

Putting the quantum to work: Otto Sackur's pioneering exploits in the quantum theory of gases

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Upon its inception within the context of radiation theory, the quantum hypothesis had rapidly diffused into other fields. By 1910, the unravelling of the classical traditions of physics and chemistry in the light of the quantum had become increasingly evident. Quantum theory was catapulted to the forefront at the First Solvay Conference (1911), in the wake of which many leading physicists embraced the quantum hypothesis as a key to solving outstanding problems in the theory of matter. The quantum approach proved successful in tackling the thermal properties of the solid state, resulting in the nearly definitive theories of Debye (1912) and of Born & von Karman (1912-13). However, the application of the old quantum theory to gases was hindered by conceptual difficulties, which were due to a lack of a straightforward way of reconciling the frequency-dependent quantum hypothesis with the aperiodic motion of gaseous molecules.

The emergent quantum perspective compelled a host of young researchers to approach quantum theory with a pragmatic attitude: without an interest or resources to partake in the big foundational debates of the time, they ventured to squeeze out from the nascent

quantum theory an essence that could serve the specific goals of their research. This pragmatic attitude spurred a variety of applications of the quantum that, to a modern eye, may appear gross, sloppy, and naive, but that sometimes led to genuine progress.

Herein, we discuss one remarkable example of such a pragmatic approach, namely Otto Sackur's exploits in the quantum theory of gases. Sackur's bold attempt to deploy the quantum hypothesis across classical statistical mechanics eventually proved instrumental in preparing Planck's path to the theory of a quantum gas.

Sackur's work had developed along two non-orthogonal directions, driven, on the one hand, by his interest in the Nernst theorem, statistical mechanics, and the problem of chemical equilibrium, and, on the other, his goal to shed light on classical mechanics from a quantum vantage point. Inspired by the interplay between classical physics and quantum theory, Sackur chanced to expound his personal take on the role of the quantum in the changing landscape of physics. In this paper, we tell the story of this enthusiastic practitioner of the old quantum theory.

The paper is divided into six sections. Sections 1 and 2 serve to introduce the biographical and conceptual context of Sackur's work. The analysis of his papers on the quantum gas theory is presented in Sections 3–5. Finally, in Section 6 we draw some historiographical conclusions.

1 Biographical overview

Otto Sackur was born in Breslau (now Wroclaw), Silesia, on September 29, 1880.¹ He studied chemistry, first at the University of Breslau, whose Chemistry Department, headed by Albert Ladenburg (1842-1911) since its foundation in 1897, belonged to the most acclaimed in Germany. In Breslau, Sackur found an enlightened mentor, Richard

¹There are only few sources available about Sackur's life. Here we have especially relied on (Kipnis 2005) and the obituaries written by colleagues and friends (Auerbach 1915; Hertz 1915; Pick 1915).

Abegg (1869-1910), who introduced him to modern physical chemistry. Sackur further advanced his chemistry education at Heidelberg and Berlin before receiving his doctorate from Breslau on July 31, 1901.

Sackur's academic career at Breslau took a detour, first via the Kaiserliches Gesundheitsamt in Berlin (from October 1902 till October 1904), where he had worked under the direction of Theodore Paul on problems related to public health. Subsequently, he joined William Ramsey's laboratory at the University College London (from October 1904 till March 1905) and then Walther Nernst's brand new laboratory at the Berlin University (from March 1905 till September 1905). During the latter stays he became privy to the most up-to-date work in physical chemistry.

Upon his return to Breslau, in October 1905, he obtained his Habilitation and the title of *Privatdozent*. For some years, he had taught at Breslau and worked side by side with Abegg, with an eye at a more secure position. Sackur's hopes were shattered by two unfortunate events. In 1909 Albert Ladenburg had retired because of poor health (he died two years later) and the new director of the department, the 1907 Nobel Prize winner Eduard Buchner (1860-1917), a fermentation biochemist, had little sympathy for physical chemistry. A year later, Richard Abegg died tragically in a ballooning accident.² Without an academic sponsor and a laboratory, Sackur had to rely on his pedagogical skills to survive. He accepted minor teaching assignments, devised a course of chemistry for dentists, and wrote textbooks on thermodynamics,³ while trying desperately to keep abreast of the latest developments in physical chemistry. It was during this period of existential difficulties that Sackur had launched his research at the intersection of physical chemistry, thermodynamics, and quantum theory, in the hope of a reward in terms of a more senior academic appointment. **Some sources say that Sackur became extraordinarius at Breslau, in 1911.**

²In Tessin, near Rostock (Arrhenius 1910; Des Coudres 1910).

³During this period, Otto Stern earned his PhD under Sackur's supervision, on "generalized soda-water" (Friedrich and Herschbach 2003). On Sackur's pedagogical activity see (Badino 2011).



Figure 1: Otto Sackur, 1880-1914

His hopes were fulfilled at the end of 1913, when, thanks in part to a mediation by Clara Immerwahr, Fritz Haber's first wife and former student of Abegg's, Sackur received a call to Haber's Kaiser-Wilhelm-Institut für Physikalische Chemie und Elektrochemie in Berlin. In 1914 he was promoted to the rank of a department director. After the outbreak of the Great War, Sackur was enlisted in military research at Haber's institute, but on the side succeeded to carry on with his experiments on the behavior of gases at low temperatures. On December 17, 1914, while working on a military-related project

in his laboratory, Sackur was killed by an explosion at his work bench. He was 34 years young.

2 The problem of chemical equilibrium

In the course of the 19th century, the concept of a chemical equilibrium underwent several transformations. Around 1850, the old notion that a reaction is at equilibrium when all the “chemical forces” involved are balanced out was gradually replaced by a kinetic view: a (reversible) chemical reaction never stops completely, but only reaches a stationary state when the reaction rates in the forward and backward direction become equal.

The ratio between the forward and backward rates was called the equilibrium constant, K . In 1864 Cato Maximillian Guldberg (1836-1902) and Peter Waage (1833-1900) discovered that the equilibrium constant depends on the ratio of the concentrations of the reactants and products (‘law of mass action’). Their pioneering paper, published originally in Norwegian, was largely ignored until 1877, when Wilhelm Ostwald (1853-1932) adopted the law and corroborated it by his own experiments.⁴ Jacobus Henricus van’t Hoff (1852-1911) discovered the law independently in 1884 and two years later derived a formula that governs the temperature dependence of K .

A second breakthrough in the study of chemical equilibria occurred in the 1880s when thermodynamics – by then complete (save for Nernst’ theorem) – was applied to chemical problems. As early as 1873, Josiah Willard Gibbs (1839-1903) used the concept of the maximum work produced by a reaction to define chemical equilibrium: a reaction has reached a stationary state when it produced all the work it was capable of producing (Gibbs 1873). Curiously, the publication of Gibbs’s results in an obscure

⁴A collection of the publications of Guldberg and Waage on the topic was later published in the series *Ostwald Klassiker der Exakten Wissenschaften* in a translation by Richard Abegg (Guldberg and Waage 1899).

journal again hampered their dissemination. In 1882, Hermann Helmholtz (1821-1894) arrived at the same results independently. He distinguished between a bound and a free energy content of a system. The latter is transformed into work during a chemical reaction, whose equilibrium is reached when the free energy drops to its minimum value (Helmholtz 1882). As Arnold Eucken paraphrased it:

[T]he (maximum) work represents a quantity whose knowledge leads immediately to the solution of the [equilibrium problem]: only when a chemical process is able to perform work, it will go on spontaneously. Hence, one can also say in what direction [a reaction] develops, if it is given in which transformation [...] the maximum work has a positive sign. If in a chemical transformation no work is produced, then the system is in a state of equilibrium. (Eucken 1922, p. 123).

The concept of free energy amounted to a well-founded replacement for the old intuitive notion of “affinity.” The internal energy, U , of a chemical system is made up of free energy, A , that can be used to produce work and of bound energy (also called the ‘latent heat of reaction’), Q . At equilibrium, the reaction work and the equilibrium constant are related by the equation

$$A = RT \ln K \tag{1}$$

with R the universal gas constant.

By combining the first and second laws of thermodynamics for the case of an isothermal and isochoric gaseous reaction, it was possible to obtain the following equation, sometimes called the Helmholtz equation, for the free energy,

$$A = U + T \left(\frac{dA}{dT} \right)_V \tag{2}$$

where T is the absolute temperature and V volume (Haber 1905, pp. 18-22). The general integral of this equation is:⁵

$$A = -T \int \frac{U}{T^2} dT + T f(V) \quad (3)$$

with $f(V)$ the integration constant (integration at constant volume). Thus, in order to evaluate the free energy – and, via eq. (1), the equilibrium constant – one needs to determine, at a given temperature, the reaction energy U and the function $f(V)$. Experimentally, this task was anything but easy and much effort had been expended in the final decades of the 19th century at collecting the requisite data for various substances.⁶

The third law of thermodynamics, enunciated by Walther Nernst (1864-1941) in 1906, amounted to a third breakthrough.⁷ Nernst observed that as $T \rightarrow 0$, the slopes of the temperature dependence of the free energy and of the internal energy (heat) tend asymptotically to the same limit, namely to zero (i.e., $\lim_{T \rightarrow 0} \frac{dA}{dT} = \lim_{T \rightarrow 0} \frac{dU}{dT} \rightarrow 0$) – without concluding that A and U themselves become equal at $T = 0$ as well. Nevertheless, based on his observation, Nernst was able to set to zero the integration constant $f(V)$ in equation (3) (Nernst 1906) and thereby enable to find at any temperature T the free energy A from U which could, in turn, be determined from thermochemical data.⁸

However, Nernst held that his theorem only applied to condensed-matter systems and so the equilibria of gaseous reactions remained out of the theorem's reach. In response, Nernst devised an ingenious detour which made it possible to evaluate the equilibrium

⁵For the technique used to solve this equation see (Haber 1905, pp. 22-23).

⁶For theoretical and experimental aspects of physical chemistry at the end of the 19th century, see (Hiebert 1971, 1983) and (Kormos Barkan 1999).

⁷Julius Thomsen (1826-1909) in 1852 and Marcellin Berthelot (1827-1907) in 1869 had speculated on the behavior of the chemical reactions in the vicinity of the absolute zero. The latter, especially, had suggested that A and U become equal as the temperature decreases. See (Kormos Barkan 1999; Bartel and Huebener 2007). It is also instructive to see Nernst's personal take on the story in the opening chapter of (Nernst 1917).

⁸For a modern treatment see (Morse 1969, pp. 143-145).

constant of gaseous reactions as well. Nernst noticed that the integration constant, C , of the van't Hoff equation is the same as the integration constant of the Clausius-Clapeyron equation which governs the temperature dependence of pressure of a vapor in phase equilibrium with a liquid or solid condensate (the two equations are isomorphic). Dubbed the chemical constant, it takes the form

$$C = \frac{S^0 - c_V + R \ln R}{R} \quad (4)$$

where c_V is the specific heat of a gaseous component at constant volume and S^0 its entropy at standard conditions, also known as the entropy constant, see eq. (10). The chemical constant needs to be determined experimentally for each gaseous species i involved in the reaction, which is indeed possible thanks to the absolute character of entropy, as established by Nernst's theorem. Once the C_i 's are available, the equilibrium constant of a gaseous reaction follows,

$$\ln K = \frac{Q}{RT} + \frac{\ln T}{R} \Sigma(c_P)_i + \Sigma C_i \quad (5)$$

where c_P is the heat capacity at constant pressure. Hence, as Sackur commented (Sackur 1911b): “Only Nernst's theorem makes it possible to establish the constant C which determines the chemical behavior of gases from measurements on *pure* substances (vapor pressure of liquids or solids) and thereby ... also the entropy constant [S^0]”

However, by 1911, the chemical constants were available for only a handful of substances. Therefore, the question arose – conceptual as well as practical – as to whether one can determine the hard-to-come-by chemical constants computationally.

This is indeed the path taken by Sackur in 1911: he set out to calculate the entropy constant S^0 – and thus C – by invoking statistical mechanics. This was a bold move not only because of the rather tentative status of the statistical approach but also because

entropy itself had been perceived as difficult to define and, moreover, wedded to mysterious applications of probability. Physical chemists of the time had preferred the concept of maximum work to characterize chemical equilibrium. In the most influential physical chemistry textbook of the time, Walther Nernst's *Theoretische Chemie*, entropy appears only to be treated as dispensable. However, Sackur's move had not remained unrewarded: he was able to derive the first quantum-theoretical expression for the entropy of an ideal gas (in the limit of high temperatures and low densities). A similar expression was discovered independently at about the same time by Hugo Tetrode (1895-1931) and is known as the Sackur-Tetrode equation. The Sackur-Tetrode equation made it possible to evaluate the entropy constant and thus the chemical constant by computation alone, without the need for any experimental input.

3 The beginnings of the quantum theory of gases

At the turn of the first decade of the 20th century, many proponents of the quantum, such as Walther Nernst, Max Planck (1858-1947), and Albert Einstein (1879-1955), had come to think that kinetic theory, quantum theory, the heat theorem, statistical mechanics, and (physical) chemistry were closely related. Einstein's 1907 quantum theory of solids exemplified the power of the quantum in treating the kinetic theory of matter while Nernst, at about the same time, became convinced that the quantum implied the validity of his theorem for gases. On a more general level, it became apparent that the quantum called for new ways of applying statistical mechanics to both the theory of radiation and the theory of matter.

Sackur got to know about these developments at the meetings of German scientists, which he had attended scrupulously in those years. The approach to the theory of matter based on sophisticated mathematical techniques – which quantum theory entailed – was exactly his cup of tea. Unlike the majority of physical chemists of the time (including

major protagonists such as Nernst) who had an aversion to the formal complications of kinetic theory, Sackur was convinced that physical chemistry could not do without the most intricate mathematical tools available. During his academic career in Breslau, he taught classes in both kinetic theory (SS 1910, SS 1912) and in the ‘mathematical treatment of chemistry’ (WS 1906, SS 1908). Sackur’s lecture notes became the basis for an acclaimed book written jointly with Abegg, which was even translated into English (Abegg and Sackur 1909).

In Sackur’s time, the term ‘kinetic theory’ did not refer to the nineteenth century analysis of collisions leading to the riddle of irreversibility. Instead, ‘kinetic theory’ meant an attempt to trace back the thermal behavior of systems, chemical or other, to the arrangements of their molecules. This is illustrated by his first paper dedicated to such problems.⁹ Sackur argued that with decreasing temperature, the molecular energy disposal becomes increasingly restricted, limiting the number of ‘cells’ (states) over which the molecules can be distributed. When the temperature drops close to zero, the number of ‘cells’ tends to one, as a result of which the distribution becomes ordered: all the molecules end up herded in the last remaining ‘cell.’ Since entropy depends on the number of molecular arrangements, W , *via* the Boltzmann principle,

$$S = k \ln W \tag{6}$$

it was apparent that $S = 0$ for $W = 1$ when all the molecules are in the same cell. Since Nernst’s theorem, as Planck had shown (Planck 1911, pp. 266-286), can be expressed as $\lim_{T \rightarrow 0} S = 0$, Sackur concluded that the third law reduces to the claim that low-temperature molecules are arranged in their energy space in the most orderly fashion.

The main sources of inspiration for Sackur’s paper (Sackur 1911a) were Planck’s *Vor-*

⁹(Sackur 1911a). Attempts along a similar direction were (Nernst 1911; Jüttner 1911; Polanyi 1913); on the debate concerning the proof of the heat theorem see (Kox 2006).

lesungen über die Theorie der Wärmestrahlung and *Thermodynamik* as well as Einstein's 1907 theory of solids (Einstein 1907). Sackur was especially intrigued by the way in which Einstein had intertwined classical statistico-mechanical procedures with the new quantum hypothesis. In the second part of the paper Einstein put forward a second proof of the heat theorem, by showing that the quantum hypothesis, in the case of a solid, implied that the entropy constant is zero. For Sackur, the transition from the gas to the solid was justified by Einstein's general procedure: "a complete kinetic theory of the solid state of aggregation might perhaps be built on Einstein's presuppositions just as the van der Waals' theory was built on the presuppositions of the classical gas theory" (Sackur 1911a, p. 467).

Furthermore, Sackur's paper also shows its author's internalization of Planck's concept of absolute entropy. Classical thermodynamics defines only an entropy difference and leaves the integration constant undetermined. But Planck was convinced that entropy expresses a fundamental property of nature and, therefore, must have an absolute value. Quantum theory combined with the heat theorem affirmed that entropy's integration constant can be set to zero (Planck 1913).

Sackur adopted the concept of absolute entropy and made it into a building block of his new quantum theory of the ideal gas. In the second paper published in 1911, he tried to construct a general application of his peculiar version of kinetic theory to chemical problems. Here 'application' is the key word that expresses the second direction of Sackur's work: his attempt to transform abstract procedures into potent treatments of classical problems. To Sackur, the glue that holds together quantum theory, kinetic theory, and physical chemistry is the concept of probability, whose value had been well proven in the course of the investigations of gases but that could be applied to other problems as well:

This idea has been hitherto applied only to the variations of state of an ideal

gas, that is to physically and chemically uniform substances, as well as to radiation phenomena. Now it seems that it can be applied to any spontaneously occurring processes in nature, for example to chemical reactions and to irreversible processes of any kind that are connected with an increase of the probability of a closed system. This generalization of the concept of probability to chemically distinct states of matter appears to me a simple consequence of Boltzmann's view. (Sackur 1911b, p. 960).

Henceforth, Sackur set out to find a general way of comparing the probability of different states. The case of chemical equilibrium in an ideal gas was particularly suitable for this aim, as it went just a step beyond Boltzmann's gas theory.

In his attack on the problem of the entropy from the 'kinetic' side, Sackur follows explicitly Planck's statistico-mechanical treatment of an ideal gas (Planck 1906, pp. 140-148). The state of the gas is determined by the number of molecules whose coordinates lie between $q_1, q_1 + dq_1, q_2, q_2 + dq_2$ and $q_3, q_3 + dq_3$, while their velocity components lie between $v_1, v_1 + dv_1, v_2, v_2 + dv_2$, and $v_3, v_3 + dv_3$. Thus, if the state space of a single molecule is divided into 'elementary regions' $dq_1 dq_2 dq_3 dv_1 dv_2 dv_3 = d\sigma$, and f is the distribution function, the number of molecules in a given region is $n = f d\sigma$. Let us assume that the elementary regions $d\sigma$ can be numbered and that $n_i = f d\sigma_i$ is the number of molecules contained in the i -th region. Thus a state distribution is the sequence n_1, n_2, \dots and, according to Boltzmann, the corresponding probability distribution is:

$$W = \frac{N!}{n_1! n_2! \dots} = \frac{N!}{f_1 d\sigma_1! f_2 d\sigma_2! \dots} \quad (7)$$

where N is the number of molecules. By substituting for W in the Boltzmann principle, eq. (6), invoking the Sterling formula, setting $d\sigma_i = d\sigma$ for all i , and replacing summation

by integration,¹⁰ Sackur arrived at the formula for entropy

$$S = kN \log N - k \int f \log f d\sigma - kN \log d\sigma \quad (8)$$

whose maximum (which corresponds to equilibrium) yields the distribution function f . Under the constraints of constant energy and number of molecules, f comes out Maxwellian, and substituted back into eq. (8), a formula for the translational entropy of a monoatomic gas results:

$$S = c_V \ln T + R \ln V + c_V \left(1 + \ln \frac{2\pi R}{M} \right) - R \ln d\sigma \quad (9)$$

where M is the molecular weight. A comparison of eq. (9) with that for the entropy of an ideal gas,

$$S = c_V \ln T + R \ln V + S^0 \quad (10)$$

yields the entropy constant in terms of the universal gas constant, the molecular weight, and the ‘elementary region’ $d\sigma$,

$$S^0 = c_V \left(1 + \ln \frac{2\pi R}{M} \right) - R \ln d\sigma \quad (11)$$

But what are Sackur’s elementary regions?

4 Sackur’s ‘elementary regions’

A considerable part of Sackur’s paper (Sackur 1911b) deals with the properties of the ‘elementary regions.’ First of all, he points out that the volume $d\sigma$ must have a well-

¹⁰On the one hand, the applicability of the Stirling formula relies on the assumption that the elementary regions are large enough to contain many molecules. On the other hand, replacing summations by integration requires the regions to be infinitesimal. Classical kinetic theory hinges upon the balance between these two contravening requirements. We will discuss below Sackur’s reflections on it.

defined value because the entropy constant is related to the equilibrium constant, which is indeed a constant for any given substance. This requirement gave a hint to Sackur that the issue crosses beyond the boundaries of classical physics “since pure kinetic [theory] has hitherto not been able to say anything about the magnitude of $d\sigma$, there is a gap in the sequence of inferences that lead from the kinetic hypothesis to the equation of state of a gas” (Sackur 1911b, p. 968).

Sackur, however, did not immediately suggest that the fixed volume of the elementary region is determined by Planck’s constant, h . There might be a purely technical reason for his reluctance. Following Boltzmann and Planck, Sackur had partitioned the position-velocity space whose volume element did not have the dimension of action. In fact, Sackur carried out the dimensional analysis of the entropy constant, but he limited himself to verifying that it depended on the volume of the gas in the expected way. Although noncommittal as to the physical meaning of $d\sigma$, the peculiarity of a fixed-magnitude elementary volume did not escape Sackur’s attention. He tried to give both a visual and a conceptual interpretation of this result.

Visually, the fixed-magnitude volume seems to entail that the molecules do not pass smoothly from one state to another or, equivalently, that they do not spread out into the entire space allowed:¹¹

The gas molecules do not distribute themselves uniformly over the whole allowed space and they cannot have all possible velocities from zero to infinity, but [...] they concentrate around individual points in space, like bullets on a target, and [...] their velocity components change *in jumps*. (Sackur 1911b, p. 969).

¹¹To a modern reader, Sackur’s talk about a tendency of molecules to clump in phase regions may suggest some, albeit naive, anticipation of quantum statistics (Darrigol 1991). However the main problem that quantum statistics had to deal with, namely the extensivity of entropy, was not considered here. And when the problem came up, Sackur did not seem to recognize it as a fundamental issue.

Conceptually, Sackur relied on Planck and traced the ‘atomicity’ of the ‘elementary region’ back to the calculation of probability. In his 1900 paper where he enunciated the quantum hypothesis for the first time, Planck had argued that an actual computation of a state’s probability is possible only if the total energy is divided into elements of a finite magnitude. The ‘atomicity’ of energy then followed directly from the Boltzmann relation between entropy and probability. Sackur had subscribed to Planck’s view unconditionally: “either [we] postulate the physical reality of a finite elementary region (and of finite elementary quanta) or [we] give up the *unequivocal* relation between entropy and probability” (Sackur 1911b, p. 970).

Sackur’s prime interest, however, lay in the physico-chemical properties of the ‘elementary regions’ $d\sigma$. Coming to terms with what $d\sigma$ means is the theme of the second part of his analysis, whose conclusion is twofold: First, $d\sigma$ is not a universal constant, but must, somehow, depend on the molecular mass. By combining eqs. (??) and (11), Sackur obtained

$$C \propto \frac{c_V}{R} \ln \frac{2\pi R}{M} + \ln R - \ln d\sigma \quad (12)$$

and argued that if $d\sigma$ were the same for all gases with the same number of molecules (as c_V is), then the chemical constant C would have to decrease with increasing molecular weight. This, however, would contradict Nernst’s experiments, which had found that C in fact increases with M .

Second, Sackur concluded that $d\sigma$ depends on the number of molecules. By making use of an argument inspired by Einstein’s 1905 light-quantum paper, Sackur contended that the probability of an ideal gas consisting of N molecules partitioned into q subsystems with N' molecules each and probability W'_N has a total probability $W_N = W_{N'}^q$. An application of Boltzmann’s principle then led Sackur to the conclusion that the ratio $d\sigma/N$ – and not $d\sigma$ alone – is a universal constant. Sackur’s result contains a grain of

truth in that it renders the entropy in his formula extensive.¹² In his *Wärmestrahlung* Planck started from extensivity and the law of the composition of probabilities to derive the Boltzmann principle (Planck 1906, pp. 136-137). Apparently Sackur did not fully realize the significance of his own argument and result, but Planck did. Three years later, while struggling with the problem of making a quantum entropy extensive, he would take up Sackur's condition by stating that the elementary volume of the phase space of a gas depends on the number of molecules in the gas (Planck 1914, p. 9).

Sackur's paper (Sackur 1911b) exemplifies well the concerns of his work. As stated in the title, his prime concern was the 'application' to physical chemistry of the methods developed by Planck in radiation theory. Sackur followed Planck closely in the usage of probability and in handling the state space, but stopped short of introducing explicitly the quantum hypothesis. Instead, he attempted to clarify the properties of the elementary volume as a means to calculate theoretically the chemical constants. In the concluding section of the paper, he tested his procedure on the dissociation of iodine molecules and was able to retrieve the correct formula for the mass-action law.

5 The generalization of Sackur's statistical theory

Sackur's focus on the burning issues of physical chemistry distracted his attention from the impact his method could have had on quantum theory at large. Tetrode, whose work approached the problems of fledgling quantum statistics from a more abstract viewpoint, stressed the quantum interpretation of the elementary volume as well as the problem of extensivity right at the outset (Tetrode 1912).¹³ However, Sackur himself had realized, on a careful reconsideration, that his procedure opened up an intriguing perspective. He explored this perspective in a paper included in the Nernst *Festschrift*, published in May

¹²If $S_1 = k \ln W_1$ and $S_2 = k \ln W_2$ are the entropies of two subsystems and $W_{12} = W_1 W_2$ is the probability of the composed system, then $S_{12} = S_1 + S_2$.

¹³For a discussion of Tetrode's paper, see (Darrigol 1991; Desalvo 1992).

1912.¹⁴ Here the notion of the quantum of action and its application to the calculation of the chemical constants appear in the very title.

First, Sackur tackled the problem of extensivity. He realized that the dependence of $d\sigma$ on the number of molecules was necessary to guarantee extensivity of the entropy function, but was no longer happy with the way it came about. At this point, Sackur was already convinced that the essence of the quantum hypothesis was probabilistic. As a consequence, he thought that a reconciliation of quantum theory with thermodynamics relied on a suitable definition of probability. In order to appreciate his procedure, it is helpful to discuss briefly Sackur's peculiar concept of probability.

In (Sackur 1911b, pp. 959-960), he defined the probability of a state as “the number that measures how many times a [...] state [...] is more probable than a state of the same energy and volume in which all atoms would have the same positions, directions and velocities.” This idiosyncratic definition, Sackur's personal reading of Planck and Boltzmann, led to the usual number of possible permutations of a state distribution. To retrieve extensivity, Sackur had stated that the definition must be changed and “we must resort [...] to the concept of molecular disorder” (Sackur 1912a, p. 406). Once again, Sackur picks up this concept from the tradition of Planck and Boltzmann, but reinterprets it in a peculiar way. In an arbitrary state, it is possible that more than one molecule lies in the same energy cell (or phase-space cell). Accordingly, the probability of the state is the number of permutations of molecules between different cells. If the state is perfectly disordered, however, each cell contains exactly one molecule. In other words, the molecules are totally spread out throughout the available space. This concept of molecular disorder could not be more distant from Planck's and Boltzmann's,¹⁵ but it accomplished its intended mission. For the number of permutations in this case is $N!$

¹⁴The paper is dated March, 1912. Since also Tetrode's article was published in March, it seems that Sackur worked out the consequences of his approach independently.

¹⁵Boltzmann considered the molecular disorder as the condition for applying probability in gas theory, while Planck was convinced that disorder had the power to eliminate any violation of the second law of thermodynamics. For a discussion of these two views see (Badino 2009).

and since Sackur defines the probability as the ratio between the number of permutations of the given state and the number of permutation of the most disordered state, the term $d\sigma/N$ appears again in the entropy formula.

The second theoretical novelty of the article is the interpretation of the elementary volume in terms of the Planck constant. Sackur maintains the position-velocity space, but he relies on Sommerfeld's authority to interpret the volume as $d\sigma = h^3/m^3$.¹⁶ This expression of the elementary volume enables us "to calculate [the] characteristic quantities for the vapor pressure and the chemical behavior without their experimental determination" (Sackur 1912a, p. 409).

Hence, the last part of the paper deals with the calculation of the chemical constants for monoatomic gases and the extension of the same procedure to more complex structures. Here Sackur displayed his knowledge of the experimental data and his ability to handle them. Unfortunately, he made a mistake in the calculation of the rotational component of the energy of a diatomic molecule, a mistake that, however, did not change substantially the order of magnitude of his results.¹⁷ The good agreement between his theoretical value and the experimental data on the chemical constants reassured Sackur that his formula was correct.

Sackur's probabilistic argument was obviously unsatisfactory and he tried a much more general analysis in the following paper, which is, from the theoretical viewpoint, the most ambitious one. A striking feature of Sackur's original approach based on the division of the state space was that it solved the baffling problem of quantizing an aperiodic system with amazing simplicity. The quantum hypothesis had been introduced for strictly periodic systems and in fact expressed a relation between the energy and the

¹⁶Sommerfeld had proposed the interpretation of the elementary volume in terms of h as a general quantization condition for the periodic system in the Solvay conference and in a widely discussed paper (Sommerfeld 1911).

¹⁷Sackur wrote the energy as a sum of squares of angular velocities $E = \frac{I}{2}(u^2 + v^2)$ (I is the moment of inertia) neglecting the angle ϑ formed by the two vectors which gives the correct expression $E = \frac{I}{2}(u^2 + v^2 \sin^2 \vartheta)$.

characteristic frequency. But there is no immediate way to ascribe a frequency to a gas. To get around this issue, Sackur had worked on the space describing the system rather than on the system itself and this strategy has led him to quantize the elementary regions instead of the behavior of individual systems. However, in (Sackur 1912b) he changed tack. Following his belief that the quantum was intimately connected with the application of probability, he tried to make contact between the quantum hypothesis and the classical probabilistic procedures in use among kinetic theoreticians. The result is an interesting argument with a clear nineteenth century flavor. The argument goes as follows.

First let us consider the case of a periodic system. Sackur speaks about a set of particles oscillating around an equilibrium point, a system that resembles very much an Einstein solid. There is no assumption on the nature of these particles but that, after a very long time, they obtain all possible values of energy. Sackur tackles the problem of calculating the probability that a particle has energy between ϵ and $\epsilon + \Delta\epsilon$ when it passes through the equilibrium point.¹⁸

To illustrate the problem, Sackur imagines a microscopical observer that can watch individual particles and send a signal every time a particle passes through the equilibrium point with the correct energy. Therefore, the sought probability $w = n/N$ is equal to the ratio between the number of signals n and the total number of particles N . This probability, Sackur states, is a function of the energy and it is proportional to the width of the cell as well as to the span of time the observer watches the system $w = f(\epsilon)\Delta\epsilon\Delta t$. Remember that any value of the energy is possible and, Sackur insists, it is a fundamental principle of probability that if one waits long enough, all possible events will occur. This principle entails that if $\Delta\epsilon$ decreases, that is the energy cells becomes smaller and more difficult to observe, the same probability can be maintained by extending the observation

¹⁸The argument might be carried out for any arbitrary point of the oscillation, Sackur chooses the equilibrium because in that point the elongation is zero, therefore the energy of the particle is entirely kinetic.

time Δt . In other words, $\Delta\epsilon \cdot \Delta t = \text{constant}$, a consequence that resembles closely, and amusingly, one of Heisenberg's uncertainty relations.

At the same time, we cannot choose an arbitrary long time or, equivalently, an arbitrary small energy cell. To be properly defined, the probability w must be normalized, to wit when we sum up the probabilities for all energy values, we have to obtain 1. But if the observer is allowed to examine the system for an arbitrary long time, it will count all molecules infinitely many times, because the molecules can assume all energy values in a long time. Hence, we have to constraint the observation time and the most obvious way to do it is to take the oscillation period $\Delta t = \tau$. During an oscillation only the molecules with a specific energy will be counted. If we call h the constant mentioned above, this condition gives $\Delta\epsilon = \frac{h}{\tau} = h\nu$. Note that in this way the quantum hypothesis concerns the energy width $\Delta\epsilon$, that is to say the 'experimental error' that the microscopic observer is allowed to make.

The gist of Sackur's probabilistic argument is that the quantum hypothesis is not necessarily a new physical assumption, but rather an 'extension of the old statistical methods':

Contrary to the old picture developed by Planck, for the derivation [of the equations of this theory], it [is] not necessary to assume an atomistic structure of the energy or the action. It suffice[s] to sharpen the (physical) concept of probability, namely by the almost obvious assumption that the verification of a result is the more probable, the longer one waits for it, and therefore even an extremely unlikely but possible result will have a finite probability to arise after an infinitely long time. (Sackur 1912b, p. 85).

He tries to show that the quantum constraint emerges as soon as we tackle the problem of transforming the probabilistic formalism into a physically workable procedure. The fiction of the microscopic observer illustrates precisely this point. The attempt

at demonstrating continuity between the methods of classical statistical mechanics and the quantum theory serves two related goals. On the one hand it allows to put aside many of the conundrums that plagued the quantum hypothesis. As the quotation above shows, Sackur was much more eager to underscore the *formal similarities* between the classical methods and the new quantum business than the weird consequences stemming from discontinuity and discretization. On the other hand, these similarities justified the application of the quantum procedure to the problems left open by the classical theory. Precisely because the quantum was an extension of the statistical mechanics, it might be helpful in filling the remaining gaps in the thermodynamic and statistico-mechanical pictures of the chemical phenomena.

Upon the ground of his probabilistic argument Sackur places a calculation which is very much inspired by Planck's general treatment of the oscillators in the *Wärmestrahlung*. The entropy is calculated by applying the maximization procedure to the probability by means of the Lagrangean multipliers. The resulting entropy satisfies the Nernst theorem and, at high temperature, the expression that one would get by applying the Rayleigh-Jeans formula. Here Sackur makes an interesting consideration. It was customary to read the entropy at high temperature as the result of the replacement of the usual combinatorial summations with integrals. This procedure, however, is inconsistent with Sackur's operational-probabilistic foundation. It is difficult to conciliate the demand of infinitesimally small elementary regions with the opposite one — implicit in the Stirling approximation — that each cell contains many particles.¹⁹ The action of the microscopic observer, as we have seen, depends crucially on the finite magnitude of the cell. Sackur's conclusion is that the Rayleigh-Jeans formula should not be viewed as the limiting case of the combinatorial procedure, but rather 'only as the approximation formula for the high temperature' (Sackur 1912b, p. 75). In other words, the Rayleigh-Jeans formula

¹⁹Curiously, some historians have recently used a similar argument to claim that the Boltzmann procedure did not hold for infinitesimally small cells, but only for very small, though finite cells (Hoyer 1980; Darrigol 1988).

does not belong to the same set of statistical idea, but it is simply an approximation.

So much for general oscillating structures. Now comes the problem to extend this procedure to gases and, more importantly, to tackle the issue of extensivity. Formally the maximization of the entropy proceeds in the same way, but since the gas is an aperiodic process, one has to find out a proper replacement for the characteristic frequency ν . Sackur argues that the limitation of the observation time must be such that the velocity of the molecule does not change during that time: “we have to choose the observation time [...] so that during $\Delta t = \tau$ the molecule experiences no change of velocity, that is no collision” (Sackur 1912b, pp. 75-76). Sackur is obviously referring to the mean time that the molecule spends to cover the mean free path. In that span of time the molecules maintain their velocity and the observer will count only the ones in the given energy cell.²⁰

To obtain the extensivity, Sackur resorts to an ingenious move. He defines the three components of the velocity as the ratio between the mean free path and the mean free time. Since the mean free path depends on the number of molecules, this procedure introduces surreptitiously the same dependence in the definition of the elementary cell in the position-velocity space. In effect, Sackur treats the gas as though it consists of molecules contained into V/N independent sub-volumes defined by the mean free path. In this way he obtains the dependence of the elementary cell on the number of molecules that was crucial to arrive at the extensivity.

In the last part of the paper Sackur comes back to the extension of his approach to more complex gases. Again, the treatment of the rotational energy is wrong and a personal letter of Tetrode made him aware of the mistake. Therefore Sackur published immediately after a new paper devoted to the discussion of gaseous molecules with two or three atoms in which he corrected his previous error (Sackur 1912c).

²⁰Sackur’s idea of using the mean free path as a parameter to quantize the gas was taken up the following year by Sommerfeld and his collaborator Wilhelm Lenz (Sommerfeld 1914).

At the end of 1912 Sackur considered completed his quantum theory of ideal gas. He had conceived an original probabilistic argument according to which the quantization was presented as a further necessary step in the application of statistical techniques. This argument justified the extension of the quantum theory from periodic systems to gases. Sackur's approach also gave reason of the extensivity and his theoretical calculations of the chemical constant enjoyed good empirical confirmation. He felt it was time to move on. His contact with Fritz Haber and the Kaiser Wilhelm Institut led him to explore the possible applications of the quantum theory to more pressing physico-chemical problems, such as the behavior of gases at very low temperature. This topic occupied him in the last phase of the career, before the outbreak of the war forced him to military research.

6 Conclusions

Sackur's most lasting contribution to quantum theory remained the Sackur-Tetrode equation. It is still quoted in textbooks as the quantum expression of the thermodynamic entropy at high temperature. It played a role as important as the Nernst theorem in the path towards a complete theory of quantum gas. Furthermore, Sackur's theoretical calculation of the chemical constants was immediately and widely accepted as a standard reference to test further theories in the field. His theoretical reflections did not encounter the same fortune. Although some of his ideas were subsequently taken up and discussed — for instance the N -dependence of the elementary cell or the division of the gas volume into V/N partitions to get extensivity — nobody followed his suggestion of a purely probabilistic-operational foundation of the quantum hypothesis. Physicists and physical chemists favored Stern's approach based on the vapor-solid equilibrium (Stern 1913, 1919) which eventually triggered Fermi's analysis of the statistics of identical particles (Fermi 1923; Rasetti 1924).

But reducing Sackur's case to a story of which aspects of his work succeeded and

which failed to have an impact would mean to miss more interesting historiographical points. Here we propose two remarks that can serve as preliminary reflections on the complex landscape of the quantum physics in 1910s. First, Sackur is an example of how diverse and variegated was the scientific community that developed quantum physics. While sharing formal tools and mathematical techniques, physicists in the 1910s could see very differently the essence of the quantum hypothesis: it meant different things for different people. In the case of Sackur, for instance, his background in physical chemistry played a substantial role in shaping his interpretation of the quantum. Eager to put the quantum to the service of long-standing problems of classical thermochemistry — as well as to prove to an imaginary employer that he was professionally qualified to do so — Sackur stressed the continuity between the classical statistical techniques and the quantum procedure. It is precisely this richness of approaches and outlooks that makes the 1910s such an interesting period both from a historiographical and from an epistemological point of view.

The second point concerns the research style of this portion of the physicists community. Contrary to Planck, Einstein or Bohr, to mention just a few examples, Sackur's research was driven neither by strong philosophical tenets nor by fundamental questions about the nature of radiation. His was, so to say, a 'dirty' quantum physics coming 'from below' as the synthesis of his personal perception of abstract concepts and his very pragmatic agenda. It is important to emphasize that for a vast majority of the lesser figure, who eventually happened to provide a lasting contribution, the quantum was mainly a tool. For them, like for Sackur, quantum physics got a meaning when viewed in interplay with classical physics and with problems that were well-defined in their disciplinary background.

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