STORAGE OF CHEMICAL ENERGY AND NUCLEAR MATERIALS

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Contents

Summary

The socio-cultural evolution of humankind have gone through several breakthroughs in the past 100 000 years. The “hunter-gatherer” cultures have evolved to “farmers” once they were able to cultivate and “store” their food. Currently, the primary concern of the humankind is to be able to “store” energy when and where it is abundant to be used when and where it is scarce. In this section you will find a general review of storage of chemical energy. Storage of chemical energy encompasses different meanings to different people, thus this section is organized accordingly. After a general introduction the second section was dedicated to the storage of both thermal and solar energy in chemical bonds. The second section was concluded with a subsection on the concept of efficiency of the release of stored energy. The third section was dedicated to the utilization of the stored chemical energy for electricity generation. Issues concerning the chemical energy storage were discussed in the fourth section. Storage of chemical energy in hydrogen, gaseous, liquid fossil fuels was discussed. Storage of solid fuels and alternative fuels were also covered in this section. A future outlook of alternative fuels was presented in the fifth section. Finally the chapter was concluded with two sections on sustainability and energy conservation.

1. Introduction

In the legends the life force is represented by the fire that Prometheus stole from heaven; in history, “discovery of fire” is regarded as a turning point in human and its socio-cultural evolution. The discovery has allowed human beings to gain more independence, survive harsh climates and thus climb one step upwards in the social evolutionary ladder. Originally the source of chemical energy was limited to combustible materials available in the immediate environment. Fire was most essential during the winter. Fuel had to be accessed as needed, thus, the hunter-gatherer cultures have developed a strategy to collect and store combustible materials for winter. As the social evolution has progressed, humankind exploited coal and oil. Archeological evidences indicate the use of oil by Sumerians, Assyrians and Babylonians for illuminants. Egyptians used the oil for medical purposes. The earliest evidence of coal utilization is related to the Chinese about 5000 years ago. But the use of the chemical energy in everyday human life was limited to household heating and cooking and in the manufacture of copper, iron and ceramic objects until the Industrial Revolution which began in the 18th Century.

The Industrial Revolution, started as the large scale production of steel required the access to coal, coke being one of the raw materials in steel processing and as the source of energy for the steel manufacture. Thus the coal mines started to be exploited at an unprecedented rate in the history. Steam engine “mobilized” the energy utilization as well as completely transformed the issue of transportation. Until the discovery of the steam engine, the transportation was powered by animals on the land and wind on the sea; completely renewable and environmentally friendly solutions. But once the steam engine replaced those, the transportation was faster, so was the development. Human beings learned to exploit the power harnessed in coal not just for its heating value, but for its ability to generate mechanical energy and in turn generate electrical energy. When steam engines were driving the trains of passengers and goods, it was possible to transport coal from distant places and utilize in areas where coal once was not available as a source of energy; thus emerged the need for transportation and storage.

Similar to coal/steam engine history, oil/car story emerged at the end of the 19th century. Until the 18th century, oil collected from surface seeps was used. The commercial production of oil from underground has changed the world history irreversibly. Oil was easier to transport than coal, and easier to use in the continuous operation of burners.

The invention of internal combustion engine has led to “The Machine That Transformed The World (Womack *et al.,* 1990)”. However, oil was not available in every part of the world, but the need for oil dispersed as fast as the need for facile land, sea and air transportation. Thus the need for storage of oil in the raw and in the processed form has emerged.

2. Storage of Energy in the Chemical Bond

Chemical bonds are formed when atoms combine to form molecules. The chemical bonds in molecules can be placed in three broad categories:

- Ionic bonds are formed when the electrons are transferred from one atom to the other, ionizing both the atoms.
- Covalent bonds are formed when the atoms mutually share their electrons. A single covalent bond is formed when a pair of electrons was shared between two atoms.
- Metallic bonds are formed in metals and alloys. The metal electrons freely move in the three-dimensional structure formed by metal alloys, while maintaining the bonds between the atoms.

The energy required to form the bonds is called the bond formation energy. Conversely, the energy required to dissociate the bonds is called the bond dissociation energy. During the chemical transformations, energy is provided to dissociate the bonds between the atoms, and some of this energy is used to form new bonds between the atoms. *Chemical energy* is the net energy stored in the chemical bonds of atoms and molecules as a result of the chemical reactions.

All of the chemical reactions require a transfer of energy -called the activation energy of the reaction- to drive the chemical components from one molecular configuration to another. The products of the reaction may be at a higher energy state than the reactants, thus maintaining part of the energy provided to drive the reaction. These types of reactions are called *endothermic* reactions.

On the other hand, the product molecules may possess less energy than the energy sum of the reactant molecules. The excess energy must be released to the environment as heat. These types of reactions are called *exothermic* reactions. Therefore, it is possible to store thermal energy in the molecular bonds by endothermic reactions, and release them by exothermic reactions.

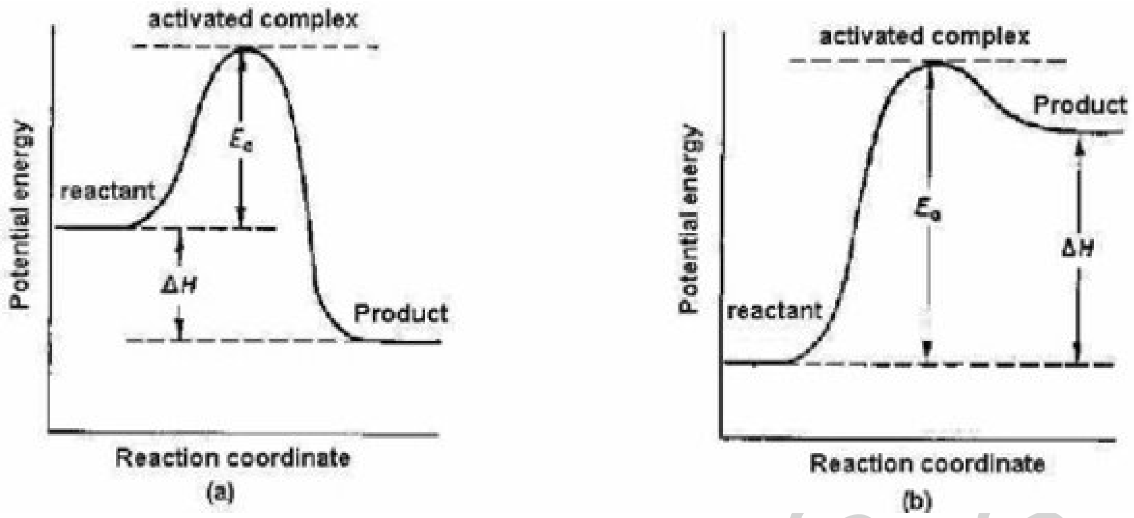

Figure 1: Energy route for (a) exothermic and (b) endothermic reactions

In biological systems, reactions that require energy transfer also take place. In such systems the chemical conversions that require net absorption of free energy are called *endergonic*, while the chemical conversions that release free energy to the surroundings are called *exergonic.*

Energy transfer to chemical bonds can be induced by physical means or by chemical means. The physical means of energy transfer can change the state of aggregation of a molecule, inducing a phase change, or can change the translational or vibrational degrees of freedom inducing an increase in temperature of the system (more detailed information can be found in *Storage of Thermal Energy*. The chemical means of energy transfer changes the molecular structure, and will be covered here in a greater depth.

Chemical bonds can be activated by thermal means, i.e., by providing heat, or by interaction with electromagnetic radiation, i.e., by absorption of radiation at a proper wave length. Chemical transformations that occur as a result of the interaction with the visible spectrum portion of the electromagnetic radiation deserves a lot of attention, because, this route enables the storage of solar energy for later utilization. In fact, this route establishes the basis for the food chain in nature. Plants can fix carbon in airborne carbon dioxide (CO_2) with water to form carbohydrates through the well known route of *photosynthesis.* In this route, plants use solar energy to provide the extra energy needed to drive the reaction through the activation barrier. The products of carbon dioxide fixation reaction store solar energy in chemical bonds for further utilization. The complete reaction route of photosynthesis is very complex and the coverage exceeds the scope of this chapter. However, a brief introduction is given in the next section, and the curious reader can refer to various biochemistry textbooks for a detailed understanding of the mechanism.

2.1. Storage of Solar Energy in Chemical Bond: Photosynthesis

Existence of living organisms on earth depends on the storage of solar energy in chemical bonds for later use. The living cells, the smallest building blocks of living organisms are defined as “self-contained, self-assembling, self-adjusting, self-perpetuating isothermal system of molecules that extracts free energy and raw materials from the environment (Lehninger *et al.*, 1993)”

The self-perpetuating nature of the living cell is the basis for life. In order to maintain the self-perpetuating nature, the cells need to extract free energy and raw materials from the environment. The living organisms have developed complex mechanisms for extraction and storage of energy through the evolutionary process. The energy storage for later use was done through chemical bonds.

Living organisms that can use atmospheric carbon dioxide as their sole source of carbon and construct their carbon containing bio-molecules are called *autotrophs*. *Heterotrophs*, on the other hand, can not use atmospheric carbon dioxide, and they must obtain their carbon from the products of autotrophs, in the form of complex molecules such as glucose or carbohydrates. Most autotrophs are photosynthetic; they harvest the energy from solar light for carbon dioxide reduction reactions.

The overall photosynthesis reaction is an oxidation-reduction reaction where water donates electrons for the reduction of carbon dioxide to carbohydrate

$$\mathrm{CO_2 + H_2O \xrightarrow{light} O_2 + (CH_2O)} \qquad (1)$$

Photosynthesis reaction takes place in two general steps. In the fist step, called the light reactions, chlorophyll and other pigments of the photosynthetic cells absorb light energy and conserve it in chemical form in ATP and NADPH, while releasing oxygen. ATP (adenosine tri-phosphate) is the major carrier of chemical energy in all cells while NADPH (nicotinamide adenine dinucleotide phosphate) assists in the electron and proton transfer reactions. In the second step, called the dark reactions, ATP and NADPH are used to reduce carbon dioxide, to fix carbon in the form of glucose and other organic products. The carbohydrates synthesized as such are used in complex biochemical reactions in the metabolism for purposes ranging from self perpetuation to combustion to maintain the cell isothermal.

It is worth noting here that an enormous amount of energy is stored as products of photosynthesis. Each year, an estimated 10^{17} kJ of solar energy is harvested by photosynthetic organisms and used in biosynthesis. This amount is about ten times as large as the fossil energy used by the people through out the world. The fossil fuels themselves are also the products of photosynthesis. Coal, oil and natural gas are formed from the fossilized remains of vegetation and fish, thus called the fossil fuels.

2.2. Release of Energy Stored in Chemical Bonds

Energy stored in chemical bonds can be released through electron transfer reactions or through heat releasing exothermic reactions. Since the chemical bonds are formed by exchange (ionic bonds) or sharing (covalent bonds) of electrons, during the chemical energy release by electron transfer processes route, the chemical bond transformations result in direct generation of electricity. The operation of batteries and that of fuel cells depend on this principle. If a circuit is established between an electron donor reaction and an electron acceptor reaction, the flow of electrons can be utilized to drive electric motors, for illumination or for muscular movement in animals.

The energy stored in chemical bonds is also released through combustion. Combustion processes are exothermic reactions. The reactants entering the combustion reactions are usually hydrocarbons and oxygen. When the hydrocarbon molecules are oxidized to form carbon dioxide (CO_2) and water (H_2O) energy stored in the carbon-carbon and carbon-hydrogen bonds are released as heat. In the metabolism of living organisms, combustion reactions take place to provide the necessary energy to do work. This fact was first noted by the French Chemist Antoine Lavoisier (1743-1794):

"… in general respiration is nothing but a slow combustion of carbon and hydrogen, which is entirely similar to that which occurs in a lighted lamp or candle, and that, from this point of view, animals that respire are true combustible bodies that burn and consume themselves… One may say that this analogy between combustion and respiration has not escaped the notice of poets, or rather, philosophers of antiquity, and which they had expounded and interpreted. The fire stolen from heaven, this torch of Prometheus, does not only represent an ingenious and poetic idea, it is a faithful picture of operations of nature, at least for animals that breath; one may therefore say, with the ancients, that the torch of life lights itself at the moment the infant breathes for the first time and it does not extinguish itself except at death" (Lehninger *et al.*, 1993).

2.3. The Concept of Efficiency of Releasing Stored Chemical Energy

The efficiency of releasing the stored chemical energy depends on the pathway taken. The efficiency of utilization of the released chemical energy via the combustive pathway depends on the end use of the heat and the limitations are quantified via the tools of thermodynamics.

2.3.1. A Thermodynamic Analysis of Thermal Energy to Mechanical Energy Conversion Efficiencies

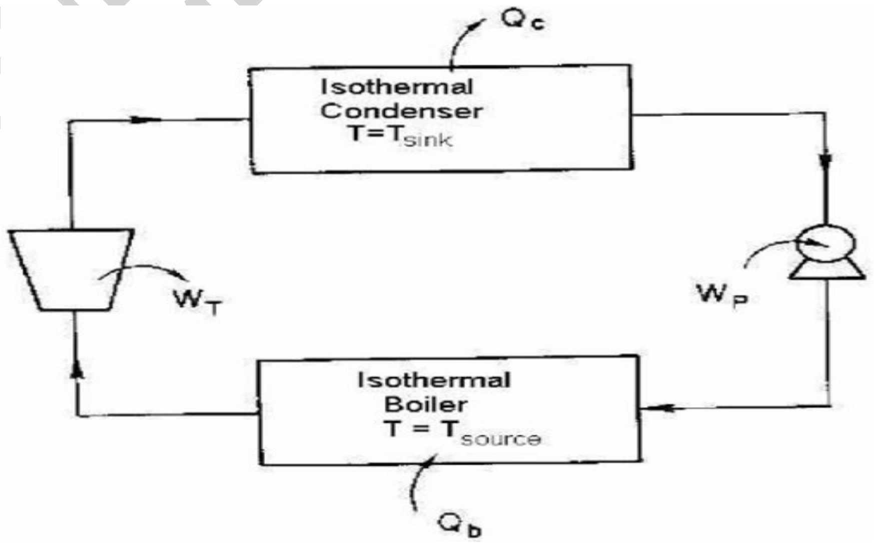

Figure 2: Carnot cycle.

The science of thermodynamics has emerged along with the invention of the steam engine. In the steam engine, heat (thermal energy) is converted to work (mechanical energy). The conversion of thermal energy to mechanical energy can be done directly, as in the case of internal combustion engines, or through a medium that carries the energy such as steam in steam power cycles. The capability of extracting work from heat depends on the engine or cycle design. The most efficient hypothetical cycle, known as Carnot cycle is given in Figure 2.

Carnot cycle being the ideal one puts certain limits on how much energy one can extract from heat. If the efficiency of a cycle is defined as

$$\eta = \frac{-\mathrm{W_{net}}}{\mathrm{Q_b}} = -\frac{\mathrm{W_T} - \mathrm{W_P}}{\mathrm{Q_b}}, \qquad (2)$$

where η is the fractional efficiency of the cycle, Q is the heat given to the system at the high temperature zone and W_{net} is the net work extracted from the system and is equal to the difference between the work extracted from the turbine, W_{T}, and the work spent to drive the pump, W_{P}. Q_{b} in equation (2) refers to the heat input to the boiler.. As one examines the cycle, it is clear that the cyclic operation is based on the heat input and heat extraction from the system. In fact, the conservation of energy and the 2nd law of thermodynamics together require that the amount of net work generated must always be less than the amount of heat input to the system, since for cyclic operation some amount of heat must be released outside the cycle. Another observation one can make from the Carnot cycle is the relationship between the cycle efficiency and the temperatures of the heat source and the sink:

$$\eta = \frac{-\mathrm{W_{net}}}{\mathrm{Q_b}} = \frac{\mathrm{T_{source}} - \mathrm{T_{sink}}}{\mathrm{T_{source}}}, \qquad (3)$$

Thus one immediately concludes that the higher the heat source temperature, the higher the cycle efficiency. Hence, if one can reach infinitely high temperatures, the efficiency of the ideal Carnot engine can be as high as 100%. In reality in thermal to mechanical energy conversion cycles, the upper limits in temperature are limited by the adiabatic flame temperature of the fuel and by the resistance of the material of construction of the equipment to high temperatures. So, typical efficiencies of conversion of thermal energy to mechanical energy range from 25 to 40 %. At, this point it should be obvious to the reader that energy at high temperatures is more valuable than energy at lower temperatures.

Another concept that needs to be introduced here is entropy. The term entropy literally means “the change within”. The change in entropy is used to measure the degree of disorder as a result of a process. According to the second law of thermodynamics, the entropy always increases as a result of the processes taking place in the universe. One of the many definitions identifies entropy with the irreversibility of the arrow of time. In fact, the concept of entropy is used to specify the regular path that a process can take. The quantitative definition of entropy is:

$$S = \frac{Q}{T}, \qquad (4)$$

where S denotes the entropy, Q, the amount of heat transfer and T the absolute (Kelvin or Rankine scale) temperature at the point of contact of heat transfer between the system and the surroundings. During a process, in addition to entropy increase as a result of direct heat transfer interactions, entropy is also generated due to the irreversibilities. This generated entropy is released to the universe as unrecoverable and unusable heat. For example, the bearings of machinery warm up due to the friction. In this process, the mechanical energy is irreversibly converted to heat and released to the environment, thus resulting in entropy generation. Entropy generation is also known to be proportional to the speed of the process. Faster processes generate more entropy than slower processes for the same net process yield. Thus, faster processes consume more energy than slower processes and therefore less efficient.Another example of entropy generation is the resistive heating. When current is flowing through a charge carrier with finite resistance, some of the electrons get dissipated in the material lattice while releasing heat. The lost electrons indicate decreased efficiency of electron transport process and the released heat indicates the increase in the entropy of the universe.

If the chemical energy is to be released to generate electricity, the traditional pathway is to release the thermal energy in the form of heat and utilize this thermal energy in a power generation cycle to generate work. Work generated can be used to produce electricity. On the other hand, the stored chemical energy can be released through electron transfer reactions for the direct production of electricity. It must be clear to the reader that in the thermal to electrical energy generation route, the cycle efficiency requires that some of the heat generated must be discarded to produce work. The losses due to the non-idealities in the equipment result in further loss of useful energy in terms of heat, thus reducing the efficiency of the overall process. It is worth remembering that the efficiency of an ideal cycle discussed above, the Carnot cycle, is around 25-40%. The actual efficiencies of power generation cycles are about half of these values. On the contrary, the direct electrical energy generation routes through electron transfer reactions can be close to 90% for ideal instruments. In other words, it is, in principle, possible to utilize the chemical energy stored in every electron exchange bond.

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Biographical Sketch

Prof. Deniz Uner was born in 1964 in Elazig, Turkey. She received BS and MS degrees in Chemical Engineering from the Middle East Technical University (METU), Ankara, Turkey. Her doctoral study was on catalysis, she received PhD degree from Iowa State University, Ames, IA, USA. Prof. Uner has joined the Chemical Engineering Department of METU in 1995. Since then, 13 MS degrees were granted under her supervision. In 2004, she supervises 3 PhD candidates and 7 MS candidates. Prof. Uner's primary research interests are in the field of supported metal catalysis. She has conducted industrial projects towards emission control catalysis from mobile sources. Her interest in environmental catalysis is emphasized with the current research projects focusing on exhaust emission control catalysis, hydrogen generation reformer catalysts for fuel cell applications and artificial photosynthesis. Prof. Uner has co-authored 27 technical articles in national and international journals, and 50 presentations in national and international conferences. She teaches graduate and undergraduate courses on Thermodynamics, Catalysis and Chemical Reaction Engineering at METU. Prof. Uner is proud mother of her four children, Imre, Esen, Sedef and Firat Ozbay.