. This process is presented  in (Fig.1).
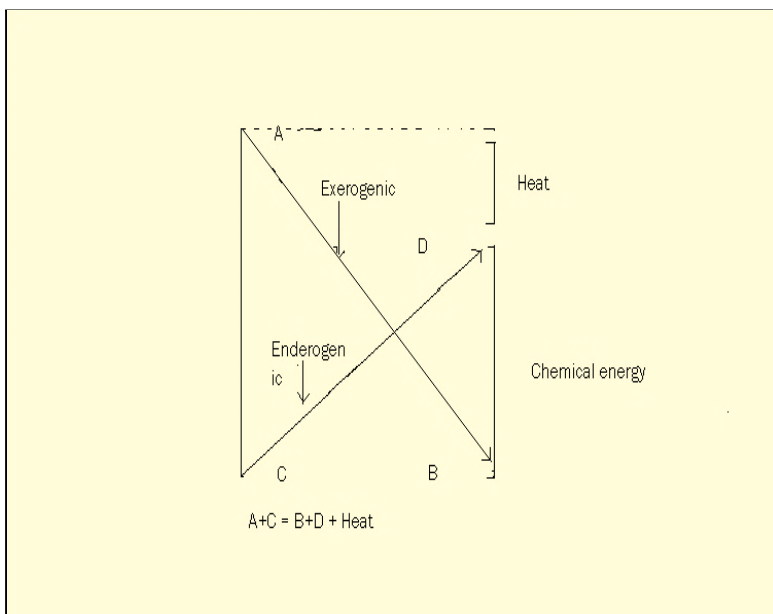


**Fig. 1. Coupled exergonic and endergonic reaction.**

The conversion of metabolites/biomolecules A into B is taking place with release of energy and which is utilised in coupling of another reaction where energy is required in conversion of C into D.

In biological systems the terms exergonic and endergonic are used in chemical reactions rather than the common terms viz. exothermic and endothermic used in chemical sciences. Exergonic reactions are those reactions in which there is release of free energy whereas in endergonic reactions, there is gain in free energy. These energy gain or loss may be in the form of heat, chemical or even in form of electrical energies. An endergonic reaction always occurs in combination of a coupled exergonic/endergonic reactions and energetically, the overall complete process is exergonic. The exergonic reaction happens in catabolism ( which involves breaking down of molecules, e.g, glucose and releases energy by oxidation) where as the synthetic reactions in which molecules are synthesized is termed as anabolism and the complete process which include catabolism and anabolism is known as metabolism. The biosynthesis of DNA is an example of anabolism, where energy is converted into useful work in the form of information which is used during protein synthesis and as the genome of the organism. Biochemically, catabolism is a highly controlled combustion process which is achieved by the oxidation of nutrients (mostly of glucose) in the cell and energy is liberated mostly in form of work and in trace as heat. Thus substrates such as carbohydrate and fat are broken down into carbon dioxide, water by oxidative process is a highly exothermic and released energy is used in doing useful work and some excess energy is lost as heat from the organism which can be easily explained on the basic principle of thermodynamics. Hence, in discussing about the phenomena of bioenergetics, it is necessary to know basic ideas of thermodynamics.[1-3]

**2.Thermodynamic Approach**

All the natural processes occurring in nature are accompanied by change in energy. The various principles of

thermodynamics have been used to study the interconvertibility of the different forms of energy into heat, in finding out the relationship between the different properties of the matter which are deduced from these thermodynamics laws. All laws of thermodynamics are postulated on three facts which had been accumulated from the experience of humans with energy. These laws have been tested from time and are valid but do not depend on any theory pertaining to atomic and molecular structure.

**2.1. Scope of Thermodynamics.**

All three laws of thermodynamics including zeroth law of thermodynamics have been deduced from rigorous mathematical treatment which are used to correlate the various properties of matters in gas laws, chemical equilibrium, Phase rule, Distribution law, Vant Hoff's law for dilute solutions, Raoult's laws of thermodynamics. It also provides the theories for predicting whether a particular change or transformation which may be either physical or chemical will be possible to occur or not under a given set of variables temperature, pressure and concentration until the equilibrium condition has been achieved.

**2.2. Limitations of thermodynamics.** The limitations of thermodynamics can be summarised as follows.

Thermodynamics are based on assumptions experienced by the human through years about the behaviour of matter in macroscopic systems or as such in bulk. Hence, the prediction from thermodynamics is applicable to macroscopic properties of systems which consider matter in bulk instead of the microscopic properties of a system accounting with individual atoms or molecules at quantum levels and ignores the internal structures of atoms and molecules.

It does not bother about the time factor for completion of a process and also does not predict the rate at which a physical change or chemical reaction will occur. Thermodynamics is

concerned only with the preliminary and the final state of a system during a change. Laws of thermodynamics provide relationships between various observed properties which have been obtained from experiments. But it is unable to provide the actual values of these properties and also fails in offering any plausible theory to validate why these properties are appearing in a system. For example, kinetic molecular theory of gas explain the pressure of a gas  is due to the impacts of individual molecules on the walls of the container,  and is a measured as force  exerted by these impacts per second of time whereas in thermodynamics, pressure of a gas is only a property of the state of the system regardless of its constitutions.

**3.Thermodynamic terms and basic concepts**

In study of thermodynamics following terms such as  system, boundary, surroundings are often used and they are defined as-

**3.1 System.** It is the part of the universe in which thermodynamic investigation/study is carried out and the remaining part of the universe is called as surrounding or it may be described as the specific portion of the universe, larger or smaller, on which effects of certain properties such as temperature and pressure are being studied. (Fig. 2)

**3.2. Surrounding.** The real or imaginary line/surface which separates a system from  the surrounding is known as the boundary of the system. In such a way a system is  separated from the rest of the universe, i.e. with the surrounding and across it heat and/ or matter or other form of the energy may or may not pass through it.
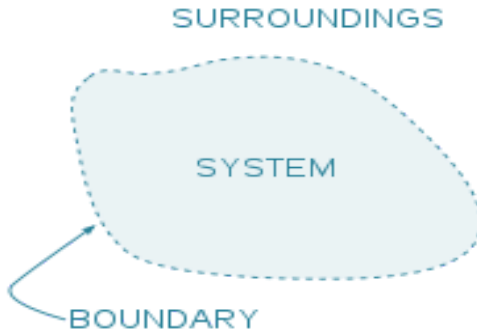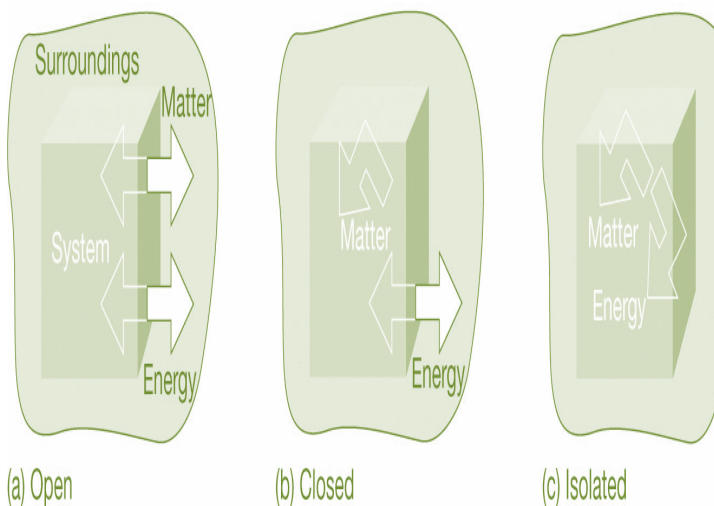
**Fig. 2. A typical thermodynamic system.**



**Fig. 3. Direction of flow of energy and matter in open, closed and isolated systems.**

### 3.3. Systems in Thermodynamics.

Chemical composition of a system is uniform in a homogenous system. There is only one phase in a homogenous system. For example, pure solid, liquid or gas, solution of salt in water and

mixture of gases. Heterogeneous system is made up of more than one phase and constituent particles are not uniformly distributed throughout the system. Examples- a piece of ice in contact with water and vapour, etc.

On the nature of the boundary of a thermodynamics system and possibility of exchange of heat and mass to the surrounding, thermodynamic systems have been classified into three categories.

**Isolated system.** In an isolated system, the boundary of the system is both sealed and insulated and so no exchange of energy and matter can passthrough the system to the surrounding and vice versa. Isolated systems are thermally isolated and mechanically isolated.

**Closed system.** Only exchange of energy is possible in closed system across its boundary to the surrounding but there is no exchange of mass from system to surrounding.

**Open system.** Boundary of an open system is open and uninsulated, hence in an open system exchange of both energy and matter occurs from system to surrounding. (Fig. 3 and 4) Cell in living organisms is an example of an open system because exchange of nutrients, harmful substances and energy takes place through the cell membrane.[4-7]
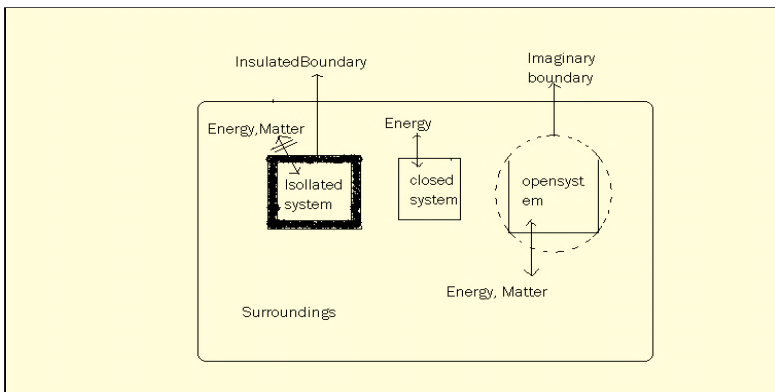
**Fig. 4. Diagramatic representation of three types of thermodynamic systems.**

The three thermodynamics systems are diagrammatically represented in (Fig. 4).

**3.4. Intensive and extensive properties.**

Physically observable macroscopic properties of a system in bulk are mainly of two types:

**Intensive properties:** Physical properties whose values are independent of the quantity of matter present in the system are called intensive properties e.g., pressure, temperature, density, and concentration are intensive properties of the system and these are additive properties.

**Extensive properties**: Physical property whose value is dependent on the quantity of the matter present in the system under consideration is known as extensive properties e.g., mass, volume, internal energy, enthalpy, entropy and Gibbs' free energy and these are not additive properties.

**4. Thermodynamic equilibrium**

The laws of thermodynamics for a given system is only concerned with its equilibrium states and a system is present in thermodynamic equilibrium only when any of its observable properties such as temperature, pressure, volume, etc. does not vary with time. In thermodynamic studies, three types of thermal, chemical and mechanical equilibrium must exist simultaneously in a system. In thermal equilibrium temperature must remain constant, in chemical equilibrium, compositision should not change with time and in mechanical equilibrium no matter in any form such as its fragments/ particles/ constituents should exchange from the system. The system in which diffusion or fast chemical reactions are happening is not in thermodynamic equilibrium and as such is not chosen for thermodynamic studies.(Fig.5)
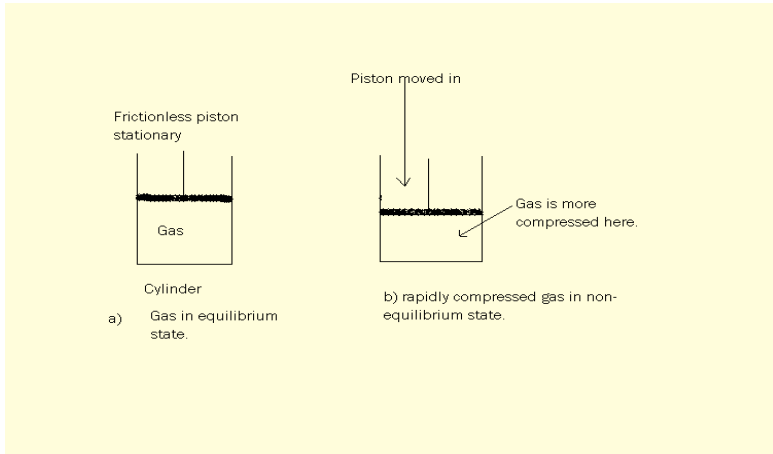
**Fig. 5. (a) Equilibrium state  and (b) Non- equilibrium state.**

**4.1. Non-equilibrium state of thermodynamics system.**
Non-equilibrium state of thermodynamics in a given system does exist when different parts of the system possess different  values of state variables. A typical example of non-equilibrium state can be seen when a gas taken in a cylinder is subjected to compression  rapidly by moving down the piston where it  passes through states in which pressure and temperature cannot be specified because they vary throughout the gas. (Fig. 5) The gas in the vicinity of  the piston is rapidly compressed, consequently gets heated while at the farther end of the cylinder gas is not heated and this state is known as non-equilibrium state of gas. [8-10]

**4.2. Thermodynamic processes**.

The thermodynamic processes in which the changes in state  of a system are observed by change in temperature, pressure and volume, then following different types of processes have been carried out. ( Fig. 6) (1) Isothermal process. During isothermal process temperature of a system remains constant and it is carried out  by keeping the system in a thermostat.

During the isothermal process, change in temperature (dT) is zero. (2) Adiabatic Process. During adiabatic process, no heat exchange into the system from the surrounding and system is kept in an insulated container or in a high vacuum flask and or in highly polished surfaces. In an adiabatic process change in heat (dq) is zero. (3) Isobaric process. This process is carried out at constant pressure. Melting of water at freezing point at constant atmospheric  pressure is an example of an isobaric process. In an isobaric process change in pressure (dp) is zero. (4) Isochoric process. In this process the volume of a system remains constant during operation. When a gas is heated  in a non-expanding chamber then its volume remains constant. In an isochoric process change in volume (dV) is zero.(5) Cyclic process. In a cyclic process, a system in a given state goes through a number of different processes and finally  returns to its initial state. In the cyclic process dE = 0, dH= 0.
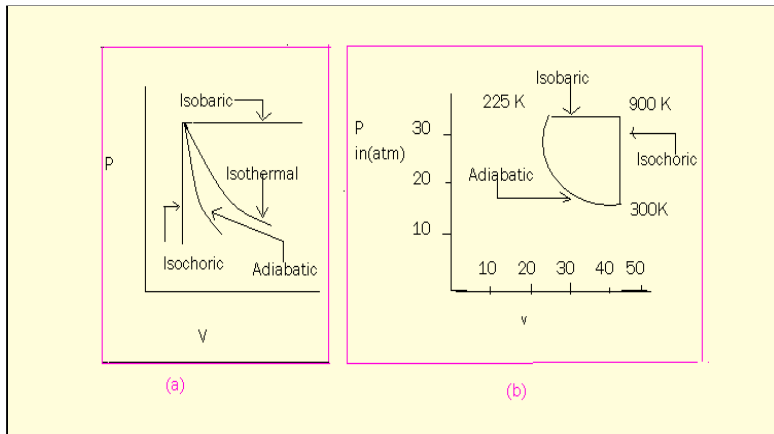


**Fig. 6. (a) Four Basic thermodynamic processes and (b) A cyclic process.**

**5. Application of thermodynamics in biological systems.** In the biological system molecular complexity and orderliness is

found in contrast to the randomness in the nonliving system. The concept of energy is important prior to describing the application of thermodynamics in biological systems.

**5.1. Energy.** Energy is defined as the property which can be produced from or converted into work or capacity to do work is energy. In mechanics, work (W) is a force  applied on a  body and is a product of   force (f) into displacement (s) i.e.,   W= f.s

Many examples of energy and its interconversion in work can be seen in biological systems e.g., during muscular contraction and relaxation stored energy in   protein fibres is released which is utilised in work during movement, in uplifting a weight, and so on. Constant exchange of food materials, ions, water and electrons in biological cells by diffusion/active transport mechanism across cell membranes from one cell to another, synthesis of biomolecules and cell division are also examples of work at the molecular level. Energies for all these biological works and processes  are provided from foods.

Erg (in CGS system)  is a smaller unit of energy and work and  a bigger unit  used is Joule (J). 1.0 joule is equal to $10^7$ ergs and Calorie is unit of heat (q).  When a system absorbs heat from the surrounding then heat is considered as positive and symbolised as (+q) and opposite to it, when heat is transferred from the system to the surrounding then it  is considered as negative and symbolised as (-q); w is symbol of work. If work is done by the surrounding on a system  and consequently increase energy of a system, then work is positive (+w). When work is done on the surrounding by the system and energy of the system is decreased, then work is negative (-w). (Fig. 7) Different laws of thermodynamics are as follows which are very useful in predicting the feasibility of a process in non living and living systems.
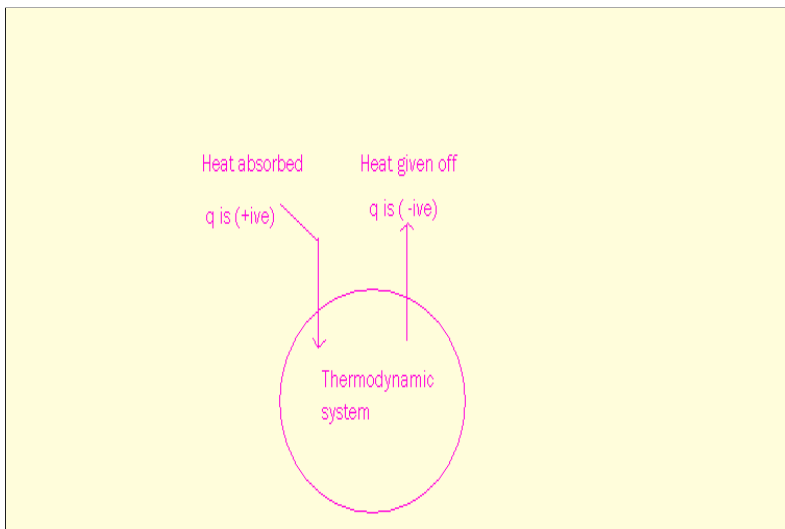
**Fig. 7. The direction and sign convention of heat flow in a thermodynamic system.**

**5.2. 1st law of thermodynamics.** In simple words, it is the law of conservation of energy and manifest conservation principle of energy. This law has been defined in various ways as follows keeping the basic idea that energy neither can be created nor can be destroyed but it only transforms from one form to another form.

The total energy of an isolated system always remains constant and it may change from one form to another form or total energy of a system and the surrounding remains constant. So, energy in the biological system is not consumed rather than it is transformed into different forms of energy.

**5.3. 2nd law of thermodynamics.** 2nd law of thermodynamics predicts the randomness in a system. During all physical/chemical changes there is an increase in the disorderliness or randomness in the system and surrounding which is measured as entropy. In the living system, it is an

intricate problem to maintain orderliness in an environment that is relatively disordered  and it increases more as time gradually changes. In the biological system two laws of thermodynamics are followed and there is a high degree of molecular orderliness that must be paid for in some way since it can not arise spontaneously from disorder. According to the laws of thermodynamics the biological system has the following properties.

i. **It utilises the useful free energy.** The living organism takes the energy  directly or indirectly which is used as useful  work under special conditions of temperature and pressure in which they live and they return the equivalent amount of energy to the environment in some other form. The less useful type of energy which a  living cell returns back to the environment in form or in other forms which are quickly randomised in the environment and thus increase its entropy.

ii**. They  usually exist in a steady state (Physiological steady state).** Precisely living organisms are in the steady state rather than in equilibrium state. This is a condition of open state where the rate of transfer of matter and energy from the environment into the system and vice versa is exactly counter balanced in a steady way. Living organisms are efficiently prone in handling energy and matter. They greatly exceed most man made machines in the manner in which they convert input of energy into work.

The environment in which the living system lives is absolutely suitable for them. They derive energy as well as raw food materials for their sustenance. In view of thermodynamics, the living system behaves as an  open system because exchange of matter and energy to the environment occurs in such a way that they easily assimilate the energy in the form of biomolecules.  Living system is not in equilibrium to the

environment because they are not changing over a period of time as it appears. But they exist in a steady state (Fig.8). Molecular machine is an example of a non-equilibrium system and the cell extracts free energy from the environment in such a way that it increases the randomness. Here it is pertinent to emphasise that the living system reflects an example of the principle which is known as the principle of maximum output. This principle explains why a living system is highly efficient in handling energy and matter.

The analysis of the magnitude and the efficiency of energy exchange in the steady state or open system is much more complex than the closed system. Here, equilibrium thermodynamics may be applicable in the case of a closed system. But for open or steady state non equilibrium or irreversible thermodynamics can be used for analysis.[11-15]
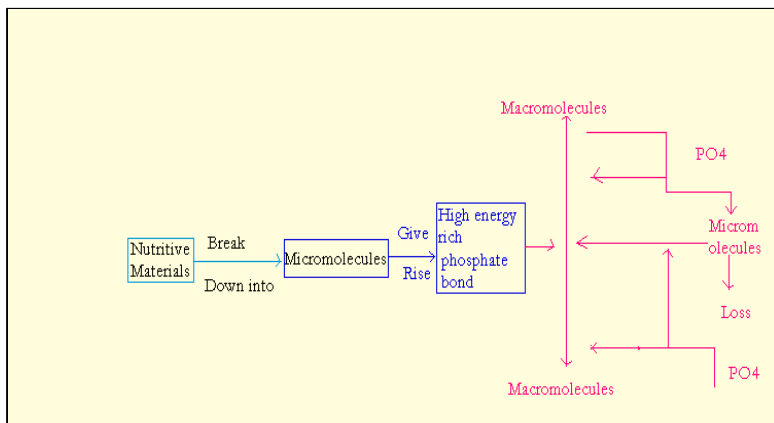


**Fig. 8. The diagrammatic representation of a cell in steady state.**

iii. Living organism is an example of a non-equilibrium system. Had it been in an equilibrium system then it would have not performed the work. Many physical as well as biological processes e.g., the transport of molecules, energy and electricity,

nerve conduction, muscle contractions, and other complex coupled reactions are occuring in open systems with irreversible changes in non-equilibrium state. Many of these biochemical reactions take place by coupled reactions from where they derive free energy. So, the non-equilibrium thermodynamics theory is used to describe the biological processes. Because of the non-equilibrium system it performs work. Living organism is an example of the isothermal system which can be understood by the fact that at any given time all parts of the cell have the same temperature.

iv. It also does not behave like a heat or electrical engine but it works like an isothermal chemical engine. The energy that a cell extracts from the environment is transformed into chemical energy to perform the biochemical work for synthesis of cells constituents, osmotic work, transport of materials into the cells, nerve conduction, mechanical work of muscle contraction and energy for movement i.e. for locomotion. [16-18]

**5.4. Internal energy.** Any system containing some definite quantity of matter always possesses some definite amount of energy within itself and all possible kinds of total energy present in a system is termed as internal energy (E). Its magnitude is the algebraic sum of the transnational, rotational, vibrational energies of motion of molecules as well as kinetic and potential energy of the nuclei and electrons within the individual atoms of those molecules. It is a  state function of the system and an extensive property. It is not possible to calculate the  absolute values of internal energy of a system and change in internal energy (ΔE) is measured when a system goes from one state to another state.
 (ΔE) is given by following expression,

ΔE  = Final - Initial

ΔE is (+ive) when Final >  Initial  and  ΔE is ( -ive )  when Final ₍  Initial.

In general, there are many ways or paths of carrying a system from one state a to another state b. At each stage, different values might be expected to be obtained the values of ΔE a→b for each of these different processes.This statement can be verified by fact that if we consider the path 1 by which system is changing from state a to b where system is gaining the energy from the surrounding. Again consider the case in which the system is restored to state a by path 2 ( shown in Fig. 9), the system is paying back less energy to the surroundings and here, it is gaining energy in the process.
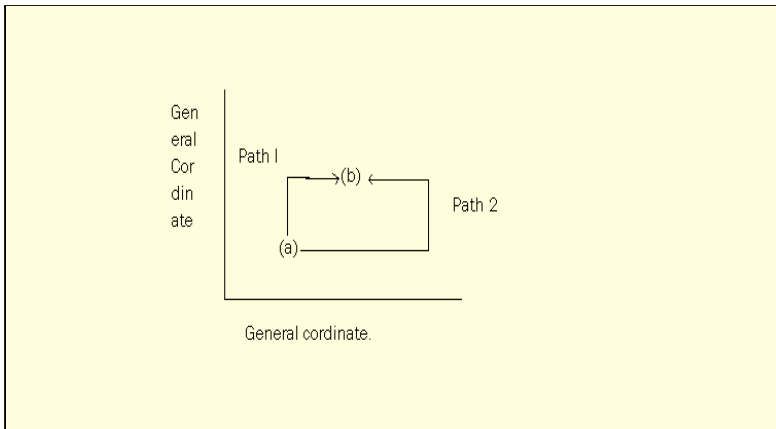


**Fig.9. Path of Processes.**

Hence,        ΔE        a→b            =        $E_b$        $-E_a$ ...1

**5.5. Enthalpy.** The heat content of a system at constant pressure is equal to the internal energy (E) and  product of the Pressure Volume work and is called as enthalpy (H) of a system. Enthalpy is the state function and does not depend on the path by which change is done in the state of the  system.

Numerically,

  H =   E + PV                                            ...2

The change in enthalpy ($\Delta H$) from initial state (1) to final state (2) of a system is given by the following expression.

$$\Delta H \qquad = H_2 \qquad\qquad - \qquad\qquad H_1 \quad ...3$$

$$= \Delta E + \Delta PV$$

When pressure is constant, then $\Delta H = \Delta E + P\Delta V$

or, $\qquad \Delta H = \Delta E + w \qquad\qquad [w = P\Delta V]$ ....4

the 1st law of thermodynamics defines $\Delta E = q - w$. Hence equation (4) is expressed as $\Delta H = q_p$. $\Delta H$ will be (+ive) when $H_2 > H_1$ and the process is called an endothermic reaction and $\Delta H$ (–ive) when $\Delta H = H_{1>} H_2$ and the process is called an exothermic reaction. The changes in enthalpy during a process arises due to change in ionic, covalent bonding, van der Waals, hydrogen bonding and change in charge interactions from product to reactant.

## 6. 2nd law of thermodynamics

The 1st law of thermodynamics states the principle of conservation of energy but does not say anything about whether a process of change occurs then what will be its direction. It also does not predict the circumstances and to what extent it is possible to change one form of energy into another led to the formulation of the 2nd law of thermodynamics which predicts direction from which heat will flow and the extent to which heat will be converted into the work. It is defined as follows: Spontaneous process takes place by increase in entropy.

or

It is not possible to make a machine which will transform all heat into an equivalent amount of work without making some changes in other parts of the system.

## 6.1. Spontaneous Processes

The process or a reaction which is occurring automatically without any external assistance is called a spontaneous process. Opposite to it is a nonspontaneous process, which does not occur on its own and it happens with aid of external assistance. The examples of spontaneous processes are 1) Toppling of spherical body, 2) Flow of heat. If a metal rod is heated from one end    and the other end is kept cold then at equilibrium, the temperature of the whole rod will be the same by spontaneous flow of heat from the hotter end to the colder end.

## 6.2. Characteristics of spontaneous process.

The important characteristics of the spontaneous processes are as follows as represented in (Fig. 10).

-Spontaneous process is unidirectional and work has to be done when change is made in reverse direction.

-Time is not a factor for spontaneous processes. It may happen in a short time or it may take a long period of time.
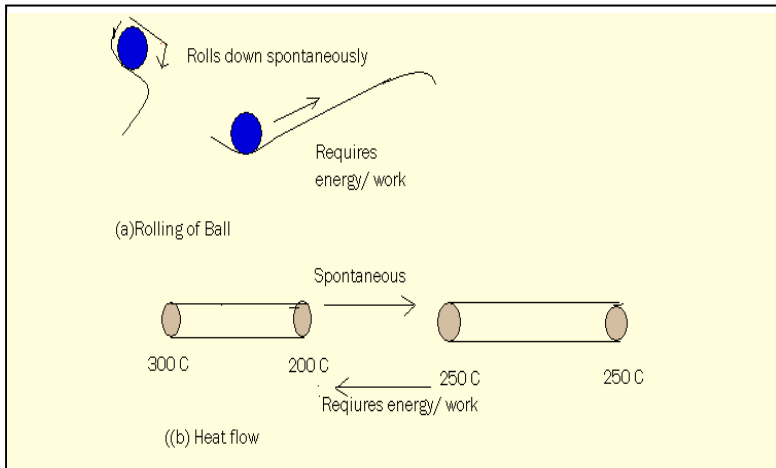


**Fig. 10. Spontaneous Processes.**

The spontaneous process occurs till equilibrium has not been achieved.  Once equilibrium has been attained, no further

307

spontaneous process occurs at equilibrium unless it is not disturbed.

During spontaneous processes, decrease in internal energy ($\Delta E$) and or enthalpy ($\Delta H$) take place and processes are exothermic. Whereas melting of ice is an endothermic process which is also spontaneous. So, it clearly indicates that apart from enthalpy there are some other factors too, which  govern the spontaneity of a process or reaction; and this spontaneity is the basis of the 2nd law of thermodynamics which incorporates another term entropy to explain spontaneity of the process.

**6.3. Entropy.** It is a measure of degree of disorder or randomness in the system and ranomness becomes maximum when equilibrium has been attained.The 2nd law of thermodynamics predicts that total entropy of a system must increase during spontaneous  process. In  a reversible change which is taking place at constant temperature (T), then change in entropy ($\Delta S$) becomes equal to heat absorbed or evolved divided by temperature. It will be expressed as follows.

  Heat absorbed at Temperature($T_2/T_2$) + Heat absorbed at Temperature ($T_1/T_1$) = 0   ...5

Mathematically, entropy is expressed as

 $\Delta S$ = Heat absorbed reversible/Temperature at which the heat is absorbed

= $q_{rev}$ / T                                    ...6

 Equation (6) can be written as follows.

($\Delta S$).$T_2$ + ($\Delta S$).$T_1$  = 0 ( for a complete cyclic process). This equation states that the sum of all  $\Delta S$ for any reversible cyclic process will be zero and entropy is the state function of a system. When heat is absorbed, $\Delta S$ becomes positive and if heat is evolved, $\Delta S$ is negative. In the SI system, the unit of entropy is J mol$^{-1}$ K$^{-1}$. Changes in entropy of a process arises due to change in  the arrangement of the solvent or counterions, reflecting the

degrees of freedom, rotational & translational energy in final state (products) as compared to initial state of process (reactant).

**6.4. Molecular interpretation of entropy.**

The entropy can be identified with some function like probability and entropy is quantitatively related to the probability. Thermodynamics is based on human experience and is not concerned with structure of matter/ molecules structure, it is very logical to consider the molecular basis of entropy. Since all natural processes lead to net increase in entropy and also since there exists a natural tendency for an order set to get disordered through interplay of natural forces, it leads to increase in entropy. In a natural or spontaneous process, there is a tendency of a process to go from a state of lower probability to higher probability and probability is the driving force for spontaneity. [19, 20]

**6.5. Carnot cycle.** The numerical values of entropy is determined by the principle of Carnot cycle which is constructed by using a heat engine.
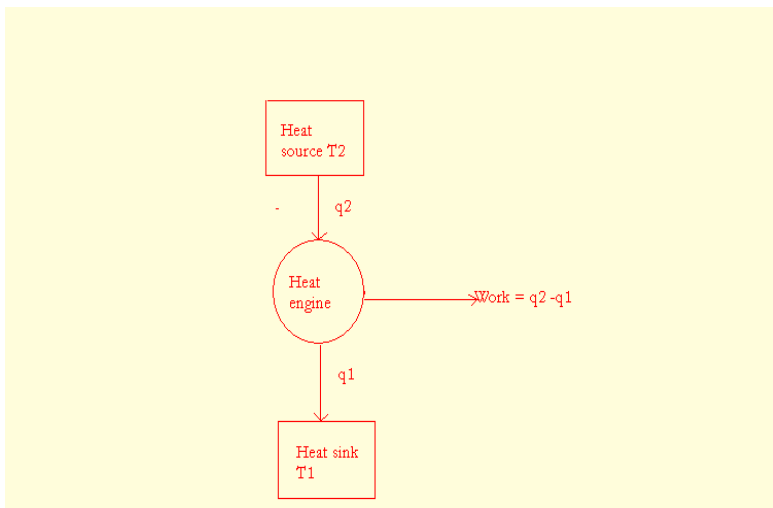


**Fig. 11. Diagramatically representation of a Heat Engine.**

Heat engine is a machine which runs in a cyclic process and yields work continuously. Here, heat flows spontaneously from a hotter body source to a colder body sink and work is  harnessed. The steam engine is an example of a heat engine (Fig.11) where heat is taken from a boiler at high temperature and converts some part of  heat into work and returns the remaining unused heat to the surrounding at lower temperature.

**6.6.The efficiency of a Heat Engine.**

Efficiency of a heat engine is defined as the ratio of the maximum work (w) obtained in   a cyclic process when heat is taken (q) from the source which is at high temperature. Practically, it is not possible for any heat engine, no matter how efficiently made, to convert all heat taken from the source (high temperature) completely into work without giving some part of the heat to sink. Efficiency of such a type of engine will be 100%. Theoretically, Sadi Carnot (1824) proposed a heat engine whose  efficiency is based on the temperature difference in between which it operates.

In the Carnot engine, each cycle consists of a series of operations on an ideal gas and on completion of a cycle, the gas is restored to its original state. Kelvin had postulated that it would not be possible to transform heat in the work taken from a source of uniform temperature. For such a transform two different temperatures $T_2$ and $T_1$ source and sink must be needed during operation. Consider an ideal gas in a frictionless piston whose different state can be represented as in (Fig. 12) of P-V graph in which two reversibly isothermally and two adiabatics processes are taking place at temperatures $T_1$ and $T_2$ respectively. (Fig. 12)

The performance of the Carnot cycle depends on four processes.

1)      Isothermal reversible expansion (Operation 1)

2)      Adiabatic reversible expansion  (Operation 2)

3)      Isothermal reversible compression (Operation 3)

4)      Adiabatic reversible compression (Operation 4)

This reversible cycle transformation (from state A to B, B to C, C to D and finally D to A  in a cyclic manner is called the Carnot cycle.
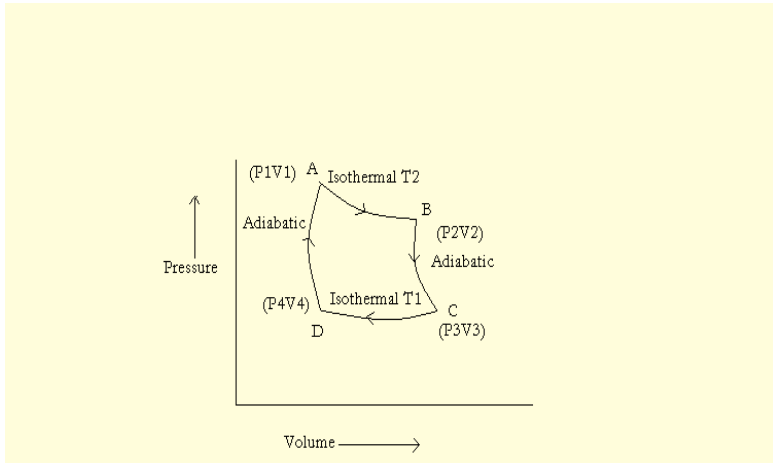


**Fig. 12. Process in Carnot cycle.**

The 1st process is isothermal reversible expansion in which 1.0 mol ideal gas at pressure $P_1$ and volume $V_1$ is enclosed in a frictionless cylinder and it is kept   in the hot reservoir at temperature $T_2$. Gas is allowed to expand isothermally reversibly in which volume of gas  increases from the volume $V_1$ to $V_2$ along path AB (Fig. 12) and it is shown by path AB in the figure.

Since $\Delta E$ =0, then work done ($w_1$) in  isothermal reversible expansion process when it absorbs heat $q_2$ at temperature $T_2$ will be from 1st law of thermodynamics,

$$\Delta E = q_2 - w$$
$$0 = q_2 - w$$
$$q_2 = w_1$$

But,            $(w_1) = RT_2 \ln V_2 / V_1$

Hence, $q_2 = RT_2 \ln V_2 / V_1$                    ....7

The 2nd process is adiabatic reversible expansion of gas at temperature $T_1$ volume $V_2$ to $V_3$ along path BC (Fig. 12)  under the new pressure $P_2$. Work done ($w_2$) in adiabatic reversible expansion process when q = 0.  Then from the 1st law of thermo equation ($\Delta E = q-w$).

$$\Delta E = -w_2$$

Since   $\Delta E = Cv (T_1-T_2)$ ,where Cv is the heat capacity of ideal  gas.

Then, $w_2 = Cv (T_2-T_1)$      ....8

The 3rd process is isothermal reversible compression of gas which is done by keeping the cylinder in contact with a heat reservoir (sink) at a lower temperature $T_1$. On compression volume of gas becomes $V_4$ from $V_3$ along path CD (Fig. 12)  and $w_3$ is the  work done during isothermal reversible compression process.

Heat obtained during compression is transferred to the reservoir at the lower temperature. Change in   $\Delta E = 0$ when $q_1$  heat is given to the reservoir and   the values of $w_3$  work done  with proper sign is given as,

$- q_1 = -w_3 = R T_1 \ln V_4 / V_3$        ..... 9

Finally, in the 4th process which is an adiabatic reversible compression where gas with volume $V_4$ ,  at temperature $T_1$ is compressed adiabatically and returns to its original state along path DA (Fig. 12). Then volume of gas becomes $V_1$ and temperature $T_2$.

Work done ($w_4$) in adiabatic reversible compression process is :

$-w_4 = -Cv (T_2-T_1)$          .... 10

Total work done W in one complete cycle will be obtained by summation of all work done in each operation of cycle as shown in the equation (7, 8,9 and 10) we get

$W = (w_1) + (w_2) + (- w_3) + (- w_4)$

W $= RT_2 \ln V_2 / V_1 + RT_2 \ln V_4 / V_3$

The quantity of heat absorbed in one cycle q $= q_2 - q_1$

On putting the values of $q_2$ and $q_1$ from equation (9) and (11),

q $= q_2 - q_1 = RT_2 \ln V_2 / V_1 - RT_1 \ln V_4 / V_3$ ....11

According to the equation governing adiabatic changes,

$T_2/T_1 = \{V_3 / V_2\}^{Y-1}$                    ....in adiabatic expansion

$T_1/T_2 = \{V_1 / V_2\}^{Y-1}$                    ....in adiabatic compression

or        $V_3 / V_2 = V_4 / V_1$

or        $V_3 / V_4 = V_2 / V_1$

So,   q $= R(T_2 - T_1) \ln V_2 / V_1$   ....12

Thermodynamic efficiency of carnot cycle will be given as

From equation (7) w = q

w $= R (T_2 - T_1) \ln(V_2 / V_1)$     ...13

The heat absorbed $q_2$ at temperature $T_2$ will be from equation (1)

$q_2 = RT_2 \ln(V_2/V_1)$  ....14

on dividing eq (13) by eq (14)

η$= w / q_2$

$= (T_2 - T_1) / T_2$  ...14

The factor ($w/q_2$) is called as thermodynamic efficiency (η) of an engine. It is the fraction of the heat taken at higher temperature from the reservoir and is converted into work by a heat engine. Theoretically, the efficiency of a Carnot engine, which is the most ideal of all engines, depends on the difference in temperature of source to sink. Larger temperature difference ($T_2 - T_1$) between the source and sink means higher efficiency of the heat engine.

**6.7. Entropy from Carnot cycle.**

Entropy (S) was introduced by Claussius, and its numerical value is given by dS = dq /t .

When( q) heat is transferred reversibly then dS is the infinitesimal changes in entropy.The Carnot equation, therefore, may be written as:

$(q_2 + q_1)/ q_2 = (t_2 – t_1) / t_2$
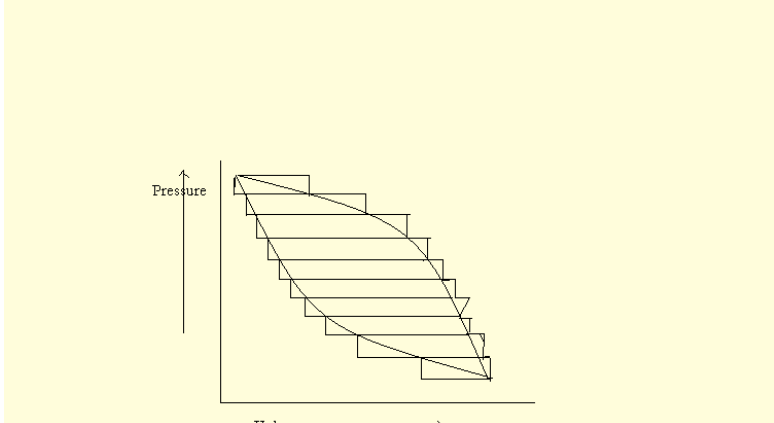
Or $\Sigma q/t = 0$



**Fig. 13. Reversible Processes in Carnot cycle.**

The reversible cycle process can be assumed as it consists of many Carnot cycles (Fig. 13), and in each Carnot cycle the sum of the two q /t terms will be zero i.e.

$q_1 /t_1 + q_2/t_2 = 0$

**8. Free energy.** Free energy is energy which is available for doing work i.e, there is available useful energy and a relationship exists between the change in free energy and the entropy change during a process. It can be easily seen by consider a system at constant temperature and pressure is undergoing the reaction, then change in free energy change (ΔG) of the system and the change in entropy (ΔS) is expressed as

ΔG = ΔH – T ΔS  ...15

Where ΔH is the change in the enthalpy and T is absolute temperature. In biochemical process, ΔH is approximately equal

to ΔE, then it becomes

ΔG = ΔE – T ΔS   .... 16

Following conclusion can be drawn from the above equation.

If   ΔG = (-ive) negative, reaction occurs spontaneously with decrease in free energy; i.e, an exergonic process. At higher ΔG reaction will go to completion and it will be irreversible.

If   ΔG =(+ive) positive, reaction will be possible only when free energy is gained; and it will be endergonic. At higher  ΔG, indicating stability in system.

If ΔG = zero, then equilibrium has been attained by the system and no net change takes place.

| If | Fate of process |
|---|---|
| (-) ive | Thermodynamically possible and will be favoured |
| zero | Reaction will be at equilibrium and reversible |
| (+) ive | It will be thermodynamically favoured and revere process will happen |

## 10. Relationship between equilibrium constant and Standard free energy change.

  Relationship between equilibrium constant and standard free energy change of a process can be easily seen by considering a general equilibrium equation.

$$aA + bB \leftrightarrows cC + dD$$
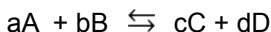
The change in free energy for such a reaction  can be given by the following expression.

ΔG = Product - Reactant    ...17

 $ΔG^0$ = - 2.303RT log K     ...18

        The equation (18) is also called the Van't Hoff isotherm. It can be used  in calculating the change in free energy of a reaction in the standard ($ΔG^0$) when the value of equilibrium constant is known or vice versa. The sign ΔG0 predicts the

feasibility of forward or backward reaction spontaneously. Three possibilities arise from equation (18) which depend on the sign of $\Delta G^0$ for the reaction.

1. When $\Delta G^0$ is positive, log K must be negative, and K< 1, reaction in reverse direction will be spontaneous and if $\Delta G^0$ is a large positive value, it means K will be very small and reverse reaction will proceed almost to completion.

2. When $\Delta G^0$ is negative, log K must be positive and reaction spontaneously proceeds in forward direction. If $\Delta G^0$ is a large negative value, K >> 1 and the forward reaction will proceed nearly to completion.

3. And when $\Delta G^0$ = 0, logK must be zero, and K will be 1. Equilibrium has been attained.

In the biochemical system, physiological reactions occur at pH 7.0 hence a standard state has to be defined at this pH because $\Delta G$ may be larger or smaller as compared to $\Delta G^0$ depending on various reactants concentration.
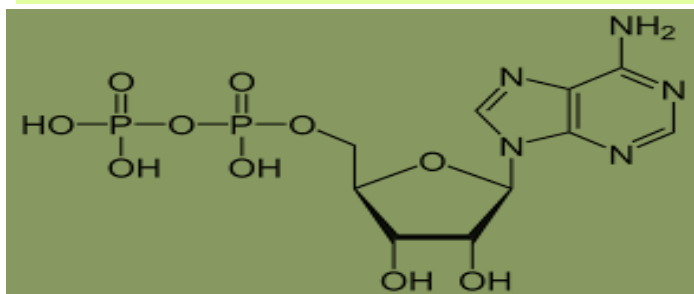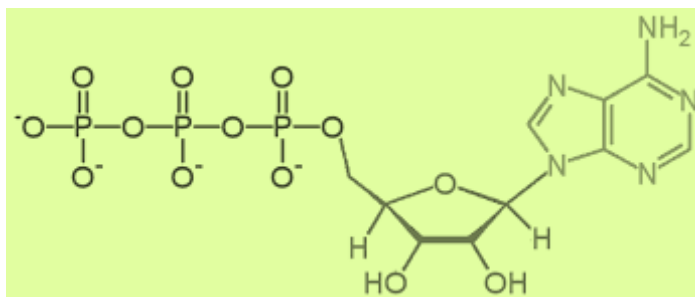
**8.1. Function of high energy phosphates molecules in living Cells.**

ATP molecule is the principal currency of the energy in a cell used as free energy in a biological system for performing different biological processes. Part of required free energy is obtained from the oxidation of highly accessible molecules present in the foodstuffs. ATP which has been synthesised in mitochondria either by aerobic or anaerobic cellular respiration in a cell ( and by fermentation in yeast and bacteria) is the main source of energy utilised in important biological functions e.g., in muscle contraction, in transmission of nerve impulse, and in protein biosynthesis. Structurally, ATP is a nucleotide made up of a nitrogenous base adenine, ribose sugar, and a triphosphate unit bound to ribose. Phosphates plays an important role in metabolism of carbohydrates which was demonstrated in the

period between 1930 and 1940 with the chemical details of glycolysis and the role of ATP, ADP, inorganic phosphate (Pi) during this process was discovered by Fritz Albert Lipmann and Herman Kalckar (1941). ATP was recognised as a means of transferring phosphate radicals during phosphorylation. Another evidence about the role of ATP in biochemical energetics was indicated in experiments which demonstrated that ATP and creatine phosphate were broken down during muscular contraction and its resynthesis depended on energy supplied from oxidative processes occuring in the muscle. In 1929, Cyrus H. Fiske and Yellapragada Subbarow had isolated ATP from mammalian muscle and liver and Karl Lohmann identified it role in muscle tissues. [19-21]

The active part of ATP contains a complex of ATP with cofactor of $Mg^{+2}$ or $Mn^{+2}$. ATP acts as an energy carrier in which the triphosphate unit is made up of two phosphoanhydride bonds. During hydrolysis of ATP into adenosine diphosphate (ADP) and orthophosphate (Pi) or into adenosine monophosphate (AMP) and pyrophosphate (PPi), a large amount of free energy is evolved.

Hydrolysis of ATP forms ADP and one phosphate group is removed with release of -7.3Kcal/mol of energy. When ATP is hydrolysed to AMP with formation of diphosphate then it releases -11 kcal/mol of energy. In adenosine diphosphate (ADP) there is diphosphate instead of triphosphate and in adenosine monophosphate (AMP )there is monophosphate respectively.(Fig. 15)

Structure of ATP.

Structure of ADP.
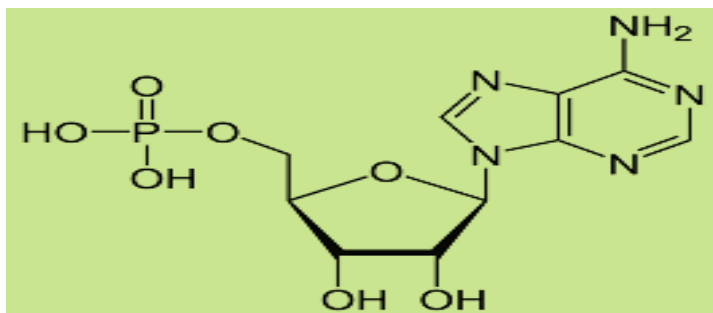


Structure of AMP.

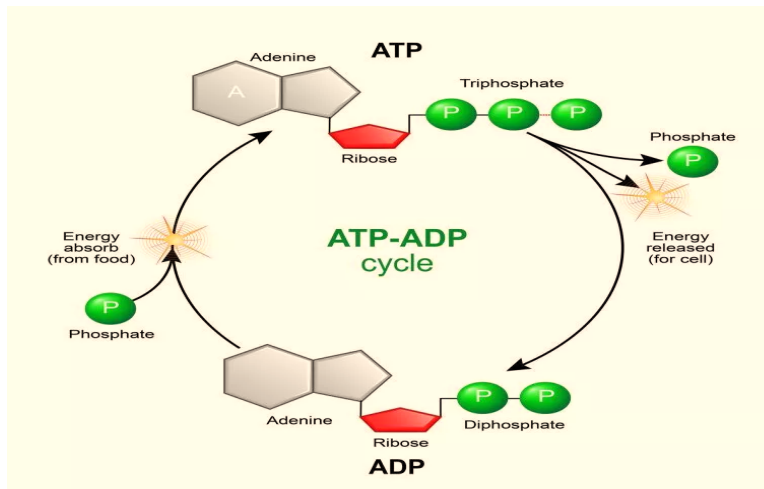**Fig. 14. Structure of ATP, ADP and AMP.**

**Fig.15  ATP-ADP Cycle.**

The symbol (~P) was  introduced  by Lipmann which indicates the presence of high energy phosphate bond in ATP molecules which  on transferring to an appropriate acceptor results in release of larger quantity of free energy. Hence, the term 'group transfer potential' has been commonly used in place of  high energy bonds. The precise values of $\Delta G^{o'}$ during hydrolysis mainly depend on the value of  ionic strength of the medium, on the concentration of $Mg^{+2}$ and other metal ions which is nearly -12 kcal/mol. The free energy liberated during hydrolysis of ATP has been used in biochemical reactions where an input of free energy is required. ATP is synthesised from ADP and Pi during oxidation of fuel molecules in chemotrophs and  from sunlight during photosynthesis in autotrophs. ATP-ADP cycle is the fundamental mode of energy carrier in biological systems.

It has also been found that some of the biosynthetic reactions are mediated by  hydrolysis of other nucleoside triphosphates structurally analogous to ATP molecule e.g. Guanosine triphosphate (GTP), uridine triphosphate (UDP), and cytidine triphosphate (CTP) whose  diphosphate and monophosphate units are represented as (GDP,UDP, CDP); (GMP,UMP and CMP) respectively.

**8.2. Role of ATP in the biological System.**

Although  the role of ATP in living organisms is diverse, its role in the human brain, intracellular transduction of signals and other processes has been summarised in brief. The human brain consume  nearly 25%  of the total energy available of ATP in the body and mostly spent in maintaining ion concentrations for proper neuronal signalling and synaptic transmission.[22,23]

 ATP is used in intracellular transduction of signal which requires energy. ATP acts as a substrate for numerous ATP- binding protein kinases which during phosphorylation in presence of the magnesium ion, modulate diverse intracellular signalling pathways and in such a way controls the activity of kinase. It also triggers the release of intracellular messengers' viz. hormones, neurotransmitters, various-enzymes, lipid mediators, growth factors and reactive oxygen species.  Synthesis of DNA and RNA takes place in presence of ATP where ATP is utilised as one of four nucleotide-triphosphate monomers during synthesis of RNA, with an analogous mechanism in DNA synthesis but one difference   involved in DNA synthesis   is removal of an oxygen atom from the sugar moiety of ATP which forms deoxyribonucleotide dATP molecule.  [24]

ATP is also used in purinergic signalling in which extracellular paracrine signalling is mediated by purine nucleotides. It triggers the    activation of purinergic receptors within proximity of cells by inducing several purinergic responses

in sympathetic and parasympathetic nerves; consequently controls the autonomic functions, neural glial interactions, pain, and the vessel tone.[25, 26]

　　　Role of ATP in muscle contraction is very important because contraction plays an important function in daily life. Three primary roles played by ATP during muscle contraction are i) production of force through the cycling of myosin cross-bridges in actin filaments, ii) mediate pumping of $Ca^{2+}$ ions by active transport from the mycoplasma across the sarcoplasmic reticulum against concentration gradients, iii) active transport of sodium and potassium ions by the hydrolysis of ATP across the sarcolemma and release of calcium ions. [27]

**8.3.The free energy of hydrolysis of ATP and other organophosphates.**

Free energy released during hydrolysis of important phosphates biomolecules have been shown in table 1. The comparative tendency of each biomolecules to transfer a phosphate group to a suitable acceptor has been derived from the $\Delta G^{o\prime}$ during hydrolysis occurring at standard state 25$^0$C, pH 7.0 e.g., the values of free energy released in hydrolysis of the terminal phosphate moiety in ATP is (-8.8) kcal/mole. One molecule having a group of low energy phosphates is ester phosphates found as intermediate during glycolysis, possess smaller $\Delta G^{o\prime}$ values as compared to ATP while in other group designated as high energy phosphate group have equal or higher $\Delta G^{o\prime}$ values than that of ATP, which is due to presence of an anhydrides (e.g. the 1-phosphate of 1,3- bisphosphoglycerate) and phospho guanidines residues in ATP and ADP.

**Table. 1. Standard free energy in organophosphates molecules during  hydrolysis.**

| S.N. | Molecules | $\Delta G^{o'}$ (Kcal mol$^{-1}$) |
|------|-----------|----------------------|
| 1 | Glycerol -3- phosphate | -2.2 |
| 2 | Glucose-6- phosphate | -3.3 |
| 3 | Fructose -6- phosphate | -3.8 |
| 4 | Glucose 1- phosphate | -5.0 |
| 5 | ATP →ADP + Pi | -8.8 |
| 6 | Creatine phosphate | -10.3 |
| 7 | 1,3-          Bisphosphoglycerate(to 3-phosphoglycerate) | -11.8 |
| 8 | Carbamoyl phosphate | -12.3 |
| 9 | Phosphophenol Pyruvate | -14.8 |

**9. Bioenergetics of Coupled Reactions.**

Some of the exergonic and endergonic reactions in biological systems are coupled. Such a mechanism in the biological system is seen when oxidative processes are allowed to occur. Since the presence of a common obligatory intermediate for both the exergonic and endergonic reactions allow the rate of utilisation of the product in  synthesis  which is determined by law of mass action and the rate at which (A) is oxidised ( as shown in Fig.1).

Coupled reaction controls an organism from burning out of control because a huge quantity of energy is released during oxidative processes. The concept of coupling can be extended in the dehydrogenation reactions, where it is coupled with hydrogenation by an intermediate carrier. The coupling of an exergonic with an endergonic process can be achieved by different methods. In one most common  method, a compound of high energy potential is synthesised in the exergonic reaction and  is incorporated into the endergonic reaction which effectively transfers the   released free energy  in  the  exergonic  to  the endergonic pathway (Fig. 16). [28-30]
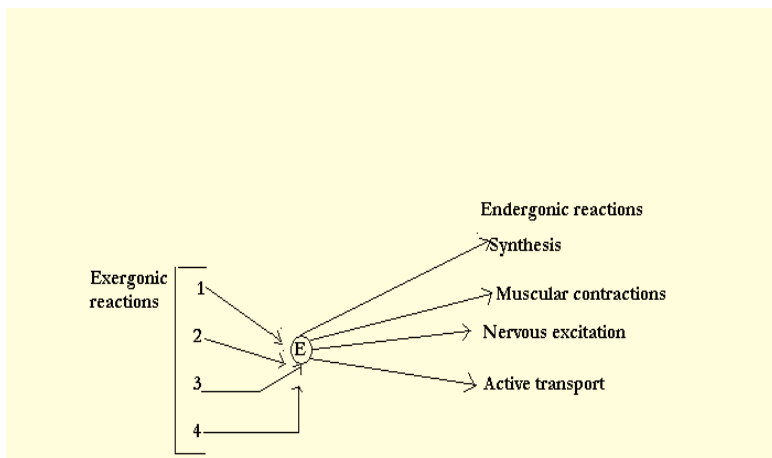


**Fig 16. Transduction of energy through a common high energy compound to energy.**

**References**

1.  *Donald T., Haynie, Biological Thermodynamics Cambridge University Press. (2 ed.). 2008, 26.*

2.  *Caplan S. R. , Essig A.,  Bioenergetics and Linear Nonequilibrium Thermodynamics. The Steady State, Harvard University Press, Cambridge.1983.*

3. *Grandy W.T. Jr., Entropy and the Time Evolution of Macroscopic Systems, Oxford University Press, Oxford. 2008. ISBN 978-0-19-954617-6.*

4. *Zotin, A. I., & Lamprecht I., Aspects of Bioenergetics and civilization. Journal of Theoretical Biology. 1996. 180, 207–214.*

5. *Schmidt-Rohr K., Expansion Work without the External Pressure, and Thermodynamics in Terms of Quasistatic Irreversible Processes. J. Chem. Educ. 2014, 91,3, 402–409.*

6. *Callen H.B., Thermodynamics and an Introduction to Thermostatistics, second edition, John Wiley & Sons, Hoboken NY. 1960/1985, 11–13. ISBN 9780471862567.*

7. *Lieb E. H., Yngvason J., "The Physics and Mathematics of the Second Law of Thermodynamics". Physics Reports.1999, 310,1, 1–96.*

8. *Kondepui D., Introduction to Modern Thermodynamics,Wiley, Chichester. 2008, Sections 3.1, 3.2, 97-108.*

9. *Bridgman P,W., The nature of Thermodynamics,Harvard University Press, Cambridge Press, MA,1943, 48.*

10. *Liu J. S., Marison I., von Stockar U., Microbial growth by a net heat up-take: A calometric and thermodynamic study on acetotrophic methanogenesis by methanosarcina barkeri. Biotechnology and Bioengineering. 2001,75, 170–180.*

11. *Hasse R., Survey of Fundamental Laws,chapter 1 of Thermodynamics, ed. W.Jost. of Physical Chemistry. An Advance Treatise.1971,1, 1-97.*

12. *Kondepui D., Prigogine I., Modern Thermodynamics. From Heat Engines to Dissipative Structures, John Wiley & Sons, 1998, ISBN 0-471-97393-9.*

13. *Kelvin, William T., "An Account of Carnot's Theory of the Motive Power of Heat – with Numerical Results Deduced from Regnault's Experiments on Steam." Transactions of the Edinburgh Royal Society, XVI. 1849.*

14. *Patel B. D., Hildebrandt, Glasser D., An overall thermodynamic view of processes: Comparison of fuel producing processes. Chemical Engineering Research and Design. 2010,88, 844–860.*

15. *Nielsen, J. and J. Villadsen (1994). Bioreaction engineering principles. New York: Plenum press.*

16. *Lebon G., Jou D., Casas-Vázquez, J., Understanding Non-equilibrium Thermodynamics. Springer, Berlin, 2008, ISBN 978-3-540-74251-7.*

17. *Lems S., van der Kooi H. J. A., de Swaan J.,. Thermodynamic optimization of energy transfer in biochemical reaction systems. Chemical Engineering Science. 2003,58, 2001–2009.*

18. *Yaşar D., Nonequilibrium Thermodynamics, Transport and Rate Processes in Physical and Biological systems. 2002, 239-355.*

19. *Dufour E. and N.-G. Larsson, Biochim. Biophys. Acta. 2004,1658, 122.*

20. *Garby L., and Larsen P.S., Bioenergetics. Its Thermodynamic Foundations, Cambridge University Press, Cambridge, 1995.*

21. *Aledo J. C., Lobo C., Esteban del Valle A.,Energy diagrams for enzyme-catalysed reactions: Concepts and misconceptions, Biochem. Mol. Biol. Educ. ,2003,31, 234 –236*

22. *Coco S., Calegari F., Pravettoni E., etal., Storage and release of ATP from astrocytes in culture. J Biol Chem. 2003, 10,278,2,1354-62.*

23. *Attwell D., Laughlin S.B., An energy budget for signalling in the grey matter of the brain. J Cereb Blood Flow Metab. 2001,21,10,1133-45.*

24. *Bonora M., Patergnani S., Rimessi A.,etal., ATP synthesis and storage. Purinergic Signal. 2012,8,3,343-57.*

25. *Cárdenas C, Miller R. A,, Smith I., Bui T., etal., Essential regulation of cell bioenergetics by constitutive InsP3 receptor Ca $^{2+}$ transfer to mitochondria. Cell. 2010,23,142,2,270-83.*

26. *Pablo Huidobro Toro J, Verónica Donoso M., Sympathetic cotransmission: the coordinated action of ATP and noradrenaline and their modulation by neuropeptide Y in human vascular neuroeffector junctions. Eur J Pharmacol. 2004,500, 1-3,27-35.*

27. *Wong-Riley MT., Cytochrome oxidase: an endogenous metabolic marker for neuronal activity. Trends Neurosci. 1989, 12,3,94-101.*

28. *Juan Carlos Aledo., Coupled Reactions versus Connected Reactions. Biochemistry and Molecular BiologyEducation. 2007, 35, 85–88,*

29. *Kondepudi D., Prigogine I., Modern Thermodynamics: From Heat Engines to Dissipative Structures, John Wiley & Sons, Chichester, UK, 1999, 233–250.*

30. *Voet D., Voet J.G., Biochemistry, 3rd Ed., John Wiley & Sons, New York, 2004,. 438 – 440.*