CHAPTER 1

HISTORY OF CHEMICAL REACTIONS

INTRODUCTION

Until the last century, most chemicals were discovered more or less by accident. Their potential uses were based on short-term observations and their syntheses based on sketchy and simple theoretical ideas. Much of the recent progress in chemical syntheses occurred because of an increasing ability of chemists to determine the detailed molecular structure of substances and also to better understand the correlations between structure and properties. A review of how this industry arrived at its present state is presented below. Sections to follow include:

Early History
Recent History
The Chemical Industry Today
Microscopic vs Macroscopic Approach

EARLY HISTORY

As noted in the Introduction, most chemicals were discovered by accident. No one can assign with certainty a birth date to what one would classify as a "chemical reaction." However, some have claimed that the first known chemical processes were carried out by the artisans of Egypt and China. These individuals worked with metals such as gold or copper, which often occur in nature in a pure state, but they learned how to "smelt" metallic ores by heating them with carbon-bearing materials. In addition, a primitive chemical technology arose in these cultures as dyes, potting glazes and glass making were discovered. Most of these inventors also developed astronomical, mathematical, and cosmological ideas that were used to explain some of the changes that are today considered chemical.

The first to consider such ideas scientifically were the Greeks at about 600 BC. They assumed that all matter was derived from water, which could solidify to earth or evaporate to air. This theory was later expanded into the idea that the world was

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Chemical Reactor Analysis and Applications for the Practicing Engineer. By Louis Theodore

composed from four elements: earth, water, air, and fire. It was Democritus who proposed that these elements combined to form atoms.

Aristotle believed that the elements formed a continuum of mass. He became the most influential of the Greek philosophers, and his ideas dominated science for nearly 1500 years. He believed that four qualities were found in nature: heat, cold, moisture, and dryness. He proposed that elements were made up of these with each element containing variable amounts of these qualities. These, in turn, combined to form materials that are visible. Because it was possible for each element to change, the elements could be combined because it was possible that material substances could be built up from the elements.

At approximately the same time a similar alchemy arose in China. The aim was to make gold, since it was believed to be a medicine that could offer long life or even immortality on anyone who consumed it. Nevertheless, the Chinese gained much practical chemical knowledge from incorrect theories.

After the decline of the Roman Empire, Greek writings were no longer studied in western Europe and the eastern Mediterranean. However, in the 7th and 8th centuries Arab conquerors spread Islam over Asia Minor, North Africa, and Spain. The Greek texts were translated into Arabic, and along with the rest of Greek learning, the ideas and practice of alchemy once again flourished.

A great intellectual reawakening began in western Europe in the 11th century. This occurred due to the cultural exchanges between Arab and Western scholars. Later, knowledge of Greek science was disseminated into Latin and ultimately reached all of Europe. Many of the manuscripts concerned alchemy.

Among the important substances discovered were alcohol and mineral acids such as hydrochloric, nitric, and sulfuric. The Chinese discovery of nitrates and the manufacture of gunpowder also came to the West through the Arabs. Gunpowder soon became a part of warfare. Thus, an effective chemical technology existed in Europe by the end of the 13th century.

During the 13th and 14th centuries the principles of Aristotle on scientific thought began to decline. The actual behavior of matter cast doubt on the relatively simple explanation Aristotle had prescribed. These doubts spread further after the invention of printing in 1450; these doubts increased into the 16th century.

It was during the first half of the 17th century that scientists began to study chemical reactions experimentally. Jan Baptista van Helmont laid the foundations of the law of conservation of mass. Van Helmont showed that in a number of reactions an "aerial" fluid was liberated which he defined as a "gas. " A new class of substances with their own physical properties was shown to exist. A kinetic–molecular theory of gases began to develop. Notable in this field were the experiments of Robert Boyle whose studies, later known as Boyle's law, provided an equation describing the inverse relation between pressure and volume of gas (see the ideal gas law in Chapter 3).

During the 18th century, chemists noted that certain substances combined more easily with, or had a greater affinity for, a given chemical than did others. Tables were developed showing the relative affinities of different chemicals. The use of these tables made it possible to predict many chemical reactions before testing them in the laboratory.

It was Joseph Priestley who discovered oxygen. He realized that this gas was the component of ordinary air that was responsible for combustion and made animal respiration possible. Priestley told the chemist Antoine Laurent Lavoisier about his discovery of oxygen. He at once saw the significance of this substance and the door was opened for the chemical revolution that established modern chemistry.

RECENT HISTORY

Lavoisier showed by a series of unique experiments that combustion was due to the combination of a burning substance with oxygen and that when carbon was burned, fixed air (carbon dioxide) was produced. An earlier proposed substance phlogiston therefore did not exist, and the phlogiston theory soon disappeared to be replaced by the carbon cycle. Lavoisier used the laboratory balance to give quantitative support to his work and he used chemical equations in his papers. He further defined elements as substances that could not be decomposed by chemical means and firmly established the law of the conversation of mass. He developed a chemical nomenclature that is still used today and founded the first chemical journal.

By the beginning of the 19th century, it was shown that more than one compound could be formed between the same elements. Joseph Gay-Lussac demonstrated that the volume ratios of reacting gases were small whole numbers, implying the presence of atoms. Dalton assumed that when two elements combined, the resulting compound contained one atom of each. He arbitrarily assigned to hydrogen the atomic weight of 1 and could then calculate the relative atomic weight of oxygen. Applying this principle to other compounds, he calculated the atomic weights of other elements and actually drew up a table of the relative atomic weights of all the known elements.

In the early 19th century (1803), Dalton proposed his atomic theory. In 1811, Amedeo Avogadro made clear the distinction between atoms and molecules of elementary substances. In addition, the concepts of heat, energy, work, and temperature were developed. The first law of thermodynamics was set forth by Julius Robert von Mayer and the second law of thermodynamics was postulated by Rudolf Julius Emanuel Clausius and William Thomson (Lord Kelvin). Later in the century, Clausius, Ludwig Boltzmann, and James Clerk Maxwell related the ideal gas law in terms of a kinetic theory of matter. This led to the kinetics of reactions and the laws of chemical equilibrium.

It was Carnot who proposed the correlation between heat and work. Josiah Willard Gibbs discovered the phase rule and provided the theoretical basis of physical chemistry. And, it was Walther Hermann Nernst who proposed the third law of thermodynamics and contributed to the study of physical properties, molecular structures, and reaction rates. Jacobus Hendricus van't Hoff related thermodynamics to chemical reactions and developed a method for establishing the order of reactions. Nearing the end of this century, Syante August Arrhenius investigated the increase in the rate of chemical reactions with an increase in temperature.

The development of chemical kinetics continued into the 20th century with the contributions to the study of molecular structures, reaction rates, and chain reactions by Irving Langmuir. Another advance in chemistry in the 20th century was the foundation of biochemistry, which began with the simple analysis of body fluids; methods were then rapidly developed for determining the nature and function of the most complex cell constituents. Biochemists later unraveled the genetic code and explained the function of the gene, the basis of all life. The field has now grown so vast that its study has become a new science—molecular biology.

THE CHEMICAL INDUSTRY TODAY

The growth of chemical industries and the training of professional chemists are intertwined. In the early 19th century during the Industrial Revolution, a number of universities were established in Germany. They drew students from all over the world and other universities soon followed suit. A large group of young chemists were thus trained just at the time when the chemical industry was beginning to exploit new discoveries. This interaction between the universities and the chemical industry resulted in the rapid growth of the organic chemical industry and provided Germany with scientific predominance in the field until World War I. Following the war, the German system was introduced into all industrial nations of the world, and chemistry and chemical industries progressed rapidly.

This scientific explosion has had an enormous influence on society. Processes were developed for synthesizing completely new substances that were either better than the natural ones or could replace them more cheaply. As the complexity of synthesized compounds increased, wholly new products appeared. Plastics and new textiles were developed, energy usage increased, and new drugs conquered whole classes of disease.

The progress of chemistry in recent years has been spectacular although the benefits of this progress have included corresponding liabilities. The most obvious dangers have come from nuclear weapons and radioactive materials, with their potential for producing cancer(s) in exposed individuals and mutations in their children. In addition, some pesticides have potential damaging effects. This led to the emergence of a new industry—environmental engineering. Mitigating these negative effects is one of the challenges the science community will have to meet in the future.(1,2)

MICROSCOPIC vs MACROSCOPIC APPROACH

The history of Unit Operations is interesting. Chemical engineering courses were originally based on the study of unit processes and/or industrial technologies; however, it soon became apparent that the changes produced in equipment from different industries were similar in nature, i.e., there was a commonality in the operations in the petroleum industry as with the utility industry. These similar operations became known as *Unit Operations*. This approach to chemical engineering was promulgated in the 1922 A. D. Little report (1922) submitted to the American Institute of Chemical Engineers (AIChE), and has, with varying degrees and emphasis, dominated the profession to this day.

The Unit Operations approach was adopted by the profession soon after its inception. During the 130+ years (since 1880) that the profession has been in existence as a branch of engineering, society's needs have changed tremendously and so has chemical engineering.

The teaching of Unit Operations at the undergraduate level has remained relatively unchanged since the publication of several early- to mid-19th century texts; however, by the middle of the 20th century, there was a slow movement from the unit operation concept to a more theoretical treatment called *transport phenomena* or, more simply, engineering science. The focal point of this science is the rigorous mathematical description of all physical rate processes in terms of mass, heat, or momentum crossing phase boundaries. This approach took hold of the education/curriculum of the profession with the publication of the first edition of the Bird et al. book.(3) Some, including the author of this text, feel that this concept set the profession back several decades since graduating chemical engineers, in terms of training, were more applied physicists than traditional chemical engineers. There has fortunately been a return to the traditional approach to chemical engineering, primarily as a result of the efforts of ABET (Accreditation Board for Engineering and Technology—see also Chapter 21). Detractors to this pragmatic approach argue that this type of theoretical education experience provides answers to what and how, but not necessarily why, i.e., it provides a greater understanding of both fundamental physical and chemical processes. However, in terms of reality, nearly all chemical engineers are now presently involved with the why questions. Therefore, material normally covered earlier has been replaced, in part, with a new emphasis on solving design and open-ended problems; this approach is emphasized in this text.

The following paragraphs attempt to qualitatively describe the differences between the above two approaches. Both deal with the transfer of certain quantities (momentum, energy, and mass) from one point in a system to another. There are three basic transport mechanisms which potentially can be involved in a process. They are:

1. radiation
2. convection
3. molecular diffusion.

The first mechanism, radiative transfer, arises as a result of wave motion and is not considered, since it may be justifiably neglected in most engineering applications. The second mechanism, convective transfer, occurs simply because of bulk motion. The final mechanism, molecular diffusion, can be defined as the transport mechanism arising as a result of gradients. For example, momentum is transferred in the presence of a velocity gradient; energy in the form of heat is transferred because of a temperature gradient; and, mass is transferred in the presence of a concentration gradient. These molecular diffusion effects are described by phenomenological laws.(3)

Momentum, energy, and mass are all conserved. As such, each quantity obeys the conservation law within a system (including a chemical reactor) as provided in Equations (1.1) and (1.2):

$$\left\{\begin{matrix}\text{quantity}\\ \text{into}\\ \text{system}\end{matrix}\right\} - \left\{\begin{matrix}\text{quantity}\\ \text{out of}\\ \text{system}\end{matrix}\right\} + \left\{\begin{matrix}\text{quantity}\\ \text{generated in}\\ \text{system}\end{matrix}\right\} = \left\{\begin{matrix}\text{quantity}\\ \text{accumulated}\\ \text{in system}\end{matrix}\right\} \tag{1.1}$$

This equation may also be written on a time rate basis

$$\left\{\begin{matrix}\text{rate}\\ \text{into}\\ \text{system}\end{matrix}\right\} - \left\{\begin{matrix}\text{rate}\\ \text{out of}\\ \text{system}\end{matrix}\right\} + \left\{\begin{matrix}\text{rate}\\ \text{generated in}\\ \text{system}\end{matrix}\right\} = \left\{\begin{matrix}\text{rate}\\ \text{accumulated}\\ \text{in system}\end{matrix}\right\} \tag{1.2}$$

The conservation law may be applied at the macroscopic, microscopic, or molecular level.

One can best illustrate the differences in these methods with an example. Consider a system in which a fluid is flowing through a cylindrical tube reactor (see Figure 1.1) and define the system as the fluid contained within the reactor between points 1 and 2 at any time. If one is interested in determining changes occurring at the inlet and outlet of a reactor, the conservation law is applied on a "macroscopic" level to the entire system. The resultant equation (usually algebraic) describes the overall changes occurring to the system (or equipment). This approach is usually applied in the Unit Operation (or its equivalent) courses, an approach that is, as noted above, highlighted in this text and its three companion texts.$^{(4-6)}$

In the *microscopic/transport phenomena approach*, detailed information concerning the behavior within a system is required; this is occasionally requested of and by the engineer. The conservation law is then applied to a differential element within the system that is large compared to an individual molecule, but small compared to the entire system. The resulting equation is differential and can then be expanded via an integration in order to describe the behavior of the entire system.

The *molecular approach* involves the application of the conservation laws to individual molecules. This leads to a study of statistical and quantum

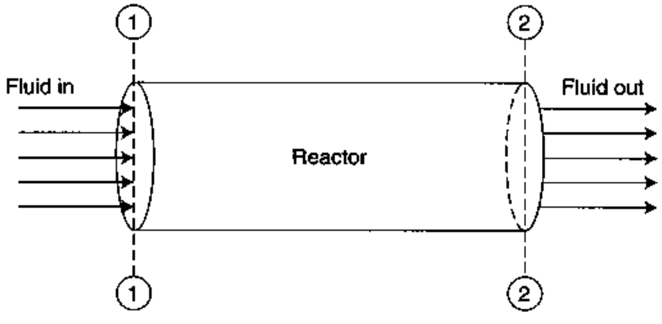

Figure 1.1 Flow reactor system.

mechanics—both of which are beyond the scope of this text. In any case, the description at the molecular level is of little value to the practicing engineer; however, the statistical averaging of molecular quantities in either a differential or finite element within a system can lead to a more meaningful description of the behavior of a system.

Both the microscopic and molecular approaches shed light on the physical reasons for the observed macroscopic phenomena. Ultimately, however, for the practicing engineer, these approaches may be justified but are akin to attempting to kill a fly with a machine gun. Developing and solving these equations (in spite of the advent of computer software packages) is typically not worth the trouble.

ILLUSTRATIVE EXAMPLE 1.1 Explain why the practicing engineer/scientist invariably employs the macroscopic approach in the solution of real world chemical reactor problems.

Solution. The macroscopic approach involves examining the relationship between changes occurring at the inlet and the outlet of a reacting system. This approach attempts to identify and solve problems found in the real world, and is more straightforward than, and preferable to, the more involved microscopic approach. The microscopic approach, which requires an understanding of all internal variations taking place within a reacting system that can lead up to an overall system result, simply may not be necessary. ■

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