Sackur-Tetrode equation

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The Sackur-Tetrode equation is important historically, because it suggests quantization (and a value for Planck's constant h) based solely on experimental work in thermodynamics. The result provides a basis for quantum theory that is independent of Planck's first conception of it, which he developed in the theory of blackbody radiation, and from Einstein's conception of quantization based on the photoelectric effect.

The **Sackur–Tetrode equation** is an expression for the entropy of a monatomic classical ideal gas which incorporates quantum considerations which give a more detailed description of its regime of validity. The Sackur–Tetrode equation is named for Hugo Martin Tetrode (1895–1931) and Otto Sackur (1880–1914), who developed it independently as a solution of Boltzmann's gas statistics and entropy equations, at about the same time in 1912.

1. Calculation of $Z_{C1}(\beta)$

Now we calculate the partition function (canonical ensemble) using the density of state for the one particle system

$$
\begin{aligned}
Z_{C1}(\beta) &= \sum_{\boldsymbol{k}} \exp(-\beta\varepsilon_{\boldsymbol{k}}) \\
&= \frac{V}{(2\pi)^3}\int d\boldsymbol{k}\exp(-\beta\varepsilon_{\boldsymbol{k}}) \\
&= \frac{V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk\exp(-\frac{\beta\hbar^2k^2}{2m}) \\
&= \frac{V}{2\pi^2}\sqrt{\frac{\pi}{2}}\frac{1}{\hbar^3}\left(\frac{m}{\beta}\right)^{3/2} \\
&= V\left(\frac{mk_BT}{2\pi\hbar^2}\right)
\end{aligned}
$$

2. *N* particle system (identical case)

The difficulty encountered in the Gibbs paradox is due to the treatment of the gas molecules as individually distinguishable. The interchanging positions of two identical molecules would lead to a physically distinct state of the gas. This is not true. In fact, if we treat the gas by quantum mechanics, the molecules would have to be regarded as completely indistinguishable.

The distinguishability of the molecules must be taken into account explicitly in calculating the partition function. This can be done by dividing the classical partition function by the permutation $N!$.

$$
\begin{aligned}
Z_C(\beta) &= \frac{1}{N!}\left[Z_{C1}(\beta)\right]^N \\
&= \frac{V^N}{N!}[\frac{1}{2\pi^2}\sqrt{\frac{\pi}{2}}\left(\frac{m}{\hbar^2\beta}\right)^{3/2}]^N \\
&= \frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2} \\
&= \frac{V^N}{N!}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3N/2} \\
&= \frac{V^N}{N!}\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}
\end{aligned}
$$

Note that

$$
\frac{1}{2\pi^2}\sqrt{\frac{\pi}{2}} = \sqrt{\frac{1}{8\pi^3}} = \frac{1}{(2\pi)^{3/2}}, \qquad \hbar = \frac{h}{2\pi}
$$

The Helmholtz free energy:

$$
\begin{aligned}
F &= -k_BT\ln Z_C(\beta,T,V) \\
&= -k_BT[N\ln V - \ln N! + \frac{3N}{2}\ln T + \frac{3N}{2}\ln(\frac{2\pi mk_B}{h^2})] \\
&= -k_BT[N\ln V - N\ln N + N + \frac{3N}{2}\ln T + \frac{3N}{2}\ln(\frac{2\pi mk_B}{h^2})] \\
&= -Nk_BT[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln(\frac{2\pi mk_B}{h^2})]
\end{aligned}
$$

or

$$
F = -Nk_BT[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln(\frac{2\pi mk_B}{h^2})]
$$

$\ln Z_C(\beta,T,V)$ is obtained as

$$
\ln Z_C(\beta,T,V) = N[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln(\frac{2\pi mk_B}{h^2})]
$$

The average energy

$$\begin{aligned} U &= -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V \\ &= k_B T^2 \left(\frac{\partial}{\partial T}\ln Z\right)_V \\ &= -\left(\frac{\partial}{\partial \beta}\ln Z\right)_V \\ &= \frac{3}{2} N k_B T \end{aligned}$$

or

$$U = \frac{3}{2} N k_B T$$

The heat capacity at constant volume:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B$$

For $N = N_A$, we have $C_V = \frac{3}{2} R$, where R is the gas constant. The heat capacity at constant pressure is

$$C_P = Cv + R = \frac{5}{2} R, \qquad \text{(Mayer's relation)}$$

The entropy S is

$$\begin{aligned} S &= \frac{E - F}{T} \\ &= \frac{3}{2} N k_B + N k_B [\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln(\frac{2\pi m k_B}{h^2})] \\ &= N k_B [\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(\frac{2\pi m k_B T}{h^2}) + \frac{5}{2}] \end{aligned}$$

or

$$S = Nk_B[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(\frac{2\pi m k_B T}{h^2}) + \frac{5}{2}]$$ (Sackur-Tetrode equation)

The pressure P is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{V}$$

or

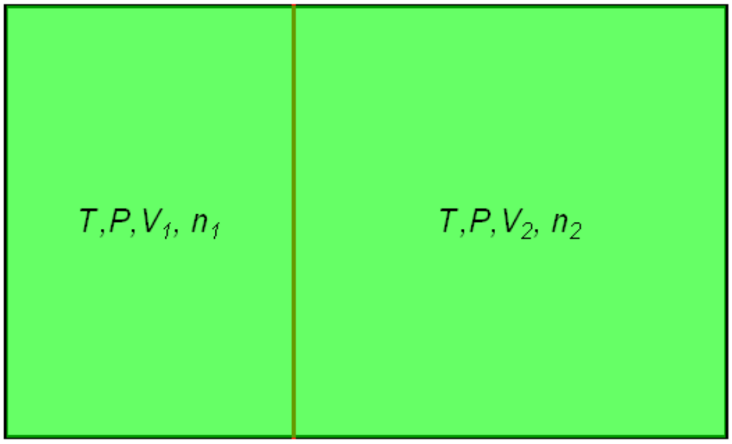
$$PV = Nk_B T$$

3. Gibbs paradox

We need to use the Sackur–Tetrode equation for the identical gases

$$S = Nk_B[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(T) + C]$$

where C is a constant, and $N = nN_A$. The entropy of the system indeed becomes a true extensive quantity. Thus the very root of the trouble has been eliminated by the recipe of Gibbs.



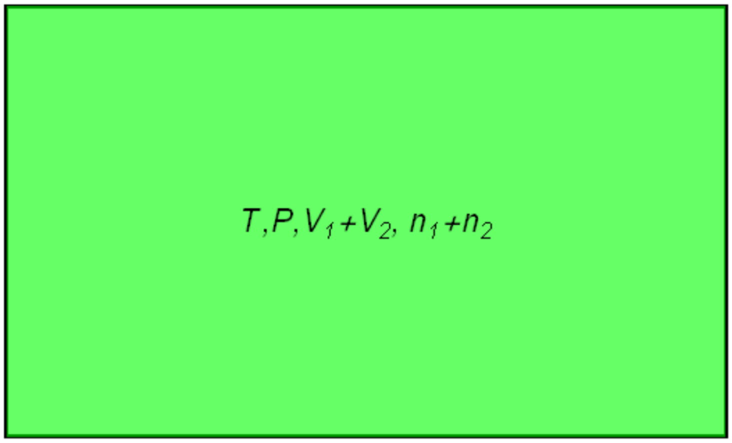


Fig. The initial state before mixing and the final state after mixing.

The entropy in the initial state before the mixing

$$\begin{aligned}
S_i &= n_1R[\ln\left(\frac{V_1}{n_1N_A}\right)+\frac{3}{2}\ln(T)+C] \\
&\quad + n_2R[\ln\left(\frac{V_2}{n_2N_A}\right)+\frac{3}{2}\ln(T)+C] \\
&= n_1R[\ln\left(\frac{RT}{PN_A}\right)+\frac{3}{2}\ln(T)+C] \\
&\quad + n_2R[\ln\left(\frac{RT}{PN_A}\right)+\frac{3}{2}\ln(T)+C] \\
&= (n_1+n_2)R[\ln\left(\frac{k_BT}{P}\right)+\frac{3}{2}\ln(T)+C]
\end{aligned}$$

since $PV_1 = n_1RT$ and $PV_2 = n_2RT$

$$S_i = n_1R[\ln\left(\frac{V_1}{n_1N_A}\right)+\frac{3}{2}\ln(T)]+C$$

The entropy in the final state after the mixing is

$$
\begin{aligned}
S_f &= (n_1 + n_2)R[\ln\left(\frac{V_1 + V_2}{(n_1 + n_2)N_A}\right) + \frac{3}{2}\ln(T) + C] \\
&= (n_1 + n_2)R[\ln\left(\frac{RT}{PN_A}\right) + \frac{3}{2}\ln(T) + C] \\
&= (n_1 + n_2)R[\ln\left(\frac{k_B T}{P}\right) + \frac{3}{2}\ln(T) + C]
\end{aligned}
$$

since $P(V_1 + V_2) = (n_1 + n_2)RT$. So we have

$$S_i = S_f .$$

The Gibbs paradox is no longer a paradox. No entropy changes

4. Comment by Huang

Gibbs resolved the paradox in an empirical fashion by postulating that we have made an error in calculating the partition function. Gibbs assumed that correct answer is $N!$ times smaller than we thought it was. It is not possible to understand classically why we must divide $(Z_{C1})^N$ by $N!$ to obtain the correct counting of states. The reason is inherently indistinguishable in the following sense. A state of the gas is described by an *N*-particle wave function, which is either symmetric or antisymmetric with respect to the interchange of any two particles. A permutation of the particles can at most change the wave function by a sig, and it does not produce a new state of the system, From this fact it seems reasonable that we should divide $(Z_{C1})^N$ by $N!$.

5. Calculation of entropy using the Sackur-Tetrode equation

Calculation of entropy for argon, neon and helium gas at *T* = 300 K and *P* = 1 atm. We use the Sackur0Tetrode equation.

S(Kr) = 164.106 J/(K mol)	for krypton gas
$S(Ar) = 154.867$ J/(K mol)	for argon gas
$S(Ne) = 146.35$ J/(K mol)	for neon gas
$S(He) = 126.174$ J/(K mol)	for helium gas

```
Clear["Global`*"];
rule1 = {cal → 4.19, atm → 1.013 × 10^5, NA → 6.02214179 × 10^23,
   R → 8.314472, me → 9.1093821545 × 10^-31, u → 1.660538782 × 10^-27,
   eV → 1.602176487 × 10^-19, qe → 1.602176487 × 10^-19,
   kB → 1.3806504 × 10^-23, c → 2.99792458 × 10^8,
   h → 6.62606896 × 10^-34, ℏ → 1.05457162853 × 10^-34,
   mNe → 20.1797 u, mAr → 39.948 u, mHe → 4.002602 u,
   P1 → 1 atm, T1 → 300};
```

$$S1 = NA\,kB\left(\mathrm{Log}\left[\frac{kB\,T1}{P1}\right] + \frac{3}{2}\,\mathrm{Log}\left[\frac{2\,\pi\,m\,kB\,T1}{h^2}\right] + \frac{5}{2}\right);$$

```
S1 /. m → mAr //. rule1

154.867

S1 /. m → mNe //. rule1

146.35

S1 /. m → mHe //. rule1

126.174
```

6. Entropy of neon at 27.2 K (Kittel)

We consider the phase transion on Ne at $P = 1$ arm.

(i) Solid (for 0 K<T<24.55 K)

$$S_{solid} = 14.29\ \text{J/(mol K)}\ .$$

(ii) Melting point T= 24.55 K. The entropy of melting is

$$\Delta S_{melting} = \frac{335}{24.55} = 13.64\ \text{J/(mol K)}$$

(iii) Liquid (24.55<T<27.2 K)

$$S_{liquid} = 3.85 \text{ J/(mol K)}$$

(iv) Vaporization at T= 27.2 K. The entropy of vaporization is

$$\Delta S_{vaporization} = \frac{1761}{27.2} = 64.62 \text{ J/(mol K)}$$

So the experimental value of entropy of neon gas at 27.2 K at 1 atm is

$$S_{gas} = S_{solid} + \Delta S_{melting} + S_{liquid} + \Delta S_{vaporization} = 96.40 \text{ J/(mol K)} \qquad \text{(experiment)}$$

The calculate value of the entropy of neon at 1 atm at 27.2 K is

$$S_{gas} = 96.4515 \text{ J/(mol K)} \qquad \text{from Sackur-Tetrode equation)}$$

There is an excellent agreement between the experiment and theory

((**Mathematica**))

```
Clear["Global`*"];
rule1 = {cal → 4.19, atm → 1.013 × 10^5, NA → 6.02214179 × 10^23,
  R → 8.314472, me → 9.1093821545 × 10^-31, u → 1.660538782 × 10^-27,
  eV → 1.602176487 × 10^-19, qe → 1.602176487 × 10^-19,
  kB → 1.3806504 × 10^-23, c → 2.99792458 × 10^8,
  h → 6.62606896 × 10^-34, ℏ → 1.05457162853 × 10^-34,
  mKr → 83.798 u, mNe → 20.1797 u, mAr → 39.948 u,
  mHe → 4.002602 u, P1 → 1 atm};

S1 = NA kB (Log[(kB T1)/P1] + 3/2 Log[(2 π m kB T1)/h^2] + 5/2);
S1 /. m → mNe /. T1 → 27.2 //. rule1

96.4515
```

7. Entropy of Kr

From
Francisco Jos´e Pa˜nos Exp´osito

The Sackur-Tetrode equation and the measure of entropy
http://diposit.ub.edu/dspace/bitstream/2445/59903/1/TFG-Pa%C3%B1os-Exp%C3%B3sito-FranciscoJos%C3%A9.pdf

T(solid-liquid)= 115.77 K (Kr)
T(liquid=gas) = 119.93 K)Kr)

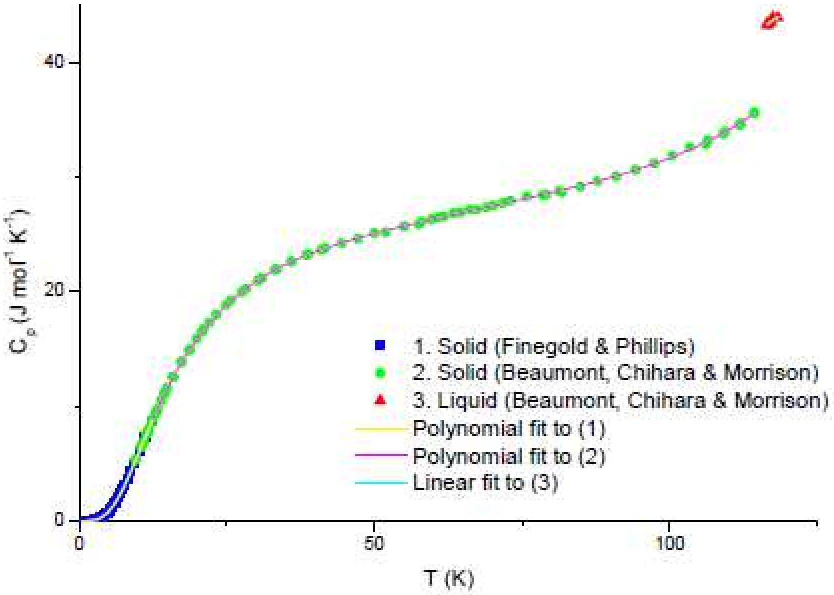


Fig. Heat capacity of krypton as a function of temperature.

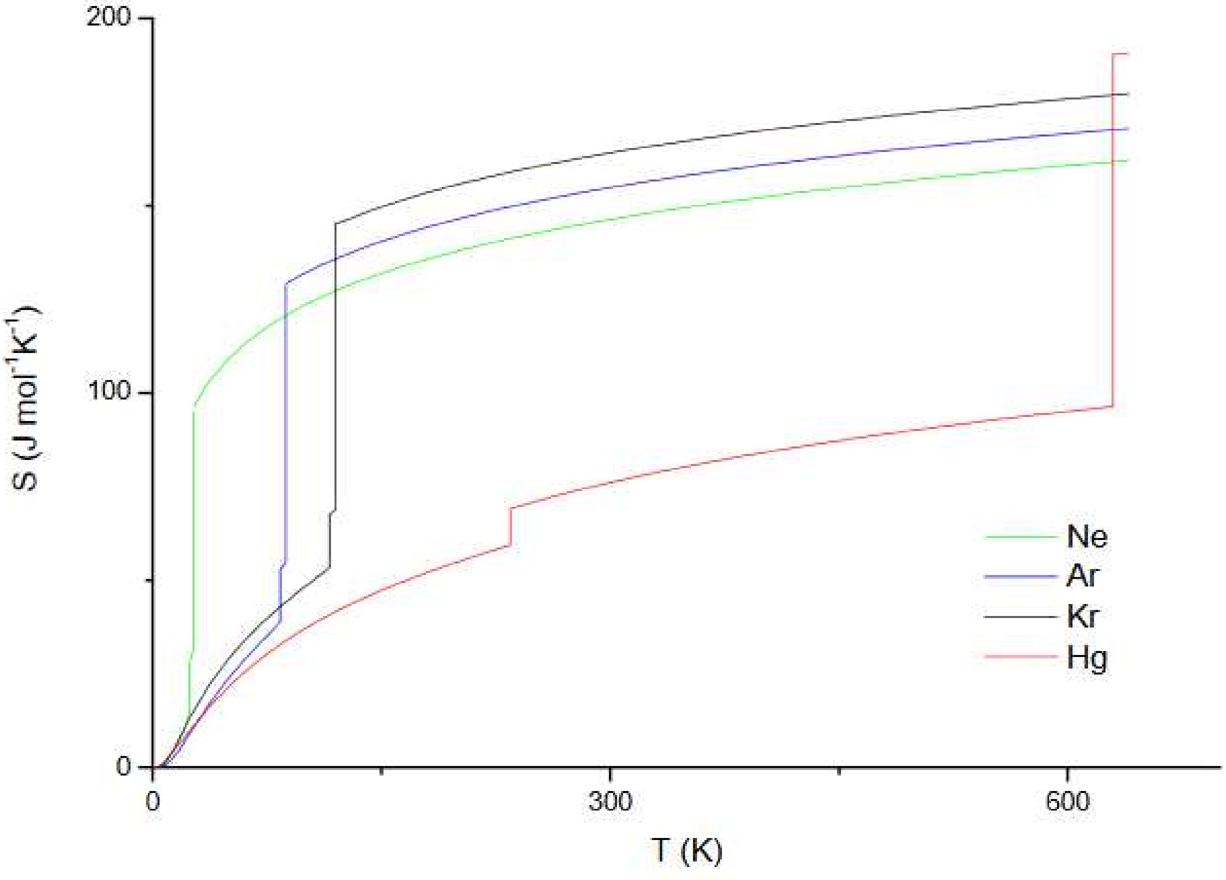


Fig. Entropies as a function of temperature for Ne, Ar, Kr, and Hg.

$$S(1K) = 0.002 \text{ J/(mol K)}$$

$$\Delta S(1K \rightarrow 12K) = 3.518 \text{ J/(mol K)}$$

$$\Delta S(12K \rightarrow 115.77K) = 49.712 \text{ J/(mol K)}$$

$$\Delta S_{melting} = \frac{1640}{115.775} = 14.166 \text{ J/(mol K)}$$

$$\Delta S(115.77K \rightarrow 119.81K) = 1.500 \text{ J/(mol K)}$$

$$\Delta S_{vaporization} = \frac{9080}{119.81} = 75.787 \text{ J/(mol K)}$$

So the experimental value of entropy of krypton gas at 119.81 K at 1 atm is

$$S_{gas}(Kr) = S_{solid} + \Delta S_{melting} + S_{liquid} + \Delta S_{vaporization} = 144.683 \text{ J/(mol K)}$$

The calculate value of the entropy of krypton at 1 atm at 119.81 K is

$$S_{gas} = 145.048 \text{ J/(mol K)}$$ from Sackur-Tetrode equation)

There is an excellent agreement between the experiment and theory.

8. Problem and solution (I)

K. Huang

Introduction to Statistical mechanics

((**Problem 3-6**))

A mixture of two ideal gasses undergoes an adiabatic transformation. The gases are labeled 1, 2. Their densities and heat capacities are denoted by n_j, C_{Vj}, C_{Pj} (j = 1, 2). Show that the pressure P and volume V of the system obey the constraint

$$PV^{\xi} = \text{constant}$$

where

$$\xi = \frac{n_1 C_{P1} + n_2 C_{P2}}{n_1 C_{V1} + n_2 C_{V2}}$$

((**Solution**))

$$dU = TdS - PdV = nC_V dT$$

$$dS = \frac{P}{T}dV + \frac{nC_V}{T}dT = Nk_B \frac{dV}{V} + \frac{nC_V}{T}dT$$

$$S = Nk_B \ln V + nC_V \ln T = n(R\ln V + C_V \ln T)$$

Using this equation

$$\begin{aligned}\Delta S &= \Delta S_1 + \Delta S_2 \\ &= [n_1 R \ln(\frac{V_f}{V_i}) + n_1 C_{V1} \ln \frac{T_f}{T_i}] + [n_2 R \ln(\frac{V_f}{V_i}) + n_1 C_{V1} \ln \frac{T_f}{T_i}] \\ &= (n_1 + n_2) R \ln\left(\frac{V_f}{V_i}\right) + (n_1 C_{V1} + n_2 C_{V2}) \ln \frac{T_f}{T_1} = 0\end{aligned}$$

or

$$\frac{(n_1 + n_2)R}{(n_1 C_{V1} + n_2 C_{V2})} \ln\left(\frac{V_f}{V_i}\right) + \ln \frac{T_f}{T_1} = 0$$

or

$$\ln \frac{T_f}{T_i} + \varsigma \ln\left(\frac{V_f}{V_i}\right) = 0$$

where

$$\varsigma = \frac{(n_1 + n_2)R}{(n_1 C_{V1} + n_2 C_{V2})}$$

or

$$TV^{\varsigma} = \text{constant}$$

Putting $PV = nRT = (n_1 + n_2)RT$

$$PV^{\xi} = \text{constant}$$

where

$$\begin{aligned}\xi &= 1 + \varsigma \\ &= 1 + \frac{(n_1 + n_2)R}{(n_1 C_{V1} + n_2 C_{V2})} \\ &= \frac{(n_1 + n_2)R + (n_1 C_{V1} + n_2 C_{V2})}{n_1 C_{V1} + n_2 C_{V2}} \\ &= \frac{n_1 C_{P1} + n_2 C_{P2}}{n_1 C_{V1} + n_2 C_{V2}}\end{aligned}$$

APPENDIX-I

APS (American Physical Society) News: This month in Physics History

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

https://www.aps.org/publications/apsnews/200908/physicshistory.cfm

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

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 $S = k_B \ln W$, 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_B, 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.