This Month in Physics History

September, 1911–The Sackur-Tetrode Equation: How Entropy Met Quantum Mechanics

Editor's note: *This month's column has been contributed by guest author Richard Williams.*

The Sackur-Tetrode Equation

$$S = N\,k\{ \ln M^{3/2}\,T^{5/2} / P + \ln [\,(2\,\pi / N_{Av}\,h^2\,)^{3/2}\,k^{5/2}\,] + 5/2\,\}$$

Early in the twentieth century, leading physicists were struggling to get a deeper understanding of the concept of entropy. Entropy is at the heart of the all-encompassing Second Law of Thermodynamics and can be used to establish the absolute temperature scale, so it needs to be fully understood. But a troubling question remained unanswered. Could its absolute value be determined, or would it always involve an unknown additive constant?

Attention began to focus increasingly on Ludwig Boltzmann's ideas. His long work on the problem is summarized in the terse epitaph, $S = k \ln W$, that is carved on his tombstone in Vienna. The equation expresses entropy, S, as the logarithm of W, the number of possible states of motion available to the atoms in a system, consistent with their energy, and multiplied by the constant, k, named for Boltzmann. However, according to classical theory, there was no limit to how close to one another, in momentum and space, the neighboring states of motion could be, and, therefore, no limit to the number of states that could exist. How then could W be enumerated to give a unique result? Thus, the question about the arbitrary additive constant.

The answer would come in two separate articles in the premier German physics journal, *Annalen der Physik*, one published in September, 1911, and the other a few months later. One author was Otto Sackur, 31 years old, a rising young physical chemist at the University of Breslau. The other was Hugo Tetrode, 17 years old, the precocious son of the president of the Dutch National Bank. Both focused on how to count the number of possible distinguishable states of motion of the atoms of a monatomic gas. In similar, but not identical, analyses, they argued that the number of allowed states in a given energy range depended on how close the states of motion could get to one another–in position and momentum, for example. They considered pairs of coordinates that define the motion of atoms, either momentum and position, or energy and time. If a lower limit existed for the possible size of the elements of the space representing the pair of coordinates, this would give an upper limit to the magnitude of W, and allow a definite count to be made.

Tetrode started with an equation from the classical statistical mechanics of J. Willard Gibbs. He required the product of the elements, momentum–position, to be not smaller than Planck's constant. Sackur adhered more to the style of Max Planck's school of thermodynamics. By similar reasoning, he limited the spacing of the allowed states for the elements, energy–time. This, together with Boltzmann's Equation, gave them an expression for the absolute entropy, the Sackur-Tetrode Equation.

Their equation can be used today without modification to calculate the standard entropy for ideal monatomic gases. Knowing only the temperature, pressure, and atomic weight of the atoms, an extremely simple calculation gives the entropy value so accurately that the calculated value is preferred to experimental values in tabulations of best values of thermodynamic data, such as the *CRC Handbook of Chemistry and Physics*.

After his work on this problem, Tetrode wrote some other theoretical papers, but none achieved comparable recognition. He lapsed into scientific obscurity, little remembered even among the community of Dutch physicists. In 1932, his compatriot, the physicist H.G.B. Casimir, spent a year as an assistant to Wolfgang Pauli at the Technische Hochschule in Zurich. Once, Pauli goaded him, "You Dutch people are strange birds. You have the example of Tetrode. He has done outstanding work, but no one knows about him, and it seems that no one wants to know." Casimir realized that he, too, knew little about Tetrode's life, and he began to learn more about it. In 1984 he wrote an article summarizing Tetrode's life, entitled, "A Forgotten Genius." Tetrode's higher education was brief, obviously at 17 years of age, when he wrote his article for *Annalen*, but also, later, his education was irregular for a scientist. He spent 1912 at the University in Leipzig, but apparently attended few lectures and did not take the usual exams. He corresponded with the major Dutch physicists at times, but did not form lasting scientific relationships. Nor did he cultivate those who might advance his scientific career. At one point, Albert Einstein and Paul Ehrenfest called at his home, but the maid told them that he could not receive them. He died of tuberculosis in 1931.

Sackur's career advanced more along the normal course for a scientist. After his doctorate from the University of Breslau, he worked there with Rudolph Ladenburg, then in London with William Ramsay, and finally in Germany with Walther Nernst, whose heat theorem was at the center of efforts to resolve the concept of absolute entropy, leading eventually, with some help from the work of Sackur and Tetrode, to the Third Law of Thermodynamics. Sackur wrote well-received books on thermodynamics, and in 1914 he joined Fritz Haber's prestigious Institute in Berlin. Haber's reputation at the time was golden, after his stunning achievement of the fixation of nitrogen from the air to form ammonia. It would bring him the Nobel Prize. His reputation began to suffer when he led Germany's project to use poison gas as a weapon in World War I. He focused the Institute's work on this project, bringing in Sackur, James Franck, and others. In late 1914, Sackur was killed in a lab explosion, prematurely ending a promising career. But this was not all. Haber's wife, Clara Immerwahr, was a close personal friend of Sackur. She opposed Haber's poison gas work on moral grounds and had long protested bitterly. When she learned of Sackur's death, from what she saw as coerced work on an immoral project, she was inconsolable. Finally, distraught, she committed suicide, using her husband's service pistol, completing a tragedy of Shakespearean dimensions.

Otto Sackur and Hugo Tetrode died too young, victims of the scourges of their time, tuberculosis and war. Despite their disparate backgrounds, they, like Boltzmann, left an equation as an epitaph, one that endures and joins them together.

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