THE WORLD OF CHEMISTRY

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Contents

Summary: An Inevitable and Pervading Science

Fuel, fertilizers, plastics, drugs, paints, and the whole range of chemical products widely employed in human activity are obtained from raw materials thanks to chemistry and its technological application. In some circumstances—life sciences for example—chemistry's contribution is more obvious, but on closer examination it is apparent that it also plays an important role in many other fields. One striking example is the current astounding development of the micro- and opto-electronics industries. These have benefited from the application of chemistry in the synthesis of advanced materials with peculiar physical properties, most of them (nanostructures for example) non-existent in a natural state. As already pointed out, the application of chemistry in life sciences is the

more compelling, both in the elucidation of the stimulating and intriguing problem of the origin of life, and through the valuable understanding of the molecular structure of living matter and the mechanisms that control its behavior. Here, the development of "drug design" seems to offer a rational approach to the design of pharmaceutical products with well-defined finality, and with substantially reduced side effects.

Chemistry is not limited by dimensions: the repetition of a large number of different atomic groups joined by chemical bonds creates so-called polymeric macromolecules. These are usually classified as natural or synthetic, the latter being widely employed as materials for structural applications. What is more, complex macromolecules with well-defined electrical and optical properties, and interesting potential perspectives in the manufacturing of new and sophisticated electronic devices, have recently also been synthesized. Finally, in recent years the appearance of new techniques for replication, on the laboratory scale, of large bio-polymers (such as proteins and DNA) is a definite indication of how chemistry has the potential to pervade our lives.

All this progress bears significant testimony to one of the fundamental achievements of modern chemistry: the theoretical possibility of interpreting, and in some cases predicting, the structure and the reactivity of molecules. This finding relates to the application of quantum mechanics to the study of the electronic configuration of molecules. With modern supercomputers it is now possible to obtain reliable information on molecular energy and its evolution in chemical transformation. This approach, associated with statistical thermodynamics, allows the theoretical evaluation of the rate of chemical processes. These findings have an interesting impact on different fields, including pyrolitic combustion processes, atmospheric chemistry, catalysis, advanced materials preparation, and cosmo-chemistry.

All the abovementioned subjects are treated from the central perspective that chemistry can be considered a mature subject which is still at the cutting edge of scientific and technological enterprise. Without any doubt, all aspects of the living universe are attributable to their building blocks: the atoms and the molecules. Their interaction and modification (or what chemists call "reaction") obey all the basic laws of chemistry, and thus can be understood by reference to this fascinating framework.

1. Centrality of Chemistry in Human Activities, Life, and Culture

> Before the word for it (in any language) came to be, there was chemistry. For a defining aspect of human beings has always been the meld of mind and hands in transforming matter.
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> (Roald Hoffman)

The understanding of most of the natural phenomena and the design of industrial processes relies on a deep knowledge of their chemical implications. This statement can be easily supported by significant examples.

Fuels, fertilizers, plastic materials, drugs, paints, and all the variety of chemical products widely employed in human activity are obtained from raw materials through suitably devised chemical reactions. The everyday applications of these materials in some way hide the way they are produced to the final users, but indeed most of what is called the “man-made world” pays a significant tribute to chemistry, and the whole of the knowledge implied in such achievements represents the heritage of modern chemistry.

Although for polymers and fertilizers (which are usually actually called chemical products) the link to chemistry is more obvious, chemistry also makes an important contribution in other fields such as the information technology world. In fact, the present micro- and opto-electronics technologies are mainly based on the peculiar properties of some solid materials characterized by a well defined structure and functionality. These materials are obtained by the accurate management of specific chemical reactions involving the deposition of solids containing silicon, gallium, arsenic, and other atoms with semiconductor properties, starting from vaporized precursor compounds. Another example not usually linked to chemistry is energy production, the availability of which nowadays supports our industrial activity, and feeds our heating and air-conditioning services. In fact, energy is mainly produced through combustion reactions whereby gaseous, liquid, and solid fuels are substantially converted to carbon dioxide and water. The advances in combustion chemistry and in exhaust post-treatments strongly contribute to the reduction of pollutant emissions in the atmosphere.

Moving towards the earth and life sciences, it is possible to state that the present structure of the planet, including atmosphere, is a consequence of a set of transformations through which geochemical evolution has occurred. These transformations occurred naturally for several geological eras, and it was only in the last century that human activities started to interact with them. The atmosphere in particular, besides holding the original compounds such as oxygen, nitrogen, water, carbon dioxide, and sulfur dioxide, also contains a cocktail of different chemical compounds, mostly stemming from anthropogenic activities. Their presence, accumulation, and transformations could affect the thermal and ecological equilibrium of the earth. This means that, if they are not carefully controlled, there are some unpleasant consequences that could threaten our lives. This management is the focal point of what is commonly indicated by the term “sustainable growth.”

Without any doubt all living systems are made by molecules whose complexity ranges from the simpler (water) to the more complex (proteins, enzymes, DNA, cell tissues). The day-by-day interaction of these molecules that span our lives occurs in harmony with the laws of chemistry, and it can be connected with an evolutionary process starting from very simple molecules. In fact, life itself may be considered to have emerged from an ensemble of molecules originally present in a prebiotic “soup” subjected to a process of evolution consistent with the laws of chemistry. The understanding of the mechanism of molecular evolution that produced living species represents an intellectual challenge on which many researchers are engaged.

2. The Impact of Chemistry on Technological Development

When it comes to analyzing the role of chemistry in the development of new technologies, a significant and classic example is the direct synthesis of ammonia from its constituent elements. The combination of hydrogen with nitrogen yields to ammonia through the reaction:

$$N_2 + 3\,H_2 \rightarrow 2NH_3 \qquad (1)$$

The industrial application of this reaction harks back to the first half of the twentieth century, and its application represented a significant breakthrough in the development of modern chemical technology. The need for low-cost fertilizers, where nitrogen is in a form that can be used directly by growing plants, is what lies behind the studies on how to transform nitrogen present in the atmosphere to ammonia. To some extent, it could be said that the stability of western society depends on the solution of that particular problem, since ammonia is the fundamental building block for fertilizers. Consequently, were it not for low-cost supplies of ammonia and fertilizers, agricultural efficiency would dramatically decline, and our economy could be thrown into disarray with starvation to follow.

The formation of ammonia is actually a very reluctant reaction in normal circumstances, since it proceeds at a negligible rate. The large-scale realization of the process required extensive investigation, both when it came to searching for a catalyst able to increase the reaction rate, and in order to establish operative conditions where the process could be performed economically. The first fundamental step for the implementation of the direct synthesis was the discovery of an appropriate catalyst apt to speed up the reaction rate. Porous iron stabilized with a small amount of dispersed potassium was the catalyst that solved the problem. Following its discovery, by an extensive “trial and error” process involving many metallic elements of the Periodic Table, its formulation underwent continuous optimization in parallel with advancement of the knowledge of the process kinetics. The result of these investigations was the demonstration that ammonia synthesis takes place through a series of intermediate steps involving the interaction of the two reactants with the surface of the catalyst, and whose rate-determining step is the nitrogen adsorption onto the catalyst surface. The information on the dependencies of reaction rate to operative conditions led, as a consequence, to the design of reactors of increasing productivity up to the current 75,000 kg/h.

Ammonia synthesis represents one of the first large-scale applications of catalysis to industrial production. Catalysis became a major industrial enterprise in the first half of the twentieth century through its applications in the oxidation of sulfur dioxide to SO_3 (for the production of sulfuric acid), steam reforming of methane (mainly used for the large scale production of hydrogen and carbon monoxide mixtures), and synthesis and oxidation of ammonia (for the large-scale production of fertilizers and nitric acid). Inevitably, commercial interest in the application of heterogeneous catalysis stimulated academic and industrial research on the chemical and physical nature of substances with potential catalytic activity. Consequently, in addition to chemical properties, the influence of physical properties such as surface area, particle porosity, and structural strength was also addressed. Thus it was possible to establish how the catalyst works in promoting the desired reaction. In fact, the developing of the metal-supported catalyst (a catalyst where the active compound, usually a metal, is dispersed onto a porous substrate) can be viewed as the first application of nanotechnology. It was noticed that the catalytic effect is proportional not to the absolute amount of active element placed on the support, but, instead, to its surface area available to the reactants. The catalytic activity is, therefore, mainly a function of the fine dispersion of the active element. That result, it should be noted, was arrived at in the early 1960s.

Accordingly, frontier research in chemistry had shifted, by the 1960s, to the study of surface chemistry at molecular level, mainly through taking advantage of the availability of surface characterization techniques based on new instrumentation. This allowed the investigation of surface properties at the atomic scale, some of which are described in Table 1.

Name	*Description*	*Surface information*
Adsorption or selective chemisorption	Chemisorption of atoms or molecules onto surface sites	Concentration of surface area sites
Scanning tunnelling microscopy (STM)	The topography of a surface is measured from the surface tunnelling current to the probe	Atomic structure
Low-energy electron diffraction (LEED)	Mono energetic electrons with energies below about 500 eV are elastically back-scattered from a surface and detected as a function of energy and angle	Atomic and molecular structures
Secondary-ion mass spectroscopy (SIMS)	Ions and ionized clusters ejected from a surface during ion bombardment are detected with a mass spectrometer	Surface chemical composition
Reflection high energy electron diffraction (RHEED)	Mono-energetic electrons, about 1-20 keV, are elastically scattered from a surface and detected as a function of angle and energy for small forward-scattering angles	Composition
Extended X-ray absorption fine structure (EXAFS)	Mono-energetic photons excite a core hole. The modulation of the adsorption cross section yields information on the radial distances to	Local surface structure and coordination numbers

	neighbouring atoms	

Table 1. Examples of some of the most used surface science techniques to characterize the catalyst surface. By means of these analytical methods it is possible to obtain information on surface catalyst structure, on its surface area, on the energetic of its interaction with the reacting species and, for the more advanced ones, also on the structure of the species adsorbed on the catalyst surface

In addition to newly designed catalysts, this fresh knowledge of surface science generated a steady state stream of high technology products, the development of which is strictly connected to all the gains made in catalyst evolution. Some examples of new materials developed thanks to the analytical methods originally studied for catalysis science are: hard coatings which can passivate surfaces and thus inhibit the corrosion process; polymeric coatings that significantly alter surface wetting and permeability; adhesive polymers used to link different parts of a structure; and, finally, the metallic and semiconductor films widely adopted in the microelectronic industry. In all those applications the surface properties usually tend to be more interesting than the bulk ones, leading to the production of devices with interesting new technological properties and uses.

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Biographical Sketches

Sergio Carrà was born in Milan in 1929 and is married with two sons and one grandson. He obtained a doctorate in Industrial Chemistry at the University of Milan in 1953, and has served as assistant professor and associate professor at the University of Milan. In 1968 he become full professor of physical chemistry at the University of Messina and two years later at the University of Bologna. At the present he is full professor of Chemical Engineering Thermodynamics at the Polytechnic of Milan. Some of his research and teaching activity has been carried out in USA.Sergio Carrà has been President of the Italian Association of Physical Chemistry, Vice President of the Italian Chemical Society and is a member of the “Accademia Nazionale dei Lincei” and of the “Academia Europeaea. He won the “Antonio Feltrinelli” award in 1991, the “Mario Giacomo Levi” in 1997, and the “Bonino” of the Divisione di chimica fisica della Società Chimica Italiana, and the Gold Medal of Scuola Normale Superiore di Pisa in 1999.Sergio Carrà has had important responsibilities in the organization of research activities performed with public financial support. He has also been a consultant for different companies (Montedison, ENI, SnamProgetti, ENEL, SISAS, Atochem, Dow and others) for the development of industrial projects.His research interest focuses on some aspects of molecular thermodynamics, applied chemical kinetics, catalysis, and modeling of chemical processes. He has published about 370 papers, six patents, and seven books.

Maurizio Masi (born in 1960) is associate professor in Applied Physical Chemistry at the Department of Chimica Fisica Applicata of Politecnico di Milano. His activity is centered on reaction kinetics and chemical reaction engineering, on the study of production processes for advanced inorganic materials for microelectronics, optics and optoelectronics, and generally on the simulation of the chemical and physico-chemical processes and separation processes. In 1992 he was Visiting Scientist at Massachusetts Institute of Technology. He has co-authored about 100 scientific papers on the above topics.