

THE CONTRIBUTION OF NOBEL LAUREATES TO CHEMISTRY

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Summary

This chapter deals with the contribution to the development of chemistry of all the Nobel Prize winners in chemistry up to the end of the twentieth century, together with some in physics and medicine or physiology that have had particular relevance for the advances achieved in chemistry. The contributions of the various Nobel laureates cited are briefly summarized. The Nobel laureates in physics dealt with in this chapter are those who made important contributions toward the understanding of the properties of atoms, the development of theoretical tools to treat the chemical bond, or the development of new analytical instrumentation. The Nobel laureates in medicine or physiology cited here are those whose contributions have been in the area of using chemistry to understand natural processes, such as the physiological aspects of living organisms through electron and ion exchange processes, enzymatic catalysis, and DNA-based chemistry. Eight areas of thought or thematic areas were chosen into which the contributions of the Nobel laureates to chemistry can be subdivided. The thematic areas chosen are the following:

- the discovery of new elements,
- the properties of atoms with the birth of quantum mechanics,
- the properties of molecules with the emergence of quantum chemistry,
- the expansion of thermodynamics,
- the dynamics of chemical reactions,
- new synthetic routes,
- the understanding of natural processes, and
- the identification of chemical entities.

At the end of the nineteenth century many revolutionary ideas were developed in chemistry. Consequently, for all these thematic areas the first Nobel laureates cited were truly pioneers in their fields, laying the foundation for further development. Analysis of the contributions of the successive Nobel laureates in each thematic area provides a step-by-step picture of the evolution of the ideas and chemical thought from the time of the foundation of the subject area to the present.

1. Introduction

An analysis of the contribution of Nobel laureates to chemistry is also a way of tracing the evolution of the major ideas, concepts, and theoretical and experimental tools developed, starting from the end of the nineteenth century and continuing throughout the entire twentieth century. Indeed, many scientists whose scientific contributions can be considered milestones in the development of chemistry have been awarded the Nobel Prize. Only a few were not considered by the commissions responsible for evaluating potential candidates for the prizes, while others, such as Harry Moseley, Richard Abegg, and Wallace Carothers, died prematurely before their contributions were recognized. The contributions of not only Nobel laureates in chemistry will be examined in this chapter, but also those in physics regarding the development of the model of the atom and quantum mechanics, and those in medicine or physiology regarding the development of DNA chemistry and understanding the chemistry of natural processes.

Some main areas of study have been chosen into which the various Nobel laureates can be categorized, based on their specific contributions as described in the official motivation for the award (Sections 2–9). It is worth remembering that between the end of the nineteenth century and the beginning of the twentieth century basic modifications occurred in many sectors of chemistry and related sciences. For this reason, in most cases the first Nobel laureate considered in each sector is either one of the main pioneers or the founder of the thematic area. Therefore, beginning with the first Nobel laureate and continuing throughout all the other awards over the years, it is possible, step by step, to trace the evolution of the different sectors of chemistry from its beginning to the scientific achievements of today.

2. The Discovery of New Elements

2.1. The Filling and Expansion of the Periodic Table

At the end of the nineteenth century the periodic table was not very much different from the one conceived by Mendeleev. Its modifications up to the final elaboration accepted today have been due, with only a few exceptions, to research carried out by Nobel laureates in chemistry.

William Ramsay (Nobel Prize (NP) in chemistry, 1904) first discovered argon in the nitrogen fraction of air, together with John Rayleigh (NP in physics, 1904) and later helium in uranium rocks. Ramsay hypothesized the existence of a group zero in the periodic table, between that of halogens and alkali metals. He predicted the existence of another three gasses, which he later isolated from liquefied air: krypton, neon, and xenon. The last gas of the zero group, radon, was discovered jointly by Ernest Rutherford (NP in chemistry, 1908) and Frederick Soddy (NP in chemistry, 1921) in the gaseous emanations of radium. Henri Moissan (NP in chemistry, 1906) isolated the element fluorine—the existence of which had been previously hypothesized—by electrolyzing at low temperature a solution of potassium fluoride in hydrofluoric acid. Marie Curie (NP in chemistry, 1911) and Pierre Curie, who died prematurely, discovered radium and polonium. They carefully studied several radium compounds and succeeded in preparing radium in the metallic state. With the identification of hafnium by Georg von Hevesy (NP in chemistry, 1943) in some minerals of zirconium; the discovery of technetium and astatine by Emilio Segrè (NP in physics, 1959); and of rhenium, francium, and praseodymium by other non-Nobel laureates, the first 92 positions in the periodic table were completed.

Edwin McMillan and Glenn Seaborg (joint NP in chemistry, 1951) received their prize for the discovery of actinides. By bombarding uranium with neutrons, McMillan first found the element with mass 93, which he called plutonium, and later with Seaborg, using the same technique, they found element 94, which they called neptunium. Seaborg found another four elements: 95, americium; 96, curium; 97, berkelium; and 98, californium. They also realized that these new elements belonged to a new family similar to that of the lanthanides, starting from element 89, actinium, and therefore the new family was called actinides. Seaborg also discovered, contemporaneously with other scientists, the remaining actinides—mendelevium, nobelium, fermium, and einsteinium—with the exception of the last in the series, lawrencium, discovered by one

of his co-workers. The final missing actinide, protactinium, was discovered by Frederick Soddy.

2.2. The Isotopes

The discovery of natural and artificial isotopes destroyed the historical assumption of the atomic theory that each element always had the same atomic weight. The discovery of isotopes continued throughout the first half of the twentieth century. By 1937, of the 88 elements investigated only 22 were found to be without isotopes.

Frederick Soddy (NP in chemistry, 1921) was the first to realize that certain elements exist in two or more forms that are indistinguishable chemically. These elements occupy the same position in the periodic table but differ in their atomic weight and in some physical properties. Francis Aston (NP in chemistry, 1922) found many naturally occurring isotopes of several elements using a mass spectrometer, which he developed, and formulated the so-called tumbler rule. This rule stated that the mass of several isotopes is a whole number of the mass of isotope 16 of oxygen, and explained the reason for some historical inversions in the positions in the periodic table as well as the fractional number of atomic weights. Harold Urey (NP in chemistry, 1934) discovered the presence of an isotope of hydrogen. On the basis of the hypothesis that it must differ in volatility, he succeeded in isolating the isotope, deuterium, by distillation of liquid hydrogen. Frédéric Joliot and Irène Joliot-Curie (joint NP in chemistry, 1935) produced the isotope 13 of nitrogen, the isotope 30 of phosphorus, and the isotopes 27 and 28 of aluminum by bombardment of boron, aluminum, and magnesium, respectively, with alpha particles.

3. The Properties of Atoms

At the beginning of the twentieth century the periodic table was more or less only a useful cryptogram and atoms were considered as indivisible entities. The scientific explanation of periodic law, the basis of the electronic structure of atoms and their reactivity, as well as the quantum mechanics model of the atom have essentially been due to the contributions of Nobel laureates in physics.

3.1. The Birth of Nuclear Chemistry

Antoine Becquerel (joint NP in physics, 1903, shared with the Curies) discovered a natural emission of rays in uranium minerals (different from X-rays), which were able to ionize gas and were deflected by electric or magnetic fields. Pierre Curie and Marie Curie (joint NP in physics, 1903, shared with Becquerel) confirmed the findings of Becquerel by observing the same types of rays in other substances (compounds of thorium, radium, and polonium), where the radiation was much more intense. Based on the fact that the radioactivity did not depend on external conditions, such as temperature, pressure, and type of compound and magnetic or electric field, the Curies suggested that radioactivity was a property of the atom. The discovery of radioactivity constituted the beginning of all the research on the properties of atoms and of the nucleus that characterized the twentieth century.

Joseph Thomson (NP in physics, 1906) not only discovered the electron but also was the first to formulate a model of the atom, and to propose an electronic explanation of the periodic table. His model of the atom consisted of a positive sphere in which electrons moved, neutralizing the positive charge. This model, however, was inadequate to explain the strong deviation of alpha rays by the atoms. The law of periodicity was explained by assuming the addition of electrons one by one to the outermost ring of an atom until it was full, after which a new outer ring formed and again started to be filled. This concept explained well the return of periodicity of the elements after a certain sequence.

Ernest Rutherford (NP in chemistry, 1908) discovered that the rays observed by Becquerel were constituted by alpha rays (material in nature) and beta rays (electrons), and those radioactive elements have a gaseous emanation. He formulated that radioactivity occurs through the disintegration of the atoms, leading to other elements. This discovery showed that the former concept of the stability and indivisibility of the atom was not correct. Rutherford then proposed a new model of the atom: a sphere of negative charge with a positive kernel, the nucleus, where practically all the mass is concentrated. This model explained the strong deviation of alpha rays exerted by atoms very well. Though Rutherford's model was different from Thomson's model there were still difficulties in explaining the stability of the atom. First, electrons rotating around the nucleus in an orbit would fall into the nucleus because of electrostatic attraction. Second, a sphere uniformly filled with negative charge was incompatible with the concept of the electron as a particle localized in the sphere. Charles Barkla (NP in physics, 1917) observed that sufficiently strong irradiation of different elements with X-rays resulted in an emission of monochromatic secondary X-rays. He found that by increasing the atomic weight starting from aluminum, the X-rays emitted by the successive elements become progressively stronger. He called this series the K series. After reaching mass 100 a new series, named the L series, starts with soft rays that become progressively stronger. Moseley—who died when he was only 28—measured the wavelength of the principle lines of the Barkla K and L series for the successive elements and observed as a general rule the progressive shortening of wavelength and increase in frequency when passing, step by step, from one place to another in the periodic table. Thus it became clear that the law of periodicity was a natural law in the function of the atomic number, and not of the atomic weight as Mendeleev thought. These observations were very useful to Bohr for his model of the atom.

Enrico Fermi (NP in physics in 1938) is considered the real founder of nuclear chemistry. He discovered that bombarding atoms with neutrons and fixing them in their nucleus produced a lot of new radioactive atoms. Fermi's modifications were only slight modifications in the mass of the atom, while Otto Hahn (NP in chemistry, 1944) discovered that bombarding uranium atoms with neutrons produced the fission of atoms. The atomic weight was halved and barium atoms were formed. By fission of thorium and uranium he observed at least 100 bodies that were connected to 25 elements lying between selenium and praseodymium. This discovery made it possible to believe that matter could be transformed into energy.

3.2. The Development of Quantum Mechanics

Niels Bohr (NP in physics, 1922) further developed the planetary model of the atom suggested by Rutherford. Bohr's model eliminated all the difficulties created by the application of Maxwellian theory. Bohr assumed that electrons can move around a nucleus only in certain orbits, which are in the stationary state. Electrons do not radiate energy while they move in the same level, but only emit radiation when they change level. The frequency of the radiation absorbed or emitted is given by the difference in energy between two stationary states and h , Planck's constant. Using this model it was possible to calculate spectra and to elaborate a periodic chart that predicted the existence of element 72, which was later discovered and named hafnium. With Bohr's model, the frequency could be calculated only for the hydrogen atom, but the model failed for multielectron atoms. Classical mechanics was found to be inadequate to explain many properties of the atom, such as the existence of X-rays, the movement of electrons around the nucleus, and radioactivity. Quantum mechanics is the theory that explains all the phenomena and properties related to atoms. Several Nobel laureates in physics made key contributions to the development of the quantum mechanics model of the atom, starting from the quantum theory of Planck, through the uncertainty principle of Heisenberg, the exclusion principle of Pauli, the wave mechanics of de Broglie, the quantum mechanics of Schrödinger and Dirac, and the final formulation of quantum mechanics elaborated by Born.

Max Planck (NP in physics, 1918) hypothesized that the emission and absorption of electromagnetic radiation occurs through pieces of energy, multiples of a specific unit named a light quantum or photon h (Planck's constant). He was a pioneer in quantum mechanics, which, however, required 30 years to reach a final, widely accepted formulation. Planck interpreted the emission of black-body radiation, assuming that each event of energy was related to the frequency through Planck's constant. The hypothesis of the existence of a quantum of energy was strongly supported by Albert Einstein (NP in physics, 1921), who applied it to explain the photoelectric effect and for the calculation of the heat capacity of solids at low temperature. With his hypothesis of the wave nature of matter, Louis de Broglie (NP in physics, 1929) initiated the theoretical construction to explain the movement of electrons within the atom. An electron presents a value of wavelength $\lambda = h/mv$ where h is the constant of Planck, m is its mass, and v its velocity. This last relation summarizes well the corpuscular and the wave nature of the electron.

Werner Heisenberg (NP in physics, 1932), together with Max Born and Pascual Jordan, used matrix mechanics as the basis of their equations to calculate physical quantities, such as the frequencies and intensities of the lines of the spectra. On the basis of the equations he developed, Heisenberg proposed that the hydrogen atom could exist in two allotropic forms, which later was confirmed. His work led to the formulation of the uncertainty principle, which states that it is impossible to determine precisely the position and the velocity of an electron at the same time.

Erwin Schrödinger (joint NP in physics, 1933, shared with Dirac) starting with the ideas of de Broglie, proposed wave equations, such as those for the propagation of light, to characterize the motion of electrons in atoms. It turned out that these equations gave

finite solutions when the energy of the system had discrete values determined by Planck's constant. The Schrödinger equations are the basis of quantum mechanics. Paul Dirac (joint NP in physics, 1933, shared with Schrödinger) proposed a more general form of quantum mechanics that also included the concept of relativity. He was able to justify the spin of electrons and proposed the existence of positive electrons.

Wolfgang Pauli (NP in physics, 1945) made it possible with his exclusion principle to describe the structure of complex atoms. Each electron is characterized by a set of quantum numbers, the same that describe the electron in the hydrogen atom; in one atom two electrons cannot exist with the same quantum number. In order to realize the structure of complex atoms, the electrons are positioned in the lowest energy level compatible with the Pauli restrictions. Using the Pauli restrictions and the Hund's rules it was possible to elaborate the electronic structure of all atoms. Max Born (joint NP in physics, 1954, shared with Walther Bothe) developed a comprehensive theory to calculate the energy states of electrons. According to Born, wave theory gives only the probability of measuring the results. Quantum mechanics is statistical in nature and determines the probability that a possible phenomenon at the atomic level has occurred. The final model of the atom is that of a central nucleus with electron clouds of different intensities, which become less and less as the distance from the central nucleus increases.

4. The Properties of Molecules

The discovery of new molecules with peculiar shapes, dimensions, types of bonds, and properties led in many cases to the birth of new sectors of chemistry. The Nobel laureates cited in this section are the pioneers or the founders of molecular biology, macromolecular and supramolecular chemistry, and the chemistry of coordination and metallorganic compounds. Quantum mechanics was the theory that explained the nature of chemical bonds in a molecule, and the forces that keep it stable.

4.1. The Discovery of Coordination and Metallorganic Compounds

Alfred Werner (NP in chemistry, 1913) discovered and explained the nature of many complex molecules—called coordination compounds—where a central atom is linked with small molecules (NH_3 , H_2O), expanding and modifying the old concept of valence. The coordination number is the number of atoms or groups of atoms that can be linked with a central one. Werner investigated compounds where the coordination number is six—the most usual—and four. He showed that the coordination number does not depend on the valence of either the central atom or interconnecting atoms. According to Werner, affinity is an attractive force exerted by the center of an atom that acts uniformly towards all parts of the atom, in contrast with Friedrich Kekulé's concept of constant valence. By separating the coordination number of an element and its valence, he initiated the modern approach to chemical bonding as an alternative to electrostatic theory. The fact that an element can form bonds with molecules was contrary to the theory of electrostatic bonding of his time. Werner also synthesized complexes of platinum and cobalt with asymmetric coordination that were able to rotate polarized light, thus creating the field of inorganic stereochemistry. Indeed, Alfred Werner can be considered the founder of coordination chemistry. Ernst Fischer and Geoffrey

Wilkinson (joint NP in chemistry, 1973) synthesized new molecules containing a central atom between two organic molecules. Fischer synthesized a chromium complex with benzene, cyclopentadiene, and cycloheptatriene. Wilkinson synthesized a complex of iron with cyclopentadiene, as well as a sandwich complex of rhodium, and sandwich compounds with a direct bond between a rhenium atom and atom hydrogen or a methyl group. With their molecules Fischer and Wilkinson created a bridge between organic and inorganic chemistry, and they can be considered the founders of metallorganic chemistry.

4.2. The Discovery of New Organic Molecules

Theodor Svedberg (NP in chemistry, 1926) can be considered the founder of molecular biology for his investigations of many natural colloids and for the isolation of the first natural macromolecules, using the ultracentrifuge he developed. He proved that Einstein's explanation of the Brownian movement of colloids was correct, thus providing strong support for the real existence of molecules, an idea that was still doubted in his time. Applying Einstein's formula, Svedberg was able to calculate the value of N (Avogadro's number) with very high accuracy. He proved that colloids are macromolecules that obey a law similar to the gas laws, and the title of a book he wrote in 1912, *Die Existenz der Moleküle*, explains very well the importance of his work at the time.

Hermann Staudinger (NP in chemistry, 1953) was the first to realize that what in many cases in organic synthesis were considered tars, sparingly insoluble, or insoluble resinous pitch-like masses were indeed polymers (i.e., covalently linked macromolecules that form when the ring closure of a molecule is not possible). In the late 1920s, he clearly stated that molecules existed, formed by chains of 10 000–100 000 atoms, and that they could be identical, differing only in the length of the chain. Indeed his work is the foundation for the field of macromolecular chemistry.

Donald Cram, Jean-Marie Lehn and Charles Pedersen (joint NP in chemistry, 1987) were awarded the Nobel prize for the discovery of molecules with relatively low molecular weights and internal cavities. Such molecules have the ability to recognize cations, anions, and neutral molecules selectively, and in some way to mime the activity of enzymes. Pedersen synthesized cyclic polyethers—crown ethers that have remarkable properties to bind alkali elements. Lehn developed bicyclic crown ethers, which he called cryptands and that have a high selectivity in trapping alkali ions. Cram synthesized several crown ethers, which could also trap organic molecules, and made an important contribution to the understanding of the mechanism of host–guest interaction. He developed new molecules, named spherands, which have a higher regularity and indeformability of the cavity, so they can distinguish between closely related guests. Cram, Lehn, and Pedersen can be considered the founders of supramolecular chemistry. Robert Curl Jr., Harold Kroto, and Richard Smalley (joint NP in chemistry, 1996) discovered molecules with 60 and 70 atoms of carbon and the shape of truncated icosahedral cages—an icosahedron is a polyhedron with 20 hexagonal surfaces and 12 pentagonal surfaces. These molecules are very symmetric, have a high stability with both simple and double bonds, and are not aromatic compounds. Applications for such molecules can be found in the field of nanotechnology related to the electronics industry.

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<<http://www.nobel.se>> [The motivation of the commission in awarding the Nobel Prize and a short biography of each of the laureates is provided.]

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Biographical Sketch

Ferruccio Trifirò obtained his degree in Chemical Engineering in Milan, Italy, in 1963 with a thesis on the polymerization of alpha olefins with Ziegler–Natta catalysts, with Professor G. Natta. From 1975 he has been Professor of Industrial Chemistry at the Faculty of Industrial Chemistry, University of Bologna, Italy. His main research activity is in the field of heterogeneous catalysis, especially for the oxidation and hydrogenation processes. He is the author of 300 publications, including three recent books on catalytic oxidation technology. He is Director of the magazine *Chimica e L'Industria* of the Italian Chemical Society. His hobbies are collecting old books on chemistry and tennis.