UWThPh-2011-34

On the 100th anniversary of the Sackur–Tetrode equation

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16 December 2011

Abstract

In 1912, Otto Sackur and Hugo Tetrode independently developed an equation for the absolute entropy of a monoatomic ideal gas. The grand achievement in the derivation of this equation was the discretization of phase space for massive particles, expressed as $\delta q \delta p = h$, where q and p are conjugate variables and h is Planck's constant. Moreover, Sackur and Tetrode succeeded in corroborating their equation by ingeniously utilizing thermodynamic data on mercury. In essence, they determined h from the equilibrium of liquid and gaseous phases of mercury and compared it with the value previously obtained by Planck from black-body radiation. In this paper we discuss the arguments leading to the derivation of the Sackur–Tetrode equation and describe also the way how they made their equation amenable to an experimental test. Doing a numerical computation similar to that of Sackur and Tetrode, we demonstrate that, with modern mercury data, Planck's constant can be determined with an accuracy of about one percent.

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1 Introduction

The formula for the absolute entropy of a monoatomic ideal gas is named after Otto Sackur and Hugo Tetrode who independently derived it in 1912 [1, 2, 3]. In classical thermodynamics the entropy of a monoatomic ideal gas is

$$S(E,V,N) = kN\left(\frac{3}{2}\ln\frac{E}{N} + \ln\frac{V}{N} + s_0\right), \tag{1}$$

where E, V and N are the kinetic energy, the volume and the number of atoms, respectively. In classical physics the constant s_0 is undetermined. The achievement of Sackur and Tetrode was to compute s_0. At first sight this does not look very exciting, however, in order to compute s_0 they had to work out the size of "elementary cells or domains" in phase space. Only with this knowledge it is possible to count the number of states in classical phase space which is a prerequisite for the computation of Boltzmann's absolute entropy given by [4, 5]

$$S = k\ln W. \tag{2}$$

In this formula, W is the number of possibilities to realize a system compatible with some given boundary conditions. Sackur and Tetrode determined the volume of phase space cells as h^n where h is Planck's constant and n is the number of degrees of freedom. Until then, h was associated mainly with photons, i.e. with massless particles. With the work of Sackur and Tetrode it became clear that Planck's constant was relevant also for massive particles. In this way h became ubiquitous in statistical physics, more than ten years before the advent of quantum mechanics.

This was an amazing result because a priori Planck's constant in the expression $h\nu$ for the energy of a photon has nothing to do with the phase-space volume associated with massive particles. This connection was clarified only later by quantum mechanics. We want to stress that the elegance of the work of Sackur and Tetrode derives from the combination of theoretical considerations and usage of experimental data with which they were able to lend credibility to their result. They did so by successfully applying their equation to the then available data on mercury, whose vapor is monoatomic and behaves in good approximation as an ideal gas,

Below we list the articles of Sackur and Tetrode and the achievements therein, written in the course of the development of their equation. The titles are literal translations from the German titles.

i. O. Sackur, *The application of the kinetic theory of gases to chemical problems* [6] (received September 1911): In this paper Sackur develops the formula for the entropy S of a monoatomic ideal gas as a function of the size of the elementary cell.

ii. O. Sackur, *The meaning of the elementary quantum of action for gas theory and the computation of the chemical constant* [1] (no "received date", must have been written in spring 1912): Here Sackur postulates that the size of the elementary cell is h^n and obtains the absolute entropy S of a monoatomic ideal gas. Using S, he computes the vapor pressure over a solid and makes a comparison with data on neon and argon. The numerical results, are, however, not completely satisfying.

iii. H. Tetrode, *The chemical constant and the elementary quantum of action* [2] (received March 7, 1912): Tetrode gives an illuminating derivation of S, assuming that the size of the elementary cell is $(zh)^n$. He fits the parameter z by using data on the vapor pressure of liquid mercury. Due to some numerical mistakes he obtains $z \approx 0.07$.[1]

iv. H. Tetrode, erratum to *The chemical constant and the elementary quantum of action* [2] (received July 17, 1912): Tetrode corrects the numerics and obtains now $z \sim 1$. He acknowledges the papers [1, 6] of Sackur by noting that the formula for S has been developed by both of them at the same time. More precisely, he refers to a formula for the so-called "chemical constant" pioneered by Nernst [7], which we will define later.

v. O. Sackur, *The universal meaning of the so-called elementary quantum of action* [3] (received October 19, 1912): He obtains good agreement ($\pm 30\%$) with the data on the vapor pressure of mercury and comments on the paper by Tetrode.

The paper is organized as follows. In section 2 we describe the different approaches of Sackur and Tetrode to derive their equation and add some comments. Since historically the corroboration of the Sackur–Tetrode equation by using data on the vapor pressure of (liquid) mercury was crucial, we give a detailed account of it in section 3. Moreover, we redo the numerics by using modern mercury data in section 4 and obtain a reasonably good value of Planck's constant. In section 5 our conclusions are presented. A derivation of Kirchhoff's equation, which is used in the numerical computation, is found in the appendix.

2 The Sackur–Tetrode equation

2.1 Tetrode's derivation

The starting point of Tetrode's reasoning is the entropy formula (2) which should, according to Nernst's heat theorem [7], give the correct value of the entropy without any additive constant. Then he considers a system with n degrees of freedom and phase space coordinates $q_1, \ldots, p_n$, for which he connects W with the number of configurations of phase space points. In order to have a finite entropy, it is necessary to discretize phase space, which Tetrode does by introducing "elementary domains" of volume

$$\delta q_1 \, \delta p_1 \cdots \delta q_n \, \delta p_n = \sigma = (zh)^n, \tag{3}$$

where h is Planck's constant and z is a dimensionless number. Then he argues that, in a system of ν identical particles, configurations which are related only by exchange of particles should not be counted as different. Therefore, denoting by W' the number of configurations in phase space, the entropy for such a system is

$$S = k \ln \frac{W'}{\nu!}. \tag{4}$$

[1] Actually, from Tetrode's equations (12) and (13) we would rather deduce $z \approx 0.02$.

This is to avoid the Gibbs paradox and obtain S as an extensive quantity, though Tetrode does not mention Gibbs in this context. Moving on to the monoatomic gas consisting of $\nu \equiv N$ atoms with mass m and spatial volume V, the number of degrees of freedom is $n = 3N$ and, for a given maximal energy E of the gas, the volume occupied in phase space is computed by

$$\mathcal{V}(E,V,N) = \int \mathrm{d}^3x_1 \int \mathrm{d}^3p_1 \cdots \int \mathrm{d}^3x_N \int \mathrm{d}^3p_N \quad \text{with} \quad \frac{1}{2m}\left(\vec{p}_1^{\,2} + \cdots + \vec{p}_N^{\,2}\right) \leq E. \tag{5}$$

Utilizing the gamma function, this phase space volume is expressed as

$$\mathcal{V}(E,V,N) = \frac{(2\pi m E)^{\frac{3N}{2}}\, V^N}{\Gamma\left(\frac{3N}{2}+1\right)}. \tag{6}$$

According to the arguments above, the entropy is then given by

$$S = k \ln \frac{\mathcal{V}(E,V,N)}{(zh)^{3N} N!}. \tag{7}$$

In the last step Stirling's formula is used, to wit the approximations

$$\ln N! \simeq N(\ln N - 1) \quad \text{and} \quad \ln \Gamma\left(\frac{3N}{2}+1\right) \simeq \frac{3N}{2}\left(\ln \frac{3N}{2} - 1\right) \tag{8}$$

for large N. This leads to Tetrode's final result

$$S(E,V,N) = kN\left(\frac{3}{2}\ln\frac{E}{N} + \ln\frac{V}{N} + \frac{3}{2}\ln\frac{4\pi m}{3(zh)^2} + \frac{5}{2}\right) \tag{9}$$

for the entropy of a monoatomic ideal gas.

This derivation is of an amazing lucidity. No wonder that 100 years later it is one of the standard methods in modern textbooks. The only amendment to Tetrode's derivation comes from quantum mechanics which fixes the size of the elementary domain to h^n, i.e. requires $z = 1$; the latter result was obtained by Tetrode through a fit to the data of the vapor pressure of mercury.

From equation (9) with $z = 1$ we infer that the constant s_0 of equation (1) is given by

$$s_0 = \frac{3}{2}\,\ln\frac{4\pi m}{3h^2} + \frac{5}{2}. \tag{10}$$

2.2 Sackur's derivation

It is much harder to follow Sackur's line of thoughts. Here we sketch the derivation of the entropy formula in [3], because there he gives the most detailed account of his derivation. In this paper he first derives Planck's law of radiation by considering a system of radiators, before he moves on to the ideal monoatomic gas. In both cases Sackur defines a time interval τ in which the system is monitored and an energy interval $\Delta\varepsilon$ for the discretization of energy. For the gas the time τ is assumed to be so small that during this time collisions between atoms can be neglected. Therefore, during the time interval

of length τ, each of the kinetic energies associated with the three directions in space, ε_x, ε_y, ε_z, of every atom can be assumed each to lie in a well-defined energy interval of length $\Delta\varepsilon$. In other words, Sackur imagines a three-dimensional energy space with x, y and z-axis referring to the kinetic energies ε_x, ε_y and ε_z, respectively, and with energy unit $\Delta\varepsilon$ on every axis. In this way, the energy space is divided into cubes of volume $(\Delta\varepsilon)^3$ and the kinetic energy of every particle lies, during the time interval τ, in a well-defined cube. If the i-th cube is defined by $n_k\Delta\varepsilon \leq \varepsilon_k < (n_k+1)\Delta\varepsilon$ $(k = x, y, z)$ with integers n_k, the energy ε_i associated with this cube is, for instance, given by

$$\varepsilon_i = (n_x + n_y + n_z)\Delta\varepsilon. \tag{11}$$

If in the i-th cube the number of atoms is denoted by N_i, such a number will be the smaller the smaller τ and $\Delta\varepsilon$ are. Consequently, Sackur makes the Ansatz

$$N_i = N f(\varepsilon_i)\,(\tau\Delta\varepsilon)^3\,, \tag{12}$$

which corresponds to the lowest order in an expansion in $\tau\Delta\varepsilon$ because there is one factor $\tau\Delta\varepsilon$ for each axis. In this Ansatz, N is the total number of atoms. The number of possibilities to distribute a total of N atoms into r energy cubes is given by[2]

$$W = \frac{N!}{N_1!N_2!\cdots N_r!} \quad \text{with} \quad N = N_1 + N_2 + \cdots + N_r. \tag{13}$$

According to Boltzmann and Planck, the entropy is obtained by

$$S = k\ln W = kN\ln N - k\sum_i N_i \ln N_i \tag{14}$$

for large numbers N_i and the most probable distribution is given by the maximum of S under the conditions

$$\sum_i N_i = \sum_i N f(\varepsilon_i)\,(\tau\Delta\varepsilon)^3 = N, \quad \sum_i N_i\,\varepsilon_i = \sum_i N f(\varepsilon_i)\,(\tau\Delta\varepsilon)^3\,\varepsilon_i = E. \tag{15}$$

This procedure resembles the derivation of the canonical ensemble. However, the difference is that in this case the *total* energy of the system is divided into energy intervals of length $\Delta\varepsilon$ whereas Sackur distributes the energies of *single* particles among cubes in energy space. Finding the maximum of S of equation (14) amounts to computing the stationary point of the functional $-\int \mathrm{d}\varepsilon f\ln f$, under the conditions of a fixed total number of atoms and a fixed energy, where the function f is defined in the Ansatz (12). The sought for stationary point is obtained from the maximum of

$$\Phi(f,\varepsilon) = -f\ln f + (\alpha'+1)\,f - \beta\varepsilon f, \tag{16}$$

where the parameters α' and β are Lagrange multipliers:

$$\frac{\partial\Phi}{\partial f} = -\ln f + \alpha' - \beta\varepsilon = 0 \quad \Rightarrow \quad f(\varepsilon) = e^{\alpha'-\beta\varepsilon} = \alpha e^{-\beta\varepsilon} \quad \text{with} \quad \alpha = e^{\alpha'}. \tag{17}$$

[2]Note that the usage of this formula implies that Sackur assumes that the atoms are *distinguishable* because for indistinguishable atoms one would simply have $W = 1$, for the reason that then every decomposition of N into a sum $N_1 + \cdots + N_r$ would correspond to a *single* state.

Eventually, Sackur arrives at the Boltzmann distribution

$$N_i = N\alpha e^{-\beta\varepsilon_i} \tag{18}$$

for the number of atoms in an energy box. Plugging this expression into formula (14) for the entropy and using equation (15), the simple expression

$$S = -3kN\ln(\tau\Delta\varepsilon) - kN\ln\alpha + k\beta E \tag{19}$$

for the entropy ensues.

In equation (19) there are three unknowns: $\tau\Delta\varepsilon$, α and β. At this point, referring to Sommerfeld [8], Sackur states that the smallest action that can take place in nature is given by Planck's constant h. Therefore, he makes the bold assumption that

$$\tau\Delta\varepsilon = h, \tag{20}$$

which he had already made successfully for the derivation of Planck's law of radiation in the same paper. The other two parameters are in principle determined by equation (15). Sackur then argues that, for simplicity, in the two integrals of equation (15) summation can be replaced by integration. For this purpose he makes the following step:

$$\varepsilon_k = \frac{p_k^2}{2m} \quad (k = x, y, z) \quad \Rightarrow \quad \mathrm{d}\varepsilon_k = \frac{p_k}{m}\,\mathrm{d}p_k = \frac{\bar{x}_k}{\tau}\,\mathrm{d}p_k, \tag{21}$$

where the $\bar{x}_k$ are the average Cartesian components of the distance covered by the atoms during the time τ. Then Sackur connects the product of the three average distances with the volume V of the gas by equating it with the volume per atom:

$$\bar{x}\bar{y}\bar{z} = \frac{V}{N}. \tag{22}$$

It is hard to understand why this equation should hold, but with equations (21) and (22) he effectively introduces an integration $\mathrm{d}^3x\,\mathrm{d}^3p$ in phase space.[3] Moreover, since Sackur nowhere introduces the concept of indistinguishable atoms, he needs the factor $1/N$ in equation (22) for avoiding Gibbs paradox, as we will see shortly. So he ends up with

$$\tau^3\mathrm{d}\varepsilon_x\mathrm{d}\varepsilon_y\mathrm{d}\varepsilon_z = \frac{V}{N}\,\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \tag{23}$$

for the integration in equation (15) and obtains

$$1 = \frac{\alpha V m^3}{N}\left(\frac{2\pi}{m\beta}\right)^{3/2} \quad \text{and} \quad E = \frac{3\alpha V m^3}{2\beta}\left(\frac{2\pi}{m\beta}\right)^{3/2}. \tag{24}$$

These two equations are easily solved for α and β. Plugging the solution

$$\beta = \frac{3E}{2N} \quad \text{and} \quad \alpha = \frac{N}{V}\left(\frac{3N}{4\pi mE}\right)^{3/2} \tag{25}$$

[3]These manipulations introduce an ambiguity in the integration boundaries: In $\mathrm{d}\varepsilon_k$ the integration is from zero to infinity, while in $\mathrm{d}p_k$ Sackur integrates from minus infinity to plus infinity.

into equation (19), Sackur arrives at his final result

$$S(E,V,N) = kN\left(\frac{3}{2}\ln\frac{E}{N} + \ln\frac{V}{N} + \frac{3}{2}\ln\frac{4\pi m}{3h^2} + \frac{3}{2}\right). \tag{26}$$

Comparing this expression with Tetrode's result (9), we see that there is a difference in the last term in parentheses; Sackur has 3/2 while while Tetrode has the correct number 5/2. Thus

$$S(z=1)|_{\text{Tetrode}} - S|_{\text{Sackur}} = kN, \tag{27}$$

which Sackur observed and commented upon in [3]. It is interesting to note that in his previous paper [1] Sackur actually had the correct number. It is kind of amazing that Sackur, with his line of reasoning, arrives at nearly the correct result, being off only by kN. This difference is indeed important for the comparison of the entropy formula with the data from vapor pressure of mercury [2, 3]; anticipating equation (38), we see that a determination of Planck's constant with Sackur's formula would result in a value which is too low by a factor of $e^{-1/3} \approx 0.72$ where e is Euler's number.

We conclude this section with a comment on equation (22). We know that S is an extensive quantity, i.e. $S(\zeta E, \zeta V, \zeta N) = \zeta S(E,V,N)$ holds for all $\zeta > 0$. If the factor $1/N$ had been absent in equation (22), we would have to replace V by NV in equation (26); but then S would not be an extensive quantity, as one can easily check.

2.3 Discussion

Let us present here, in particular, for comparison with Sackur's treatment, the derivation of the entropy of a monoatomic ideal gas by using the canonical partition function Z. Since we are dealing with non-interacting particles, Z is given by

$$Z = \frac{Z_1^N}{N!}, \tag{28}$$

where Z_1 is the partition function of a single particle. The factor $1/N!$ is present to take into account that the particles are indistinguishable. Then the entropy is given by

$$S = k\left(\ln Z + \beta E\right) = kN\left(\ln\frac{Z_1}{N} + 1 + \frac{\beta E}{N}\right), \tag{29}$$

where E is the total energy of the N particles and $\beta = 1/(kT)$. Furthermore, Stirling's formula has been used to replace $\ln N!$ by $N(\ln N - 1)$. If E/N does not depend on N, which is the case for the ideal gas, this equation displays the full dependence on N. For the monoatomic ideal gas, in the classical approximation, the single-particle partition function is given by the integral

$$Z_1 = \frac{1}{h^3}\int_{\mathcal{V}} \mathrm{d}^3x \int \mathrm{d}^3p\, \exp\left(-\beta\frac{\vec{p}^{\,2}}{2m}\right) = \frac{V}{\lambda^3} \quad \text{with} \quad \lambda = \frac{h}{\sqrt{2\pi m k T}} \tag{30}$$

being the thermal de Broglie wave length. The integration domain $\mathcal{V}$ is the space taken by the gas, i.e. the container with volume V. Plugging Z_1 into equation (29) yields the desired entropy

$$S(T,V,N) = kN\left(\ln\frac{V}{\lambda^3 N} + \frac{5}{2}\right) \tag{31}$$

as a function of temperature, volume and particle number.

We compare Tetrode's and Sackur's result with the entropy formula (31) by substituting

$$E = \frac{3}{2} NkT \tag{32}$$

in equations (9) and (26).[4] We find what we have announced earlier: Tetrode's result exactly agrees with equation (31), while Sackur's result differs by kN. We can easily locate the origin of the difference. Considering the definitions of α and Z_1 and taking into account equation (15), we find that

$$\alpha = \frac{N}{h^3 Z_1}. \tag{33}$$

Insertion of this expression into equation (19) leads to the entropy (29), with the "1" within the parentheses being absent. Effectively Sackur replaces $\ln N! \simeq N(\ln N - 1)$ by $N \ln N$ in his derivation and does, therefore, not fully take into account indistinguishability of the atoms.

The entropy of the monoatomic ideal gas as a function of the pressure p instead of the volume V is obtained with the ideal-gas equation by the substitution $V = NkT/p$.

As mentioned in the introduction, Sackur and Tetrode tested their equation on mercury vapor. This element has seven stable isotopes with various nuclear spins s_k [9]. Therefore, in principle for mercury one has to add the corresponding residual entropy

$$S_{\mathrm{res}}(\mathrm{Hg}) = Nk \sum_{k=1}^{7} P_k \left(-\ln P_k + \ln(2s_k + 1)\right), \tag{34}$$

where the P_k are the isotopic abundances ($\sum_k P_k = 1$), to the Sackur–Tetrode formula. Of course, in 1912 the mercury isotopes were not known. However, as we will see in the next section, in the mercury test only the entropy difference between gaseous and liquid phases is relevant. For both phases, however, the same residual entropy is expected and thus $S_{\mathrm{res}}(\mathrm{Hg})$ of equation (34) drops out.

3 The vapor pressure of mercury and Planck's constant

How to subject the *absolute* entropy of a monoatomic ideal gas to experimental scrutiny? Sackur and Tetrode applied the following procedure. Consider the latent heat $L(T)$ of a monoatomic substance for the phase transition from the liquid to the gaseous phase. In terms of the absolute molar entropies, the latent heat is given by

$$L(T) = T\left(s_{\mathrm{vapor}}(T, \bar{p}(T)) - s_{\mathrm{liquid}}(T, \bar{p}(T))\right), \tag{35}$$

[4] In Tetrode's formula we set $z = 1$.

where $\bar{p}(T)$ denotes the pressure along the coexistence curve, i.e. the vapor pressure. If the vapor behaves in good approximation like a monoatomic ideal gas, then the Sackur–Tetrode equation in the form

$$s_{\text{vapor}} = R\left(\ln\frac{kT}{\bar{p}\lambda^3} + \frac{5}{2}\right) \tag{36}$$

with the molar gas constant R can be substituted for $s_{\text{vapor}}(T, \bar{p}(T))$. For the liquid phase, neglecting the p-dependence, the absolute entropy can be expressed as an integral over the heat capacity:

$$s_{\text{liquid}} = \int_0^T \mathrm{d}T'\,\frac{c_p(T')}{T'}. \tag{37}$$

Note that here the integration includes the solid and liquid phases, and the latent heat of melting. After insertion of s_{vapor} and s_{liquid} into equation (35), one obtains an expression for the vapor pressure:

$$\ln\bar{p}(T) = -\frac{L(T)}{RT} + \ln\frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3} + \frac{5}{2} - \int_0^T \mathrm{d}T'\,\frac{c_p(T')}{RT'}. \tag{38}$$

Similar derivations can be found in [10, 11]. Since equation (38) is a direct consequence of equation (36), it serves as a testing ground for the Sackur–Tetrode equation. For this test not only data on the vapor pressure $\bar{p}(T)$ are needed, but also data on the latent heat $L(T)$ and the heat capacity $c_p(T)$ in the condensed phase must be available. While for $\bar{p}(T)$ and $L(T)$ it is sufficient have data in a certain temperature interval, one needs to know $c_p(T)$ as a function of T down to absolute zero. In 1912 the most comprehensive set of data was available on mercury. This was utilized by Sackur and Tetrode to test their equation. In this test they followed slightly different approaches. Both employed the value of Planck's constant h as determined from black-body radiation and inserted it into equation (38). Then Sackur directly computed the vapor pressure of mercury from equation (38) and compared his results with the experimental data, whereas Tetrode replaced h in equation (38) by zh and carried out a fit of z to the data.

Now we want to delineate how Sackur and Tetrode actually performed the numerical evaluation of equation (38). We follow the exposition of Sackur in [3] because his account is sufficiently detailed and easy to follow. On the right-hand side of equation (38) we have to discuss the term with $L(T)$ and the integral. In treating the latent heat as a function of T, Sackur uses Kirchhoff's equation—see equation (A10) in the appendix. Furthermore, he assumes that in the temperature interval he considers, which is from 0° C to 360° C, the heat capacity in the liquid phase can be regarded to have the constant value c_p^{liquid}. If at a reference temperature T_1 the latent heat is L_1, then due to Kirchhoff's equation

$$L(T) = L_1 + \left(\frac{5}{2}\,R - c_p^{\text{liquid}}\right)(T - T_1). \tag{39}$$

The integral on the right-handed side of equation (38) is treated by splitting it into the part in the solid phase, the contribution of the phase transition, and the part in the liquid phase. Denoting the latent heat of melting by L_m and the melting point by T_m, this integral reads

$$\int_0^T \mathrm{d}T'\,\frac{c_p(T')}{T'} = \int_0^{T_m} \mathrm{d}T'\,\frac{c_p^{\text{solid}}(T')}{T'} + \frac{L_m(T_m)}{T_m} + c_p^{\text{liquid}}\ln\frac{T}{T_m}. \tag{40}$$

Again the approximation that the heat capacity of the liquid is temperature-independent has been used. Implicitly the additional approximation that the melting temperature T_m is independent of the pressure has been made. The final form of the vapor pressure, prepared for the numerical evaluation, is thus

$$\begin{aligned}\ln \bar{p}(T) &= -\frac{L_1 + \left(c_p^{\text{liquid}} - \frac{5}{2}R\right) T_1}{RT} + \frac{5}{2}\ln T - \int_0^{T_m} \mathrm{d}T' \, \frac{c_p^{\text{solid}}(T')}{RT'} \\ &\quad - \frac{L_m(T_m)}{RT_m} - \frac{c_p^{\text{liquid}}}{R}\ln\frac{T}{T_m} + \ln\frac{(2\pi m)^{3/2}k^{5/2}}{h^3} + \frac{c_p^{\text{liquid}}}{R}. \qquad (41)\end{aligned}$$

This equation corresponds to Sackur's equation on top of p. 82 of [3] and we have written the terms in the same order as there. We have refrained, however, from converting the natural logarithm to the logarithm to the base of ten, which was used by Sackur. As mentioned earlier, Sackur and Tetrode actually determine the *chemical constant*, defined as

$$\mathcal{C} = \frac{1}{\ln 10} \times \ln\frac{(2\pi m)^{3/2}k^{5/2}}{h^3} = \log\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}, \qquad (42)$$

from the data and compare this value of $\mathcal{C}$ with the value computed with Planck's constant obtained from black-body radiation. At that time, the chemical constant was a commonly used quantity. It appears not only in the vapor pressure but also in the law of mass action of chemical reactions in the gas phase [7]. Note that the conversion of the logarithm mentioned above brings about a division by $\ln 10 \approx 2.3026$ in many places in the equations in [2, 3].

In equation (41), in the integral over $c_p^{\text{solid}}(T)/T$ both Sackur and Tetrode use a model by Nernst [12] for the specific heat of solid mercury. This model is a kind of Einstein model [13] but is sums two frequencies, ω and 2ω. It is interesting to note that the paper of Debye concerning the Debye model [14] has a "received date" July 24, 1912, and is thus prior to Sackur's paper [3]. Actually, Sackur refers to it in [3], but only in the part concerning Planck's law of radiation; in the integration over the solid phase of mercury he uses nevertheless Nernst's model.

We conclude this section by summarizing and commenting on the approximations which lead to equation (41). In essence the following approximations have been made:

i. The vapor is treated as a classical ideal gas.

ii. The molar volume v_l of the liquid is neglected compared to the molar volume v_g of the vapor.

iii. In the liquid phase the dependence on p of the isobaric heat capacity is negligible in the considered temperature interval.

iv. There are two technical assumptions which facilitate the numerics: The temperature dependence of the heat capacity in the liquid phase is neglected and the melting temperature T_m is pressure independent.

From the first assumption it follows that the heat capacity of a monoatomic vapor is constant with the value

$$c_p^{\text{vapor}} = \frac{5}{2}\,R, \tag{43}$$

which is an important ingredient in equation (39). The thermal equation of state,

$$pV = n_m RT, \tag{44}$$

where n_m the number of moles of the gas, has been used in equation (36) and in the derivation of Kirchhoff's equation—see appendix. The second assumption, which occurs only in the derivation of Kirchhoff's equation, is well justified because the order of magnitude of the ratio of the molar volumes is $v_g/v_l \sim 10^3$. To discuss the third assumption we note that via the Gibbs potential we obtain the relation

$$\left.\frac{\partial c_p^{\text{liquid}}}{\partial p}\right|_T = -Tv\left(\alpha^2 + \left.\frac{\partial \alpha}{\partial T}\right|_p\right) \quad \text{with} \quad \alpha = \frac{1}{v}\left.\frac{\partial v}{\partial T}\right|_p, \tag{45}$$

where α is the thermal expansion coefficient. This equation leads to a linear approximation of the heat capacity with respect to the pressure:

$$c_p^{\text{liquid}}(T,p) \approx c_p^{\text{liquid}}(T,p_0) - T\left(\alpha^2 + \left.\frac{\partial \alpha}{\partial T}\right|_p\right)_{p=p_0} v(T,p_0)\,(p-p_0). \tag{46}$$

The pressure p_0 is a reference pressure. It is well known that the p-dependence of c_p for liquids is suppressed for two reasons. First of all, the product $vp \sim 1\,\text{J}\,\text{mol}^{-1}$ where v is the molar volume of the liquid and $p \sim 1\,\text{bar}$ is rather small. Secondly, also the thermal expansion coefficient α is quite small. Thus, the third assumption is very well justified. The assumption of a constant heat capacity for the liquid is not so good. For mercury it drops between the melting point at -38.84° C and 200° C by 4% [15].

4 Our fit of Planck's constant to mercury data

It is worthwhile to use the thermodynamic data on mercury available at present and employ a slight variation of the method of Sackur and Tetrode described in the previous section in order to check the accuracy with which Planck's constant can be determined in this way. We follow Tetrode's approach in replacing h by zh in equation (38). In the following we will plug in the modern meanvalue of h and determine z from the data. The best modern value of h, recommended by CODATA [16], is

$$6.62606957(29) \times 10^{-34}\,\text{J}\,\text{s} \tag{47}$$

In order to account for the slight temperature dependence of the heat capacity of liquid mercury we make the ansatz

$$c_p^{\text{liquid}}(T) = a_0 + a_1 T + a_2 T^2 \tag{48}$$

and fit the coefficients a_0, a_1 and a_2 to the input data from the table presented in [15]. In this table one can also read off that from the melting point up to a temperature of about 200° C the heat capacity of gaseous mercury agrees exactly with the ideal-gas value (43). Thus we confine ourselves to the temperature interval from −38.84° C to 200° C, in which the ansatz (48) should be sufficient. With equations (35) and (48), and taking into account Kirchhoff's equation, we obtain

$$L(T) = L_0 + \frac{5}{2}\,R(T - T_0) - a_0\,(T - T_0) - \frac{1}{2}a_1\left(T^2 - T_0^2\right) - \frac{1}{3}a_2\left(T^3 - T_0^3\right), \qquad (49)$$

while inserting equation (48) into the entropy formula (37) gives

$$s_{\text{liquid}}(T) = s_0 + a_0 \ln\frac{T}{T_0} + a_1(T - T_0) + \frac{1}{2}a_2\left(T^2 - T_0^2\right). \qquad (50)$$

As a reference temperature we take $T_0 = 298.15\,\text{K}$, which allows us to use the enthalpy of formation and the standard molar entropy from the CODATA Key Values for Thermodynamics [17]:

$$L_0 = 61.38 \pm 0.04\ \text{kJ mol}^{-1}, \quad s_0 = 75.90 \pm 0.12\ \text{J K}^{-1}\,\text{mol}^{-1}. \qquad (51)$$

The value of s_0 saves us from the non-trivial task of determining the integral in equation (37) with the boundaries $T = 0$ and $T = T_0$.

The input data for the vapor pressure of mercury we take from the table in [18]. In the legend of this table estimated uncertainties of the vapor pressure values are given, which we use in the method of least squares in order to fit the parameter z. A further input parameter is the atomic weight of mercury, $A = 200.95(2)$ [9]. The mass value for mercury is then $m = Au$ where u is the atomic mass unit. For the determination of h from mercury data we can safely neglect errors in the physical constants R, k and u.

With the above input, our best fit value for z is $\bar{z} = 1.003$ at $\chi^2_{\text{min}} = 4.2$. Since we have at disposal vapor pressure measurements at 75 temperatures [18] in the considered interval, but we determine only one parameter, the number of degrees of freedom is 74. For such a large number of degrees of freedom the above value of the minimal χ^2 tells us that the fit is perfect. We take into account the following sources of uncertainties in z: the statistical error determined by $\chi^2(z) = \chi^2_{\text{min}} + 1$, the errors in A, L_0 and s_0, and an error in c_p. We obtain the uncertainties ± 0.0002 for the statistical error and ± 0.0005 for the error in A. These errors are one order of magnitude smaller than the errors originating in L_0 and s_0 which are ± 0.004 and ± 0.005, respectively. We have no information on the error in the heat capacity of liquid mercury in [15]. Therefore, we simply vary a_0 by $\pm 1\%$ as a generous error estimate [19]; the resulting uncertainty, however, is smaller than the statistical error. In summary, our value of z is

$$z = 1.003 \pm 0.004\,(L_0) \pm 0.005\,(s_0). \qquad (52)$$

Of course, the error estimate above is not a sound statistical computation, but we can safely argue that, with existing thermodynamic data on the equilibrium of liquid and gaseous phases of mercury, Planck's constant can be determined with an accuracy of about one percent. Improving the accuracy of L_0 and s_0 might improve the determination of h, but due to the approximations pointed out in the previous section, thermodynamic data can most probably never compete with quantum physics data for this purpose.

5 Conclusions

Planck's quantum hypothesis in 1900 was a revolutionary step which he justified by referring to Boltzmann, because in this way he could count the number of different photon states and compute the entropy of a photon gas by using formula (2). The importance of the quantum hypothesis became clear only gradually. In the beginning, Planck's constant played a role in loosely connected or seemingly unconnected phenomena. The unified perspective was achieved only later with quantum mechanics and quantum field theory. However, the importance of the quantum hypothesis for atomic and molecular physics, including thermodynamic quantities like heat capacities, was suspected quite early, for instance, by Sommerfeld [8] who connected Planck's constant with the "action[5] in pure molecular processes."

In the beginning, apart from black-body radiation, the phenomena to which the quantum hypothesis could be applied were scarce. In 1905 Einstein could explain the photoelectric effect and in 1907 he put forward the "Einstein model" of the heat capacity of solids which could account for deviations from the Dulong–Petit law but gave the wrong behavior at low temperatures. This flaw was cured by Debye [14] who developed his model practically at the same time as Sackur and Tetrode derived their equation. The Bohr model of the atom was to follow in 1913. As a side remark, Ernest Rutherford's paper on the atomic nucleus appeared in 1911, in the same year when Heike Kamerlingh Onnes discovered superconductivity. For an extensive account of the evolution of the "old quantum theory" we refer the reader to [20].

Just as Planck more than ten years earlier, Sackur and Tetrode referred to Boltzmann in the derivation of their equation. One can view the Sackur–Tetrode equation and its successful test with thermodynamic data as one of the very first confirmations of Planck's quantum hypothesis. This equation was a quite fundamental step towards modern physics as it demonstrated the ubiquity of Planck's constant in statistical physics. We stress once more that the outstanding feature of the papers of Sackur and Tetrode was the combination of theoretical ideas with an ingenious usage of experimental data.

One may speculate why the work by Sackur and Tetrode is not that well known in the physics community as one would expect from its importance in the development of quantum theory and statistical physics. One reason is certainly that both died rather young. Sackur (1880–1914), who was actually a physical chemist, died in an explosion in the laboratory of Fritz Haber, hardly two years after the Sackur–Tetrode equation. On the other hand, Tetrode (1895–1931) was a wunderkind who published his first research paper, namely the paper on the Sackur–Tetrode equation, at the age of 17. Later on he rather lived in seclusion, though he did publish a few papers which were appreciated by the community and kept some contact with eminent contemporary physicists before he prematurely died of tuberculosis.

Acknowledgements: The author thanks E.R. Oberaigner for useful discussions and P.O. Ludl for a critical reading of the manuscript.

[5]Here action means the time integral over the Lagrangian.

A Kirchhoff's equation

For the transition from the liquid (or solid) to the gaseous phase, this equation relates the slope of the latent-heat curve to the difference of the heat capacities across the coexistence curve. We derive it here because it is not that well known and also because we want to give a fairly self-contained account of the physics around the Sackur–Tetrode equation. A derivation of Kirchhoff's equation is also found in [10, 21].

The starting point is the equation

$$L(T) = T\left(s_2(T, \bar{p}(T)) - s_1(T, \bar{p}(T))\right) \tag{A1}$$

for the molar latent heat of the transition from phase 1 to phase 2. In order to simplify the notation we define

$$\Delta s(T) = s_2(T, \bar{p}(T)) - s_1(T, \bar{p}(T)), \tag{A2}$$

and analogously Δv and Δc_p, the molar volume and heat capacity differences, respectively, along the coexistence curve. Taking the derivative of equation (A1) with respect to T, we obtain

$$\frac{\mathrm{d}L}{\mathrm{d}T} = \Delta s + T\left.\frac{\partial \Delta s}{\partial T}\right|_p + T\left.\frac{\partial \Delta s}{\partial p}\right|_T \frac{\mathrm{d}\bar{p}}{\mathrm{d}T}. \tag{A3}$$

Though along the coexistence curve the entropy difference is a function of the temperature alone because the pressure along this curve is given by $p = \bar{p}(T)$, the partial derivatives in equation (A3) refer to the original dependence of the entropy on temperature and pressure; of course, after performing the derivatives, p has to be replaced by $\bar{p}(T)$. Next we perform three substitutions in equation (A3). Firstly, we note that the molar heat capacity is given by

$$c_p = T\left.\frac{\partial s}{\partial T}\right|_p. \tag{A4}$$

Secondly, we use the Maxwell relation

$$\left.\frac{\partial s}{\partial p}\right|_T = -\left.\frac{\partial v}{\partial T}\right|_p. \tag{A5}$$

Thirdly, we apply the Clausius–Clapeyron equation

$$\frac{\mathrm{d}\bar{p}}{\mathrm{d}T} = \frac{L}{T\Delta v}. \tag{A6}$$

With these substitutions equation (A3) reads

$$\frac{\mathrm{d}L}{\mathrm{d}T} = \frac{L}{T} + \Delta c_p - \frac{1}{\Delta v}\left.\frac{\partial \Delta v}{\partial T}\right|_p L. \tag{A7}$$

So far this equation is general for a phase transition of first order. Now we argue that, in the case of the vapor pressure over a liquid (or solid), the third term on the right-hand

side of equation (A7) cancels the first term to a very good approximation. To this end we consider the thermal expansion coefficient defined by

$$\alpha = \frac{1}{v}\left.\frac{\partial v}{\partial T}\right|_p \tag{A8}$$

which, for an ideal gas, is simply $1/T$. Then, using $v_l/v_g \ll 1$, we derive

$$\left.\frac{1}{\Delta v}\frac{\partial \Delta v}{\partial T}\right|_p = \frac{\alpha_g - \frac{v_l}{v_g}\alpha_l}{1 - \frac{v_l}{v_g}} \approx \alpha_g \approx \frac{1}{T}, \tag{A9}$$

which proves the cancellation announced above.[6] With this step we finally end up with Kirchhoff's equation for the latent heat of vaporization:

$$\frac{\mathrm{d}L}{\mathrm{d}T} \approx \Delta c_p. \tag{A10}$$

[6]Note that for a liquid far below the critical point usually not only $v_l \ll v_g$ holds but also $\alpha_l \ll \alpha_g$.

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