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# How Did the Tree of Knowledge Get Its Blossom? The Rise of Physical and Theoretical Chemistry, with an Eye on Berlin and Leipzig

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history of chemistry  $\cdot$  physical chemistry  $\cdot$  theoretical chemistry  $\cdot$  quantum mechanics

Dedicated to Hans-Joachim Freund and Matthias Scheffler on the occasion of their 65th birthday and to Gerhard Ertl on the occasion of his 80th birthday

#### Introduction

Physical and theoretical chemistry came about with a purpose, namely to save chemistry from becoming a collection of little disconnected facts. Its founders, Jacobus van't Hoff, Wilhelm Ostwald, and Svante Arrhenius, set out, at the end of the 19th century, to seek the general rather than cherish the particular by focusing on the processes of forming chemical compounds—that is on chemical reactions—rather than on the compounds themselves. They co-opted the methods of physics, especially thermodynamics, and their effort gave rise to the fields of physical and theoretical chemistry, which were here to stay and become a part of any chemistry of the future. The success of physical and theoretical chemistry in providing a common ground for chemistry was celebrated by Ostwald in his proclamation, "Physical chemistry is not just a branch on but the blossom of the tree of knowledge." The fragrance of this blossom proved irresistible to scores of scientists who would lead chemistry through the quantum revolution and beyond, and find a new gratification in the premise that the road to general chemistry goes through physics and mathematics. Herein, I provide a tour along the timeline of the developments of physical and theoretical chemistry from its dawn in the 17th century to its triumphs during the post-quantum revolution era, up to about 1940, with an eye on the developments in Berlin and Leipzig.

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# 1. The Dawn of Physical and Theoretical Chemistry (1650–1840)

Chemistry as a science came about in a long process with only few revolutionary moments. Perhaps one such moment was the publication of Robert Boyle's book, The Sceptical Chymist, in 1661. In it, Boyle attempted to liberate chemistry from the grip of the "vulgar chymists" (as he called them), who were concerned with commerce and medicine, and make chemistry into a tool for the study of the workings of nature.<sup>[1]</sup> Wielding skepticism against the Aristotelian elements and Paracelsian principles, Boyle strived to elevate chemistry to the status of a fundamental experimental science. His outlook is well captured by the statement: [2] "I look upon experimental truths as matters of great concernment [importance] to mankind." In keeping with this outlook, Boyle carried out countless experiments. Some were of general, enduring value. The inverse relationship between the pressure and volume of gases, known as Boyle's law, is perhaps the best example. He discovered it with a "pneumatic engine" built by his assistant Robert Hook (Figure 1). Boyle's law smacks of physics and mathematics—the other tools for understanding nature, which would prove to be not only interrelated but inseparable from each other and from chemistry.

The term physical chemistry appeared for the first time in the work of the Russian polymath Mikhail Lomonosov. Here is his definition (1752):<sup>[3]</sup> "Physical chemistry is the science that must explain under provisions of physical experiments the reason for what is happening in complex bodies through chemical operations." This definition sounds quite modern. However, it took more than a hundred years to become widely accepted as such.

One of the first feats of chemistry that bore on all of science was the establishment of the law of the conservation of mass. Although its ur-form can be found already in the work of Lomonosov, it was put on a firm footing by the accurate experiments of Antoine Lavoisier and his wife, Marie-Anne, shown in Figure 1 in a double portrait<sup>[\*]</sup> by

<sup>[\*]</sup> The 1788 depiction of Mme. Lavoisier—a partner of her husband both in life and in the research laboratory—as a muse whose touch guides Mr. Lavoisier's hand, delightfully contradicts the stereotype about women as ill-suited for scientific work.







Figure 1. Timeline of the developments in physical chemistry during its dawn period 1650–1840. See text.

Jacque Louis David. Apart from being a scientist, Marie-Anne was also an artist, as alluded to by the folio seen in the background. Her artistic training was provided by David himself.

The faith in the ability of physics and mathematics to aid in explaining chemical phenomena is reflected in this musing of Lavoisier's found in his correspondence with Pierre-Simon Laplace (1782):<sup>[4]</sup> "Perhaps ... some day ... the mathematician will be able to calculate at his desk the outcome of any chemical combination, in the same way ... as he calculates the motions of celestial bodies." This sounds like a manifesto of theoretical chemistry: calculate in order to predict.

In his 1789 masterpiece *Traité élémentaire de chimie* (*Elements of Chemistry*) illustrated by Marie-Anne, Lavoisier



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provided a list of 33 chemical elements that included light and caloric, the latter as the element of heat. Lavoisier's list signified a definitive departure from the Aristotelian—or prescientific—view of matter.

The law of constant proportions, discovered by Joseph Proust, [5] espoused Lavoisier's chemical elements and established the notion of a chemical compound as a combination of chemical elements in a particular ratio of integral amounts. When Joseph Gay-Lussac subsequently discovered the law of constant proportions for gases, he was smitten with it to the point that he declared: [6] "We are perhaps not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation."

A further step in elucidating the nature of matter was taken by John Dalton. In his work A New System of Chemical Philosophy, published in 1808, Dalton identified chemical elements with atoms—which he characterized as indivisible and indestructible particles that preserve their identities in chemical reactions. What added weight to Dalton's argument was that he declared atoms to have, well, weight, and proceeded to infer it from the law of multiple proportions, stoichiometry, etc. A major influence on Dalton was Isaac Newton, who in his mechanical derivation of Boyle's law<sup>[7]</sup> assumed the existence of small particles (interacting via repulsive forces inversely proportional to their distance) but fell short of calling them atoms. Newton may have sought to avoid the stigma of atheism, which in his day was still attached to the atomistic views of Epicurus and Lucretius.[8] However, Dalton was fearless and eloquent, as attested by his state-







Figure 2. Timeline of the key conceptual (on the left) and institutional (on the right) developments in physical and theoretical chemistry during the period 1845–1940. See text.

ment: <sup>[9]</sup> "We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, [than] to create or destroy a particle of [say] hydrogen."

A table of 49 chemical elements ordered according to their atomic weights was drawn up by Jöns Jacob Berzelius in 1818. [10] Berzelius, who enriched chemistry with many modern terms and discovered a number of chemical elements, also came up with the notion of isomer [11] for what was discovered by his pupil Friedrich Wöhler (silver cyanate) and by Justus von Liebig (silver fulminate, an explosive). Wöhler, together with his friend Liebig, were engaged in a systematic study of mainly organic compounds within the framework of the above-mentioned chemical laws. The discovery of isomerism helped to cement the status of atomic theory in chemistry and foreshadowed the work of Alexander Butlerov, Emil Fischer, and others on chemical structure.

## 2. Key Conceptual and Institutional Developments Concerning Physical and Theoretical Chemistry (1845–1940)

Robert Boyle's goal to elevate chemistry to the status of a fundamental science was taken up during the last third of the 19th century by a trio of chemists who would become the founders of physical chemistry proper: Jacobus van't Hoff, Wilhelm Ostwald, and Svante Arrhenius. Trained primarily as organic chemists but with a predilection for physics and mathematics, they shared two pivotal views: Firstly, that chemistry was in need of a reform as it was drifting towards taxonomy—a collection of disconnected little facts bred mainly by organic chemists. Secondly, that chemistry should, like physics, speak the language of mathematics and seek the general rather than relish the particular. [\*] Key moments of the effort that ensued are captured in the timeline of Figure 2.

The term "physical chemistry" that could—and would—be used for the chemistry of the future was, as we know, already in existence although not in circulation. However, some of the pioneers of physical chemistry preferred, at least for a while, the terms "general" or "theoretical" chemistry.

But how does one seek the general in chemistry? To the trio, which would eventually become a triumvirate, the answer was: by focusing on the processes of forming chemical compounds—that is on chemical reactions—rather than by studying the compounds themselves. The pioneering paper on the key characteristic of a chemical reaction, the equilibrium constant, was published by two Norwegians, Cato Guldberg and Peter Waage, in Norwegian. [12] The law they discovered, known as the law of mass action, remained well hidden until Ostwald finally came across it a dozen years later.

<sup>[\*]</sup> Justus von Liebig, in his Chemische Briefe [Letters on Chemistry] compared the usefulness of chemistry for understanding nature to that of mathematics, whose role he extolled as "indispensable" (first letter. 1841).





According to Guldberg and Waage, the equilibrium state was the result of a balancing act between the forward and reverse reaction forces, characterized by chemical affinities. Ostwald corroborated the validity of the law by his own experiments and made it, along with the notion of chemical affinity, into a mainstay of his future work.

Van't Hoff, who was among the first to apply thermodynamics to chemical problems, discovered the law independently and derived a formula that describes the temperature dependence of the equilibrium constant. [13] Van't Hoff's work on the temperature dependence inspired Arrhenius to propose a relationship between the reaction rate and temperature—and to introduce the key notion of activation energy on the way. [14] In addition, Arrhenius applied the theory of chemical equilibrium to electrolytes, [15] which, from then on, would become one of the triumvirate's chief preoccupations and earn them the label "Ionists."

During the formative years of physical chemistry, the notion of chemical affinity underwent an overhaul—from its vague beginnings as a "chemical force" to being equated with the concept of free energy as developed by Herrmann von Helmholtz. [16] The attempt of the Ionists to elevate chemistry as a science largely relied on applying the methods of thermodynamics to chemical processes. They spoke of "chemical dynamics," a term later replaced by "thermochemistry." "Chemical dynamics" still appears in van't Hoff's Nobel citation from 1901. In Nernst's citation, from 1920, it is already "thermochemistry."

During the same period, the thermodynamic work of Josiah Willard Gibbs, later characterized as the "principia of thermodynamics", was blissfully ignored by chemists (including the Ionists), although it had answered all the questions that the chemists were asking—from chemical forces to the nature of the electromotive force. [17] The reason was that Gibbs worked in splendid isolation in rural Connecticut and communicated with his European colleagues—mainly physicists—by mailing them reprints of his papers. [18] He had to, as these appeared in the then (and now) obscure *Transactions of the Connecticut Academy*. In 1892, Ostwald translated Gibbs' magnum opus into German. [19]

James Clerk Maxwell was among the most appreciative recipients of Gibbs's reprints. He was fascinated by Gibbs's work to the point that he sculpted, out of clay and plaster, a Gibbs energy surface as a function of volume and entropy for a water-like substance and traced the isotherms and isobars on the surface. Apparently Gibbs was quite pleased when the famous Maxwell sent him—a "chemical engineer from Connecticut" —a copy of the sculpture. Maxwell also shared with Gibbs a predilection for statistical methods in physics. Maxwell's velocity distribution anticipated Gibbs's work in that area and inspired Ludwig Boltzmann. Here's what Gibbs said about the benefits of statistical methods: [20] "We avoid the gravest difficulties when ... we pursue statistical inquiries as a branch of ... mechanics."

Let me now briefly outline the institutional framework of physical chemistry. The first research university—based on the Humboldtian principle of the unity of teaching and research—was the Berlin University, founded in 1810 (and named only in 1949, during the political skirmishes in divided Berlin, after the Humboldt brothers). However, it wasn't the Berlin University that established the first research laboratory for chemistry, but rather Justus von Liebig's operation at the University of Gießen, in the 1820s. Liebig's school combined a well-equipped laboratory with a body of students enlisted in active, creative research. Liebig's school became a widely adopted model throughout Germany's roughly 30 universities (including 10 technical colleges). As a result, by the mid-19th century, German universities played a pace-setting role in chemical research worldwide. [\*][23]

The first university to establish a chair in physical chemistry was Leipzig University. [\*\*\*] Its recipient was Wilhelm Ostwald, who would become a most vocal advocate of his field and founder of a highly influential international school of physical chemistry. [\*\*\*\*] Ostwald would also cofound, with van't Hoff, a tribune of the chemistry of the future, namely *Zeitschrift für Physikalische Chemie*, [\*\*\*\*] with an international editorial board. In his introduction to the first issue of the journal, [24] Ostwald declared that "Physical Chemistry is not just a branch on but the blossom of the tree [of knowledge]."

More chairs in physical chemistry quickly followed: for Hans Landolt in Berlin and Ostwald's pupils Walther Nernst and Arthur Noyes in Göttingen and at the Massachusetts Institute of Technology (MIT), respectively. By 1910, about a half of the German universities had a chair or section of physical chemistry.<sup>[22]</sup> This reflected the view that physical chemistry was not just a core discipline of chemistry but also the basis of chemical technology. In contrast, Oxford and Cambridge established their chairs in physical chemistry only after World War I.

The first journal outside of Germany dedicated to the new field was the *Journal of Physical Chemistry* (JPC), edited by Ostwald's pupil Wilder Bancroft. During its first decade JPC published 300 research papers, written almost entirely by Americans and Canadians. One quarter of these were Ostwald's pupils, among them Gilbert Newton Lewis, Arthur Noyes, and Theodore Richards. American physical chemists

<sup>[\*]</sup> Ref. [23] concluded that during the period from 1492 until 1897, about 5000 theses on chemical subjects were submitted in Germany, compared with 1500 theses in France, 600 in Switzerland, 120 in Russia, and fewer than 100 in any other country.

<sup>[\*\*]</sup> However, Hermann Kopp (1817–1892), a chemistry professor at Heidelberg, trained by Justus von Liebig, was concerned with one of the later preoccupations of physical chemistry, namely the relationship between chemical composition and the physical properties of substances, cf. "Kopp's rule."

<sup>[\*\*\*]</sup> Ostwald had 147 pupils who achieved independent scientific success; 34 became professors. Einstein and Haber could have been among them, had Ostwald not turned them down when they applied for positions in his laboratory. However, he was the first to nominate Einstein for a Nobel Prize, already in 1909, the year he himself received it.

<sup>[\*\*\*\*\*]</sup> The journal became one out of six periodicals on chemical subjects published in Germany at the time.

<sup>[\*]</sup> Gibbs was Professor of Mathematical Physics at Yale University.





published in the *Journal of the American Chemical Society* (JACS) as well—and by 1926, over a quarter of all papers published by JACS were in physical chemistry. As a witness observed: "Physical chemistry now seems about to swallow up chemistry proper."

And what will, in turn, swallow up physical chemistry? Well, arguably, in all but name, chemical physics and theoretical chemistry. But in order to get there, we must gloss over the quantum revolution first.

As Helge Kragh noted, [25] "Quantum theory owes its origin to the study of thermal radiation, in particular to the 'black-body' radiation that Robert Kirchhoff had first defined in 1859-1860." The experimental investigation of black-body radiation is a legacy of Helmholtz and his leadership at the Physikalisch-Technische Reichsanstalt (PTR). The discovery of the black-body radiation law by Max Planck, [26] signified in the words of Abraham Pais<sup>[27]</sup>—the first "coming" of Planck's constant. Three more comings of Planck's constant were needed in order for quantum mechanics to emerge: The second coming was in Einstein's paper on the light quanta<sup>[28]</sup> (often incorrectly referred to as the photoeffect paper)[\*] and the third in his paper on the heat capacity of solids. [29] This paper caught the eye of Walther Nernst, who saw in it a clue to his Heat Theorem. In response, Nernst co-organized the first Solvay conference.[\*\*] The fourth coming was in Bohr's model of the atom, [30] which combined the extant quantum ideas with the discoveries of the electron and of the atomic

The discovery of quantum mechanics by Werner Heisenberg, Erwin Schrödinger, and Paul Dirac was surrounded by a host of other discoveries relevant to physical and theoretical chemistry. Among them was Einstein's analysis of Brownian motion<sup>[31]</sup> and its experimental validation by Jean Perrin.<sup>[32]</sup> This led to the definitive recognition of the particulate or atomic structure of matter—even by diehard physicists (with the exception of Ernst Mach) and physical chemists (including Ostwald). It also helped to precipitate the demise of the theory that proteins and other macromolecules were colloids. Max von Laue's discovery of X-ray diffraction by crystals<sup>[33]</sup> had repercussions for the study of structure and the understanding of strong electrolytes—both key preoccupations of physical chemistry at the time and beyond. William Lawrence and William Henry Bragg's discovery of a law governing Xray diffraction provided a key to the analysis of crystal structures.<sup>[34]</sup> The work of Gilbert Newton Lewis<sup>[35]</sup> and Irving Langmuir<sup>[36]</sup> foreshadowed the theory of the covalent bond as due to a shared electron pair. The discovery of space quantization of angular momentum<sup>[37]</sup> and of spin<sup>[38]</sup> led eventually to NMR spectroscopy and other marvels of quantum science. On the heels of Schrödinger's wave mechanics came Friedrich Hund's discovery of tunneling.<sup>[39]</sup> Moreover, the Pauli principle and Hund's rules-along with adjusted hydrogenic energy levels-proved capable of making sense of Mendeleev's periodic system of the elements.[40] By deploying group theory across quantum mechanics, Eugene Wigner recast selection rules as the observable signature of an underlying physical symmetry.<sup>[41]</sup> The Fifth Solvay conference, in 1927, consolidated quantum theory.

When the dust of the quantum revolution settled, Dirac famously stated that: [42] "The underlying physical laws necessary for the mathematical theory of ... the whole of Chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved." So the key question of theoretical chemistry became: How can these these equations be solved? The quite astounding flurry of activity that ensued provided some answers.

The 1927 paper by Walter Heitler and Fritz London on the homo-polar bond launched quantum chemistry. [43] Apart from demonstrating that chemical bonding owes its existence to a quantum effect, Heitler and London provided the first example of the fine art of approximation that would be in such high demand in quantum chemistry. This paper was quickly followed by the introduction of the Born–Oppenheimer approximation, [44] the consequential Thomas–Fermi model, [45,46] and Hartree's method of self-consistent field. [47]

The year 1931 can be, for good reason, characterized as the *annus mirabilis of* theoretical chemistry. [48] The recasting by Fritz London, [49] Henry Eyring, and Michael Polanyi [50] of Arrhenius's activation energy in terms of an electronic eigenenergy surface, along with the idea of rolling a ball on this surface, introduced a completely new way of visualizing and interpreting a chemical reaction. [\*\*] The rival valence-bond and molecular-orbital theories proved essentially complementary, as first emphasized, in conciliatory terms, by John Van Vleck. [51] Charles Coulson would put it succinctly 20 years later: [52] "[There is] a kind of uncertainty relation about our knowledge of molecular structure: the more closely we try to describe the molecule, the less clear-cut becomes our description of its constituent bonds."

Eugene Wigner was apparently the first to calculate the electronic energy beyond the Hartree–Fock approximation (this was for metallic sodium) and he coined the term "correlation energy" for the correction that he had found.<sup>[53]</sup>

The next step in developing a quantum-mechanics-based theory of chemical reactions was taken by Polanyi and Eyring, who worked separately at that time. They combined their semiempirical potential-energy surfaces with considerations from quantum-statistical mechanics into the "transition-state" (Polanyi)<sup>[54]</sup> and "activated-complex" (Eyring)<sup>[55]</sup> theory.

In the same year, John Van Vleck laid the foundations of ligand-field theory, [56] by showing that in coordination compounds "electrons from a paramagnetic cation are allowed to wander onto the anions and vice versa, so that there is incipient covalence." [57]

The timeline of Figure 2 also includes the discovery of nuclear fission, as it tops the development of the notion of the chemical element, discussed above.

<sup>[\*]</sup> This is the only paper from his "annus mirabilis" series that even Einstein considered revolutionary. See below.

<sup>[\*\*]</sup> At the First Solvay conference, Einstein, until then an unknown quantity from Bern, became well known among physicists.

<sup>[\*]</sup> This work was also a harbinger of chemical reaction dynamics, which would emerge in America in the 1960s.





On the institutional side, the rise of physical and theoretical chemistry was fostered by the following developments:

- The Faraday Society<sup>[58]</sup> was founded in London, named after a founder of electrochemistry.
- The German Society for Electrochemistry (since 1902 the Bunsen Society), dedicated to physical chemistry and electrochemistry,<sup>[59]</sup> was founded, with Ostwald serving as its first president.
- In Germany, the Kaiser Wilhelm Society for the Advancement of Science (today the Max Planck Society) was founded. One of its first two institutes was dedicated to physical chemistry, with Fritz Haber as its founding director.<sup>[60]</sup>
- The first chair in theoretical chemistry was established at the University of Cambridge, for John Lennard-Jones who would speak of his operation as a "mathematical laboratory." [61]
- Additional journals for physical chemistry were established, *Journal de Chimie Physique* in France and *Faraday Transactions* in Britain, among others.

The most important development in terms of publication venues for the post-quantum-revolution physical chemistry was perhaps the founding of the Journal of Chemical Physics (JCP), with Harold Urey as Editor-in-Chief. JCP provided a venue for publishing purely theoretical papers, which the competing Journal of Physical Chemistry (JPC) had scoffed at. In any case, Harold Urey would characterize publishing in the then-failing JPC as "burial without a tombstone." [62] In the very first issue of JCP one can find such gems as John Slater's analysis of the covalent bond in terms of the quantum virial theorem, apart from contributions by Langmuir, Debye, Pauling, G. N. Lewis, Eyring, and others. JCP became a triumph of physical chemists oriented towards physics and mathematics. Ostwald's 19th century premise that the road to general chemistry goes through physics and mathematics thus found a new gratification.[22]

This concludes the tour of the first heroic eras of physical and theoretical chemistry, characterized by the co-optations of thermodynamics and quantum mechanics.

Figure 2 also contains an admonition that affects the current era, which is characterized by the co-optation of computational techniques and a reliance on the digital computer. It comes from none other than Richard Feynman. Feynman was a one-time theoretical chemist himself—he discovered what's known as the Hellmann–Feynman theorem as an undergraduate working with John Slater. Here's his advice: [63] "[I]f you want to make a simulation of nature, you'd better make it quantum mechanical ..." Well, possibly—or hopefully—the quantum simulator or quantum computer will render the arsenal of approximations developed to treat chemical problems redundant *as computational tools* and make theoretical chemistry truly predictive. [64] Of course only if there will ever be a universal quantum computer ...

Henceforth, I will take a somewhat myopic view and describe the key developments concerning physical and theoretical chemistry in Berlin and Leipzig. In doing so, I

will present a gallery of the main contributors to these developments working out of these two centers.

# 3. Physical Chemistry Chairs in Imperial and Weimar Leipzig

A gallery of the Leipzig professors of physical chemistry is shown in Figure 3.

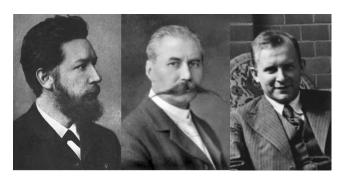


Figure 3. The first physical chemistry chairs at Leipzig. From left to right: Wilhelm Ostwald (1853–1932), Max Le Blanc (1865–1943), and Karl Friedrich Bonhoeffer (1899–1957).

The beginnings of **Wilhelm Ostwald**<sup>[\*]</sup> at Leipzig, upon his arrival from Riga, were less than glamorous: the building was "an old pile in every way unfitted for the carrying on of those delicate experiments which brought Ostwald to the forefront of scientific workers."<sup>[65]</sup> Moreover, Ostwald had to teach freshman analytical and pharmaceutical chemistry, a job beneath the dignity of Johannes Wislicenus, the dominant chemist at Leipzig at the time.

Then finally, in 1898, the university and the government of Saxony provided Ostwald with the present, much more adequate building, designed by Ostwald himself. As a commentator writing for the journal *Nature* put it at the time, the building was "a proof of the appreciation of the importance of the new science and of Ostwald's services." The well-attended inauguration of Ostwald's institute (Figure 4) served to celebrate the new field of physical chemistry.

Following his early retirement, in 1906, Ostwald continued to flourish in a great number of areas, ranging from philosophy to painting to peace activism. His credo, "Don't squander energy, utilize it" is modern in both its literal and figurative sense.

Max Le Blanc<sup>[\*\*]</sup> was something of a Fritz Haber doppelgänger, in that he studied in Berlin under August Wilhelm von Hofmann and held a professorship at the Technische Hochschule Karlruhe. However, in the intervening years he was, unlike Haber, admitted by Ostwald as his assistant and *Habilitand*. After Ostwald's retirement in 1906, Le Blanc became Ostwald's successor at Leipzig. Thereby he

<sup>[\*]</sup> W. Ostwald was *Ordinarius* at Leipzig University 1887–1906 and member of the Prussian Academy of Science since 1905.

<sup>[\*\*]</sup> M. Le Blanc was an electrochemist, working mainly on decomposition potentials and other aspects of electrolysis. He was Ordinarius at Leipzig since 1925.







Figure 4. Inauguration of Ostwald's institute in Leipzig, with Ostwald at the lectern and S. Arrhenius, J. van't Hoff, W. Nernst, M. Planck, G. H. Wiedemann, H. Landolt, J. Wislicenus, and others in the audience.

vacated the professorial slot at Karlsruhe, which had been filled by appointing Haber as *Ordinarius*.

Karl Friedrich Bonhoeffer [\*] was a pupil of Walther Nernst, assistant of Fritz Haber and Le Blanc's successor at Leipzig. The Bonhoeffer family—particularly Karl Friedrich's brother Dietrich and sister Christine—put up a heroic resistance to the Hitler regime. [67] After World War II, Karl Friedrich Bonhoeffer was intensely involved in the reconstruction of German Academia, which he served in various capacities—mostly simultaneously. His wide-ranging scientific pursuits included the kinetic studies of chemical and biochemical reactions, in which he pioneered the use of deuteration as a means to unravel reaction mechanisms.

## 4. Physical Chemistry Chairs in Imperial and Weimar Berlin

A gallery of the Berlin professors of physical chemistry is shown in Figure 5.

Hans Landolt<sup>[\*\*]</sup> was the first occupant of the newly created chair for physical chemistry at the Berlin University. A pupil of Robert Bunsen, Landolt dedicated his life to the study of the relationship between chemical composition and the physical properties of substances.<sup>[68]</sup>

His name is connected with the standard reference work, the Landolt–Börnstein tables, whose first edition appeared in 1883. Today, the tables comprise about 400 volumes and are available as a database. [69]

It was at the occasion of Landolt's induction into the Prussian Academy that Emil du Bois-Reymond, its perpetual secretary, used the phrase that "physical chemistry is the chemistry of the future." [24]



Figure 5. The first physical chemistry professors in Berlin. Clockwise from top left: Hans Landolt (1831–1910), Jacobus van't Hoff (1852–1911), Walther Nernst (1864–1941; portrait by Max Liebermann, 1911, Max Volmer (1885–1965), Max Bodenstein (1871–1941), and Fritz Haber (1868–1934).

**Jacobus van't Hoff**<sup>[\*]</sup> came to Berlin in 1896 when his accomplishments were legion.<sup>[70]</sup> Here I will mention just a few more, in addition to his pioneering work in chemical thermodynamics outlined above.

In his 1874 dissertation, van't Hoff laid the foundations of stereochemistry, by introducing the prescient hypothesis that the bonds of carbon atoms are directed towards the vertices of a tetrahedron.<sup>[71]</sup> Pauling would justify it 57 years later by his theory of directed valence.<sup>[72]</sup>

Van't Hoff's work on osmotic pressure established an analogy between gaseous mixtures and solutions and became a basis for the accurate determination of molecular weights. Van't Hoff also cared about the implications of his work for plant as well as animal biology.<sup>[73]</sup>

Van't Hoff played a truly unique role in chemistry: When he was a student, organic structural chemistry dominated much of the field. There were zillions of useful rules to guide the synthesis of new compounds—but no chemical theory. By unleashing thermodynamics on chemical problems, van't Hoff established a lasting theoretical basis for chemistry. Chemical thermodynamics became the theoretical chemistry of van't Hoff's day and a component any theoretical chemistry of the future.

From this perspective, it is perhaps less surprising that van't Hoff was chosen to be the recipient of the very first Nobel Prize in Chemistry. The great organic chemist Emil Fischer received only the second. The two other members of the Ionist triumvirate would be honored likewise, all during

<sup>[\*]</sup> K. F. Bonhoeffer was Ordinarius at Leipzig University 1934–1947; Ordinarius at the Berlin University 1947–1949; director of the Kaiser Wilhelm Institute (KWI) for Physical Chemistry and Electrochemistry, Berlin, 1948–1949; founding director of the Max Planck Institute for Physical Chemistry, Göttingen, 1949–1957.

<sup>[\*\*]</sup> H. Landolt was Ordinarius at Berlin University 1891–1905 and member of the Prussian Academy since 1881.

<sup>[\*]</sup> J. van't Hoff was Honorarprofessor at Berlin University 1896–1911 and member of the Prussian Academy since 1896.





the first decade of the award. Along with the Chemistry Nobel Prizes for William Ramsay and Ernest Rutherford, one-half of the chemistry prizes during the first decade went to physical chemists or physicists. According to my count, over the long term about one-third of the Chemistry Nobels have gone to physical/theoretical chemists or physicists.

Landolt's successor at Berlin University was Ostwald's former assistant Walther Nernst.[\*] After a stint at Göttingen, Nernst arrived, in his automobile, in Berlin in 1905 (Figure 6), to take up the vacated chair. The next year, Wilhelm Ostwald retired from his post in Leipzig, thereby clearing the way for Berlin's dominance of the field of physical chemistry. Moreover, Nernst heralded his arrival in Berlin with a roar-by enunciating his Heat Theorem (or Third Law of Thermodynamics). The experimental and theoretical basis for the Third Law remained at the focus of his research in subsequent years, which also cemented Berlin's position as one of the early centers of the young quantum theory.<sup>[74]</sup>



Figure 6. Walther Nernst reaching Berlin on his automotive voyage from Göttingen in 1905.

The name of **Fritz Haber**[\*\*] may serve as an apt reminder of the Janus face of modern science. On one side the industrial process for the catalytic synthesis of ammonia from its elements, developed by Haber jointly with Carl Bosch and Alwin Mittasch, is the basis for the large-scale production of fertilizers—or "bread from air." Current estimates indicate that about two-sevenths of humankind would not be able to survive in the absence of the Haber-Bosch process. About one-half of the nitrogen atoms in the body of today's European or American went through the Haber-Bosch process.<sup>[75]</sup> On the other side, the Haber-Bosch process is also the basis for the production of explosives and munitions-or "gunpowder from air." Moreover, in the course of

Prior to his arrival in Berlin as the founding director of the KWI for Physical Chemistry and Electrochemistry, Haber spent 17 years at the Technische Hochschule Karlsruhe. There he not only laid the scientific foundations for the Haber-Bosch process, but also became a well-known protagonist of physical chemistry—in particular through his contributions to the thermodynamics of gas-phase reactions.

The Kaiser Wilhelm Society was another institutional innovation that came out of Prussia during the "long" 19th century (which ended with the outbreak of World War I). Its stated purpose was to accelerate the production of knowledge beyond what was achievable at research universities. Unlike the research university or the national metrology institute (see below), the Kaiser Wilhelm Society was not widely emulated. The institutions directly inspired by it were the RIKEN in Tokyo and the Weizmann Institute in Rehovot.

During the Weimar era, Haber's institute would become a world-renowned center of research at the intersection of chemistry and physics (see below). An influential spokesman-along with Einstein-for German academia abroad, Haber would also co-found the forerunner of the Deutsche Forschungsgemeinschaft. [60]

In contrast to many of his colleagues, Haber embraced the Weimar Republic and was one of its open supporters. Still, neither his great scientific merits nor his unbridled patriotism sufficed to stave off his loss of status once the Nazis rose to power. Ill and heart-broken, Haber died in Basel less than a year after being driven out of Germany.<sup>[77]</sup>

Max Bodenstein[\*\*] was another of Ostwald's former illustrious assistants. Prior to receiving a call from Berlin University to become Nernst's successor, Bodenstein established himself by saving Einstein's law of photochemical equivalence. This law seemed at odds with experiment and Bodenstein saved it by introducing the concept of a (photoinduced) chain reaction.[78]

Bodenstein, like Ostwald and Nernst, had a large international following that included the influential Harvard physical chemist George Kistiakowsky. Here's Kistiakowsky's characterization of Bodenstein, as told by Dudley Herschbach:<sup>[79]</sup> "[Upon his emigration from Russia, Kistiakowsky] went directly to Bodenstein in Berlin and said 'I want to work with you'. Bodenstein was a Geheimrat-type professor, typically visited his lab wearing white spats and carrying a cane. On his first visit to see Kisty, his new student, Bodenstein admired the nice glass vacuum apparatus Kisty had set up; that was

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World War I, Haber became the "father of chemical warfare" by redirecting his KWI toward the development of chemical weapons—or "poison instead of air." We note that in Haber's view, chemical weapons were supposed to break the stalemate of trench warfare by forcing the adversary to surrender—and thereby preclude the slaughter of millions by artillery and machine gun fire.[\*][76]

<sup>[\*]</sup> W. Nernst was Ordinarius at Berlin University 1905-1934, member of the Prussian Academy since 1905, and president of the PTR 1923-1924

<sup>[\*\*]</sup> F. Haber was director of the KWI 1911-1933, Honorarprofessor 1912-1920 and Ordinarius 1920-1933 at Berlin University, and member of the Prussian Academy since 1914.

 $<sup>\</sup>c|\ensuremath{^{\star}}\c|$  Chemical weapons, eventually adopted by all principle World War I belligerents, did not work this way. As pointed out in Ref. [76], they became weapons of (mutual) harrassment, adding to the unspeakable suffering of the troops on both the western and eastern fronts.

<sup>[\*\*]</sup> M. Bodenstein was Ordinarius at Berlin University 1923-1936 and member of the Prussian Academy since 1925.





essential for all gas-kinetics experiments in those days. He asked Kisty if he had made it, and Kisty admitted he'd the glassblower do it. Bodenstein promptly smashed it to bits with his cane, saying 'No student of mine will have the glassblower build his apparatus,' and walked out. That led Kisty to become a legendary glassblower."

Max Volmer<sup>[\*]</sup> was known in his early years for his studies of photochemical reactions under high vacuum. During World War I he was enlisted in Nernst's operation at the Berlin University. Immediately after armistice—while still in Nernst's laboratory—he was joined by Otto Stern to work on the kinetics of intermolecular deactivation processes, such as the quenching of fluorescence. It is governed by what is now known as the Stern–Volmer relationship. In 1922, Volmer became Professor of physical chemistry at the Technische Hochschule Charlottenburg (today Technische Universität Berlin), where he worked on the kinetics of phase transitions until the end of World War II.

In 1943, he was elected member of the Prussian Academy, but his induction was thwarted by the notorious Nazi minister of education, Bernhard Rust, with the words: "[Volmer's] political attitudes are not clear-cut enough in order for him to be able to represent the National Socialist state." Also, charges for aiding Jewish scientists were leveled against him. [80]

After World War II, he was drafted, along with about half a dozen other prominent German scientists, to help the Soviets to develop nuclear weapons. Upon his return from the Soviet Union he was resettled in the GDR and lived in Potsdam-Babelsberg. Among the offices he held in the GDR was the presidency of the Academy of Sciences. Volmer was an amateur entomologist; his collection of butterflies can be found in Potsdam's Naturkundemuseum.<sup>[81]</sup>

# 5. Hermann von Helmholtz, Max Planck, and the Discovery of the Black-Body Radiation Law

Hermann von Helmholtz<sup>[\*\*]</sup> was a polymath of a breadth that was unmatched in his time. He greatly contributed to many diverse areas of science—physics, chemistry, medicine, astronomy, and more. Helmholtz was called the *Reichskanzler der Physik*—and the portrait by Ludwig Knaus (Figure 7) does some justice to this title. Of particular relevance to physical chemistry was his work in thermodynamics, which included a definitive formulation of the energy-conservation law.<sup>[82]</sup>

The momentous discovery that energy can only be subdivided into finite quanta is connected with Helmholtz, albeit indirectly, through his leadership role as the founding president of the PTR. The PTR was another institutional



Figure 7. Hermann von Helmholtz (1821–1894) in a portrait by Ludwig Knaus, from 1881, commissioned by the Berlin National Gallery.

innovation, along with the research university and the Kaiser Wilhelm Society, that came out of Prussia during the "long" 19th century. This national metrology institute, funded by the Berlin industrialist Werner von Siemens, undertook to develop luminosity standards for the sprawling lighting industry, in which Siemens had a vested interest. With Helmholtz's blessing, investigation of the black-body radiation problem came into the focus of the PTR during the 1890s. [83]

Gustav Kirchhoff, who formulated the black-body radiation problem already in about 1860 while still in Heidelberg, became a Berliner in 1875, when he finally accepted a repeated call from the Berlin University. As a result, Max Planck could attend lectures by both Helmholtz and Kirchhoff as a student in Berlin and become Kirchhoff's successor as professor of theoretical physics at the Berlin University.

The circle of physicists working on the black-body radiation problem at the PTR, most of them Helmholtz's former students, included Otto Lummer, Heinrich Rubens, Ernst Pringsheim, Ferdinand Kurlbaum, and Willy Wien. Friedrich Paschen was working on the black-body radiation problem out of his laboratory in Hannover. These scientists, along with Max Planck, were from the same generation.

Figure 8 shows the historic Radiation Laboratory at the PTR. The black body consisted of a porcelain pipe inside another porcelain pipe, with heating wires and thermocouples

<sup>[\*]</sup> M. Volmer was Ordinarius at the Technische Hochschule Charlottenburg 1922–1945, elected to the Prussian Academy in 1943 but not inducted, and president of the Academy of Sciences of the German Democratic Republic 1955–1958.

<sup>[\*\*]</sup> H. von Helmholtz was Ordinarius at Berlin University 1871–1894, member of the Prussian Academy since 1870, and founding president of the PTR 1887–1894.





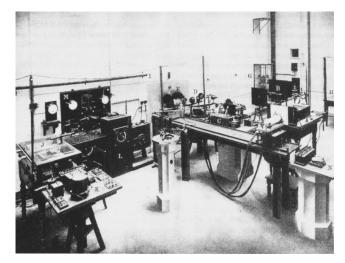
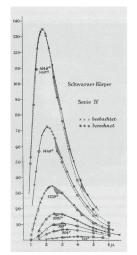


Figure 8. Radiation Laboratory at the PTR. The black body is on the optical bench supported by pillars left over from the building's construction.

attached to it. The contraption was manufactured by the Royal Porcelain Factory, founded in Berlin under the patronage of Frederick the Great. The thermally insulated black body could be shifted around on an optical bench to various measurement positions.

Here's a summary of what the quest was all about: Once quantitative results became available on the spectral distribution of the black body, Willy Wien noticed that the maxima of the distribution curves move towards the blue proportionately with temperature and that the maximum spectral energy densities increase with the fifth power of temperature. This is known as Wien's displacement law. He and Friedrich Paschen then found a fit to the known spectral distributions at short wavelengths, which was consistent with Wien's displacement law. The Wien-Paschen curve received strong backing from Planck who declared in 1899 that it was a consequence of the second law of thermodynamics.<sup>[83]</sup> That could have been the end of the story, but it wasn't, thanks to the accurate measurements by the team at the PTR in the previously unexplored long-wavelength range (that was marred by air absorption). These measurements revealed that the Wien-Paschen fit becomes irreconcilably inadequate there and that the classical Rayleigh-Jeans theory becomes in fact asymptotically correct at long wavelengths (see Figure 9).

Enter Max Planck again, this time as the "reluctant revolutionary", [84] to commit his "act of desperation", as he called it. Planck set out to find the black-body formula "at any price, no matter how high that might be."[83] In order to do so, Planck had to "fit physics" to the reality of the black-body radiation: Firstly, he had to give up the premise that "natura non facit saltum" and introduce a "nonclassical" constant of nature in the process (i.e., Planck's constant). Secondly, he had to make use of a statistical argument,[\*] moreover one pertaining to the nonclassical statistics of indistinguishable bosons.



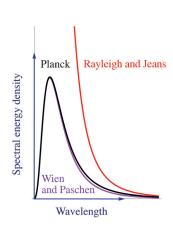


Figure 9. Left: Spectral energy density distribution of the black body published by Otto Lummer and Ernst Pringsheim in 1899 with the Wien-Paschen distributions shown by dashed curves. Right: Theoretical curves of Rayleigh and Jeans (red), Wien and Paschen (violet), and Planck (black) as well as the definition of the coordinate axes.

Wien's displacement law, along with the accurate experimental results provided by the PTR, served Planck as a reality check throughout his quest. Wien would receive a Nobel Prize for this contribution to the discovery of the black-body radiation law in 1911, nine years before Planck would be honored in the same way.

Friedrich Hund described Planck's quantum hypothesis as a premature birth, as most manifestations of Planck's constant were unknown or poorly understood at the time. [85]

## 6. The Principal Contributors to Quantum Mechanics in Berlin and Leipzig

Quantum mechanics emerged as a result of a more or less uncoordinated international collective effort, until then quite unprecedented in the history of science in its scope and achievement. Figure 10 displays a gallery of the founders of quantum mechanics who worked out of Berlin.

The first photo captures Max Planck, in the fateful year of 1900, when he was 42 years old. Planck succeeded Gustav Kirchhoff at the Berlin University 13 years earlier and had already been a member of the Prussian Academy for six years. Remarkably, Helmholtz, in his nomination of Planck to the Academy, emphasized Planck's contributions to "thermochemistry."[83]

Albert Einstein came to Berlin in 1914 to assume a professorship at the Prussian Academy and the directorship of the KWI for Physics. Upon his arrival, he likened himself to a "rare postage stamp" [86] collected by his Berlin sponsors— Planck, Nernst, Rubens, and Emil Warburg, then president of the PTR. What I find quite telling is that Planck, in his nomination of Einstein for membership in the Prussian Academy, apologized for Einstein's paper on the light quanta, although he had accepted it for publication in Annalen der Physik as the journal co-editor about a decade earlier. Planck

<sup>[\*]</sup> Statistical mechanics was anathema to Planck at the time.







Figure 10. The founders of quantum mechanics affiliated with Berlin institutions. Clockwise from top left: Max Planck (1858–1947), Albert Einstein (1879–1955), Peter Debye (1884–1966), Max von Laue (1879–1960), John von Neumann (1903–1957), Eugene Wigner (1902-1995), James Franck (1882–1964), and Erwin Schrödinger (1887–1961).

and his co-sponsors said in the letter: "The hypothesis of the light quanta should not be held against [Einstein] too much; after all, it is hard even in the natural sciences to introduce a true innovation without taking a risk." [87] Apparently, blaming quantization on the black body was still somehow digestible, but ascribing quantum nature to what was known to be electromagnetic waves was too much for too many, including Planck.

The KWI for Physics never materialized during Einstein's tenure in Berlin, but came about belatedly in 1935—at first as a construction site—with **Peter Debye** as director. The institute was sponsored by the Rockefeller Foundation and under Debye's liberal leadership started work in atomic and low-temperature physics. Debye managed to escape from Germany after the outbreak of World War II with the help of his colleagues—and his Dutch passport. [88] However, his stint in Berlin under the Nazis would become the subject of fierce—albeit ill-justified—criticism more than half a century later. [89]

Max von Laue was a fixed star on Berlin's firmament since assuming tenure at Berlin's university in 1919, side by side with his mentor Planck. [\*] In 1943 he was forcefully retired for his overt opposition to Nazism by a decree signed by Hitler. [\*\*] The immediate pretext was a lecture series on Einstein's general relativity theory he had held in Sweden. After World War II, von Laue's scientific reputation and irreproachable past would make him one of the key figures in the reconstruction of German academia and the restoration of its international relations. He would serve as director of Haber's KWI and be the force, along with Bonhoeffer, behind the renaming of the institute for its founding director. [90,91]

**Erwin Schrödinger** became Planck's successor at the Berlin University in 1927. He would leave this post and Germany six years later, in disgust over Nazi policies, especially their anti-Semitism. [91]

It was in the laboratory of Heinrich Rubens at the Berlin University that **James Franck** and Gustav Hertz devised their much admired experiment, in 1914, which provided strong support for Bohr's model of the atom. [92,93] In the years immediately following World War I, James Franck led the Physics Department at Haber's KWI. [60] Together with Gustav Hertz, Erich Einsporn, Walter Grotrian, and Paul Knipping, he concentrated primarily on the careful measurement of absorption spectra and ionization energies and the correlation of these measurements with the Bohr–Sommerfeld model of the atom. Their results also triggered later investigations at the institute, such as the pivotal 1922 work by Haber and Walter Zisch on chemiluminescence and research by Hans Beutler and others on the quantum mechanics of atomic collisions. [60]

There are two more founders of quantum mechanics featured in Figure 10: They are the "Hungarian Martians," [94] **Eugene Wigner** and **John von Neumann**, who both spent extended periods of time in Berlin. Friends since high school, they both—on the wish of their parents—studied chemical engineering, Wigner at the Technische Hochschule Charlottenburg and von Neumann at the ETH Zurich. Later on, as *Privatdozenten* in Berlin, they pursued related scientific agendas. Their Berlin years ended in 1932, when they were both hired by Princeton. Wigner later recollected that Princeton was really interested in von Neumann, but the administration thought that it would be wiser to transplant both of them—as they would be happier in each other's company, like a pair of rabbits. [95]

The encounter between group theory and quantum mechanics that Wigner arranged—with some help from von Neumann—during his time in Berlin had a profound and long-lasting impact. Group theory endowed quantum mechanics with a new type of argument, in which selection rules, rather than conservation laws, were regarded as the observable signature of an underlying physical symmetry. [41] In 1927, Wigner articulated what is today referred to as the quantum version of Noether's theorem. When asked in the early 1930s by Max von Laue what group-theoretical result derived so far was the most important one, Wigner replied: the explanation of the Laporte rule (the concept of parity) and the quantum theory of vector addition (angular momentum). [60]

A gallery of the founders of quantum mechanics who worked out of Leipzig is shown in Figure 11.

**Gregor Wentzel**, a Sommerfeld pupil, came to Leipzig as *Extraordinarius* for mathematical physics in 1926. It was here that he developed, independently of Leon Brillouin and Hendrik Kramers, the semiclassical method. In 1928 he left for Zurich, where he succeeded Schrödinger.

**Werner Heisenberg** received a call from the University of Leipzig to became *Ordinarius* for theoretical physics in 1927. He was just 26 years old. Together with Peter Debye and Friedrich Hund, he would make Leipzig into one of the world's centers of physics, in particular of nuclear physics. He

<sup>[\*]</sup> Max von Laue ran the Berlin biweekly Physics Colloquia, now named after him.

<sup>[\*\*]</sup> Christian Matthaei, von Laue's grandson, showed me the decree in 2005





Figure 11. The founders of quantum mechanics affiliated with the University of Leipzig. From left to right: Gregor Wentzel (1898–1978), Werner Heisenberg (1901–1976), and Friedrich Hund (1896–1997).

would stay at Leipzig until 1942, when he moved to Berlin to take over the directorship of the KWI for Physics after Debye's escape from Germany.

**Friedrich Hund** became Wentzel's successor as professor of mathematical physics at Leipzig in 1929 and would stay there until 1946. During the Nazi era he would defend physics and Heisenberg against attacks orchestrated by the proponents of the so-called "Deutsche Physik." [96]

#### 7. Principal Contributors to the Post-Quantum-Revolution Theoretical Chemistry from Berlin and Leipzig

Figure 12 displays a gallery of the key contributors to the post-quantum-revolution theoretical chemistry from Berlin and Leipzig. Eugene Wigner and Friedrich Hund would belong in this gallery as well.



Figure 12. Key contributors to the post-quantum-revolution theoretical and physical chemistry affiliated with institutions in Berlin and Leipzig (other than those shown in Figures 4, 5, 10, and 11). From left to right: Otto Sackur (1880–1914), Michael Polanyi (1891–1976), Fritz London (1900–1954), Henry Eyring (1901–1981), and Rudolf Ladenburg (1882–1952).

Wigner's mentor in Berlin was **Michael Polanyi**, another "Hungarian Martian". Acclaimed as a physical chemist, neo-Keynesian economist, philosopher of science, sociologist of science, and public intellectual, [97] Michael Polanyi left behind a legacy that still inspires numerous scholarly articles and monographs. [98] Dudley Herschbach told me that "no one else impressed [him] as living 'the life of the mind' so intensely" as Michael Polanyi did. [99] At Haber's KWI since 1920, Polanyi put his mind to the study of the structure of cellulose, crystals, physisorption, heterogeneous catalysis, and chemical kinet-

ics—his foremost preoccupation. With his mutually "trusting but critical" team of young theorists, Polanyi laid the conceptual foundations for kinetic theory consistent with the new quantum mechanics. The team included Eugene Wigner, **Fritz London**, who was Schrödinger's assistant at Berlin University, and **Henry Eyring**, who came from the U.S. on a National Research Council Fellowship as a guest.

It was in their landmark 1931 article<sup>[50]</sup> on the quantum mechanics of the making and breaking of chemical bonds that Polanyi and Eyring introduced the visual metaphor for understanding the process: "the chemical initial and final states are two minima of energy which are separated by a chain of energy mountains." As a model reaction, Polanyi and Eyring considered the hydrogen-atom exchange in the reaction H+H<sub>2</sub>, presumed to play a part in the ortho-to-parahydrogen conversion. This conversion was investigated at Haber's KWI by Karl Friedrich Bonhoeffer and his illustrious collaborators, among them the Farkas brothers. Soon thereafter, Polanyi and Eyring introduced the semiempirical method that made use of spectroscopic data to refine estimates of electronic energies. Wigner, along with Hans Pelzer, then combined the semiempirical potential-energy surfaces with considerations from statistical mechanics into an analysis of reaction rates. This analysis would form the starting point for the "transition-state" or "activated-complex" theory. [60]

Polanyi's Berlin years, of which Wigner said, [97] "I doubt [Polanyi] was ever again as happy as he had been in Berlin," came to an end with the rise of the Nazis to power and Polanyi's forced emigration from Germany in 1933. In his later work in the sociology of science (whose founder he's considered to be), he made use of his Berlin experiences as the foundation for his thoughts on the freedom of research and the self-organization of an ideal scientific community.

**Rudolf Ladenburg** took over James Franck's Physics Department in the early 1920s upon Franck's departure for Göttingen. Ladenburg and his collaborators undertook pioneering work on dispersion which played a central role in the development of quantum theory in general, and in the formulation of matrix mechanics by Werner Heisenberg in particular. In a series of articles from about 1930, Ladenburg presented the first evidence for stimulated emission. [60]

The literature on chemical physics and spectroscopy teems with references to **Friedrich Hund**'s contributions, such as Hund's rules and Hund's cases. His contribution to the molecular orbital theory received much recognition from Hund's more internationally appreciated *doppelgänger*—Robert Mulliken. Mulliken, after becoming the sole recipient of a Nobel Prize (in 1966) for the molecular orbital theory, started referring to it as the "Hund–Mullikan theory." [100]

The left-most photo in Figure 12 shows Otto Stern's PhD adviser, **Otto Sackur**. Sackur was a pioneer of quantum statistical mechanics known for deriving an expression for the entropy of a gas, the Sackur–Tetrode equation. At the end of 1913, Sackur received a call to Haber's KWI, where, after the outbreak of World War I, he was enlisted in military research. In December of 1914, he was killed in a laboratory accident at his work bench—while trying to tame cacodyl chloride for use as an irritant and propellant.<sup>[101]</sup>





#### 8. The Empyrean—the Highest Heaven—of Science

In order to mark the departure of James Franck for Göttingen in 1920, a memorable gathering took place in Berlin, a glimpse of which is offered by the photograph shown in Figure 13. Perched on the armrests, Mr. Physics and Mr.



Figure 13. Farewell party in 1920 for James Franck before his departure from Berlin-Dahlem for Göttingen. Left to right, seated: Hertha Sponer, Albert Einstein, Ingrid Franck, James Franck, Lise Meitner, Fritz Haber, and Otto Hahn; standing: Walter Grotrian, Wilhelm Westphal, Otto von Baeyer, Peter Pringsheim, and Gustav Hertz.

Chemistry—Einstein and Haber. James Franck, flanked by his wife and Lise Meitner, jokes with his assistant, Hertha Sponer, while Otto Hahn makes himself ready to jump in the conversation. Standing in the back are Gustav Hertz, Peter Pringsheim, Otto von Baeyer, Wilhelm Westphal, and Franck's assistant Walter Grotrian. Such a photo embodies what the distinguished biochemist and essayist Erwin Chargaff must have meant when he characterized Berlin during the Weimar era as the "very empyrean [highest heaven] of science." [102]

Walter Grotrian, a well-known spectroscopist at the time the photo was taken, would make the study of the heavens and the nearest star the subject of his work. [103] Grotrian became a solar scientist at the Potsdam Astrophysical Observatory in 1922 and a professor at the Berlin University in 1927. The call from the Observatory came at a time when its *Einsteinturm*, designed by the star expressionist architect, Erich Mendelsohn, was becoming operational. The Einsteinturm housed a solar telescope with one of the largest spectrographs of its time. Its main intended purpose was to test general relativity by measuring shifts of spectral lines due to the gravitational field of the sun. The observatory was inaugurated in 1924 in Einstein's ex officio presence—as chairman of the Observatory's advisory board.

Walter Grotrian had a hobby, namely writing theater plays. One of them was a "physikalischer Einakter" (Figure 14), produced for a "Physics Fest" occasioned by Max Planck's 80th birthday, in 1938. [104] As we can—or cannot—imagine, it must have been quite difficult to come up with something that was both humorous and politically correct in 1938 Germany. The problem was exacerbated by a lack of willingness on the part of the Nazi authorities to suffer the

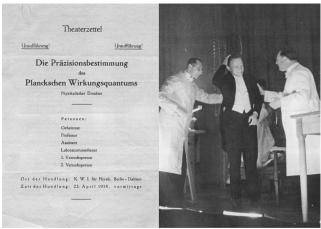


Figure 14. Program for and a stage photo from a play by Walter Grotrian at the "Physics Fest" in Harnack House to celebrate the 80th birthday of Max Planck. The photo shows, from left to right, Herbert Stuart, Werner Heisenberg, and Peter Debye as actors in the one-act play.

birthday party at all. So the play displayed a mixture of childish and scientific humor (which some people would argue is the same thing), while dealing with the issue of determining the value of Planck's constant. This was done by reading (undisclosed) jokes to test subjects on stage, whose "ha, ha, ha" served in the determination of "ha," i.e., h. The value found was then delivered by telegram to Max Planck, seated near the stage. The play featured a star-studded cast comprising Arnold Sommerfeld, Peter Debye, Werner Heisenberg, Walter Gerlach, Herbert Stuart, and Ernst Ruska, the last representing a folksy Berlin character speaking Berlinerish—and making the best jokes.

Well, Max von Laue had a famously raucous laughter and perhaps it was his laughter that inspired the play's plot. Anyway, at that time Berlin was hardly the highest heaven of science anymore and would become, within a few years, an outright hell. Thank heavens that the von Laues, Bonhoeffers, Grotrians, and their likes made it through—and could be called upon to begin restoring the empyrean of science to its pre-Nazi and pre-war splendor.

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