

CHEMISTRY PAST, PRESENT, AND FUTURE

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Contents

- 1. Introduction
 - 1.1. The Central Science
- 2. Chemistry Past
 - 2.1. Metals and Alloys
 - 2.2. Glass
 - 2.3. Pigments
 - 2.4. Drugs and Chemotherapeutic Agents
- 3. Chemistry Present
 - 3.1. Engineering
 - 3.2. Industrial Chemistry
 - 3.3. Biology
 - 3.4. Green Chemistry
 - 3.5. Environmental Chemistry
 - 3.6. Sustainable Development
- 4. Chemistry Future
 - 4.1. Energy
 - 4.2. The Environment
 - 4.3. Food
 - 4.4. Health
 - 4.5. Materials
- 5. Transitions to the Future
- Glossary
- Bibliography
- Biographical Sketch

Summary

Chemistry is a science, the principles of which are central to understanding all phenomena at a molecular level. Many of the other “science disciplines,” and the technology-oriented disciplines—engineering—also deal with the things of the world, from advanced composites that find potential use in internal combustion engines to body functions, including thought processes as well as the thoughts themselves. Thus, understanding in such diverse fields of human endeavor, ultimately, rests on the application of fundamental chemical ideas associated with the properties of molecules.

Historically, chemistry and humanity have existed in a symbiotic relationship because of the perceived societal usefulness of the subject. Initially, when the principles of chemistry were unknown, the “chemical arts” were primarily used to benefit the ruling

classes, e.g. in the development of decorative items, which represented a relatively small fraction of humanity. But chemistry slowly, then rapidly, became an important, if invisible, component of a widening circle of humanity until now, when we find that the results of the application of chemistry are pervasive in our global society. It is safe to say that there is no single person on earth that is not—or cannot be—affected by the application of chemical ideas. The worldwide need for energy, food, and materials to make things from machines to bone-compatible substances, and health needs are all affected by the careful and clever applications of core chemical ideas. The widespread societal needs in these areas of human activity have engendered an important international chemical enterprise and, with it, the potential to affect the environment adversely. Environmental issues themselves are responsive to solutions based on chemical ideas, as are the implications of resource depletion driven by the widening needs of a global society.

The future of the chemical enterprise—the developing subject, the practitioners of chemistry, and the chemical industry—is now faced with sustaining the development of the promise of chemistry. “Sustainability” implies the promotion of growth for the benefit of humanity and its attendant benefits for society without depleting resources or adversely affecting the environment.

1. Introduction

Chemistry is a science—a system of knowledge covering truths or operations of fundamental laws that are concerned with the physical world. It has not always been so. Since recorded time began, what we now call “chemistry” was an art—a system of methods employed in a set of activities, a craft, or a trade. As such it became intertwined with human development from the earliest times, a condition that persists today.

1.1. The Central Science

Chemistry has achieved the status of the central science since it deals explicitly with the molecularity of the world (Figure 1). Everything in the world—from material objects to the storage of thoughts in the human mind (including the brain itself)—has a molecular basis. Thus, it should not be surprising that, as mankind faces problems, whether they be practical ones or those associated with subjects that are key to understanding the development of basic ideas in ancillary and associated disciplines, solutions arise from considerations of molecular-level arguments; in other words, from the application of core chemical principles. The question marks (??) on the Venn diagram in Figure 1 represent a molecular-level discipline that has not yet been defined. When this unknown discipline arises in the future and it has a molecular basis, progress will be dependent on the application of chemical concepts.

A very large number of chemistry-driven applications can be delineated, but only a few will be presented to illustrate the basic relationships of chemistry to other areas of societal interest.

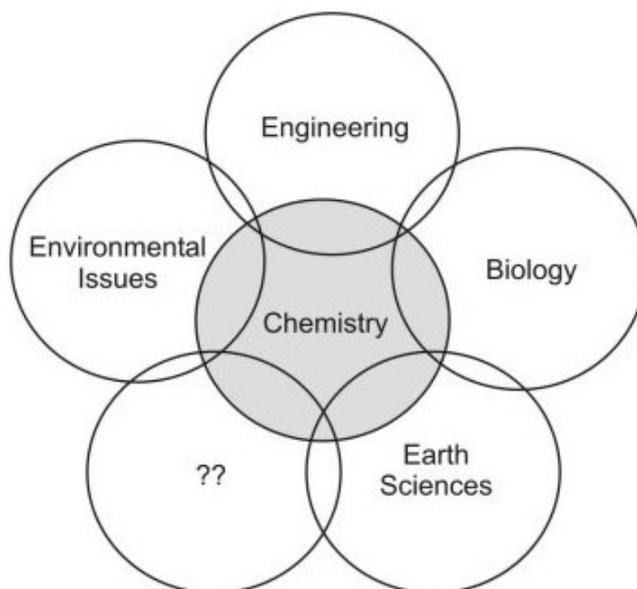


Figure 1. A Venn representation of the centrality of chemical thought to associated disciplines

2. Chemistry Past

Historically, the art of chemistry was employed to create or produce chemical substances that are intermediates used to make a variety of useful materials and for other important societal uses, e.g. for agriculture, soaps and detergents, dyes, and pharmaceuticals. That trend continues today and is expected to continue into the future. In this section, we present a brief review of historically significant, chemically-related, vignettes as a preview of a discussion of the future uses of chemical concepts.

2.1. Metals and Alloys

The “chemical arts” reach back to antiquity. Our historical records begin only about 3000 B.C.; before this era, methods used by early practitioners were handed down orally. Worked gold objects are known from earliest times, the Neolithic age, but little of the chemical arts was necessary in the use of gold because the substance is often found as the native metal. Similarly, copper, which also can be found in its native state, was worked by North American aborigines. Copper objects appear with the earliest human remains (*c.* 3500 B.C.) found in Egypt and Mesopotamia. The invention of bronze—an alloy of copper and tin—represents an important event in the evolution of the chemical arts because elemental tin is not found in nature and to make bronze requires the winning—the chemical extraction—of tin from an appropriate ore followed by the alloying procedure. The most common naturally occurring compounds are oxides, e.g. cassiterite, which is essentially SnO_2 ; the elemental tin can be won using an appropriate reducing agent, to use modern terminology. Extracting elemental tin from one of its compounds is a chemical process. Most of the early chemistry developed without theory to guide it. The earliest bronze pieces have been dated at about 3000 B.C. Interestingly, Egyptian and Mesopotamian bronzes sometimes contain lead in place of tin and, occasionally, antimony, as do some early Chinese bronzes.

2.2. Glass

Glass is the hard, inert, transparent material made by heating together a mixture of substances such as sand (SiO_2), limestone (CaCO_3), and soda (Na_2CO_3) at a sufficiently high temperature—about 1400 to 1500°C, just below the melting point of iron. These materials react to form a viscous liquid. When this liquid is taken from the furnace, it becomes more viscous as it cools until about 500°C when it becomes a transparent solid—the material we call “glass.” The history of glass reflects the symbiosis of chemistry with the needs of society. Initially, glass making was an art that produced materials of variable properties. But the chemical compositions of modern glasses, in contrast, are carefully controlled to produce materials with appropriate physical and chemical properties for specific applications.

From one point of view, glass is as old as the vitreous glaze on pottery, which can be described as “a glass.” It is thought that glass making originated in western Asia around 3000 B.C.; initially, only beads and similar small objects were made of glass, but glass vessels appeared around 1500 B.C. Fragments of glass vessels have been found on western Asiatic sites in strata of the late sixteenth and early fifteenth centuries B.C. Egyptian glass appears to have first been made in the reign of Thutmose III (1504–1450 B.C.). Thutmose achieved a series of Asiatic conquests in 1481 B.C. and glass workers brought back to Egypt from those conquests were probably used to set up a glass industry in Egypt. This “transfer by conquest” is probably one of the earliest examples of a very efficient method of diffusion of technology/science from one people to another. The development of Egyptian glass technology itself was also strongly influenced by knowledge derived from Mesopotamia. For example, the decorations on all Egyptian glass from about 1300 B.C. onward is very similar to that found on glass objects from Ur, an ancient Sumerian city in Mesopotamia on a site in present-day Iraq. The extensive use of cobalt in Egyptian glass—the cobalt blue glass—also supports this idea because the nearest sources of cobalt were in southern Mesopotamia. By A.D. 50 glass had become as widespread as pottery in Rome. It had become a utilitarian material—cheap, attractive, impermeable, and widely available—and formed a new class of material culture that continues today. Glass making was a closely held secret, but the ability to make glass moved relentlessly from the Middle East to Europe and England. Each part of the world added to the overall art, and many of these improvements involved chemistry. Thus, glass that contained (accidentally) iron compounds had an undesirable greenish to brown cast as the compounds became oxidized and, in effect, decolorized the glass. The Venetians used pyrolusite to make glass as clear as fine rock crystal. Pyrolusite contains manganese dioxide (MnO_2), an oxidizing agent, which reacts with the iron compounds that cause the green-brown color. At the same time that the Venetians were producing a fine clear glass, they discovered how to make glasses in many beautiful colors—blue, white, green, purple, and turquoise—by adding certain inorganic substances that reacted with the components of glass to produce colored compounds. In England, the rapidly expanding glass industry competed, often unsuccessfully, with iron making for a diminishing fuel supply. The switch from charcoal to coal in iron smelting was a benefit not only to the iron makers but also to the glass industry. The English contribution to glass making was the development of lead crystal glass, which had a very high transparency and a high refractive index, giving it an ability to sparkle in the light falling on faceted or angular cut surfaces.

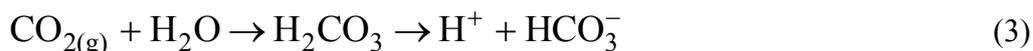
In the nineteenth century, “glass works” were generally forest-related industries. Wood was required for the fires to melt the mixture that would become glass; it also yielded potash, one of the basic glass components, which was extracted from wood ashes by leaching. Glass workers near the sea used sea plants as sources of soda, which gradually replaced potash. The French chemist Nicolas Leblac (1742–1806) succeeded in making soda from common salt, sulfuric acid, and limestone, which is a form of calcium carbonate. Leblac went bankrupt as a result of the French Revolution, but the need for soda continued to increase. That need was satisfied by Ernest Solvay (1838–1922), a Belgian chemist. In the Solvay process, brine (a saturated aqueous solution of NaCl often found naturally) is treated with ammonia and carbon dioxide, produced from the thermal decomposition of limestone (CaCO_3):



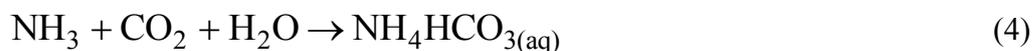
The dissolution of ammonia produces ammonia hydroxide.



And the dissolution of CO_2 produces bicarbonate ion.



Steps 2 and 3 correspond to the production of a solution of ammonium bicarbonate:



which in the presence of the brine solution yields sodium bicarbonate.

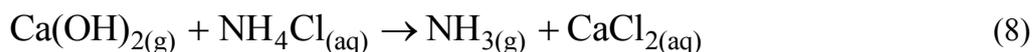


Of all the possible species present in this solution, NaHCO_3 is the least soluble and this substance precipitates. The solid NaHCO_3 , when heated, produces soda, Na_2CO_3 , and CO_2 .



An interesting characteristic of the Solvay process is its chemical efficiency in producing a desired product, soda (Na_2CO_3), from relatively common materials—salt (NaCl), limestone (CaCO_3), and ammonia (NH_3). The CO_2 from in Step 6 can be recycled in Step 4. Ammonia can be obtained from the other product of Step 5— $\text{NH}_4\text{Cl}(\text{aq})$ —by treating the aqueous solution with calcium oxide obtained as the second product of Step 1.





The ammonia obtained in Step 8 is recycled to Step 2. Thus, the net result of the Solvay process is the consumption of salt (NaCl) and limestone (CaCO₃), and the production of soda (Na₂CO₃); CaCl₂ (Step 8) is the only byproduct. Note that ammonia is not consumed chemically; its only loss occurs during mechanical handling.

The Solvay process (like the earlier Leblac process) is an early example of the epitome of the symbiosis of chemistry and society: to take relatively simple substances that are easily obtained and produce more desirable substances. The Solvay process became the source of inexpensive soda, which advanced the production of inexpensive glass.

Glasses with a wide variety of compositions exist. Chemical science has produced a large number of specialty variants: special formulations are used for lens making; a glass containing boric acid as a flux, replacing most of the soda in the standard glass composition, is used for ovenware and other high temperature uses; and glasses containing no soda are used for mercury vapor street lamps and for fiberglass used in light pipe applications.

2.3. Pigments

The decorative arts, especially painting, have been dependent on the interaction of what we now call “chemistry” since the beginning of recorded history. Indeed, that interaction originally defined the “chemical arts.” Perhaps one of the oldest recorded pigments is Egyptian Blue, found on a sarcophagus dated from the Fourth Dynasty (2613–2494 B.C.). Egyptian Blue is a copper silicate that can be produced by heating a copper-containing ore (like malachite) with sand (SiO₂), limestone (calcium carbonate), and soda (Na₂CO₃). A mineral with the same composition (namely, CuO • 2SiO₂ • (CaO, Na₂O) • 2SiO₂), called cuprorivaite, exists in nature, but is so scarce that it could not have been collected in sufficient quantities to be used as a pigment by the Egyptians (or the other peoples that are known to have used it as a pigment). Thus, Egyptian Blue must have been a manufactured product. (The pigment should not be confused with the cobalt blue glass so prized by the Egyptians.)

Other naturally occurring minerals with interesting colors have been used as pigments. Examples include orpiment, the yellow arsenic sulfide (As₂S₃), and realgar, the red arsenic sulfide (AsS), which were known to the ancient Greeks and Romans. We do not strive to be exhaustive concerning the identity and nature of minerals used in art through the ages. Suffice it that the use of a number of such substances stretches to antiquity and humans have learned to produce materials that are naturally occurring if nature does not yield sufficient quantities of the desired substances. This is another hallmark of the symbiosis of chemistry with humanity.

The highly specialized use of pigments as artists’ materials has been expanded to include modern coatings (paints) that are designed to protect surfaces of all kinds from the effects of weathering. Both artists’ colors and the colors used in coatings have been expanded by using organic materials (dyes, *vide infra*) to increase the spectrum of colors available. Thus, the original artists’ interests in naturally occurring colorants is no

longer the purview of the art community, but now extends to the “common person,” and it is not limited to naturally occurring substances. As with many substances of historical interest, modern pigments (and dyes) are human-made equivalents or are entirely new substances with superior qualities.

2.4. Drugs and Chemotherapeutic Agents

Humankind's ills, historically, have been dealt with using naturally occurring substances: most often associated with plants. Folk remedies involving plants abound even today. Galen (130–200), the Greek physician, and Avencenna (980–1037, also known as Abdullah Ibn Sina), a Persian physician, are the historic written sources of ancient drug lore that is mainly plant based. Indeed, Avencenna's writings were based on Galen's ideas and, when Avencenna's books were translated into Latin, his and Galen's ideas became the source of the most important medical information in Europe until the time of Harvey. Theophrastus Philippus Aurelous Bombastus von Hohenheim, known simply as Paracelsus (1493–1541), a Swiss physician and alchemist, decided that the purpose of alchemy was not to discover methods for manufacturing gold, but to prepare medicines with which to treat diseases. Indeed, Paracelsus' ideas initiated an historic era formally described as iatrochemistry—or, chemistry associated with medicine. In a sense, that era continues today in its more sophisticated manifestation known as genetic engineering. More about genetic engineering and chemistry later. Before Paracelsus' time, medicines used to treat ailments were derived from plant sources, but he stressed the importance of mineral substances and became renowned for the use of mercury, arsenic, antimony, and tin salts for the treatment of syphilis, intestinal worms, and a variety of other conditions endemic in medieval Europe. Paracelsus probably killed more patients than he cured with these very toxic metal salts. Four hundred years later, Paul Ehrlich (1854–1915) discovered the arsenic containing drug “606” which was later called Salvarsan—the magic bullet—the first true anti-syphilitic. Salvarsan, or its derivatives, such as neosalvarsan and mapharsen, remained the mainstay of treatment for syphilis until the arrival of the “wonder drug,” penicillin. Ehrlich coined the term “chemotherapy” and the concept of the “magic bullet,” which was a substance aimed exclusively at a dangerous intruding parasite and not the host organism itself.

Chemistry has always been in the forefront of fighting bacteria such as the microorganism that caused the “Great Pestilence” of 1347–52 known as the Black Death, which was caused by a bacillus carried by fleas that infected the black rat. It is believed that the plague started in the late 1330s in the black rat population of the Gobi desert in Mongolia. The flea responsible for carrying the bacillus was passed to nomadic Mongolian horsemen who traveled the caravan routes of Asia and the Middle East, and by 1347 the infection had reached the Black Sea. From there it was a short trip *via* the Italian merchant fleet to Constantinople, Alexandria, Messina, Cagliari, Genoa, and Marseilles. During 1348, the disease raged throughout southern Europe. Between 1349 and 1352, virtually the whole of northern Europe, including parts of Scandinavia and Russia was in the grip of the plague. It has been estimated that around a quarter of the population of Europe died as a result of infection. From 1350 to the late seventeenth century, the plague was endemic in Europe. Outbreaks between 1504 and 1505 killed about one-third of the population of London. Other major epidemics occurred between

1558 and 1569, in 1603, 1625, and, for the last time in 1665–66, at which time in London 20 percent of the population died. In 1894, the causative bacillus was identified. Earlier, in 1864, Louis Pasteur (1822–1895) had enunciated the “germ theory of disease” on the way to disproving the doctrine of spontaneous generation which held that living things arose spontaneously from dead organic matter. In the course of the studies that disproved spontaneous generation, Pasteur solved problems of the French wine industry (wine and beer soured if the wrong yeast cells were present), the silk industry (silkworms were infected by tiny parasites), the cattle industry that was being decimated by anthrax, chicken cholera, and hydrophobia (rabies). Pasteur’s fight against these diseases involved two ideas: create an immunity by inoculation with a mild version of the disease (that is, create a vaccine); or stop the disease with a disinfectant. The vaccine approach does not appear to be a chemical solution, however, modern genetic engineering techniques that are arguably based on chemical concepts, could indicate that the principle of “weakening of the infectious agent” is a chemical process. The disinfectant approach clearly involves chemical substances (antiseptics) that are toxic to bacterial agents.

This idea, like many, had very old antecedents. Historically, the ancient Egyptians were the first to be concerned with putrefaction—the decay of organic matter caused by microorganisms (bacteria) or fungi—when they employed aromatic plant extracts, tree resins, pitch, and spices to mummify their dead. The famous Greek physician, Hypocrites (460–370 B.C.), used tar and wine on wound dressings. We now know that all these mixtures contain many chemical substances, including phenols and terpenes, which have antimicrobial properties. Indeed, Joseph Lister (1827–1912) showed that the systematic use of carbolic acid (phenol) markedly decreased the deaths of surgical patients from subsequent infections. Eventually, chemical substances less irritating to tissue and more effective against microbes were discovered and are in use today.

The recognition that “a chemistry” was responsible for interactions with parts of bacterial cells can be derived from the observations of Robert Koch (1843–1910) a German bacteriologist who experimented with dyestuffs as a means of helping with the identification of microorganisms. His observations eventually led to the division of bacteria into two main classes. The one class comprised the gram-positive organisms like streptococci (responsible for pneumonia, ear and throat infections, etc.), staphylococci (causing boils, endocarditis, meningitis, etc.), and pneumococci (causing pneumonia). The gram-negative organisms, like *salmonella*, *typhimurium* (which causes typhoid fever), and *escherichia coli* (causing food poisoning, urinary tract infections, etc.) formed the second class. The dye test is quite simple; the gram-positive organisms react irreversibly with the dye methyl violet; the subsequent violet coloration of the bacteria resists washing out and reaction with other dyestuffs. The chemical implication is that the gram-positive organisms contain chemically reactive sites (probably in the cell walls) that interact with specific atom groupings on the methyl violet molecule. The gram-negative microorganisms do not contain such sites at which chemical reactions occur. In other words, the test with methyl violet produced early evidence that the parts of a microorganism could interact with relatively simple organic molecules, which suggested that vital life processes of bacteria could be influenced by chemical reactions. The synthesis of a variety of molecules carrying different functional groups and the subsequent testing of these substances for anti-microbial activity eventually led to the

discovery of the highly effective antibacterial sulfonamides. Slowly, the chemistry of biological processes—biochemistry—was developed and founded on enduring chemical principles. With an understanding of the details or the chemistry of critical biological processes came the ability to attack bacteria with chemical agents that were highly specific. This ability is clearly a restatement of Ehrlich's "magic bullet" ideas.

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Biographical Sketch

Joseph J. Lagowski is Professor of Chemistry (since 1967, in the Department of Chemistry and Biochemistry) and Professor of Education (since 1973, in the College of Education) at The University of Texas, Austin. He received his Ph.D. in inorganic chemistry (non-aqueous solutions) from Michigan State University. An appointment as a Marshall Scholar at Cambridge University led to a second Ph.D. (organometallic chemistry) from that institution. Lagowski's scholarly interests include both "bench chemistry" and various aspects of chemical education. His work in the former area has focused on the influence of the solvent on the chemistry of unusual species, from the point of view of aqueous chemistry. His work in organometallic chemistry includes various aspects of Π -complexes. Lagowski's other major scholarly work has been in chemical education. In the early 1960s, he became interested in the use of interactive computing to assist the educational process. He and his students have identified those areas of teaching for which computer methods are maximally effective. Lagowski's research and education interests have also manifested themselves in his service to the professional community. Lagowski served as Editor of the *Journal of Chemical Education* (1979–96), where he was instrumental in the realization of the advantages of technology in teaching chemistry. Lagowski received the CMA Award for Excellence in Chemistry Teaching (1981); he was elected a Fellow of the AAAS (1982); he was named a Piper Professor for Outstanding Scholarly and Academic Achievement (1983); he received the ACS Award in Chemical Education (1989), the Southwest Regional ACS Award (1996), and the James Flack Norris Award (1999).