

Chapter 1

Development of Physics and Physical Chemistry from about 1800 until 1870

In his statement addressed to CASPAR VOGHT at the beginning of the 19th century, *“The sciences move forward not in a circle, but in a spiral – the same returns again, but higher and farther.”* (quoted after [Dobel (1968)]), JOHANN WOLFGANG VON GOETHE had expressed his opinion on the development of the sciences, which at the same time implied the importance of the pre-occupation with the history of science. In the introduction to the historic part of his *«Farbenlehre»* GOETHE has remarked *“Indeed, a history of the sciences, as long as it is treated by human people, shows quite a different and highly educative meaning, than if discoveries and opinions are only arranged one after another.”* [Goethe (1893): XII].

So it is necessary and rewarding at the same time to illuminate with a few words the historic development preceding the scientific activity and work of WALTHER NERNST, in which physical chemistry as a special discipline of physics occupies the central place.

The development of chemistry into an exact science happened around the turn of the 18th to the 19th century. Still in 1786 IMMANUEL KANT had denied chemistry this status: *“So as long as no concept, which can be constructed, is found regarding the ‘chymischen’ actions of matter upon one another, i. e., no law about getting closer or more apart of the parts can be formulated, according to which, say, in proportion to their densities ... their movements including their consequences can be made clear and be depicted a priori in space (a requirement which hardly ever*

will be fulfilled), so 'Chymie' can never become more than a systematic art, or an experimental doctrine, but never a proper science, since its principles are only empirical and do not allow a description a priori in a clear picture, hence, it cannot make the principles of 'chymischer' phenomena in the least understandable, because they are incapable of applying mathematics." [Kant (1786): X]. Although at this time to a large extent this remark had lost already its validity, it still emphasizes the necessary connection of the chemistry with the mathematics and due to the latter with the physics as a requirement for its transformation into an exact science. In Section 4.12 a few aspects of the historic development of the relations between chemistry and mathematics or mechanics, at the time treated as part of this discipline, will be discussed. Here only a few points from the history of physics and chemistry from the end of the 18th until about the third quarter of the 19th century shall be mentioned, which were important for the rise of the classical physical chemistry, for the completion of which NERNST then played a decisive role.

The early history of these mutual relations extends to the time before 1600. During this period great scientists have demonstrated close relations between the chemical substances and their mutual transformations and measurable quantities such as weight (mass), temperature, and time.

ANDREAS LIBAVIUS, the founder of the quantitative chemical analysis and the discoverer of the *spiritus fumans Libavii* (SnCl_4), connected the relationship (affinity) between salts with their crystal size, mass, and magnetism, as well as smell and taste.

For the 17th century above all ROBERT BOYLE must be mentioned. His law of gases, which was discovered independent of him also by EDME MARIOTTE, and which, hence, is named after both scientists, quantitatively connects the pressure p , the volume V , the temperature T , and the amount n of the substance with one another: $p \sim V^{-1}$ for $T = \text{const.}$ and $n = \text{const.}$ BOYLE considered the qualitative and the quantitative determination of the compositions of the substances as the main task of the chemists. Also he had introduced the vacuum into the chemical experimental technique.

The natural scientist HERMAN BOERHAAVE from Leiden was similarly versatile and brilliant as the British BOYLE. His work «*Elementa chimiae*» of 1732 contains data on the freezing and boiling points, on the values of the heat of solution, mixture, and reaction, as well as on the thermal expansion of the materials. BOERHAAVE distinguished between purely chemical compounds and their mixtures.

The Russian universal scholar MIKHAIL LOMONOSOV advanced the mathematical and physical side of chemistry. He is credited with the discovery of the conservation of mass in the case of chemical reactions, one of the most fundamental laws of chemistry. The French scholar ANTOINE LAURENT LAVOISIER had also discovered this law a little later independent of his Russian colleague. It is said that LOMONOSOV had coined the word “Physical Chemistry” for the first time. He had emphasized: “*The chemistry of mine is mathematical.*” (see also Section 4.12).

The activity of CARL FRIEDRICH WENZEL working in Saxony was highly important. In Freiberg he had recognized the influence of the amount of substance upon the result of a chemical reaction. The relationship between chemical substances he assumed to be inversely proportional to their time of solution in a given solvent.

These examples and names in place of many others may be sufficient in order to demonstrate how strongly chemistry was dominated by quantitative and thereby actually by physical ideas until the end of the 18th century. Of course, this was a great advance for its development. Now quantitative laws with far-reaching consequences could be discovered.

At the beginning of this development one can place the dissertation of JEREMIAS BENJAMIN RICHTER from 1789 of the University of Königsberg, which was devoted to the application of mathematics in chemistry (see Section 4.12). The law of the equivalent proportions (1792) also originates from RICHTER. In 1807 WILLIAM HYDE WOLLASTON formulated its general version: “Chemical elements always combine with each other following the ratio of certain compound masses (so-called equivalent masses) or integer multiples of these masses leading to chemical compounds.” At this time also two additional fundamental laws of the mass balance of chemical reactions were found. We refer to the law of

constant proportions by JOSEPH LOUIS PROUST from 1799 (“In a certain chemical compound elements always appear in the same mass ratio.”), which JOHN DALTON extended in 1803 in terms of the law of the multiple proportions (“If two different chemical compounds contain the same elements, then there appear simple number ratios between the element masses.”). Based on these laws in the beginning of the 19th century DALTON justified the model of the elementary nature of chemical compounds based on the assumption of atoms, which he treated in his book “*A New System of Chemical Philosophy*” published in 1808. Thereby the foundation was created for quantifying and mathematizing the chemistry. Therefore, more than LAVOISIER, DALTON is to be counted as the true founder of chemistry as an exact science, as has been noted already by the philosopher FRIEDRICH ENGELS: “*The new epoch starts in chemistry with the atomistics (so Dalton, not Lavoisier, the father of the newer chemistry) and correspondingly in physics with the molecular theory ...*” [Engels (1968): 552].

Essentially, the only common feature of the atomic theory of DALTON and the classical antique theory of DEMOCRITUS was the name of the treated objects, which goes back to the Greek ἄτομος (‘indivisible’). Also this doctrine had been highly controversial. Prepared during the 16th century, perhaps during the 17th century the opinions collided with each other most strongly. For example, RENÉ DESCARTES represented the doctrine of the continuity; on the other hand his contemporary PIERRE GASSENDI followed the leading Greek atomist DEMOCRITUS. If the existence of atoms and, hence, a discontinuous structure of matter would be physically real, then between the atoms there should exist the empty space, i.e., the vacuum so strongly opposed by DESCARTES. The reality of the vacuum was demonstrated by the investigations by OTTO VON GUERICKE, in particular by his famous experiment performed in 1654 at the *Reichstag* in Regensburg using the Magdeburg hemispheres, by his construction of a vacuum pump, and also by the first proof of the chemical effect of the empty space by means of the extinction of a candle. In this way the validity of the atomic opinion had gained special weight. ROBERT BOYLE criticized the qualitative doctrines of the elements by

ARISTOTLE and by PARACELTUS, which were dominating during his time. He taught that the corpuscular or the atomic theory best explains the experimental experience and the existence of the vacuum. According to his opinion the atoms represent matter without any special quality, an idea which was contested, for example, by his contemporary NICOLAS LÉMERY.

AMADEO AVOGADRO from Piedmont worked out a molecular hypothesis, which is expressed in the law published in 1811 and named after him: "Under the same conditions (pressure, temperature) the same volumes of gases contain the same number of particles." Since initially AVOGADRO's paper remained unrecognized, in 1814 ANDRÉ MARIE AMPÈRE expressed the same hypothesis. Although the atomic or the corpuscular understanding of matter turned out to become an essential basis of chemistry and physical chemistry, even up to the times after 1900 one could find important scientists such as ERNST MACH and WILHELM OSTWALD, who considered the existence of atoms and molecules to be physically unreal, in contrast to, say, WALTHER NERNST.

In addition to the atomic theory, in particular thermodynamics and the theory of electricity represented further pillars upon which the structure of physical chemistry could be erected. The development of thermodynamics started from the interest to understand the physics of heat engines, in order to improve their efficiency. During the first half of the 19th century the most essential theoretical foundations have been created. Among the most important scientists who had contributed to these advances we must mention in particular SADI CARNOT, RUDOLF CLAUSSIUS, JULIUS ROBERT MAYER, HERMANN VON HELMHOLTZ, JAMES PRESCOTT JOULE, and JOSIAH WILLARD GIBBS. In Section 5.5.1 this development will be treated in more detail. Together with the thermodynamics, the thermochemistry or the chemical thermodynamics developed into one of the most important disciplines of the physical chemistry.

The evolution of the theory of electricity and of the electrochemistry was closely connected with each other in this "*electric age*", as the 19th century was called by FELIX PINNER [Pinner (1918)]. In 1780 in Bologna the medical doctor LUIGI GALVANI had discovered a new kind of elec-

tricity in the behavior of the thighs of dead frogs placed close to an electrostatic generator. This new kind could be counted in addition to the atmospheric and the frictional electricity. GALVANI interpreted his discovery in terms of a vitalistic point of view. On the other hand, during the years from 1792 until 1796 for the interpretation of the galvanism ALESSANDRO VOLTA created the concept of the contact electricity, which became highly important for the electrochemistry. In this work VOLTA had benefited from the previous studies of FRIEDRICH ALBRECHT CARL GREN and JOHANN CHRISTIAN REIL. In 1798 in Jena JOHANN WILHELM RITTER founded the electrochemistry by associating the galvanism with chemical effects [Ritter (1798)]. Only after 1810 the Englishman GEORGE JOHN SINGER coined the word "Electrochemistry". Prior to this the term galvanism had been used exclusively.

For the development of the electrochemistry during the first decade of the 19th century, in addition to the investigations by Sir HUMPHRY DAVY, JÖNS JAKOB BERZELIUS, and others, those by THEODOR GROTHUSS are important. For example, already in 1805 the latter presented first ideas about the electrolytic dissociation, where, however, he considered the electric current to represent the cause of the dissociation. In 1857 RUDOLF CLAUSIUS interpreted this phenomenon statistically. The completion of the theory of the electrolytic dissociation fundamental to the natural science was achieved about 30 years later by the brilliant Swedish physicist SVANTE ARRHENIUS (see Section 3.4).

In the history of electrochemistry we must emphasize the activity of MICHAEL FARADAY also in this field. He created the basic terms electrode, electrolyte, anode, cathode, anion, and cation (see Section 3.4), and in 1832 he discovered the fundamental laws of electrolysis:

$$(1) n = (zF)^{-1} \cdot q, \quad (2) m = (zF)^{-1} \cdot qM,$$

where n denotes the amount of substance precipitated electrolytically, z the valency of the ion, q the electric charge, m the precipitated mass, M the mole mass, and $F = e_0 N_L$ FARADAY'S constant (e_0 elementary charge, N_L LOSCHMIDT number).

For the theory of the electrolytes the investigations by WILHELM HITTORF on the transport of current within electrolytic solutions were highly

important. Based on these studies in 1853 he discovered the transport law of the ions, which allowed a quantitative treatment of the mass transport in an electric field.

In particular GIBBS and HELMHOLTZ applied thermodynamics to electrochemical systems in equilibrium or in the absence of a current. So already in 1847 HELMHOLTZ had recognized the equivalence between the so-called electromotoric force (e.m.f, potential difference between the electrodes of a galvanic cell in the state of equilibrium) and the heat of reaction. In 1882 he found that the voltage of the cell can be particularly well described in terms of the free energy of the reaction. NERNST extended these scientific advances in his fundamental studies on electrochemistry.

In the 19th century for scientific experiments and as a current source the column developed by VOLTA and named after him played an important role. The discovery of FARADAY's laws led to new current sources, the galvanic elements, of which we mention those of JOHN FREDERIC DANIELL, WILLIAM GROVE, and ROBERT WILHELM BUNSEN. During his search for a new galvanic element, in 1854 the German physician JOSEPH SINSTEDEN invented the lead-acid storage battery, which five years later was improved by the French physicist GASTON PLANTÉ. Only in 1886 the inventor HENRI TUDOR from Luxemburg developed the first technically suitable lead accumulator.

The discovery of the dynamo-electric principle was extremely important for the generation of current. It had been recognized first in 1853 by the Hungarian physicist ÁNYOS JEDLIK, who initiated its technical application in 1861 with the construction of a dynamo engine. However, this principle became widely known only in 1866 when WERNER VON SIEMENS found it independently of JEDLIK and also built a dynamo engine. This then led to a rapid upturn of the electric technology. In the subsequent "*electric age*" the major innovation initially dealt with the electric light generation, to which also NERNST contributed significantly utilizing his electrochemical and physical experience (see Section 4.9).

Among the first scientists working in the field of the classical physical chemistry in the sense of today we can count ROBERT WILHELM BUNSEN

and AUGUST FRIEDRICH HORSTMANN. Since 1859 the former worked on the spectrum analysis of the chemical elements together with GUSTAV ROBERT KIRCHHOFF. The paper by HORSTMANN on the vapor pressure and the heat of evaporation of ammonium chloride, which appeared in 1869, can be looked at as the first publication in the field of the chemical thermodynamics. Also HANS LANDOLT and HANS JAHN, which later will be mentioned several times, have achieved important results within the physical chemistry. Already in 1855 LANDOLT organized a physical-chemical colloquium at the Polytechnic Institute in Aachen.

On the completion of the classical physical chemistry the physical chemist WILHELM JOST from Göttingen has noted: "*Physical chemistry as a distinct field of chemistry, at least for practical purposes, originated in Germany during the last fifth of the 19th century. Who were the leading men of that period, i. e., born before 1860? They were Arrhenius, van't Hoff, and W. Ostwald, followed by Nernst – about ten years younger than the other three.*" [Jost, W (1966): 1]. "... *Physical chemistry in Germany started in Leipzig, and then spread by way of Göttingen to Berlin, there to experience an unprecedented flowering in a mutual exchange with all of Germany, and with the world.*" [Jost, W (1966): 14]. In this last listing mainly the academic career and the development of the scientific impact of WALTHER NERNST is sketched.