Chapter 4
Dissolving the Boundaries between Research and Pedagogy: Otto Sackur's *Lehrbuch der Thermochemie und Thermodynamik*
Massimiliano Badino

4.1 Introduction

Today, the name Otto Sackur hardly appears in historical accounts of quantum physics. Sackur was born in Breslau, in the border region of Silesia in Germany (now Wrocław, Poland) on 28 September 1880.[1] At that time, the University of Breslau was an important center for research in experimental physics, especially spectroscopy and optics. The Chemistry Department, founded by Albert Ladenburg in 1897, was one of the best equipped in the German Reich. Sackur studied physical chemistry in Heidelberg (one semester), in Berlin, and in Breslau under Richard Abegg, who was also his doctoral supervisor. After the doctorate, which he received at a precociously young age on 31 July 1901, he became Abegg's assistant.

However, as was customary in Germany, he left his *alma mater* to enrich his scientific experience. For two years, from October 1902 to October 1904, he worked on the properties of alloys at the *Kaiserliches Gesundheitsamt* in Berlin. The research of this institute, headed by Theodor Paul, focused especially on possible health risks related to the lids of typical German beer mugs, which were made of alloys of lead, zinc, tin, and copper. Then, Sackur moved to London, with a letter of recommendation from Abegg, and worked at William Ramsey's laboratory at University College. In London (October 1904–March 1905), he met Otto Hahn, with whom he worked on radioactivity, particularly on the decay of radium. Sackur's *Wanderjahre* ended with another six-month research stint in Walther Nernst's laboratory in Berlin. After his return to Breslau, on 19 October 1905, he obtained his habilitation and became a *Privatdozent*.

Sackur seemed to be headed for a quiet academic career in Breslau, but these plans were suddenly disrupted by two unexpected events. In 1909, personal problems forced Albert Ladenburg to retire from his position as director of the department, and his successor, Eduard Buchner, was anything but a supporter of physical chemistry. Moreover, in 1910, Sackur's mentor Abegg died in a ballooning accident. All of a sudden, Sackur found himself without an academic guide and in a hostile research environment. His career prospectives appeared to be at a dead end, and during 1909–1913, he had to take on minor teaching assignments to survive. This grim situation changed at the end of 1913, when Fritz Haber invited Sackur to spend a research period at the newly founded *Kaiser-Wilhelm-Institut für Chemie und Elektrochemie*. It seems that Clara Immerwahr, Haber's first wife and herself a student of

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[1] Biographical information on Sackur can be found in the entry written by Alexander Kipnis in the *Neue Deutsche Biographie* (Kipnis 2005) and in the obituaries written by personal friends and former colleagues of Sackur's at Breslau after his untimely demise in 1914 (Auerbach 1915; Hertz 1915; Pick 1915).

Abegg in Breslau, played a role in this important call.[2] The following year, Sackur became director of a department, and after the outbreak of the war, he was recruited to study the most effective way to fill the bullets of howitzers. Unfortunately, his career ended abruptly on 17 December 1914, when he was mortally wounded by an unexpected explosion in his own laboratory and died a few hours later.

His contemporaries credited Sackur with a rare gift for explaining the complexity of modern physical chemistry in simple terms. His teaching activities in Breslau included very unconventional courses, like a "Reading group on classics of physical chemistry" (Winter Semester 1906/07), a massive presence of thermodynamics and thermochemistry (Summer Semester 1907, SS 1909, WS 1910/11, WS 1911/12), kinetic theory (SS 1910, SS 1912), and some advanced classes on the "mathematical treatment of chemistry" (WS 1906/07, SS 1908). After Abegg's death, Sackur was forced to take on introductory courses on chemistry (SS 1911, WS 1912/13), a special course on chemistry for dentists (SS 1912, WS 1913/14), and he had to take care of the weekly colloquium on physical chemistry, created by Ladenburg and Abegg some years earlier.

Most probably, it was during this tough period after Abegg's death that Sackur's pedagogical skills were refined and reached the high level later acknowledged by his colleagues. His introductory courses were particularly appreciated, and Sackur developed them into a book (Sackur 1911a) that convinced the publisher Springer to assign a more ambitious project to the young *Privatdozent*, namely a textbook on thermodynamics and thermochemistry, which I will discuss in this paper. One moving recollection concerning Sackur's ability to write textbooks came from Fritz Haber, many years after Sackur's death, on the publication of the second edition of the *Lehrbuch*, edited by Clara von Simson, in 1928. In the foreword to the book, Haber pointed out that, although some of the content was outdated, the clarity of the work was still remarkable. He also added a personal evaluation on Sackur:

> He had in the highest measure those features that are necessary to the composition of a good textbook: a clear understanding of the fundamental concepts, a mastery of the subject matter, practicality and precision in judgement and, finally, lightness and simplicity in his presentation. (Haber 1928)

Apparently, Sackur was not only a born teacher, but also an innovative one. A summary of his courses at the university of Breslau (see the table at the end of the paper) reveals a wide range of interests and a careful balance between experimental and theoretical issues. His ability to master both laboratory techniques and subtleties of differential calculus was underscored by his contemporaries.

There are two lessons that the case of Sackur's textbook can teach us and that I spell out in this paper. First, Sackur's book shows us that, when studied from a historical perspective, a textbook is not only a record of established theories, but it may also reflect internal tensions of the general dynamics of knowledge. A textbook actively selects and organizes its material, a process that is never completely neutral. Research considerations might enter this process and lead to a fundamental reshaping of the pedagogical tradition. This does not happen in every case necessarily: in this paper we will encounter textbooks that separate the pedagogical tradition from up-to-date research. However, it does happen in Sackur's book, particularly in his treatment of specific heat.

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[2] Administrative letters concerning Sackur's hiring at the Institute are now collected in Haber's correspondence stored at the Archive of the Max Planck Society, Berlin (AMPG).

Second, a textbook can become a functional vehicle for research, a way to disseminate new methods, concepts, and procedures. More importantly, it can contribute to the formation of a new generation of students able not only to master established techniques, but also to recognize new priorities and new avenues of research. Sackur's discussion of chemical equilibrium and his insistence on the importance of the concept of entropy achieve precisely this goal.

4.2 The Structure of the Book

Sackur's *Lehrbuch der Thermodynamik und Thermochemie* was published by the Berlin publisher Julius Springer in 1912. Apparently, the book was well received. Extant reviews point out its innovative character and its didactical clarity. Above all reviewers remarked, that the book constitutes a useful tool for the chemist eager to find his or her way through the jungle of new developments in physical chemistry (Coehn 1913; Krüger 1914). Although it is difficult to establish with certainty, it seems that the book essentially derived from Sackur's lectures at the university in Breslau. He had been lecturing consistently on thermodynamics and thermochemistry since the summer semester 1907 and especially focused on these topics in the winter semesters 1910/11 and 1911/12, immediately before the publication of the book. Furthermore, in the preface to the first edition, he underscored the clear pedagogical aim of the book: "in the selection and the organization of the material I have been guided especially by the didactical point of view and I have deliberately relinquished completeness" (Sackur 1912a, iii). The book was thus conceived for use in the classroom.

As for content, the book consists of 13 chapters and covers the most important topics of physical chemistry, including electrochemistry and capillarity. There is a section devoted to the theory of radiation and a very long and instructive chapter on Nernst's theorem.[3] The whole edifice of physical chemistry is presented as resting on two main pillars: the first and the second principles of thermodynamics. These two principles are deployed to elaborate the fundamental equations of chemical statics and chemical equilibrium, hence Sackur discusses at length their consequences. The great importance Sackur gives the principles of thermodynamics reveals the influence of Max Planck, who had been emphasizing the foundational role of thermodynamics for physical chemistry since the end of the nineteenth century (Hiebert 1983; Kormos Barkan 1999; cf. also Hoffmann's article in this volume). However, Planck only inspired parts of Sackur's book. For instance, Sackur did not follow Planck in the thorough use of the formalism of thermodynamic potentials. More importantly, contrary to Planck, Sackur leaned more strongly on the experimental side of physical chemistry, and in his book, Sackur reported recent data as well as descriptions of the most advanced experimental techniques. This attention to the empirical basis of the discipline hints at another important source of inspiration, namely Nernst's *Theoretische Chemie* (1909).

More generally, Sackur presented physical chemistry as a discipline in flux. He repeatedly stressed the limitations of classical doctrines as well as the shaky foundations of more recent approaches. Giving shape to feelings that Nernst, Planck, and Einstein voiced at the First Solvay Conference, only one year earlier (Mehra 1975; Marage and Walleborn 1999), he portrayed the theory of matter as a field experiencing deep change, where new,

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[3] The book was translated into English by G. E. Gibson and published in 1917 by MacMillan (Sackur 1917). Curiously, the translation has an additional chapter.

interesting, and possibly revolutionary, things were about to happen. Ultimately, Sackur's book is permeated with a sense of transition.

4.3 The Reorganization of Knowledge: The Case of Specific Heats

These observations lead me to the first point of this paper: the impact of new research agendas on the organization of knowledge in a textbook. This creative process turns the textbook into a historiographical tool that allows us to understand a great deal about how ideas about relevant problems, acceptable solutions and, ultimately, the relative importance of different parts of a field of knowledge can change during a period of crisis. I illustrate this general point by considering the way Sackur coped with the issue of specific heats in his book.

The understanding of specific heat underwent a major theoretical change at the turn of the century. The nineteenth century experienced spectacular developments in kinetic models of matter. According to these models, the thermal properties of physical bodies can be traced to the mechanical behavior of the microscopical constituents of matter. In particular, conclusions regarding the specific heats of various substances could be drawn from the so-called equipartition theorem, which states that each degree of freedom, or more precisely, each quadratic term of the total energy, gets the same share of the total energy. Temperature variation is related to changes in the energy of the body, therefore to the "intensity" with which it carries out its motion, but it does not affect the kinds of motion it can perform. Thus, the amount of energy necessary to increase the temperature of the body, say, from 100° to 101° C, must be the same as that required to increase it from 0° to 1° C. In other words, the specific heat of each body must be independent of temperature, a conclusion that fit well with the Dulong-Petit phenomenological law of thermodynamics.

Kinetic models had been constructed especially for gases. The gaseous state was historically the first to be pictured as a collection of tiny particles in random motion, and this led to epoch-making progress in the understanding of the laws of thermodynamics. Extension of the kinetic approach to the solid and liquid states was not as successful, though. Bernhard Weinstein and Gustav Mie made some attempts in this direction around 1900, but it became clear pretty quickly that the solid state involved enormous formal complications and hence gave very little payoff (Weinstein 1901--1903; Mie 1903). In particular, the equipartition theorem was hopelessly at variance with the experimental outcomes of Heinrich F. Weber (1875), who had found a temperature dependence in the specific heats of many solid substances. In kinetic theory, there was no clear idea of how to explain the temperature dependence of the specific heat of a solid.

Many textbooks on thermodynamics and physical chemistry acknowledged this impasse in contemporary research by organizing the topic of specific heat according to a precise didactic scheme. This "kinetic scheme" guided the students' training first through a familiarization with the treatment of a gas as a set of particles in random motion. The application of mechanical arguments was carried out for monoatomic gases, and then more complex models for polyatomic gases were described. Then, strong cohesion forces were introduced to discuss the liquid state. Finally, the student was presented with a model of particles arranged in a lattice, vibrating around equilibrium positions, customarily used to represent a solid. In this schema, an idealized gas was presented as the paradigmatic case, the solved example, while liquids, and above all solids were handled as puzzles. Mastering the treatment of the gas was necessary first, before extending the approach to still-mysterious cases.

This scheme was generally adopted in classic books on thermodynamics used by physical chemists, such as Ludwig Boltzmann's *Vorlesungen über die Gastheorie* (1898) or Planck's *Vorlesungen über Thermodynamik* (1913), as well as in textbooks of physical chemistry that relied mostly on phenomenological thermodynamics, such as George Senter's (1912).

Though, at the beginning of the century, the emerging quantum theory offered an alternative to the kinetic scheme. Planck's theory of radiation, based on the hypothesis that energy depends on the frequency of an oscillation via a universal constant, was in stupendous accord with the experimental data, and its underlying model (electromagnetic resonators in an empty cavity) was intriguingly close to matter. Indeed, the picture of particles vibrating about fixed points of a solid lattice was a natural extension of Planck's original idea of resonators. In 1907, when Einstein applied the quantum hypothesis to a solid lattice, the resulting theory enjoyed marked success, especially because it explained the temperature dependence of specific heats. However, the quantum hypothesis had been conceived and applied primarily to periodic phenomena. It was apparently very difficult to reconcile this hypothesis with the picture of gas molecules in random motion. Thus, in the first decade after 1900, quantum theory turned the research agenda on the structure of matter upside down: while in classical kinetic theory the task had been the extension from an aperiodic to a periodic system, now the priority became the application of a formal procedure devised for periodic behavior to the gas. All of a sudden, the solid had become the paradigmatic case and the gas had become the puzzle.

Sackur's book was the first to change the pedagogical presentation of the topic of specific heat as a result of this radical change in the research agenda. He already introduced the problem of specific heat in the second chapter of his book, just after having defined the concept of temperature. He began with a summary of classical knowledge concerning the thermal behavior of solids, which basically consisted of decades of experimental observations condensed into the law of Dulong-Petit and into Kopp's rule. Both laws, Sackur insisted, have only a very limited range of validity. Next, he abruptly introduced Einstein's quantum theory of specific heats (Sackur 1912a, 26–28). According to Einstein's hypothesis, the atoms in the solid lattice can be interpreted as compounded of three oscillators that perform independent oscillations along each of the coordinate axes. If one assumes that the energy is distributed over the oscillators according to Planck's distribution law, it is easy to find an expression for the specific heat that tends to zero as the temperature decreases. This is a remarkable result, Sackur commented, because it happens to coincide with the predictions of the theorem that Nernst had put forward the previous year (in 1906). Clearly, Einstein's intuition was a step in the right direction, but Sackur was also quick to point out that it was far from being the last word on the subject: "even though Einstein's theory has been qualitatively confirmed by the experience, there can be no doubt that it only gives a rough sketch of the reality" (Sackur 1912a, 28).

Therefore, Sackur discussed techniques and results of the experiments carried out in 1910 and 1911 by Nernst, Arnold Eucken and others: these experiments gradually enlarged the empirical basis of the theory and offered clues about how it could be improved. One attempt in this direction was the Nernst-Lindemann formula, which had two characteristic frequencies that Sackur discussed in the context of these experiments. The Nernst-Lindemann formula was, however, still only a partial result because, as Sackur underscored, "it has not yet found a theoretical interpretation" (Sackur 1912a, 28). Finally, Sackur mentioned the important problem of determining the characteristic frequency, an issue that impacts on the optical and elastic properties of the solid. In particular, he touched on Frederick Lindemann's important argument concerning how to fix the frequency from the temperature of fusion (Lindemann 1910). Overall, Sackur's picture of the theory of the specific heat of a solid is excellently up-to-date and complete: the only missing piece is Peter Debye's theory which would appear at the end of 1912.[4]

The remainder of the chapter deals with specific heats in liquids, solutions, and gases. Here, the treatment becomes very classical and relies solely on thermodynamics and experiments. The kinetic approach to specific heats in gases is mentioned only later, when Sackur introduces the mechanical interpretation of the concept of entropy (Sackur 1912a, 130). In general, specific heat in gases receives much less attention.

4.4 The Quantum in Quarantine

Sackur's account of specific heat was clearly inspired by the results of quantum theory. He did not simply inform the reader that there was a new way to attack the topic: he outright reorganized the material according to the new research agenda. Quantum theory showed that there was a very natural way to handle the specific heat of a solid: Einstein's treatment, albeit incomplete, was the new paradigmatic solution. However, there was no quantum theory of a gas in 1912. The construction of such a theory was the front line of research—research to which Sackur himself was contributing. The apparently well-known gas had transformed into a *terra incognita*. The goal of his reorganization was evidently pedagogical: there was no point in getting the students acquainted with a surpassed scheme. They could contribute more effectively to the advancement of knowledge if they knew from the beginning what the new starting points and the new problems were.

Other textbooks on thermodynamics and physical chemistry had a far less open-minded attitude toward quantum theory. To be sure, almost none of the major textbooks published after 1910 ignored quantum theory altogether. However, at the same time, almost none made an effort to integrate quantum theory into their didactical structure. Instead, the most common strategy consisted of a clear-cut separation between the established, and still reliable, kinetic theory and the new quantum machinery. Usually, the quantum theory was confined to specific chapters, more often than not at the end of the book as a sort of appendix. As a consequence, the kinetic scheme in the organization of the topic of specific heat largely remained dominant: the widespread pedagogical strategy still aimed at consolidating the good old kinetic theory in the minds of students. The quantum theory persisted in a state of *quarantine*, segregated in less prominent places or, as we shall see, in separate volumes.

The fundamental justification for this pedagogical strategy was the "reasonable doubt" argument. After all, the quantum hypothesis was young and imported from radiation theory into the study of matter. By contrast, kinetic theory was more than half a century old, full of glory and not yet completely explored. But the reasonable doubt argument was not merely based on common sense considerations. Research also played a role. A paper published by the authoritative physical chemist Gilbert Lewis in collaboration with Elliot Adams in 1914 made this point clearly (G. N. Lewis and Adams 1914). In that paper, the authors chal-

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[4] The foreword to the book was written in April 1912; Debye's paper appeared in November (Debye 1912). It is true that the Born-von Kármán paper was published in March (Born and von Kármán 1912), but it was probably too late to include the results of that paper in Sackur's book.

lenged head-on the necessity of adopting the quantum theory to explain new experimental phenomena connected with the thermal behavior of bodies:

> Now, if there were no other way of explaining the very important facts to which attention has been called by the quantum theory, it would be proper to make such assumptions and to modify the body of physical theory in so far as might be necessary to render it consistent with them. But we believe that no such necessity exists. (G. N. Lewis and Adams 1914, 331)

They went on to argue that the most impressive results of quantum theory, including the temperature dependence of specific heat, might be obtained by supplementing the classical equipartition theorem with a new hypothesis, called the *constraint hypothesis*. According to this hypothesis, the particles in real bodies must be ascribed a smaller value of the partitioned energy because of their mutual interactions. Apparently, the paper by Lewis and Adams was very influential, both in the United States and in Europe, in conveying the message that quantum theory was not yet established enough to justify a revolution in the pedagogical organization of the knowledge in physical chemistry. Lewis and Adams's suggestion was taken up by the vast majority of textbooks on thermodynamics and physical chemistry.

One telling example is a textbook written by Edward W. Washburn in 1915. In his book, Washburn superficially reviewed the quantum developments and Debye's theory. He even began the chapter on specific heats by stating that

> the systematic investigations of specific heats at low temperatures carried out in recent years largely by Nernst and his associates at the University of Berlin have resulted in an extensive modification of former theories concerning heat capacity. (Washburn 1915, 291–292)

However, Washburn maintained a reasonable doubt about this modification. Although Lewis and Adams's hypothesis was a "qualitative interpretation only," Washburn decided to set aside the quantum theory and to base his "presentation […] upon the older principle of equipartion of energy" supplemented by the constraint assumption. Consequently, he organized the topic of specific heat according to the kinetic scheme: he set out the theory of the monoatomic gas and then introduced further complications related to the rotation and vibration of gas particles. Liquids and solids were left in a foggy state. Ironically, in the foreword, Washburn ridiculed the nineteenth-century skepticism concerning kinetic models and took a realist's stance:

> [I]nstead of considering these [models] in a special chapter as interesting but unnecessary hypothetical explanations of observed facts, they are themselves in their most essential features treated as facts already established beyond the possibility of reasonable doubt, and together with thermodynamics, are made to serve as the framework of the development of the whole subject. (Washburn 1915, viii–ix)

Ultimately, Washburn, as well as other authors, used the same "quarantine strategy" against quantum theory that their predecessors had adopted against kinetic models.

But the most significant instance of the persistent quarantine of the quantum theory was William C. Lewis's *System of Physical Chemistry* (1921). The first edition of Lewis's book was printed in 1916, as one installment in a series of textbooks in physical chemistry edited by William Ramsay. In his review of the book, Frederick George Donnan, incidentally the other editor of the series, praised the work as the treatise that would interrupt the British dependence on German texts in physical chemistry. He even went a step further by stating that: "in its arrangement of matter, lucidity of style, and comprehensive unity of design it is destined to become the standard general treatise on the subject of physical chemistry for English-speaking students" (Donnan 1916). Donnan's opinion was by and large confirmed because, for example, in the second edition of his book (1921) Washburn refers the student to Lewis's textbook as the authoritative source for more advanced discussions.

However, the general structure of the work is not revolutionary. An anonymous reviewer of the second edition commented that "the more classical portions are presented to the student in much the same manner as in several of the older text-books (and, it might be added, lecture courses)" (Anonymous 1919, 162). In effect, Lewis consistently adopted the kinetic scheme in his book because, in his pedagogical organization, kinetic theory and thermodynamics are the foundations of the system:

> The scientific treatment of any set of phenomena consists in applying the minimum of general principles or theories which can afford a reasonable explanation of the behavior of matter under given conditions, and predict its behavior under new conditions. The principles referred to as far as physics and chemistry are concerned are the kinetic theory and thermodynamics. (W. C. Lewis 1921)

It is more interesting to see how the attitude toward quantum theory evolved through the three editions of the work. In the first edition, Lewis confined the quantum theory to the end of the second volume, but in the second edition (1919), he felt that "the role which the quantum theory now plays in physical and chemical research makes it imperative for the advanced student to be familiar to some extent" with it. Therefore, he expanded his treatise to three volumes and devoted the last one completely to the quantum. In the prefatory note to the additional volume, Lewis pointed out that, although the quantum theory was born as a theory of radiation, its importance for physical chemistry was related to its application to specific heat:

> [E]ven the success which has attended Planck's treatment of radiation problems would scarcely have sufficed to gain for his views that prominence which they now have, had it not been for the satisfactory explanation which his theory offers at the same time for the heat content of the substances and the variation of the heat content with temperature. (W. C. Lewis 1921)

After this opening statement, in the third volume, Lewis consistently presented the topic of specific heat according to the quantum scheme. First, he accounted for Debye's theory of solid as the best established case and then reported on the attempts at constructing a quantum theory of gas. This structure remained unchanged in the third edition of the book (1921). So, is Lewis's textbook a turning point in attitudes about the quantum? Not quite. The quarantine is still in force: Lewis clearly separated the kinetic approach from the quantum one and highlighted that quantum theory should be reserved for the advanced student only. Also, the reasonable doubt argument was still the main reason for this separation. In the same prefatory note, Lewis wrote:

> In the present volume […] the underlying ideas—especially those involved in the quantum theory—have not yet been fully accepted, at least in their present form. The position of the quantum theory is to a certain extent undefined. The physical significance of what is meant by a quantum of energy or, in stricter sense, the quantum of action is still vague. (W. C. Lewis 1921)

Note an important difference. Sackur had also cautioned his students against premature enthusiasm and highlighted the limitations of Einstein's theory. However, this did not prevent Sackur from grasping the radical innovation of the new approach, and he therefore endorsed the general reorganizaton of knowledge entailed by the quantum theory. Lewis's caveat, instead, undermines the quantum theory as a whole. Quantum theory is a relevant piece of physics, but it has a somewhat inferior pedagogical status. It is something about which the student must be informed, but not formed. By and large, this was the prevailing strategy among the authors of physical chemistry textbooks. The quantum theory did not affect the organization of the didactic material even for those topics, such as specific heat, in which its success was patent and its superiority over the classical theory blatant. Quantum theory remained quarantined in places to which only the most zealous student would have access.

4.5 Research in the Classroom

In contemporary reviews most commentators were struck by the fundamental role that entropy played in Sackur's book. The second lesson that we can draw from his textbook hinges precisely on this concept. Although a key notion in thermodynamics, entropy encountered many difficulties in being accepted by the community of physical chemists (Kragh and Weininger 1996). The reason is that entropy is a very abstract quantity and is usually difficult to measure experimentally. Therefore, physical chemists were more inclined to use notions, such as affinity (what we now call free energy) or maximum work, to express the laws of equilibrium (Hiebert 1982; Laidler 1985). The majority of textbooks on physical chemistry simply ignored entropy altogether (Weininger 1996).

To the contrary, Sackur discussed entropy in detail, not only from a thermodynamical point of view, but also from a statistical-mechanical one. In a section devoted to the "mechanical meaning of the second principle and the concept of entropy," Sackur explicitly followed the leads of Boltzmann and Planck in relating entropy to molecular disorder and the atomic hypothesis (Sackur 1912a, 125–134). He presented Boltzmann's work as the solution to the fundamental puzzle of the compatibility between mechanical reversibility and thermodynamical unidirectionality. The key to the solution, Sackur pointed out, is that it is very easy for a mechanical system to become more and more disordered, while it is very unlikely that it will spontaneously retrieve an ordered disposition. "One understands the difference between ordered and disordered motion," Sackur stated, "by comparing the motion of a regiment of soldiers with that of a swarm of mosquitos" (Sackur 1912a, 127).

Sackur dwelled on the notion of disorder and illustrated it by means of various analogies from the mixture of gases to the behavior of a die. The message he wanted to convey to the students was that Boltzmann's statistical version of entropy was a flexible tool whose scope was not limited to gas theory. In his *Wärmestrahlung*, Planck had shown that the "Boltzmann principle"[5] had a very general validity and followed from the basic properties of entropy and probability themselves (Planck 1906). By repeating the same argument, Sackur was going far beyond the limits of usual textbooks in physical chemistry. His purpose was to present thermodynamics as an area of knowledge intimately intertwined with kinetic theory, probability and, ultimately, quantum theory. The notion of entropy, stubbornly dismissed by physical chemists, was the keystone of this conceptual network. The Boltzmann principle not only provided an effective way to calculate the entropy of a monoatomic gas. Using Planck's work on the quantum theory of radiation, it allowed the assignation of an entropy even to oscillating particles. In the final part of his discussion, Sackur showed that combining Planck's entropy of radiation and Einstein's theory of solid bodies, one can ascribe an entropy to an Einsteinian solid and develop the concept of an "ideal solid body," analogous to the ideal gas. In effect, a large part of this section was taken from Sackur's first research paper on the quantum theory of matter (Sackur 1911b).

In the last part of the book, Sackur insisted on the importance of entropy to the issue of chemical equilibrium. As mentioned above, although there was a clear analogy between thermal and chemical equilibrium, entropy had never enjoyed much success in the community of physical chemists. A telling example is Nernst's *Theoretische Chemie* (1909). The textbook went through many editions and from the beginning (1893) was considered the main transmitter of the most advanced methods in physical chemistry (Eggert 1943). However, Nernst famously hated the concept of entropy, and he hardly mentioned it in the almost 900-page volume. Entropy was not part of the standard theoretical arsenal of a physical chemist at the time.

From this perspective, Sackur's stress on the interrelations between chemical, thermal, and radiation equilibrium is unprecedented. To be sure, Sackur's book was not the only one to make wide use of statistical entropy. During the same period James Riddick Partington, who also made a name for himself as a historian of chemistry, wrote a textbook that contained a long account of Boltzmann's approach to entropy (Partington 1913). In its precision and extensiveness, Partington's account is superior even to Sackur's. However, while Partington's is a fairly complete but rather dry report, Sackur strove to show the relevance of these abstract procedures to practical physical chemistry. The pedagogical strongpoint of his treatment was not confined to making the theoretical interrelations between kinetic theory, physical chemistry, and quantum theory apparent, it went so far as displaying how these interrelations could be turned into workable tools for the physical chemist in the lab.

Sackur discussed the topic of chemical equilibrium in chapters 8 and 13. A chemical reaction is in equilibrium when the transformation of the reagents into the products and the reverse occur at the same rates. The fundamental equations of chemical equilibrium had been established by Jacobus H. Van't Hoff on the basis of general thermodynamics (Van't Hoff 1884). However, his solution was still incomplete, in that the thermodynamic equations could be solved only up to an integration constant. This meant that, to apply these equations to practical problems, one had to know the empirical values of the quantities involved at one temperature in order to calculate the corresponding values at another temperature. Hope for the general solution of the problem of chemical equilibrium lay in the numerical correlation between the various integration constants. In particular, the equilibrium constant was related

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[5] The phrase "Boltzmann principle" usually means the proportionality between the entropy of a state and the probability of that state. Boltzmann expresses this equation for a very specific case. It was Planck who, in about 1900, generalized it to the modern form.

to the chemical constant and to the integration constant of the thermodynamic entropy.[6] These numerical relations were never mentioned in physical chemistry textbooks because the entropy constant was unimportant in thermodynamics. To the contrary, Sackur perceived in these relations a way to illuminate the issue of chemical equilibrium:

> Knowing the values of the entropy constants [...], and also the specific heats and their temperature coefficients [...] for all gases, we should be able to calculate the equilibrium constant [...] from the heat of the reaction for all gas reactions at all temperatures. [...] The two laws of thermodynamics alone, however, do not enable us to express the entropy constants [...] in terms of the experimental data. This has only recently been made possible by the discovery of Nernst's heat theorem. (Sackur 1912a, 235)

In the last chapter of the book, Sackur connected this discussion of chemical equilibrium with Nernst's heat theorem and the entropy concept. Sackur explained that thermodynamics allows for the calculation of the state of a system at one temperature if the state at another temperature has been determined. With such a limitation, the problem of chemical equilibrium cannot be solved once and for all because "on the basis of the two principles [of thermodynamics] it is impossible to calculate the affinity or the chemical equilibrium from [...] thermal quantities only; it is always necessary to know the value of affinity at a certain temperature" (Sackur 1912a, 305). Nernst's heat theorem fills this gap using a specific hypothesis about the behavior of affinity and internal energy near absolute zero. In 1906 Nernst had supposed that affinity and internal energy tend to the same value as the temperature decreases (Nernst 1906). This allows for the determination of the integration constant of the so-called Gibbs-Helmholtz equation and the calculation of the affinity for each temperature.

Very soon it was understood that there is a strong connection between Nernst's heat theorem and the quantum hypothesis. As we have seen above, Einstein's theory of specific heats in solids fit surprisingly well with the theorem. Sackur returned to these connections in the last section of his book. In addition, he pointed out the importance of the Boltzmann principle, as a link between old thermodynamics and new developments. Boltzmann's idea of tracing the calculation of entropy back to the calculation of the number of ways of arranging molecules into suitable energy cells provided a representation of the behavior of substances at very low temperatures without introducing kinetic hypotheses. Ultimately, it suggested a possible strategy to derive Nernst's heat theorem:

> This derivation must obviously come out of the features that we ascribe to the absolute zero of temperature. If we now put aside the kinetic theory of heat, then we can characterize the absolute zero as that state in which a body has no heat energy whatever. (Sackur 1912a, 330)

According to the Boltzmann principle, this statement means that there is only one possible allocation of the molecules and the entropy is zero. It is exactly this insight that Sackur would use in his attempt to derive Nernst's heat theorem (Sackur 1911b). More importantly,

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[6] The equilibrium constant is the ratio between the rates of the two opposite directions of a chemical reaction and fixes the equilibrium concentrations of the reactants. The chemical constant was introduced by Nernst, and it is formally the integration constant of the Clausius-Clapeyron equation.

the last chapter of the book also anticipates Sackur's crucial work on the chemical constant. The Boltzmann principle and the quantum theory can, together, provide a theoretical expression of the entropy constant and, as a result, a solution to the problem of chemical equilibrium. How all this can be actually done, Sackur would investigate in his research papers (Sackur 1911c; 1912b; 1912c). In the last chapter, he confined himself to outlining the problem and the tools for its solution.

Thus, Sackur was bringing the tensions of advanced research in physical chemistry into the classroom and directly to his students. The foremost problem was the application of quantum physics to gas reactions and chemical equilibrium, a problem that involved a complex conceptual cluster of classical thermodynamics, Nernst's heat theorem, and the new quantum hypothesis. It was precisely this state of intellectual turmoil that Sackur wanted to convey.

4.6 A Pedagogy for Quantum Physics

Sackur's book certainly has a special position in the context of textbooks on thermodynamics and physical chemistry published circa 1912. As our cursory survey of other important textbooks has shown, cutting-edge research, and especially quantum physics, did not easily find a place in the training of students. One might suggest that this was due to the low level of formal sophistication in physical chemistry books: perhaps Sackur was proposing formal methods and procedures that were too difficult for other authors. This explanation only captures a portion of the truth. It is generally correct that quantum physics was not a subject in books that deployed very little mathematics in their approach to physical chemistry. And it is also true that many authors eschewed high mathematics because it was considered unnecessary. In his textbook, S. Lawrence Bigelow efficaciously summarized this attitude:

> An unfortunate impression has got abroad that much mathematics is needed for a comprehension of physical chemistry; unfortunate, as it deters many who want it, and would profit by it, from electing the subject. No attempt has been made to avoid the use of mathematics, but a perusal for this book will show that ordinary arithmetic and elementary algebra are sufficient, except in five or six demonstrations. One unfamiliar with the calculus must take it on faith that steps in the derivations of half a dozen formulae are correct, and that is all. (Bigelow 1912, iii)

Unsurprisingly, Bigelow organized physical chemistry according to the kinetic scheme, without mentioning quantum theory. But the level of the mathematics involved is not a decisive discriminant. Washburn's didactical perspective was, in this respect, almost literally the reverse of Bigelow's position:

> The author is aware that in many elementary textbooks of Physical Chemistry it is customary to avoid the use of the calculus as far as possible, frequently even with the sacrifice of accuracy and at the risk of conveying erroneous impressions concerning some of the most fundamental relationships; and in those cases where the use of the calculus seems to be unavoidable some authors have felt it incumbent upon themselves to assume a somewhat apologetic attitude and to explain that the student must take on faith "these few derivations" but that he

> should not allow this fact to worry him, since with the aid of the accompanying explanations and illustrations he will still be able to understand the relationships and to apply them, even though he is not in a position to appreciate clearly what is involved in their derivation. With this dilettant attitude the writer finds himself entirely out of sympathy. (Washburn 1915, v)

Yet, we have seen that Washburn did not abandon the kinetic scheme. Similarly, Lewis's book was even more advanced than Washburn's, though it carefully separated classical and quantum physics.

Another explanation of the exceptionality of Sackur's book might be based on local considerations. After all, Sackur was working in Germany, the homeland of quantum theory. Furthermore, he was educated in Breslau, one of the centers of German physics, and he was in contact with Planck and Nernst. It was only natural to absorb, so to say, the quantum theory from this environment and to imbue his pedagogical activity with it. However, this local argument looses much of its strength if we compare the case of Sackur with that of other German textbooks used by physical chemists at about the same time.

For instance, nobody could doubt Planck's engagement both in quantum theory and in thermodynamics. At the end of the nineteenth century, Planck wrote important papers on the physical chemistry of dilute solutions, and at the beginning of the twentieth, he initiated the whole quantum business. However, his celebrated book on thermodynamics (Planck 1913) does not give the student the feeling that quantum theory has anything to do with physical chemistry. Planck's book is organized around the two principles of thermodynamics and their application to chemical problems. In this setup, gases have a privileged role on the grounds of van't Hoff's famous analogy between the ideal gas and dilute solutions. Only in the third edition, published in 1911, did Planck add a chapter on Nernst's heat theorem, and only in the fifth, in 1917, did he refer briefly to Debye's theory of the specific heat of solids.

The situation improves slightly looking at Nernst's *Theoretische Chemie*, the first and most respected textbook on physical chemistry. The sixth edition, published in 1909, contains a summary in a few lines of Einstein's theory of specific heat, without any special emphasis on the quantum (Nernst 1909, 700). One has to wait until the seventh edition, in 1913, to find an autonomous chapter entitled "Molecular Theory of the Solid State of Aggregation." The chapter is largely the summary of two research papers Nernst published in 1911 (Nernst 1911a; 1911b). However, the results are basically the same as those presented in Sackur's book, and the level of formal elaboration of the arguments is even lower. Thus, even if deeply interested in the application of the quantum to the theory of matter and to chemistry, two such scientific leaders as Planck and Nernst were reluctant to change the organization of their textbooks because of the new approach.

Albeit special, the position of Sackur's book was not unique. In 1913, less than one year after Sackur, Karl Jellinek published an impressive book (more than 800 pages) which is, to the best of my knowledge, the first textbook in physical chemistry to rely explicitly and consistently on quantum theory (Jellinek 1913). Jellinek's book is divided into two parts: statics and kinetics of gaseous reactions. However, the gaseous state is by no means the only subject of the book. There is a very long chapter on radiation theory—a topic "that is becoming more and more important for physical chemistry" (Jellinek 1913, 194)—and equally long sections on the statistical concept of entropy and on Nernst's heat theorem.

The chapter on specific heats, which is completely devoted to the quantum version of the problem, is particularly interesting. Like Sackur, Jellinek began with the theory of solids which he analyzed both theoretically and experimentally. Then, he continued with the specific heats in gases and mentioned some recent papers on the quantization of the rotation of diatomic molecules. Jellinek's treatment of specific heat is exactly what a quantum account of the topic should be: solid state is the central paradigm. Interestingly, Sackur also contributed to this textbook. In the preface, Jellinek thanked him for a revision of the manuscript before its publication.

Thus, trying to represent Sackur's or Jellinek's books as the result of an idiosyncratic leaning toward abstract concepts or as local phenomena is missing an important historiographical point: it was around 1912 that the necessity gradually emerged to formulate a didactic platform for quantum physics by reorganizing the classical pedagogy. This process, which was eventually taken up by first-rank physicists like Arnold Sommerfeld and Fritz Reiche (see the articles by Michael Eckert and Clayton Gearhart in this book), was initiated by lesser actors who grasped the importance of the new research and tried to implement this research in their teaching activities.

4.7 Conclusion

One might be tempted to read into the story of Sackur's textbook a fundamental contrast between innovative and conservative pedagogy. But again, I think that this reading would conceal a more intriguing point. The two lessons I spell out in the previous sections point more decisively to the interactions between research and pedagogy as a manifestation of the more general dynamics of knowledge. I have used a Kuhnian terminology to illustrate one important novelty in Sackur's book: gas changed its status from paradigm to puzzle, while the solid underwent the opposite change. Though, it is important to stress that this was not a Gestalt switch. On the contrary, it grew out of the steady effort of negotiating the conceptual space of the new quantum theory within classical physics.

Thus, the construction of a new platform for the didactics of quantum physics that Sackur attempted in his book did not occur in a conceptual vacuum: it was developed as *a reorganization of the established platform ideated over time for classical physics*. The determining insights for this reorganization came from research in that field. The platform was ultimately conceived as a translation of new research priorities into new pedagogical priorities; these priorities modified the criteria for the selection and disposition of the material, as the example of specific heat illustrates. These contextual aspects and its fortunate temporal positioning make Sackur's book not just the receptacle of a dead doctrine, but rather a historiographical tool for understanding the transformations brought about by quantum theory.

SS 1906	Messung chemischer Affinitäten, 1 Radioaktivität mit Experimenten, 1
WS 1906/07	Einführung in die mathematische Behandlung der Chemie, 2 Lektüre klassischer Arbeiten der physikalischen Chemie, 1 g
SS 1907	Thermochemie und Thermodynamik, 2 Radioaktivität mit Experimenten, 1 Physikalisch-chemisches Praktikum (Abegg's course), 3
WS 1907/08	Physikalische Chemie technischer Prozesse, 2. Physikalisch-chemische Rechenübungen (with Abegg), 1 g Physikalisch-chemisches Praktikum (Abegg's course), 3
SS 1908	Physikalisch-chemisches Praktikum (Abegg's course), 3 Ausgewählte Kapitel der technischen Elektrochemie, 1 Einführung in die mathematische Behandlung der Chemie, 2
WS 1908/09	Physikalisch-chemisches Praktikum (Abegg's course), 3 Radioaktivität, 1 Ausgewählte Kapitel der technischen Elektrochemie, 1
SS 1909	Physikalisch-chemisches Praktikum (Abegg's course), 3 Übungen zur Thermodynamik (Abegg's course), 1 g Thermochemie und Thermodynamik, 2 Die physikalischen und chemischen Eigenschaften der Metalle und Amalgame, 2
WS 1909/10	Physikalisch-chemisches Praktikum (Abegg's course), 3 Anorganisch-chemische Technologie, 3
SS 1910	Radioaktivität mit Experimenten, 1 Kinetische Theorie der Gase und Flüssigkeiten, 2 Physikalisch-chemisches Praktikum, 3
WS 1910/11	Radioaktivität mit Experimenten, 1 Ausgewählte Kapitel der Thermochemie und Elektrochemie, 2 Physikalisch-chemisches Kolloquium (with Meyer), 1 g Physikalisch-chemisches Praktikum, 3
SS 1911	Physikalisch-chemisches Kolloquium (with Meyer), 1 g Die Beziehung zwischen chemischer Konstitution und physikalischer Eigenschaften, 2 Einführung in die Chemie, 2 Physikalisch-chemisches Praktikum, 3
WS 1911/12	Physikalisch-chemisches Kolloquium (with Meyer), 1 g Physikalisch-chemisches Praktikum, 3 Physikalische Chemie II: Elektrochemie, Thermochemie, Photochemie, 2
SS 1912	Chemische Referate für Vorgeschrittenere (Biltz's course; with von Braun, Meyer) biweekly, 2 g Kinetische und thermodynamische Theorie der Gase und Flüssigkeiten, 2 Einführung in die Chemie für Zahnärzte, 3 Kleines physikalisch-chemisches Praktikum, 3

WS 1912/13	Chemische Referate für Vorgeschrittenere (Biltz's course; with von Braun, Meyer, Koenig and Arndt), biweekly, 2 g Physikalisch-chemisches Kolloquium (with Meyer), 1 g Einführung in die Chemie, 3 Physikalische Chemie II: Elektrochemie und Photochemie, 2 Kleines physikalisch-chemisches Praktikum, 3
SS 1913	Chemische Referate für Vorgeschrittenere (Biltz's course; with von Braun, Meyer, Koenig and Arndt), biweekly, 2 g Radioaktivität mit Experimenten, 1 Bestimmung von Molekulargewicht und Konstitution nach physikalisch-chemischen Methoden, 1 Praktische Übungen, 3
WS 1913/14	Chemische Referate für Vorgeschrittenere (Biltz's course; with von Braun, Meyer, Koenig and Arndt), biweekly, 2 g Einführung in die Chemie für Zahnärzte, 3 Radioaktivität mit Experimenten, 1 Bestimmung von Molekulargewicht und Konstitution nach physikalisch-chemischen Methoden, 1 Praktische Übungen, 3 Physikalisch-chemisches Kolloquium (with Meyer), 1 g

Table 4.1: Sackur's courses at the University of Breslau (the numbers are the weekly hours, "g" means that the lecture was *gratis*, free of charge).

Abbreviations and Archives

AHQP	Archive for History of Quantum Physics. American Philosophical Society, Philadelphia
AMPG	Archive of the Max Planck Society, Berlin

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