Pathways to Modern Chemical Physics

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Preface

This book originates from the suggestion made by several colleagues to extract certain sections from a two-volume book that I recently published in Italian with the Bollati-Boringhieri publishing house. The sections concerned deal with recent developments in chemical physics and the intention was to implement them with additional material in order to produce a book in English, explicitly dealing with the progress of chemical physics, in particular that realized in the last two centuries. As a professor of chemical physics, I felt encouraged to fill this gap by producing a book that could offer to new generations of chemistry students a testimony of the commitments, hopes, and dreams that my generation has experienced throughout this fascinating adventure.

Although chemistry has its roots in alchemy, or even earlier in the old Sumerian, Babylonian, and Egyptian cultures, chemical physics became an independent discipline only in the second half of the eighteenth century. At this time the efforts of several scientists interested in developing the basic theoretical aspects of chemistry and their relationships with physics gave rise to the birth of this new discipline and to the creation of the first chairs and journals of chemical physics. A reasonable official birth date of chemical physics seems to be the year 1887, when Ostwald founded the *Zeitschrift für physikalische Chemie*. A journal which was clearly inspired by chemical physics, the *Annalen der Physik und der Physikalischen Chemie*, had in fact already been founded in 1819 by Ludwig Wilhelm Gilbert (1769–1824), but it changed its name and interests after only few years, and in 1824 it transformed into the *Annalen der Physik und Chemie* edited by J.G. Poggengorff.

The connection between chemistry and physics, however, goes back much further, as testified by the *Sceptical Chymist* of Robert Boyle in 1661, bearing the subtitle *Chymico-physical Doubts and Paradoxes* and by a lecture held at the St. Petersburg University by the Russian chemist Mikhail Lomonosov in 1752, entitled “A Course in True Physical Chemistry”. In the eighteenth century, specialization was not yet tightly structured and ties between behavior and composition of matter were such that it was often difficult to classify the contributions of different researchers in current terms. For instance, the mathematician and physicist Pierre Simon Laplace contributed, together with Lavoisier, to water synthesis, and at the beginning of the nineteenth century another mathematician, André-Marie Ampère, developed a hypothesis parallel to that of Avogadro. Newton, a physicist, was interested in alchemy, while Faraday, a chemist, had provided fundamental contributions to electromagnetism.

By the nineteenth century, however, chemical physics was already a mature science and developed along several separate directions: thermodynamics, kinetics, electrochemistry, molecular structure determination, and colligative properties of the solutions. The premises to this type of organization of the discipline had already existed since the eighteenth century: the affinity theory, born with Boerhaave, Macquer, Geoffroy, and Berthollet, assumed the form of a proto-theory of the chemical bond. The caloric theory and the study of phase transitions of Lavoisier paved the way to thermodynamics. The series of Berzelius created the basis on which the theory of electrolytic dissociation could be developed. Atomic spectroscopy originated from the works of Fraunhofer, Kirchhoff, and Bunsen, while Stanislao Cannizzaro and Hermann Kopp introduced the concepts of dissociation and chemical equilibrium from which chemical kinetics originated. With the discovery of the electron, the affinity concept found its correct interpretation and was transformed into the modern chemical bond theory that was then completely assimilated into the developing quantum mechanics. In the evolution of the different branches of chemistry, lines of thought, new methodologies, and different problems and solutions cumulated and amalgamated in time, giving rise to a science that perfectly blends the theoretical structure and quantitative exactness of physics with the necessary systematization and classification typical of the natural sciences. As a consequence of this complex and articulated situation, chemical physics represents today a natural bridge connecting very different scientific disciplines such as physics, molecular biology, geology, mineralogy, and even astrophysics.

Public opinion sees chemistry as essentially an experimental laboratory practice and a chemist as an alchemist or, at best, a dowdily clad gentleman of the nineteenth century mixing chemicals in a test tube in an old-fashioned laboratory. However, in fact chemistry possesses a very important theoretical structure, elaborated essentially in the last two centuries, that has contributed to the development of all kinds of scientific knowledge and to the formulation of the theories that now constitute the supporting framework of modern science.

The vision that the public has of chemistry results from a secular diffidence and an old form of humanism, bound to the concept of an unremitting separation between the two cultures, leading to two incompatible directions of thought and consequent mistrust of scientific conquests. The fear was that they could orient the development of modern society toward Orwellian scientific power, able to condition the freedom and the humanity of future societies. In contrast to this opinion, this book represents an attempt to convince the reader that chemistry, and in particular the more theoretical structure represented by chemical physics, is an integral part of the general culture of mankind and that, more than any other branch of science, had a profound influence on the growth of culture in modern societies. The development of chemistry, and particularly that realized in the last two centuries, coincides with the development of civilization, owing to the strong influence that chemistry has on most of the scientific, technological, and even social growth of mankind. The birth and growth of modern industrial structure and the important social transformations that arise from it, are indeed strictly connected with theoretical developments in chemistry and reflect its historical evolution, all its conceptual transformations and contradictions, and all its constant enrichments and extraordinary achievements.

The history of modern chemical physics is, in many respects, the history of the great theoretical and technological achievements that humankind has realized in developing its control of nature and in realizing its freedom from hunger, sicknesses, poverty, and sorrow. It is essentially the history of the contributions that ranks of chemists have made to improve the knowledge of the structure of our world and of the fascinating intellectual adventure represented by their participation in the development of natural philosophy. It is also the story of how the human mind has succeeded in penetrating the secrets of nature and of how knowledge and the ideas of ancient times have flowed together in the structure of modern culture, making it possible to modify a hostile nature, adapting it to the needs of modern society in continuous improvement.

It is actually inherent to the nature of chemical physics to give more space to the ideas that have produced variations of the paradigms supporting the theoretical structure of modern chemistry rather than to results obtained in practical applications. This book is therefore more a history of ideas than an account of results, and for this reason the historical development of chemical physics is presented in terms of problems, although still paying the necessary attention to the illustration of the heroes in this wonderful adventure. Svante Arrhenius, Nobel laureate for his contributions to modern electrochemistry, gave a very enthusiastic evaluation of the importance of chemical physics in scientific culture. He said:

> The theoretical side of physical chemistry is and will probably remain the dominant one; it is by this peculiarity that it has exerted such a great influence upon the neighboring sciences, pure and applied, and on this ground physical chemistry may be regarded as an excellent school of exact reasoning for all students of the natural sciences.

This book is organized into eight main chapters, each separated in turn into several sections presenting the fundamental directions in which chemical physics has evolved since its birth. The first three chapters deal with the history of the growth of classical chemical physics, particularly thermodynamics, chemical equilibrium, and electrochemistry. Classical thermodynamics describes energy transformations in terms of macroscopic variables and has always been the battle horse of theoreticians, owing to its lucid and logically perfect treatment of the transformations of any physical system. The development of classical thermodynamics is supplemented by that of statistical thermodynamics, relative to irreversible and out-of-equilibrium processes and to the interpretation of the microscopic interactions between individual particles or quantum-mechanical states. Chapter 2 treats another classical problem, that of chemical equilibrium, presenting a detailed treatment of the modern approach to the problem in terms of catalysis and including a description of the most advanced techniques utilized in the study of catalytic processes. Chapter 3 covers the strict connection between matter and electricity, the different theories of ionic processes in solution, the modern version of ionic transport in solution, and the study of colligative properties. Chapter 4 is the first in the part of the book dedicated to advanced research problems typical of modern chemical physics, including rotational, vibrational, nuclear, and electronic resonance spectroscopy, as well as x-rays and neutron diffraction. Chapters 5 and 6 are dedicated to the history of the discovery of the electron and nuclear structure, the development of models of the atom, theories of the chemical bond in the framework of the old quantum theory, and the related problems of natural and artificial radioactive substances. Chapter 7 then covers the birth of quantum mechanics and its extension to the study of the quantum behavior of molecules with particular reference to the various methods of approximation that have allowed the quantum treatment of large molecular systems. Finally, Chap. 8 illustrates how all these theoretical aspects have converged in the study of the mechanisms of chemical reactions, i.e., in offering to the organic chemists a theoretical justification of their work on synthesis.

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