Putting the Quantum to Work: Otto Sackur’s Pioneering Exploits in the Quantum Theory of Gases

Massimiliano Badino & Bretislav Friedrich

Fritz Haber Institute of the Max Planck Society
Max Planck Institute for the History of Science

HQ3 - Third International Conference on the History of Quantum Physics
Berlin, June 28 - July 2 2010
Summary

• Biographical Information
• The problem of the chemical equilibrium
• The entropy constant and the quantum gas theory
• Sackur’s theory of gas degeneracy
• Conclusions
Otto Sackur, 1880-1914

• Born in Breslau, September 28, 1880.
• Physical Chemistry at Heidelberg, Berlin, and Breslau.
• Ph.D. in 1901 under the direction of Richard Abegg.
• Experimental work at the Kaiserliches Gesundheitsamt Berlin, William Ramsey's Laboratory (London) and Walther Nernst's Institute (Berlin).
• Privatdozent in Physical Chemistry in October 1905.
• Abegg's assistant at Breslau (1905-1910).
• Ladenburg's retirement (1909).
• Abegg's death in a balloon accident (1910).
• Professor of Physical Chemistry in Breslau (1910-1914).
• Department director in Fritz Haber's Institute.
• Explosion in his laboratory, December 17, 1914.
The problem of the chemical equilibrium

Step 1: Classical Theory

- A chemical reaction is at equilibrium when it occurs in both directions at the same rate (kinetic equilibrium).
- One must know the equilibrium constant $K$, which depends on the concentrations or the partial pressures of reagents and products (mass-action law).
- Alternatively one must know the maximum affinity, or maximum work (or, today, the free energy).
- Classical thermodynamics provides a relation between max work, heat of reaction and temperature (Gibbs-Helmholtz equation). An integration constant remains undetermined.
The problem of the chemical equilibrium

Step II: The Heat Theorem

• In 1906 the Nernst theorem determines the asymptotic behavior of heat of reaction and affinity.

• Consequently, the integration constant of the Gibbs-Helmholtz equation is set to zero.

• However, the theorem held for solids and liquids only (substances that can be cooled down to zero without condensation).

• The chemical equilibrium in gases remains open.
The problem of the chemical equilibrium

Step III: Applying the theorem to gases

• Fix your attention on a vapor (considered as an ideal gas) in equilibrium with a condensate phase (liquid or solid).

• There is a thermodynamic law expressing the pressure of the vapor. Nernst dubbed the integration constant of this law ‘chemical constant’.

• From the Nernst theorem it follows that if one knows the chemical constants of the gases, it is possible to solve completely the van’t Hoff equation and to find the equilibrium constant for each reaction.

• Thus, the problem of the chemical equilibrium in gaseous reactions is reduced to measure the chemical constants.
The problem of the chemical equilibrium

Step IV: Determining the chemical constants

• The experimental determination of the chemical constants via vapor pressure was very difficult.

• About 1911 very few constants were known.

• Alternative: one can apply the second principle to the vapor-condensate system and find out a relation between chemical constant and the entropy constant.

• Thus, if one knows a theoretical expression for the entropy constant, one can calculate the chemical constant as well.
• Kinetic theory: not collisions and mechanic laws, but thermodynamic properties traced back to the allocation of the molecules into cells (order and disorder).

• Planck’s quantum theory of radiation shows that kinetic procedures works well in other fields.

• To these ingredients Sackur adds his peculiar concept of probability to get a quantum understanding of chemical equilibrium defined kinetically.

June-October 1911
The entropy constant and the quantum gas theory

Statistical Mechanics

\[ S = k \log W \]
\[ = k \log \frac{N!}{\prod n_i!} \]
\[ = kN \log N - k \int f \log f d\sigma - kN \log d\sigma \]
\[ = \frac{3}{2} R \log T + R \log V + R \left[ \frac{3}{2} + \log \left( \frac{2 \pi R}{mN} \right)^{3/2} \cdot \frac{1}{d\sigma} \right] \]

Classical Thermodynamics

\[ S = \frac{3}{2} R \log T + R \log V + S_0 \]

\[ S_0 = R \left[ \frac{3}{2} + \log \left( \frac{2 \pi R}{mN} \right)^{3/2} \cdot \frac{1}{d\sigma} \right] \]

The elementary cell determines the entropy constant as well as the chemical constant, therefore must have a universal value.
The entropy constant and the quantum gas theory

• In this first paper Sackur does not assume a quantum volume for the elementary region.

• He confines himself to study the applications of the statistical procedure (mass-action law for iodine) and the physico-chemical properties of the elementary region.

• In particular, he finds out the the elementary volume depends on the total number of molecules (because entropy must be an extensive quantity): this point influenced Planck.
The entropy constant and the quantum gas theory

Extension of the theory

• A probabilistic interpretation of the quantization.
• Entropy and chemical constants for the monoatomic gas.
• Extension to the diatomic and triatomic gas (quantization of the rotational energy).
• Calculation of the equilibrium constant for many substances: generally good results, problems with more complex molecules like CO₂.

October 1912

Massimiliano Badino & Bretislav Friedrich
Putting the Quantum to Work
The entropy constant and the quantum gas theory

Quantizing the oscillators

• Let’s a set of oscillators be given. What is the probability that an oscillator has energy in the interval \((E, E+\Delta E)\)?

• The probability is defined as the fraction of oscillators in that cell counted by an ideal observer that observes the system for a time \(\Delta t\).

• This probability depends on the energy, the width of the energy cell, and on \(\Delta t\), \(w = f(E, \Delta E, \Delta t)\).

• He assumes that \(\Delta E\Delta t = h\) (universal constant).

• The observation time must be fixed, otherwise the observer will count all energy values infinitely many times (the oscillators behave “ergodically”).

• The fixed time must be the period of the oscillator, therefore \(\Delta t = \tau\), \(\Delta E = h\nu\).
The entropy constant and the quantum gas theory

The quantum is a consequence of the probabilistic formalism and the kinetic scheme

"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."

---

1) Ramsey u. Travers, 1. c.
The entropy constant and the quantum gas theory

Quantizing the gas

• Sackur divides the total volume $V$ into subvolumes $V/N$ defined by the ‘average distance’ between the molecules.

• In this case the observation time is the time necessary to cover this average distance given the average velocity.

• The reciprocal of this time is the frequency to quantize the gas.

• This technique yields the entropy extensivity as well because the entropy of the whole gas is understood as the sum of the entropies calculated for each subvolume.
The Theory of Gas Degeneracy

• Around 1912-1913 physicists turn their attention to the behavior of gases at very low temperature.

• The most popular assumption is that near absolute zero the gas behaves like a Debye solid.

• Different ways to fix the characteristic frequency.

• Some use the zero-point energy, some don’t.
The Theory of Gas Degeneracy

- One of the first theories to introduce a degeneracy parameter.
- He works on a general equation of state by combining the quantum with the van der Waals equation.
- During the period at the KWI he carries out measurements of PV and finds good qualitative agreement for hydrogen and helium.
- His theory shows that the quantum effects turn up at very low temperature and are very small (contrary to Nernst’s for example).
Fritz Haber: The hypothesis by which the theoretical result has been obtained is that the role played by the resonator frequency in Planck’s theory, is here played by a reciprocal time defined as the ratio between the average molecular velocity and the average distance between the molecules. Do you relate this hypothesis to a specific physical mechanism?

Otto Sackur: No. I would like to conceive this hypothesis only as a dimensional consideration.
• There are two axes of Sackur’s work 1911-1914:

  (1) Exploring a constellation of intertwined problems (kinetic theory, quantum theory, Nernst theorem, thermodynamics, physical chemistry).

  (2) Getting effective tools out of this exploration to be applied to the problems of physical chemistry, especially equilibrium.

• That is: Sackur was not driven by a strong research program and did not have foundational aims, he was more interested in putting the quantum to work.
Conclusions

What lessons does this story teach us?

• If we look at lesser figures of the scientific community of 1910s, we realize that much work stemmed from the interaction between a ‘high level’ quantum physics and specific backgrounds, priorities, resources coming ‘from below’. Sackur was clearly inspired by the style of Planck and Einstein, but then combined those abstract ideas with his pragmatic agenda.

• In 1910s quantum physics meant different things for different people and it is important to highlight these differences. For instance, Sackur understood the quantum hypothesis as a sharpening of the probability concept, therefore as a more effective tool to do things that could be previously done by statistical mechanics.