

The Sackur-Tetrode equation and the measure of entropy

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Abstract: Is it really possible to measure *absolute* entropy? Motivated by this question, and taking advantage of a previous article by W. Grimus on the Sackur-Tetrode equation (2011) [1], I have studied the hypotheses behind this equation and the way it can be experimentally tested with a calorimetric method. I have also analyzed data for Ne, Ar, Kr and Hg and found that they verify the ST equation, as long as the strong version of the Third Law of thermodynamics is assumed.

I. INTRODUCTION

On the hundredth anniversary of the Sackur-Tetrode equation, in 2011, Walter Grimus wrote an article in which he explained the derivation of an expression for the absolute entropy of an ideal monoatomic gas, that is, the Sackur-Tetrode equation [1]. He also checked its validity making use of vapor pressure data for mercury, from which he obtained a value for Planck constant with an accuracy of about 1 %. Despite this fantastic result, one still can ask: is it really possible to measure *absolute* entropy? Which suppositions lie behind these measurements? Do the results depend on the election of a particular version of the Third Law of thermodynamics? Does the ST equation work so well for other elements?

In this paper I will try to answer these questions by analyzing the calorimetric method of measuring entropy. It is interesting to study how the ST equation can be experimentally tested as it is one of the first equations that connect thermodynamics with quantum mechanics. Moreover, the simple exercise of asking “how is entropy measured?” is in itself interesting, as in this case the connection between the blackboard and the laboratory is not trivial at all.

This paper is structured as follows: in the next section, I talk about the ST equation and the hypotheses that lead to it. Later, I explain the basic outline of an experimental method of measuring entropy, with special attention to all the suppositions and approximations involved (section III). A simple example of the calculation is presented in section IV. In section V, I discuss the accuracy of the results obtained for four elements. Eventually, in section VI I make some final observations on the results and discuss the relevance of the Third Law to our experiment.

II. THE ENTROPY OF AN IDEAL GAS

We know from thermodynamics that the entropy for an ideal gas can be written as [1]:

$$S(E, V, N) = kN \left(\frac{3}{2} \ln \frac{E}{N} + \ln \frac{V}{N} \right) + S_0, \quad (1)$$

where E , V and N are the energy, volume and number of particles of the system, k is Boltzmann constant and

S_0 an undetermined constant. Sackur and Tetrode, independently, obtained an equation for the entropy of an ideal gas starting from statistical mechanics. Using the well-known formula $S = k \ln W$, and computing the number of microstates W for the studied system in the usual way, one finds that [1]:

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

where m is the mass of a particle and h is Planck constant. Comparing this result with the previous equation we infer that:

$$S_0 = kN \left(\frac{3}{2} \ln \frac{4\pi m}{3h^2} + \frac{5}{2} \right). \quad (3)$$

Therefore, we have found a theoretical value for the entropy constant. It is worth to say that the derivation of (2) is not trivial at all. In fact, to obtain it, two conditions must be satisfied:

1. The phase space needs to be discretized in cells of volume h^n , where n is the number of degrees of freedom of the system ($3N$).
2. The number of configurations in phase space must be divided by $N!$ to make entropy extensive (and to take into account the indistinguishability of particles).

A modification of any of these two hypotheses leads to a different value of S_0 . For instance, Sackur used N^N instead of $N!$ in one of his papers and obtained $3/2$ (instead of $5/2$) in the last term of eq. (3) [1].

Now that we have a value for S_0 , the reader may well ask if this has any importance at all. As we always measure *variations* of entropy, the constant in (1) might seem irrelevant. However, if we assume the strong version of the Third Law ($S(T=0) = 0$), it is indeed possible to experimentally determine this constant. In this work, I will use this version and discuss later the influence of taking the less restrictive one ($S(T=0) = \text{const}$).

III. EXPERIMENTAL DETERMINATION OF S_0

Basically, there are two procedures of measuring the entropy constant for a monoatomic ideal gas: one in-

volves vapor pressure measurements as well as calorimetric ones [1], [2], whereas the other is purely calorimetric [3]. We have analyzed the latter, since the vapor pressure method relies on this one.

The idea is to measure the increment of entropy a substance has after heating it from 0 K to its ideal gas state at constant pressure. As the entropy at $T = 0$ is assumed to be 0 by the strong version of the Third Law of thermodynamics, if we measure this increment of entropy, we actually have the absolute entropy of the substance, which can be compared with the theoretical value.

From thermodynamics we know that, at constant pressure:

$$\Delta S = \int_{T_0}^T dT' \frac{C_p(T')}{T'}, \quad (4)$$

where C_p is the heat capacity at constant pressure. Thus, if we heat a solid since 0 K, measuring its heat capacity as a function of temperature, we can compute its entropy. Nevertheless, at some point the solid starts melting. This is not a problem if we know its heat of fusion, because the change in entropy is then given by:

$$\Delta S = \frac{\Delta H}{T_t}, \quad (5)$$

where ΔH refers to the change in enthalpy due to the phase transition (that is, the latent heat of fusion at constant pressure) and T_t is the temperature of the transition. If we carry on heating the substance, we can apply again eq. (4) to the liquid and then eq. (5) to the liquid-gas transition at the boiling point. Heating the gas until we are in conditions of ideality, we could compute another contribution from eq. (4) and therefore find a value for the entropy of the ideal gas obtained just by applying the definition of entropy to experimental data: heat capacities, transition temperatures and latent heats. This is the basic outline of the method. However, some considerations need to be taken into account:

- The definition of entropy is $dS = dQ_r/T$, which means that we have to measure the heat transferred in a reversible process to get the correct value of S . Of course, as entropy is a state function, the entropy difference between two given states will be the same independently of the process used to get from one to the other. But the key here is to understand that we do not measure entropy, we compute entropy from measures of heat, and therefore it is indeed important that the processes involved in the measurements of C_p are as much reversible as possible.
- The solid or liquid under study is in equilibrium with its vapor. Therefore, what we actually measure is the heat capacity of the substance in equilibrium with its saturated vapor, which is known as heat of saturation C_s . This quantity is related

to C_p by [4]:

$$C_s = C_p - T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_s, \quad (6)$$

According to [5], [6] the difference between C_s and C_p is less than 0.1 % even at the highest temperatures and one can directly take $C_s \simeq C_p$. Moreover, this C_p refers to the vapor pressure, but the corresponding values of C_p for any small fixed pressure (including 1 atm) are practically identical [4]. Of course, if vapor pressure data is available, C_p can be computed from C_s . As we can see, strictly speaking, the calorimetric method depends on vapor pressure measures, thus both methods are closely related and there is not one more fundamental than the other. However, these vapor pressure data are dispensable in the calorimetric method.

- It is usually difficult to have experimental values for the heat capacities at very low temperatures and, in case we have them, sure they will not get to 0 K. Therefore, we need to extrapolate from our lowest values to 0 K the behaviour of heat capacity. This is done supposing that the Debye Law is verified. This law states that, at low temperatures, $C_v \sim T^3$. Specifically:

$$C_v = \frac{12\pi^4 Nk}{5} \left(\frac{T}{\theta} \right)^3, \quad (7)$$

where θ is the so called Debye temperature, a characteristic parameter of the substance. C_v and C_p are related by:

$$C_v = C_p - \frac{\alpha^2 VT}{\beta}, \quad (8)$$

where α and β are the coefficients of isobaric thermal expansion and isothermal compressibility, respectively [4]. It is very useful to take into account that $C_v \rightarrow C_p$ when $T \rightarrow 0$, and in consequence:

$$S(T) = \int_0^T dT' \frac{C_p(T')}{T'} = \int_0^T dT' aT'^2 = \frac{aT^3}{3} = \frac{C_p(T)}{3}. \quad (9)$$

This saves us not only from the necessity of knowing α and β but also from doing an actual integration of expression (7), and therefore from the need of knowing the Debye temperature.

- Most articles that deal with measures of the heat capacity of a substance as a function of temperature show measurements just until the vaporization. The value of the entropy obtained when the substance becomes a gas (a real gas) cannot be directly compared with the theoretical value for an ideal gas. I will suppose that the real gas can be approximated by an equation of state such as:

$$pv = RT + B(T)p, \quad (10)$$

where $v = V/n$ and $B(T)$ is the second virial coefficient of the gas. In this case, a correction can be applied to find the ideal entropy from the real one [4]:

$$S_{ideal\ gas} = S_{real\ gas} + p \frac{dB}{dT}. \quad (11)$$

IV. AN EXAMPLE: KRYPTON

Now that we know some of the underlying suppositions and approximations of the calorimetric method, we are ready to analyze a particular case. I have taken the heat capacity data for krypton from [7] (solid at low temperatures) and [8] (solid up from 10 K and liquid), the Debye's temperature from [7], and all the latent heats and temperatures of transition (at 1 atm), as well as the second virial coefficient from [9]. We can see a plot of the heat capacity in Fig.(1).

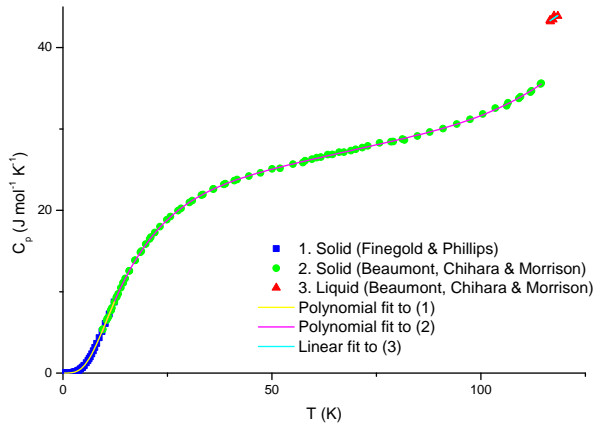


FIG. 1: Heat capacity of krypton as a function of temperature. As we can see, the data from Finogold and Beaumont overlap perfectly.

First of all, we need to extrapolate the behaviour of C_p to $T = 0$. As we have data from 0.4 K, we will use Debye's Law to calculate the entropy at $T = 1$ K. Using $\theta = 71.9$ K and utilizing (9) we get:

$$S(1\text{ K}) = 0.002\text{ Jmol}^{-1}\text{K}^{-1},$$

which, as we will see, is a negligible contribution to the total entropy.

Secondly, we need to compute the entropy increment between 1 K and the melting point using eq. (4). Two integrations have been performed: from 1 K to 12 K (ΔS_1) and from 12 K to 115.77 K (ΔS_2). A polynomial of degree 6 has been adjusted for the heat capacity data in both ranges of temperature. As the data are not very scattered, the fit is excellent. The results are:

$$\Delta S_1 = 3.518\text{ Jmol}^{-1}\text{K}^{-1}, \quad \Delta S_2 = 49.712\text{ Jmol}^{-1}\text{K}^{-1}.$$

Then, we have the melting point. With eq. (5) we get:

$$\Delta S_{fusion} = \frac{1640\text{ Jmol}^{-1}}{115.77\text{ K}} = 14.166\text{ Jmol}^{-1}\text{K}^{-1}. \quad (12)$$

We use again eq. (4) from the melting point to the boiling point. In this case I have approximated the heat capacity data by a straight line. We get:

$$\Delta S_3 = 1.500\text{ Jmol}^{-1}\text{K}^{-1},$$

We are almost done. Now we calculate the entropy of vaporization:

$$\Delta S_{vaporization} = \frac{9080\text{ Jmol}^{-1}}{119.81\text{ K}} = 75.787\text{ Jmol}^{-1}\text{K}^{-1}. \quad (13)$$

Finally, we add the second virial coefficient correction. We need the correction at $p = 1\text{ atm} = 101325\text{ Pa}$. We can obtain the derivative of $B(T)$ at $T = 119.81\text{ K}$ using the data from [9]. Some values of the second virial coefficient as a function of temperature are shown in Fig. (2). I have adjusted a polynomial of degree 3 to the points

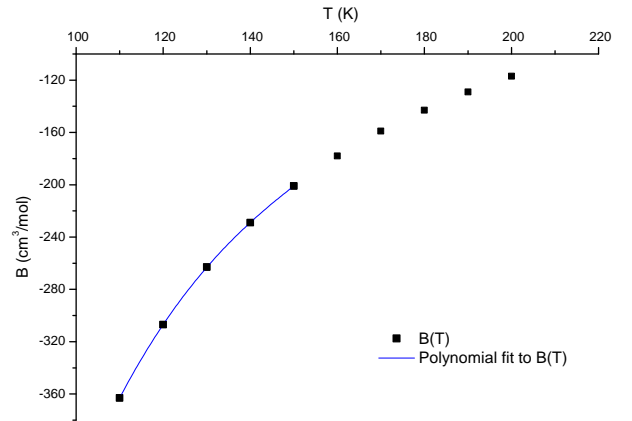


FIG. 2: Representation of some values of the second virial coefficient for krypton as a function of temperature.

between 110 K and 150 K, so that I have been able to calculate the derivative of B at the boiling point. The correction to the entropy is:

$$\Delta S_{virial} = 0.503\text{ Jmol}^{-1}\text{K}^{-1}. \quad (14)$$

Hence, the experimental value of the entropy for ideal krypton is:

$$S_{exp}(\text{Kr}) = 145.188\text{ Jmol}^{-1}\text{K}^{-1}. \quad (15)$$

It is quite clear that the major contribution to the error of this quantity will come from the entropies of phase changes. If we just consider an uncertainty of $\pm 10\text{ Jmol}^{-1}$ in the latent heats and neglect any other source of error, we get:

$$S_{exp}(\text{Kr}) = 145.19 \pm 0.12\text{ Jmol}^{-1}\text{K}^{-1}. \quad (16)$$

To compare this result with the theoretical value we need to express the entropy (2) in terms of temperature and pressure. That is:

$$S(T, p, n) = nR \left(\frac{5}{2} \ln T + \frac{3}{2} \ln M + \ln \frac{(\sqrt{2\pi})^3 R^{5/2}}{h^3 N_A^4 p} + \frac{5}{2} \right), \quad (17)$$

where R is the ideal gas constant, N_A is Avogadro's number, M is the molar mass and n the number of moles. Now we can compute the molar entropy (S/n) for krypton:

$$S_{ST}(\text{Kr}) = 145.03 \text{ Jmol}^{-1}\text{K}^{-1}, \quad (18)$$

which is in very good agreement with the experimental results.

V. RESULTS AND DISCUSSION

Proceeding similarly I have calculated the entropy of neon, argon and mercury. Apart from computing this experimental entropy and comparing it with the theoretical value, we can evaluate the accuracy of the ST equation by calculating Planck constant starting from our experimental entropies, assuming that they verify (17). All the results and the sources of the data are summarised in table I.

Element	S_{ST} ($\text{Jmol}^{-1}\text{K}^{-1}$)	S_{exp} ($\text{Jmol}^{-1}\text{K}^{-1}$)	h_{exp} (10^{-34}Js)	Sources
Ne	96.37	95.0 ± 0.7	7.0 ± 0.2	[5], [10]
Ar	129.21	128.8 ± 0.3	6.73 ± 0.08	[7], [6]
Kr	145.03	145.19 ± 0.12	6.58 ± 0.03	[7], [8]
Hg	190.40	190.26 ± 0.04	6.664 ± 0.011	[11], [12], [4]

TABLE I: Theoretical and experimental entropies, Planck constant derived from experimental entropies and references of the data used for each element. All the physical constants, transition temperatures and enthalpies of fusion and vaporization were taken from [9]. The second virial coefficients were taken from [9] too, except for the case of mercury, for which I have used the data in [4].

As we can see, the relative discrepancies, $\frac{S_{ST} - S_{exp}}{S_{ST}}$, are smaller than 1.5 % in all the cases. However, the discrepancy $S_{ST} - S_{exp}$ for mercury is more than two times the estimated uncertainty in S_{exp} . This fact points out that some of the hypotheses that we have used are not appropriate, or that we have underestimated some source of uncertainty, because we are probably making a systematic error we have not taken into account. For instance, Pickard and Simon notice in [11] that their values for the heat capacity of mercury between 10 and 14 K are lower than those obtained in a previous occasion by Simon. It must be said that in the other cases the uncertainties are higher because of their lower temperatures of transitions, which make more relevant the error on the latent

heats. These quantities, especially the heat of vaporization, vary considerably depending on the chosen tables. Just as an example, the enthalpy of vaporization of neon is 1.71 kJ/mol according to [9], but 1.76 kJ/mol if we follow [13]. With 1.75 kJ/mol we would have had a perfect agreement between theory and experiment.

The fact that most experimental entropies are lower than the theoretical prediction can be explained taking into account that our correction for the real gas was the simplest possible: a second virial coefficient. A more convenient equation of state for the real gas should add a higher correction to the entropy.

Considering all of this, it is quite clear that the results confirm the validity of the ST equation for monoatomic gases. If we take the average h_{exp} with its error (experimental plus statistical) as a global test of the ST equation, we get:

$$h_{exp} = (6.75 \pm 0.11) 10^{-34} \text{ Js}$$

The tabulated value is $h = 6.626 \cdot 10^{-34} \text{ Js}$ [9], which is inside twice the margin of error.

VI. FINAL REMARKS

It is an interesting exercise to plot together all the curves $S(T)$ for the elements we have studied. The ST

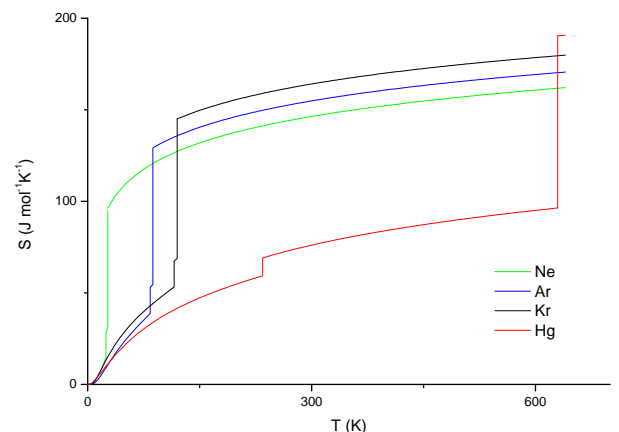


FIG. 3: Entropies as a function of temperature for neon, argon, krypton and mercury. We can see the evolution of entropy for the solid, the phase transition, the liquid state (which is ephemeral for noble gases) and the transition to ideal gas, which includes the virial correction. The representation for the gas phase has been done with the ST equation, which connects very well with the first part.

equation tells us that the difference of entropy between two different ideal gases at the same conditions of pressure and temperature is given by the difference of the logarithms of their masses. On the other side, we have seen that the calculation of entropy from experimental data involves the temperatures of fusion and vaporization, the corresponding enthalpies and the heat capacity.

Therefore, it must be noticed that all of these factors “conspire” to obtain at the boiling point a value for the entropy that only depends on $\ln M$.

For instance, we can see that, for noble gases, the increments of entropy due to phase changes are basically identical, which is a remarkable fact: both temperatures of transition and latent heats are higher for massive noble gases, but in a way that the variations of entropy are approximately equal. Hence, the “responsibility” to verify ST equation relies on the behaviour of the heat capacities: the fact that massive substances have higher transition temperatures allows a bigger increment of entropy due to contributions from heat capacity. This applies to mercury too.

There is still one question waiting for an answer. It seems clear that the ST equation has been corroborated by experience. However, to do it we have assumed the strong version of the Third Law of thermodynamics. Let us see what happens if we take a less restrictive version.

We have measured a *difference* of entropy, $S_{ideal\ gas} - S_{solid}(T = 0)$, and we have stated that this difference is equal to the ST entropy. Therefore, the ST equation gives us the difference of entropy between $T = 0$ and an ideal gas state. Hence, if we want to establish an absolute scale of entropy, $S(T = 0) = 0$ works well with $S = k \ln W$. Of course, if we prefer $S(T = 0) = const$, then we will have to say $S = k \ln W + const$ in order that the experimental results are still verified. Thus, strictly speaking, we have not measured absolute entropy, and therefore we have not measured the constant S_0 of equation (1). However, as we have measured $S_0 - S_{solid}(T = 0)$, and since this value coincides with (3), we have a reason to prefer the strong version of the Third Law, which states that $S_{solid}(T = 0) = 0$.

VII. CONCLUSIONS

We started this article posing some questions. Let us summarise the most important facts we have dealt with in order to answer them:

- We cannot measure absolute entropy, we always measure differences. However, as we have argued, this does not prevent us from testing the ST equation, as long as we understand S_0 as a constant relative to the arbitrary value of the entropy at $T = 0$. It is this fact precisely what makes the validation of the ST equation independent of the chosen version of the Third Law, and what allows us to establish the relation $S(T = 0) = 0 \Leftrightarrow S = k \ln W$. We have found an experimental justification of this famous relation.
- We have tested the validity of the ST equation for Ne, Ar, Kr and Hg.
- This gives credit, on the one hand, to the assumptions in its derivation (in particular, the discretization of phase space in domains of volume h^n and the use of $N!$ to make entropy extensive), and on the other hand, to the experimental assumptions discussed at the beginning of this paper.
- The ST equation is quite known and widely taught, but it should be stressed that solids and liquids must have certain properties regarding its heat capacities, latent heats and transition temperatures so as to verify it for their ideal gas state. This equation shows the power of statistical mechanics, and how it connects mechanics and thermodynamics.

Acknowledgments

I would like to use these final lines to thank my advisor, Enric Pérez, for his help and guidance throughout this project. His scepticism about the possibility of actually measuring the ST entropy made me think carefully about all the process, and eventually turned me into an admirer of the equation.

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