CONCEPT OF THERMODYNAMICS AND ENVIRONMENT: AN OVERVIEW

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Energy is the currency of life. The very physical existence is attributed to energy. The acceptance and dissipation of energy from a system is well understood with the help of thermodynamic laws or principle. However, the use of the thermodynamic principle to the biosphere, is being used considering it as a system. Although, all aspects of the thermodynamics analysis is still a matter of debate. But ecosystem deriving energy by electromagnetic energy from sun is subject to thermodynamic laws. The Earth is a closed system and biosphere is a closed as well as open system, poses challenges for its understanding. The laws governing the system (Living) is also attributed to the thermodynamic principle; especially, energy, entropy and exergy. The concern specifically confronted by the biosphere and human kind is their own existence in light of the climate change or change in heat energy. Thus, the energy pushes the system towards the disorder state. The understanding of the closed system, the Earth will lead to understand energy utilization and optimization in nature. The present overview is thus, an approach to understand the basic phenomenon of thermodynamic in an ecosystem.

INTRODUCTION

The term thermodynamics has its origin from Greek word “Thermes” (Heat) and dynamics (force) which is most descriptive of the early efforts to convert heat into power. Today it is used broadly to interpret and to include all aspects of energy and energy transformation (Dincer and Cengel, 2001; Wall, 1977). The science of thermodynamics is based on two laws: First law is expression of the conservation of energy principle and the second asserts that energy has quality as well as quantity and actual processes occur in the direction of decreasing quality of energy. It simply means high-temperature thermal energy is degraded as it is transferred to a lower temperature body. The attempts to quantify the quality or “work potential” of energy in the light of the second law of thermodynamics has resulted in the definition of the properties entropy and exergy. The first and second laws of thermodynamics emerged simultaneously in the 1850s, primarily out of the works of William Rankine, Rudolph Clausius and Lord Kelvin. Its importance was realized with the construction of the first successful atmospheric steam engine in 1697 by Thomas Savery and Thomas Newcomen in 1712. Though, these engines were very slow and inefficient, but they opened the way for the development of a new science. Thus, Thermodynamics is a science of “energy”. Similarly, Ecosystem is a system which depends on energy received by sun in the form of electromagnetic energy for the whole ecosystem (Dincer and Rosen, 1999). Thus, in this context this review will apprise of the thermodynamic in ecology and biosphere. Before we begin about thermodynamics, it is pertinent to overview, what is system in general, energy balances, energy, entropy and exergy in a system.

System and its energy balances

Environment is an open system: In the sense that this system is open for mass and energy transfer. Ecosystem receives energy from solar radiation and water from precipitation from the atmosphere, inputs by wind and flows of various types plus migration of species. A system that is closed for in and output of energy and mass is called an isolated system. If an ecosystem is isolated, it would move towards the thermodynamic equilibrium and becomes dead system with no gradient to do work or, dG = 0 and dS = 0 at a maximum S value. An openness explains, why an ecosystem of life requires inputs of energy, if an ecosystem is at least none isolated. The application of second law of thermodynamics is crucial to open system since; an ecosystem violates the second law of the thermodynamic by moving away from the thermodynamics equilibrium by formation of biological structure. In an isolated system neither energy /matter exchanges with its environment. In a closed system, only energy exchanges, with its environment, but no exchange of matter. An open system is the system which exchanges energy and matter both to environment. From thermodynamics point of view, any ecosystem is open which exchanges energy and matter with the environment. The biosphere is a typical closed system; since it exchanges only energy with space (matter exchange can be neglected with a good approximation). Certainly, all these classes are theoretical models of real systems. In reality, there are no purely isolated, closed and open systems. The same system can be isolated during some time intervals, but be open during the
others. For instance, the biosphere is a closed system with respect to thousands of years and it is an open system with respect to geological times, when we cannot neglect the matter exchange between the core and the mantle the main bodies in thermodynamics are the system and its environment. As a rule, this pair forms an absolutely isolated supersystem, while the system and its environment are exchanged by matter and energy through a border of the system. There are two sorts of equilibriums in thermodynamics. The first, thermodynamic equilibrium, takes place when there is no exchange of matter and energy between the system and its environment and its state does not change. The second, dynamic equilibrium (steady state) is maintained by non-zero flow of energy, matter (and entropy) across borders of the system.

Energy: Newton first introduced the concept of energy and hypothesized about forms of energies viz. kinetic and potential energies. However, the unification of energy was realized in the 20th century. Energy, being a scalar quantity, it cannot be observed directly but can be recorded and evaluated by indirect measurements. The absolute value of energy of system is difficult to measure, whereas its energy change is rather easy to calculate. The sun is the major source of the earth’s energy. It emits a spectrum of energy that travels across space as electromagnetic radiation. Energy is also called currency of existence. Everything that has physical existence has energy. Further energy is conserved i.e. total amount of energy never changes. This, means simply, that energy cannot be created nor destroyed but be converted from one form to another. Einstein, for the first time related energy to mass reasoned that mass can be converted to another form of energy. Such as, \(E = mc^2\). The amount of heat energy \(E\) equals to amount of mass \(m\) multiplied by an exchange rate \(C^2\), where \(C\) represent velocity of light in empty space (C = 671 million miles MPH). Thus, logically a small amount of mass could yield a huge amount of energy in another form. Einstein’s equation \(E = mc^2\) and its implication for generating energy namely, that almost all useful energy ultimately came from the conversion of mass into other forms of energy, such as heat. Though the conservation laws are independent of each other but according to Einstein equation matter can be transferred to matter and energy to matter and equivalent amount of mass and energy. Therefore these laws are not independent but since the conservation of matter to energy and vice versa have interest for nuclear and plasma process. In biology we can consider has independent. Thus, in conservation law Einstein equation is very important since it provides the energy positiveness \(E = mc^2\), where \(m\) is the rest mass. The energy in thermodynamic is classified into two forms:

**The macroscopic forms**: The macroscopic forms of energy are those where a system possesses as a whole with respect to some outside reference frame such as kinetic and potential energies. For example, the macroscopic energy of an up moving object changes with velocity and elevation. The macroscopic energy of a system is related to motion and the influence of some external effects such as gravity, magnetism, electricity and surface tension. The energy that a system possesses as a result of its motion relative to some reference frame is called kinetic energy. The energy that a system has, as a result of its elevation in a gravitational field is called potential energy. Kinetic energy refers to the energy possessed by the system because of its overall motion, either translational or rotational. The word “overall” is italicized because the kinetic energy to which we refer is the kinetic energy of the entire system, not the kinetic energy of the molecules in the system. If the system is a gas, the kinetic energy is the energy due to the macroscopic flow of the gas, not the motion of individual molecules. The potential energy of a system is the sum of the gravitational, centrifugal, electrical, and magnetic potential energies.

**The microscopic forms**: The microscopic forms of energy are those related to the molecular structure of a system and the degree of the molecular activity and they are independent of outside reference frames. The sum of all the microscopic forms of energy is called the internal energy of a system. The internal energy of a system depends on the inherent qualities, or properties, of the materials in the system, such as composition and physical form, as well as the environmental variables (temperature, pressure, electric field, magnetic field, etc.). Internal energy can have many forms, including, sensible and latent (i.e., thermal), chemical, nuclear, electrical, mechanical, magnetic and surface energy.

**The laws of thermodynamics**

**The first law of thermodynamics**: It is also the first law of the conservation of energy. This is stated as “energy can be neither created nor destroyed; it just changes form”. The first law defines internal energy as “a state functions and provides a formal statement of the conservation of energy”. However, it provides no information about the direction in which processes can spontaneously occur, that is, the reversibility aspects of thermodynamic processes. For example, it cannot say how cells can perform work while existing in an isothermal environment. It gives no information about the inability of any thermodynamic process to convert heat into mechanical work with full efficiency, or any insight into why mixtures cannot spontaneously separate or unmix themselves. An experimentally derived principle to characterize the availability of energy is required to do this. This is precisely the role of the second law of thermodynamics. The total energy \(E\) represents the sum of all forms of energy a system possesses and the change in the energy content of a system during a process is expressed as \(\Delta E\) system. In the absence of electrical, magnetic, surface, etc effects, the total energy in that case can be expressed as the sum of the internal, kinetic and potential energies as

\[
E = U + KE + PE
\]

\[
\Delta E\text{ system} = \Delta U + \Delta KE + \Delta PE
\]  

Energy can be transferred to or from a system in three forms: heat \(Q\), work \(W\) and mass flow \(m\). Energy interactions are recognized at the system boundary as they cross it and they represent the energy gained or lost by a system during a process. Thus, the first law of thermodynamics or energy balance for any system undergoing any kind of process can be expressed as:

\[
E_{in} - E_{out} = \Delta E\text{ system}
\]  

Net energy transfer by Change in internal, kinetic, heat, work and mass potential, etc. energies. That is, the net change (increase or decrease) in the total energy of the system during
a process is equal to the difference between the total energy entering and the total energy leaving the system during that process. This relation can also be expressed per unit mass, differential and rate forms as
\[ e_{\text{in}} - e_{\text{out}} = \Delta e_{\text{system}} \]  

\[ \delta E_{\text{in}} - \delta E_{\text{out}} = dE_{\text{system}}, \text{or } \delta e_{\text{in}} - \delta e_{\text{out}} = de_{\text{system}} \]  

\[ E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}} \]  

Rate of net energy transfer Rate of change in internal, kinetic, by heat, work, and mass potential, etc.

The only two forms of energy interactions associated with a fixed mass or closed system are heat transfer and work.

The second law of thermodynamics – Entropy: The nature is dynamic and the classical concepts of equilibrium and stability does not exist, since, we see, fluctuation, instability and evolutionary processes at all levels from chemistry, biology to cosmology. We observe irreversible process in which time symmetry is broken. The difference between irreversible and reversible processes are explained by concept of entropy where, entropy is simply a “measure of the amount of molecular disorder within a system. A system possessing a high degree of molecular disorder has a very high entropy value and vice versa. Thus, entropy is the core of second law of thermodynamics. It high lights.

1. The entropy of the system is a measure of the amount of molecular disorder within the system.
2. A system can only generate, not destroy, entropy
3. The entropy of the system can be increased / decreased by the energy transport across the system boundary.

Energy transfer or conversion are changes of the state of a system. The natural direction of change of the state of a system is from a state that is more probable than ordered ones. Thus, the natural directions of change in state of a system are from order to disorder i.e. entropy. Thus, the second law of thermodynamic is expressed more broadly in terms of entropy in the following way. In any transfer or conversion of the energy within a closed system, the entropy of the system increases.

Thus, the state of low probability have low entropy state of high probability have higher enthalpy. The overall change in entropy is positive. In the life process highly ordered structure are built from the much simpler structure of various chemicals, but to accomplish this, life takes in relatively low – entropy energy – sunlight and chemical energy and gives off high entropy heat energy. The entropy of the total system again increases in Fig. 1.

Third law of thermodynamics applied to open ecosystem: The first law is applied when energy balance of ecosystem are made. The second law is applied when we consider the entropy production of ecosystem as a consequence of the maintenance of the system far from thermodynamic equilibrium. The third law state that the entropies of pure chemical compounds are zero and that entropy production \( \Delta S_p \) by the chemical reactions between pure crystalline compounds is zero at absolute temperature, \( 0 \text{ K} \). Thus, third law states, since, \( S_p = 0 \) (absolute order) and \( \Delta S_p \) (no disorder generation) that is order does not exist and cannot be created at absolute zero temperature. But temperature higher than zero of Kelvin, disorder can exist \( (S>0) \) and be generated \( (\Delta S_p = 0) \). The third law defines the relation between entropy production \( \Delta S_p \) and the Kelvin temperature, \( T \).

\[ \Delta S_p = \int [\Delta f_c] c_p \ln T + \Delta S_o \]

Where, \( \Delta f_c c_p \) is the increase in heat capacity by the chemical reaction. Since, order is absolute at absolute zero. In high temperature, however, order can be created. Entropy, is the degradation of energy from a state of high utility \( (\text{Large } T) \) to a low utility \( (\text{Small } T) \). The ecosystem will never, reach an equilibrium as long as they occur isolated and receive energy (energy that can do work) from outside to combat the decomposition of the compounds. It is absolutely necessary for an ecosystem to transfer the generated heat (entropy) to the environment and to receive low entropy energy (solar radiation) from the environment for the formation of dissipative structure. The question that arises is, Will energy source and sink also sufficient to initiate formation of dissipative structure. Which can be used as source for entropy combating processes? The answer is yes. Morowitz (1968; 1978) showed that flow of energy from sources to sinks leads to an elements cycle. This type of organization depends upon various factors, the temperature, the element present, initial conditions, of the system, and the time available for the development of organization. The steady state of the open system do not involve chemical equilibrium. A system at 0K is without any creative potential because no dissipation of energy can take place at the temperature. A temperature \( >2.726 + 0.01K \), where, 2.726 K is the temperature of deep space, is required before order can be created. At 0 K the world is dead and still, as the temperature is a measure of velocity of atoms, is also same and behave like one single atom. The velocity is 0 at 0K by definition and therefore determined without uncertainty. At 0K there is no structure, no gradient and no complexity. No entropy can be formed because all mass is everywhere and nowhere, and without form and structure. There is no disorder to create and therefore no entropy to produce. The system is trapped between complete orders because mass occupies all the space and complete disorder because all the space is occupied by mass and complete dissipation had taken place. At 0K no creativity is possible, no difference (gradient), no structure, no physical activity, because all velocities are zero and every thing is dull and dead, even light has stopped, Time has no meaning, because time is determined by the rate of change. This extreme condition at 0K elucidates the meaning of concept of entropy. Entropy is a one side, the price we pay for order, its organization and creativity, but without entropy there would be no order, structure, organization and creativity. Thus, it explain the meaning between 2nd law of thermodynamics and because, heat is an energy from which is generated by transformation of all. Other energy forms because 100% effective transformation of heat to work cannot take place because in the Carnot cycle the cold reservoir can never be maintained at 0K. Energy that cannot do work is inexorably lost to energy that cannot do work. This is the condition which impound on us; time and all reactions are irreversible.

Ecosystem as a Biochemical Reactor

The fuel of ecosystem is organic detritus matter; hence, it is necessary to calculate the free energy of dead organic matter.
The chemical potential of dead organic matter is, indexed \(i = 1\), is expressed as in classical thermodynamics (Russel and Adebyri, 1993) as

\[
\mu_i = \mu_i^0 + RT \ln \left( \frac{C_i}{C_0} \right)
\]

The difference \(\mu_i - \mu_i^0\) is the detrital organic matter which comprises carbohydrate, fat and proteins. Enthalpy values of 18.7kJ/g are applied for the free energy content of average detritus. Coal and mineral oil have a free energy content of 30kJ/g and 42kJ/g respectively. Both coal and mineral oil are a concentration form of detritus from earth’s geology. The concentration the detritus in considered and \(C_1^0\) is the concentration of detritus in the same ecosystem but at a thermodynamic equilibrium.

When we consider the equilibrium constant for the aerobic decomposition of detritus at 300K. The molecular weight of detritus is found to be about 100000. (Precisely, 104400 (Morowitz, 1968), and its typical consumption is 3500 Carbon, 6000 Hydrogen, 3000 Oxygen and 600 Nitrogen.

\[
C_{1000}H_{6000}O_{3000}N_{600} + 42500O_2 \rightarrow 3500CO_2 + 2700H_2O = 600NO_3^- + 600 H^+ + 600 NO_3^- + 600 H^+ + \text{heat} \]

Therefore the equilibrium constant

\[
K = \frac{[CO_2]^{3500} [NO_3^-]^{600} [H^+]^{6000} [C_{1000}H_{6000}O_{3000}N_{600}] [IO_3^-]^{4350}}{[C_{1000}H_{6000}O_{3000}N_{600}]}
\]

Since, water is eliminated from the expression of \(K\), then we have \(\Delta G = RT \ln K\), so that \(\Delta G = 18.7 \text{kJ/g} \times 104400 \text{g/m} = 1952 \text{MJ/mol} = 82 \text{J/mol} \times 300 \ln K\), which suggest that \(\ln K = 793496\) or it is about 1034499. Thus, it is obvious that equilibrium constant is enormous. The spontaneous formation of detritus in the form of compound with the molecular weight of about 100000 has therefore a very small probability. Thus, it suggests the detritus, is decomposed spontaneously and thereby yields energy to the heterotrophic organisms. Fig. 2 shows the resulting biochemical reactants of an ecosystem, how an ecosystem works with biochemical reactions.

The biochemical and element cycling are cyclic and are used and resused again to build biochemically important compound, e.g., protein, lipid and carbohydrate. These compounds carry the energy of the solar radiation and thus, support the maintenance of life by cycling processes. The cycle can be compared with the Carnot cycle. The hot reservoir (the Sun) delivered the energy, which is used to work. The heat energy is delivered to the cold reservoir at the ambient temperature. The work after it has been performed is transformed into heat, which is also delivered to the environment. The Fig. 3 shows the energy of the cycle in detail. The free energy of the biologically important nitrogen compounds, protein posses the highest free energy as a result of photosynthesis or biochemical synthesis in heterotrophic organisms (Fig. 4). They play an important food compounds for the heterotrophic organism as they supply important blocks, amino acids for the energy.

In biochemistry, thermodynamic, is applied to understand the relationship between chains of biochemical processes and corresponding energy budget. The catalytic processes are important for the supply of energy for the maintenance of the life processes. The energy demand is called by catalytic process; additional energy may be used to build to cover the anabolism. The organism need to transport energy between cells, from cells. That is, they have to supply energy from cell synthesizing energy to the cells where the energy is needed. The organism use small packages of ATP, which are easily transported to enable to release 41.8kJ/mol by the following process

\[
\text{ATP} \rightarrow \text{ADP} + \text{Pi}
\]

The second law gives a deep insight into the understanding of the ecosystem. It is however, based on the irreversible processes. Energy that is used for work is lost as heat to the environment. It is nothing but cost it pays for keeping the ecological machine running. This continuous process is responsible to build new biomass. Of course the energy is derived from sun. Ecosystem thus, requires an input source of useful energy to drive the life processes. The question, do we understand ecosystem with Newtonian classics, the answer is no. Because, the processes and time are irreversible. This process is in one way. e.g. Solar radiations plant biomass (photosynthesis) the biochemical energy (Plant Biomass) in food web new biomass. Thus, an ecological models cannot be developed from Newton’s mechanics but they must be based on the thermodynamics.

**Equilibrium and steady state**

In a sun – earth system, having a temperature of 5600K and 3K respectively. The system has a mixture of water, carbon-dioxide and nitrogen. As the system ages, it results in temperature and concentration gradient between the two reservoirs, but the chemical description becomes very complex. The high temperature will lead to free radical formation and the short wavelength end of the 5750K black body spectrum will drive many photochemical and radiocidal reactions. Thus, can the system achieve a steady state? The answer would be probably, no, but it is at present unknown. For an equilibrium ecosystem, the singularity of the final state occurs as one of the postulates of theory; indeed it lies at the root of the idea of solar energy, being a state function. No such postulate exists for being far from equilibrium systems, and the required kinetic methods are complex. Earth, we know is a materially closed system. In this closed system, the flow of matter, although meteorites, comets and planetary debris arrive episodically and hydrogen and helium escapes (leak) from the upper atmosphere. It has a constant inflows of the energy (solar energy), plus the thermal energy from radioactive decay in the earth’s interior and a constant out flow of energy to the 3K could be of outer space. This is the major energy influx which drives the present day biosphere. Thus, when we say that Earth is a closed system, it means it is closed to the flow of matter and open to the flow of energy. Whereas, in open system, system is open to flux of the matter and energy from the both equilibrium or non equilibrium sources and sinks.

**Temperature range for life processes**

The ecosystem receives energy in the form called solar quanta. This suggest that energy at first can only be used at molecular levels in the hierarchy. The appropriate atoms must be transported to the place where order is created. The creation of order in liquid and gases state is much faster than solids. The temperature required for a sufficiently rapid creation of order is consequently considerably above the lower limit, 2.726K. The gaseous diffusion allows the most rapid mass
transport. Many molecules on Earth that are necessary for ordinary carbon based life do not occur in gaseous phases and liquid diffusion, even though it occurs at a much slower rate is of particular importance for biological ordering processes. The diffusion coefficient increases with temperature for gases the diffusion coefficient is approximately $T^{3/2}$ (Hirschfelder et al., 1954). Where $T$ is the absolute temperature. Thus, one should look for a system with a higher order characteristics of life at temperature higher than 2.726K. The biochemical anabolic processes on the molecular level are highly temperature dependent (Straskraba et al., 1997). The influence of temperature may be reduced by the presence of reactions specific enzymes. The relationship between the absolute temperature $T$ and the reactions rate coefficient, $k$ for a number of biochemical processes can be expressed by the following general equation

$$\ln K = -b - A/RT$$

$A$ = activation energy, $b$ is a constant, $R$ = gas constant.

**Natural conditions**

The natural conditions involves; (i) The system is open, (ii) an influx of low entropy that can do work is necessary. (iii) An out flow of high entropy energy, is necessary i.e. 2.726K,(iv)Entropy production accompanying the transformation of energy and heat in the system it is necessary cost of maintaining the order and (v)mass transport of processes at a not too high low rate are necessary. This means that the liquid /gases phase must be anticipated. A higher temperature implies better mass transfer and also a higher reaction rate/an increased temperature means faster breakdown of macromolecules, therefore a shift towards catabolism. A temperature approximately, in the range of 260- 340K therefore be anticipated for carbon – based life. Thus, the biochemical conditions of the molecules are determined by the temperature of the ecosystem of the exergy supply to the system. Hierarchical organization ensures that the reactions of the exergy available on the molecules level can be utilized on the next level, the cell level and so on through out the entire hierarchy: molecules cells organs organisms’ population ecosystem. The maintenance of each level is dependent as its openness to exchange energy and matter. The rates in the higher levels are dependent on the sum of many processes on the molecular level. Further, they depend on openness to exchange energy and matter. They are further dependent on the slowest processes in the chain: supply of energy and matter to the unit- the metabolic processes- excretion of waste heat amino waste materials. The carbon based life on earth requires abundant water to deliver two important element, H and O, as solvent for compounds containing the other needy elements as compound which is liquid at suitable diffusion coefficient, a suitable specific heat capacity to buffer temperature fluctuations and a suitable vapor pressure to ensure a suitable cycling rate of these crucial chemical compounds. Thus, the biochemical determined conditions can be summarized as 2 points. Abundant presence of unique solvent water. Water being a pre request for the formation of life form the presence of N, P, S and other metal ions seems absolutely necessarry for the formation of carbon based life.

The use of second law of the Thermodynamics for open ecosystem is crucial. At first look it appears that ecosystem violates the second law of thermodynamics, because they are moving away from the thermodynamic equilibrium by formation of a biological structure. In ecosystem steady state the formation of the biological compounds (anabolism) is in approximate balance with the decomposition (catabolism). The energy captured by the ecosystem may be in principle, be any form of energy (electromagnetic, electrical, magnetic, chemical, mechanical) but for ecosystem earth, the solar radiation (electromagnetic energy) plays a major role. All biosphere energy process uses only electromagnetic energy. If human uses only electromagnetic energy than all environmental / ecological crisis can be resolved. But, as soon as Human began to use the later forms of energy (nuclear power plant) and moreover intends to use the thermonuclear synthesis, she enters into principal contradiction with the biosphere.

The consequence of energy processes operates (Jorgenson, et al., 1997) source, solar radiation – anabolism (Charge phase) incorporation of high quality energy with enentrained work capacity, into complex bimolecular structure, entailing anti entropic system moment away from equilibrium – catabolism ( discharge phase) – sink.

**Exergy**

Energy cannot be neither created nor destroyed, it just changes form. This energy in turn is used in every day life as two distinct meaning. The first being the abstract additive conserved property that is used in modeling. The second refers to exergy which quantifies the ability to cause changes and is not certainly conserved. Thus, by definition the exergy (Ex) of a system or resource is the maximum amount of useful work that can be obtained from this system or resource, when it is brought to equilibrium with the surrounding through reversible process in which system is allowed to interact only with the environment.

$$\text{The exergy} = \text{entropy production} \cdot (S_{gen}) \times \text{temperature} (T_o)$$

$$\text{Ex}_{\text{loss}} = T_o S_{gen}$$

The exergy or work potential of a system (as resource) is usually split up into four contributions: potential energy, due to its position in the given body force field (Gravitational, magnetic, etc). Kinetic energy due to its velocity with respect to a fixed reference frame, Physical exergy due to its pressure ($P_o$) and temperature ($T_o$) being different from the surrounding, $P_s$ and $T_s$ and chemical energy due to its composition being different from the surrounding. System without kinetic, potential or physical exergy are considered to be at the environmental state, system without chemical exergy have no potential at all and are considered to be at the dead state, being in full equilibrium with the surrounding, therefore they cannot produce any work. Potential and kinetic exergy are equivalent to potential and kinetic energy; physical exergy can be calculated from the enthalpy (H) and entropy (S) of the system at its actual T and P and at environment $T_o + P_o \text{Ex}_{\text{loss}} = (h-T_sS)$

$$= (H-T_sS)$. The equation represent the physical exergy transport by a flowing system, per unit of mass flow. The physical exergy content of material per unit mass, equals $u + P_sV-T(S-g)$, where $u$ = is the internal energy $v = \text{vol and g} = \text{Gibbs free energy, each /unit mass}.$
xergy in Natural system analysis

Various workers have tried to implement the laws of Thermodynamics to natural ecosystem. Schneider and Kay (1994) reformulated the second law of thermodynamics as adaptation to another system. This they called ecosystem — xergy concept. This concept suggest that ecosystem tend to develop structural and functional attributes that lead to more effective degradation of the energy flows possibly through the system. It depends upon two axioms (a) maximum storage principle, i.e. for any site with given abiotic features and a given local gene pool. The ecosystem tend to develop towards the state with the highest possible exergy content terms of biomass, genetic information and complex structural network. (ii) The maximum dissipation principle means ‘that for any state the ecosystem strives to attain the maximum dependence of the inputs exergy flows. Both principle were linked by Svirezhev and Steinborn (2001) minimum principle Which states that during the process of self organization, ecosystem tends to maximize their exergy in respect to the increment of information and to minimize it in respect to their radiation balance, this is considered a as a generalization of Carnot cycle to open system, far from equilibrium. Comparison of energy and energy

Thermodynamics of living organisms

The process of self organization and evolution of living organisms can be explained by the thermodynamics point of view. Though the first efforts were carried out by various workers (Ostwald, 1931; Bauer, 1935; VonBertalanffy, 1942; 1952; 1956; Schrodinger, 1944; Prigogine and Wiame 1946). For an organism to be in at steady state, it is necessary that energy balance must be maintained. Apart from energy, entropy must also be fulfilled. The basic function of metabolism in a living organism is to suck the amount of entropy, which is at least equal to entropy produced within the organisms, by means of the exchange of matter and heat with the environment. The export of entropy is achieved by (i) heat transfer, (ii) matter exchange and (iii) transformation of matter within the system. The first part, heat conductivity and irradiation plays a role. This is achieved by a certain difference in temperature and is essential to maintain the difference in temperature, needed to be maintained between the organisms and its environment. $T_{org} - T_{env} = T > 0$. Based on temperature, animals are divided into two groups, poikilotherms and homotherms. Poikilotherms with $T_H$ Constant. And homotherms with $T_H H^*$Constant. The latter can transfer a quantity of heat ‘q’ in a unit time into the environment by means of heat conductivity. In addition the organisms can get radiation energy ‘q’ in the course of the same time. Presuming that, if the incoming radiation to the organism is
from a black body with temperature, $T_{rad}$, then it corresponds to the entropy in flow, $q_{rad} = 4q_{rad} \times T_{rad}$, where the factor (4/3) is Planck's form factor, which takes into account some peculiarity of entropy transport by means of radiation (Landau and Lifshitz, 1995). In a solar radiation, the energy is used by plants for photosynthesis, $q_{photo}$. Thus, the accurate description it is necessary to assume the different thermal components $q_{photo}$ with different radioactive temperature $T_{photo}$.

In nature, the Fungus extracts energy from tree stumps by oxidizing the complex molecules that make up wood. Oxidation, being a chemical process not only involves adding oxygen to molecules (or removing H), but also stopping an electron from it. Reduction is the reverse reaction, where by an electron is taken from one molecule (the reductant, or fuel) and passed to another, the oxidant. This reaction – oxidation process is called redox. Almost all eukaryotes extract energy by breaking down carbohydrate molecule (glucose) and oxidize it to produce water and carbon-dioxide. Human use oxygen because the cells use this molecule (glucose) and oxidize it to produce water and carbon-dioxide. The laws of matter conservation is used for chemical compounds that can be transformed into other chemical compounds, thus, the equation: Change of mass or energy = inputs – outputs is changed to $V_{dC/dt} = \text{input-output + formation} \rightarrow \text{transformation. Where, } V = \text{volume, } C = \text{concentration at the i}^\text{th} \text{ substance. This principle is used in the biogeochemical models. The equation is set for the replacement element, e.g. for the eutrophication models for C, N, P and perhaps Si (Jorgenson. 1976; 1992; Jorgenson and Mejer, 1977). For terrestrial ecosystem, mass per unit area is often applied in mass conservation, thus, equation, becomes, $Adm/dt = \text{input – output + formation} \rightarrow \text{transformation Where, } A \text{ is area and } m = \text{mass/unit area. The transformation of solar energy to chemical energy by plant conforms with the first law, which represent. Solar energy assimilated by plants = chemical energy of plant tissue growth + heat energy of respiration. Thus, for the herbivorous animals the energy balance can be as follows F = As – UD = Gr – Re + UD F = food intake converted into energy (J) as= energy assimilated by the animal, UD= undigested food or the chemical energy of feces, Gr= chemical energy of the animals growth and Re= heat energy of respiration. The conversion for biomass to chemical energy is shown in Table 2. The energy content per 1g ash free organic material is uniform. The energy content in the table is the energy of “dead matter” applied as fuel due to elementary composition. Thus, $^{+H}$ (increase in enthalpy) defined as $H = U - pv$. The energy being originated from the following chemical processes; organic matter + oxygen = carbon-dioxide + water + other in organic compounds nitrate, sulphate and phosphate. The biomass thus, can be translated into energy and can be

Table 1: Differences between energy and exergy

<table>
<thead>
<tr>
<th>Energy</th>
<th>Exergy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dependent on the parameters of matter or energy flow only and independent of other environment parameters</td>
<td>Is dependent on the parameters of matter or energy flow and on the environment parameters</td>
</tr>
<tr>
<td>Has the value different from zero (equal to mc² upon Einstein Equation)</td>
<td>Is equal to zero (indeed state equilibrium with the environment).</td>
</tr>
<tr>
<td>Is governed by first law of thermodynamics for all the processes</td>
<td>It is governed by the first law of thermodynamics for reversible processes only (in irreversible processes due to the second Law of thermodynamics)</td>
</tr>
<tr>
<td>Is limited to the second law of thermodynamics for all processes (include reversible ones)</td>
<td>Is not limited for reversible processes due to the second law of thermodynamics</td>
</tr>
<tr>
<td>Is motion or ability to produce motion</td>
<td>Is work or ability to produce work</td>
</tr>
<tr>
<td>Is always conserved in a process, so can neither be destroyed or produced</td>
<td>Is always conserved in a reversible process, but is always consumed in an irreversible process</td>
</tr>
<tr>
<td>Is a measure of scalar quantity</td>
<td>Is a measure of quantity and quality due to entropy</td>
</tr>
</tbody>
</table>

Table 2: Combustion heat of animal materials

<table>
<thead>
<tr>
<th>Animal</th>
<th>Heat of Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahymena pyriformes</td>
<td>-5.938</td>
</tr>
<tr>
<td>Hydra littoralis</td>
<td>-6.034</td>
</tr>
<tr>
<td>Dusera tigrina</td>
<td>-6.286</td>
</tr>
<tr>
<td>Bipalium leewense</td>
<td>-5.684</td>
</tr>
<tr>
<td>Siccinea oralis</td>
<td>-5.415</td>
</tr>
<tr>
<td>Artemia sp</td>
<td>-6.737</td>
</tr>
<tr>
<td>Leprodora kindtii</td>
<td>-5.605</td>
</tr>
<tr>
<td>Calanusgelolodnicaus</td>
<td>-5.400</td>
</tr>
<tr>
<td>Trigropus californicus</td>
<td>-5.515</td>
</tr>
<tr>
<td>Trygophlyus lintneri</td>
<td>-5.808</td>
</tr>
<tr>
<td>Tenebrio molitor</td>
<td>-6.314</td>
</tr>
<tr>
<td>Lebbistes reticulatus</td>
<td>-5.823</td>
</tr>
</tbody>
</table>

After the glucose is broken down into two Carbons and this carbon is fed into Krebs cycle. This molecule steadily oxidize by releasing an electron here and produce ATP. Thus, the process is recycled indefinitely. In principle, any redox reaction yield electrons that can be used to drive cellular metabolism e.g. Fe²⁺ ferrous iron is oxidized to give Fe³⁺ and a free electron.

$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^\cdot$. Ferrous ion is green, when it loses electron and becomes Fe³⁺ it turns red brown, rust color. The fundamental position of the carbon carrier and transport chain in the biochemistry of all cells implies that they probably formed the basis of the very first metabolism (Fig. 5).

Thermodynamics in Ecology

The laws of matter conservation is used for chemical compounds that can be transformed into other chemical compounds, thus, the equation: Change of mass or energy = inputs – outputs is changed to $V_{dC/dt} = \text{input-output + formation} \rightarrow \text{transformation. Where, } V = \text{volume, } C = \text{concentration at the i}^\text{th} \text{ substance. This principle is used in the biogeochemical models. The equation is set for the replacement element, e.g. for the eutrophication models for C, N, P and perhaps Si (Jorgenson. 1976; 1992; Jorgenson and Mejer, 1977). For terrestrial ecosystem, mass per unit area is often applied in mass conservation, thus, equation, becomes, $Adm/dt = \text{input – output + formation} \rightarrow \text{transformation Where, } A = \text{area and } m = \text{mass/unit area. The transformation of solar energy to chemical energy by plant conforms with the first law, which represent. Solar energy assimilated by plants = chemical energy of plant tissue growth + heat energy of respiration. Thus, for the herbivorous animals the energy balance can be as follows F = As – UD = Gr – Re + UD F = food intake converted into energy (J) as= energy assimilated by the animal, UD= undigested food or the chemical energy of feces, Gr= chemical energy of the animals growth and Re= heat energy of respiration. The conversion for biomass to chemical energy is shown in Table 2. The energy content per 1g ash free organic material is uniform. The energy content in the table is the energy of “dead matter” applied as fuel due to elementary composition. Thus, $^{+H}$ (increase in enthalpy) defined as $H = U - pv$. The energy being originated from the following chemical processes; organic matter + oxygen = carbon-dioxide + water + other in organic compounds nitrate, sulphate and phosphate. The biomass thus, can be translated into energy and can be
transformed through trophic chains. Thus, it implies that short trophic chains, of grain to human should be preferred to the larger and more wasteful "grain to domestic animal to human."

The problem of food shortage, though cannot be solved simply, since, animals produce proteins with a more favorable amino acid composition for human food today. But food production can to a certain extent be increased by making the trophic chains as short as possible. This relationship can be illustrated by using ecological pyramids that can either represent the number of individuals. The biomass (or energy) content or the energy flows on each level in trophic chains / trophic network. Only energy flows from true pyramid due to energy loss of heat by respiration. The pyramids based on number are affected by variations in size and the biomass pyramids by the metabolic rates of individuals. A wide spectrum of organisms exists in an ecosystem ranging in size from tiny microbes to large animals and plants. The small organisms, account for the most of the respiration (energy turnover), whereas, the larger organisms comprises almost of the biomass. It is therefore important for the ecosystem to maintain both small and large organisms as it will mean both energy turnover rate and the energy storage form of biomass are maintained.

Ecosystem theories

Boltzmann (1905) said that the struggle for existence is a struggle for free energy available for work which is by definition very close to the maximum exergy principle. Similarly, Schrodinger (1944) pointed out that organization is interpreted as system that are able to gain most exergy under the given conditions i.e. to move the farthest from the thermodynamic equilibrium will prevail. Exergy is defined as the useful or available energy of the system relative to the environment > such system will gain most biochemical energy available for doing work and therefore have most energy stored to be able to struggle at their existence. Boltzmann proposed that 'Life is a struggle for the ability to do work 'which is exergy, thus can be expressed as. Free energy = energy - temperature x entropy. That can be interpreted as (Straskraba et al., 1997). Energy – disorder = energy + order

The difference between the free energy and exergy is the ability with exergy to select a case dependent reference state.

Maximum Biomass

Biomass is a stored energy some of which can be turned into work. This portion is exergy. The inherent order in which is taken into account through multiplication by N[i]'s .The ability of a species to perform work in an ecosystem. Exergy / free energy, is proportional not only to its information content, but also to its biomass as ecological function (Margalef, 1968; Straskraba et al., 1979, 1980 Brown 1995). As biomass is storage and has exergy, its maximization would be at least partly consistent with the exergy storage hypothesis.

Maximum power

The transformation of energy to perform work is correlated with the amount of exergy available (stored / in passage) with in the system. The more the exergy stand. The more is available to be drawn on for work at a later stage, which requires conversion from storage to through flow in order to achieve storage, there must be inflows to sequester.

Minimum specific entropy

Mauersberger (1983; 1995) proposed minimum entropy principle "derived from principle of least specific dissipation from far – from equilibrium thermodynamics (Prigogine, 1947). Aoki (1988; 1989; 1993; 1995) Compared entropy production which reflect exergy utilization in terms of maintenance versus exergy storage in different lake system. Entropic lakes capture and store more exergy, then subsequently use it for maintenance (Jorgenson, 1982; Salmonson, 1992) that entropic lakes have more biomass, thus more stored exergy but following one from this also greater through flow and dissipation, loss specific dissipation, then mesotrophic or oligothrophic lakes. Biomass specific exergy in other words decreases with increasing eutrophication.

Maximumemergy

Odum (1983a, b) introduced the term "embodied energy" later contracted to "emergy ". Emergy is expressed in solar energy equivalents, though Emergy and exergy conceptually
and computationally may be different quantities and though
emergy calculates how much solar energy it cost. To build a
structure whereas exergy expresses the actual work potential
for growth the two measure co relates well when computed
for models. The difference being emergy expresses costs in
solar radiation equivalent, while exergy expresses the result
(the standard working capacity). Bastianoni and Marchettini
(1996) found that a natural lagoon has a high exergy /emergy
ratio than man made waste water lagoon. Thus, nature
apparently is better able to utilize the emergy in order to obtain
exergy then manmade ecosystem (Bastianoni, 1998).

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for their classic book on “Towards a thermodynamic theory
for ecological systems”. Which has introduced the concept of
thermodynamics and a must read for ecologists. Author has
profusely referred to sources from this book.

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