Chapter 1

Introductory Chapter: Historical and Newest Perspectives

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Additional information is available at the end of the chapter

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1. Historical background

The history of oxidation reduction reactions can be traced back to the early time of the human development, since the first time that the human knew the fire and used it in their daily life, especially the Copper-Bronze age of the human development, the early time, around 4000–8000 years ago. In that era, people were benefited by the use of copper in their life; they heated copper ores and coal in an oxidation reduction reaction by which copper ores are reduced to copper metal and coal is oxidized to carbon dioxide, and besides the production of copper, the Bronze age is also known to use clay in the production of pottery. Greeks are the first to use oxidation reduction reaction as oxidizing and reducing fire conditions for pottery making; this can be summarized as firing clay in a rich or indigent atmosphere of oxygen. Clay containing iron will turn to orange-red if fired under rich atmosphere of oxygen due to the presence of red iron oxide (higher oxidation state) or will turn to black if fired under indigent atmosphere of oxygen when black iron oxide forms (lower oxidation state). Then, the human development jumped to the Iron Age, which is around 3000–5000 years ago, when the human for the first time used iron mainly in production of knives and bayonets which were used in their daily lives and wars. A great historic jump in the oxidation reduction reactions is the use of explosives, first used by Chinese as early as 950 A.D. It was the Chinese who first developed this deadly weapon, but around the thirteenth century, the Europeans would have jumped on the technological band wagon, using it to devastate the natives of the New World during the Age of Exploration.

A modern exploration of the oxidation reduction reaction starts formally with Georg Ernst Stahl [1] in 1697 when he proposed the phlogiston theory [2], which was based on the premise that the metals often produce a calx when heated (calx is defined by Stahl as the crumbly residue left after a mineral or metal is roasted), and phlogiston is given off whenever metals or something were burned; moreover, the calxes form metals when heated with charcoal and wood, and charcoal is particularly rich in phlogiston because they leave very little ash when they are burned;

however, the theory of phlogiston was not widely accepted in the scientific media. Seventy-five years later, Antoine-Laurent Lavoisier (1743–1794) came with solid explanation of combustion [3]. In 1772, Lavoisier discovered that when phosphorus or sulfur is burned in air, the products are acidic in nature, and the products also weigh more than the original phosphorus or sulfur, and he came to the conclusion that the elements combine with something in the air to produce acids [4], but he could not recognize what was in the air that combined with phosphorus or sulfur. In 1974, he met Joseph Priestley (the father of oxygen discovery, 1733–1804) during his visit to Paris; he told Lavoisier about the gas produced when he decomposed the compound which we now call mercury oxide. This gas supported combustion much more powerfully than normal air. Priestley believed the gas was a particularly pure version of air; he started calling it dephlogisticated air, believing its unusual properties were caused by the absence of phlogiston. In 1779, Lavoisier coined the name oxygen for the element released by decomposition of mercury oxide, and from here, explanation of certain reactions as oxidation reduction officially started [5].

Coming back to the explosive materials, the year 1964 was the year that explosives, nitrocellulose and nitroglycerin, were both discovered, and later on trinitrotoluene (TNT), involved in weapon production and widely used in the First World War (1914–1919). The cheap mixture of ammonium nitrate and fuel oil was recognized as a powerful explosive in 1955, and this was used to bomb the Federal Building in Oklahoma City in 1995; finally, the explosives that were used in the fireworks are believed to be used for the first time in China in the sixth century.

Now, the five main types of redox reactions are combinations, decompositions, displacements, combustions, and disproportionations. In combination redox reactions, two elements are combined whereas one element becomes oxidant and the other reluctant; in decomposition redox reactions, a compound is broken down into its constituent parts; in displacement redox reactions, one or more atoms is swapped out for another; in combustion reactions, a compound reacts with oxygen to produce carbon dioxide, water, and heat; and in disproportionation redox reactions, a molecule is both reduced and oxidized. These types of reactions are rare, and many reactions are considered in the interface between these areas.

Concluding this historical background that chemists worldwide later recognized that other elements reacted in the same general manner as oxygen, the concepts of oxidation and reduction were extended to include other elements; electrochemistry as a new field is further broadening the definition of the oxidation reduction reaction. Investigators observed that the ferric ions could be formed from the ferrous ions by the action of oxygen gas. This consumption of oxygen, oxidation, involved a loss of electrons by the ferrous ions species, and hence, an oxidation reaction could refer also to a transfer of electrons.

2. Redox reactions in biological processes

An understanding of the redox reactions of inorganic and organic compounds is central to understanding the metabolism of living things. One of the most important processes that occurs in living organisms is photosynthesis, which consists of a series of oxidation reduction reactions; the series begins when the chlorophyll in barks or leaves of plant cells absorbs sunlight with certain wavelengths and converts carbon dioxide into carbon and oxygen in a reduction

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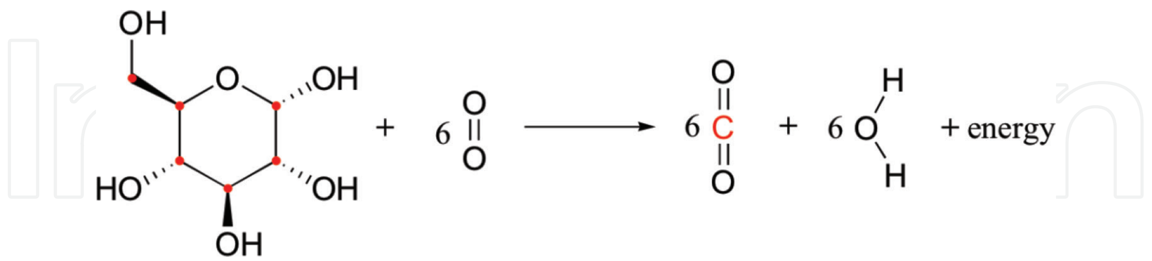
process and ends the series with the production of glucose molecules. In other organisms, glucose is being consumed to generate energy in a long series of enzyme-catalyzed reactions; in simple words, electrons can be transferred from glucose to molecular oxygen, oxidizing the carbon molecules to carbon dioxide and reducing O_2 to water.



This aspect of redox reactions in living organisms is called cellular respiration by which cells break down molecules of food (glucose) in a series of chemical reactions to produce energy, carbon dioxide, and water; the process depends heavily on the reduction of NAD^+ to NADH and the reverse oxidation reaction of NADH to NAD^+ as intermediate steps [6]. The oxidation of glucose is a thermodynamically favored process, meaning the transfer of electrons from

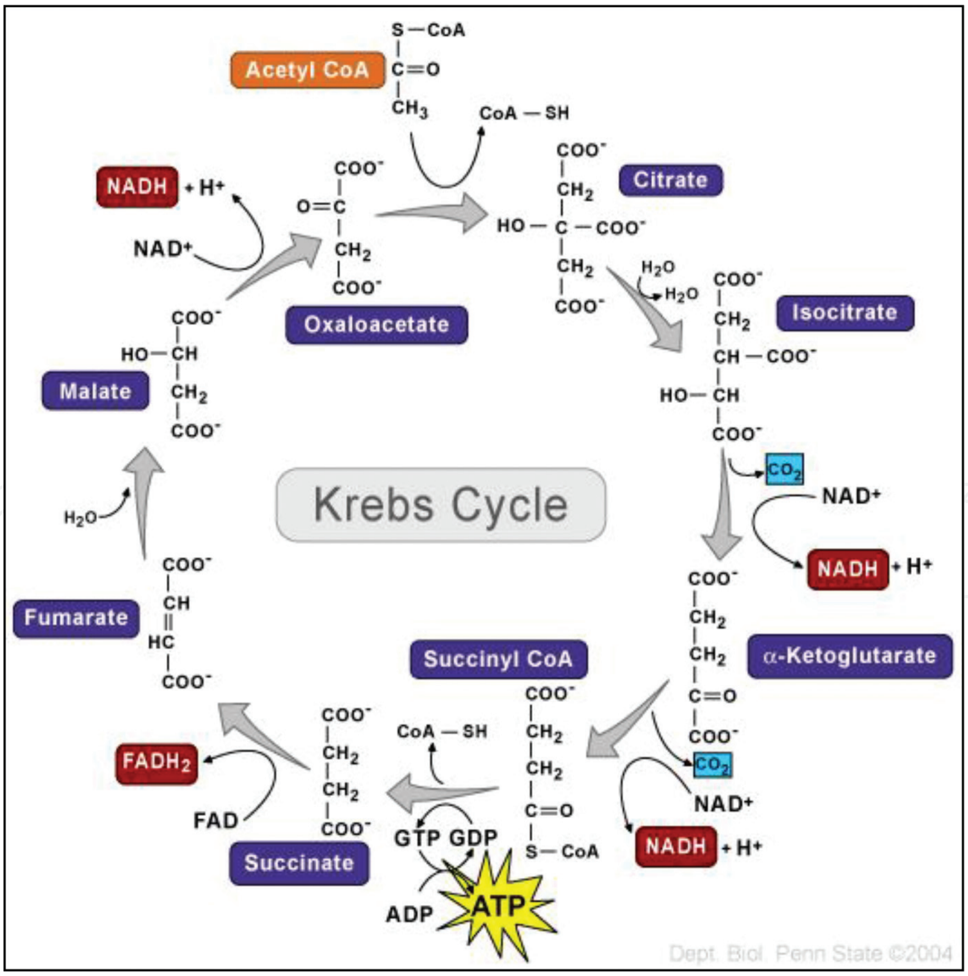


Figure 1. An illustrated diagram for Krebs cycle, copied from the website, https://wikispaces.psu.edu.

glucose to O_2 is thermodynamically downhill, and cells use this released energy to carry out a wide variety of energy-requiring activities. **Figure 1** illustrates how glucose is burned in a series of redox reactions and ends up in the formation of carbon dioxide and energy that is stored as adenosine triphosphate (ATP); in the diagram called Krebs Cycle which describes cell burning of glucose, enzymes are used in each step to lower the activation energy for each step and aid in breaking and formation of bonds; the overall reaction is a redox reaction, that is, electrons are lost or gained in each step.

Other biological processes that involve the redox reaction is the production of free radicals, which can be produced by detaching electrons from certain type of molecules and reattaching to another type of molecule instantaneously; free radicals play an important role for the programmed cell death (apoptosis), and any uncontrolled production of free radicals may lead to cause cancer [7].

3. Redox reactions in corrosion reactions

Corrosion is another type of redox reaction; it occurs when a metal comes in contact to a solution or at least moisture; the metal corrodes with evolving of electrons that move to cathodic part of the so-called localized galvanic cell, and then, cathodic reaction starts with the production of hydrogen gas if the electrolyte is acidic or conversion of water to hydroxide if the electrolyte is neutral or basic. In this case, the intensity of flow of electrons from the anodic part (metal) to cathodic part (electrolyte) is defined as the corrosion current; there may be some microscopic galvanic cells with adjacent distance or some distance apart if the electric current in the galvanic cells is huge and is more than the electrolyte capacity to allow the current to pass, then the operation is governed by the movement of electrolyte ions; on the other hand, if the electric current is less than the electrolyte capacity to allow the current to pass, then the operation is governed by activation energy. One of the famous corrosion examples is the iron rust, and in this case, iron is oxidized at the beginning to ferrous ions releasing two electrons, and the reaction will proceed as long as the metal is capable of releasing electrons and electrolytic solution to carry the ions; the corrosion current is increased by increasing the number of oxidized iron atoms, and if there is excess of oxygen in electrolyte, then ferrous ions are oxidized further to ferric ions that can give ferric oxide or ferric carbonate which is the main constituent of the iron rust. Besides iron, most of elements in the periodic table are capable to corrode, and corrosion now has become a global problem that should be controlled if it could not be stopped (according to the second law of thermodynamics); the biggest breakthrough that has been achieved in the corrosion research is the invention of the electrochemical series, a series in which ordering the periodic table elements depends on the redox potential, and the most benefit of this is trying not to gather two elements of far different reduction potential in one alloy because that is produced in fast corrosion.

4. Redox reactions in combustion reactions

To start a discussion on this, let us first ask this question, is the combustion reactions is a redox reaction? Answering this, as the oxidation state is changed from 0 in the molecular oxygen to −2

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in the species that produce in the reaction, the reaction is a redox in nature; combustion in the form of fire produces flame and a considerable amount of heat, which can make combustion self-sustaining. In case of burning metals such as mercury, copper, zinc, and so on, the product is the metal oxide; in case of burning organic molecules, the products are carbon dioxide, water, and heat, and the combustion reaction is not as easy as it looks; probably the reaction takes place in a series of more than 10 steps, and hence finding the overall rate of reaction becomes extremely complicated, and the computer softwares are the only logical solution for this. MatLab, Avogadro, Copasi, and Kintecus are some of the most powerful softwares used in this regard.

5. Redox reactions in explosion reactions

Potassium nitrate, when mixed with carbon and sulfur in correct ratios which are the constituents of gunpowder, nitrate is reduced to form nitrogen, mono and dioxides, while carbon is oxidized to form carbon mono and dioxides, and sulfur is oxidized to form di and trioxides. The reaction will not start unless it is initiated; it has been found that such reactions can be initiated by electric shocks, spark, or electric current, and the reaction is maintained in a series of complicated steps; production of all these gases increase suddenly the pressure, the contents of the reaction come to explode to relieve the pressure, and besides increase in pressure, temperature is also increased tremendously; the main mechanism of explosive reaction is the chain reaction by which one product of the reaction, called free radical, is initiated and activates other molecules in the reaction mixture, and the reaction is proceeded till all free radicals are used up.

Although nuclear explosion is one of the massive explosions on earth, but is not itself a redox reaction, and is something more complicated, as in the case of uranium, the nuclei split and form two different elements and release energy more than any ordinary explosive.

Nowadays, redox reactions fuel the most advanced form of the space transportation and the space shuttle; powdered aluminum and ammonium perchlorate are used to undergo redox reactions that produce the gases hydrogen and oxygen and give the shuttle enormous amount of extra thrust; the redox reaction is represented as follows:

$$3NH_4ClO_{4(s)} + 3Al_{(s)} \rightarrow Al_2O_{3(s)} + AlCl_{3(s)} + 3NO_{(g)} + 6H_2O_{(g)} + \text{energy} \quad (1)$$

It produces temperatures of about 5700 F and 3.3 million pounds of thrust in each rocket; thus, the redox reactions furnish the energy to launch the space shuttle.

6. Conclusions

Besides the above examples, so many examples can be drawn to prove the importance of applications of redox reactions in general life; in electrochemical cells, electrons formed from the oxidation of one element and pass through a conductor to the reduction element; bleaching solutions that are used to brightening clothes are made of oxidizing agent (clorox), and this oxidizes any constituent that is capable of being oxidized and then make clothes clean and bright, and so on.

In this summarized introduction, we aimed to draw the reader's attention to the wide range of applications as well as the importance of redox reactions; luckily, chapters of this book can be categorized into two main parts: Part (1) batteries and computer applications and part (2) drugs and biological applications, and the diverse of chapters exhibit clearly the wide range of researches in the field of redox reactions.

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