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History of Physics and Related Sciences

Max Planck's Determination of the Avogadro Constant

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O trabalho que levou à discretização da energia é certamente o trabalho mais famoso de Max Planck. Além da quantização foi introduzida uma nova constante universal, a constante de Planck, com um novo cálculo da constante de Drude-Boltzmann. A segunda parte desse trabalho, publicado de forma separada em 1901, contém o cálculo de vários constantes importantes em físico-química e será o objetivo principal do presente artigo. Usando as duas definições de entropia, a introduzida por Planck e a de Boltzmann, estabeleceu-se a relação entre as constantes, R, N_A e k. Guiado por esse resultado e pelo conhecimento prévio da constante de Drude-Boltzmann, Planck calcula o número de partículas por mol, a constante de Loschmidt e a carga do elétron. Nesse último caso utilizou-se a constante de Faraday, também conhecida em 1900. Talvez, devido à importância do primeiro artigo na discretização da energia, pouco estudo é dedicado a esse segundo trabalho. Entretanto, muito pode ser discutido e aprendido ao se abordar o contexto histórico desse segundo artigo que serve, também, como uma referência para o conhecimento das constante dos gases, constante de Boltzmann, número de partículas por centímetro cúbico, número de partículas por mol, carga do elétron e constante de Faraday, no final do século XIX.

Palavras-Chave: Constante de Avogadro, número de Loschmidt, constante de Drude-Boltzmann, carga do elétron, constante de Faraday.

The work leading to the discretization of energy is certainly Max Planck's most famous work. In addition to quantization, a new universal constant, the Planck constant, was introduced with a new calculation of the Drude-Boltzmann constant. The second part of this work, published separately in 1901, contains the calculation of several important constants in physical chemistry and will be the main objective of the present article. Using the two definitions of entropy, the one introduced by Planck and the one by Boltzmann, the relationship between the constants, R, N_A and k was established. Guided by this result. Planck calculates the number of particles per mole, the Loschmidt constant, and the electron charge. In the latter case, Faraday's constant was used, also known in 1900. Possibly, due to the importance of the first article on the discretization of energy, little study is devoted to this second work. However, much can be discussed and learned by approaching the historical context of this second article, which also serves as a reference for knowing the gas constant, Boltzmann constant, number of particles per cubic centimeter, number of particles per mole, electronic charge and Faraday constant, at the end of the XIX century.

Keywords: Avogadro constant, Loschmidt number, Drude-Boltzmann constant, electron charge, Faraday constant.

1. Introduction

The first paper by Max Planck on the blackbody radiation changed the ideias in physics. The discretization of energy and the quantum of action, known today as Planck's constant, h, was calculated numerically. The Drude-Boltzmann constant, k, was also determined since two equations in the unknowns h and k were established by Planck.

There are two ways to follow Max Planck fundamentals papers on the blackbody radiation, if one wants to read the original references. A preliminar version was read at the Physics German Society on 14, December 1900 [1–3]. For publication in the Annalen der Physik, Max Planck divided this talk in two parts. The first one contains the discretization of energy [4], together with the calculation of h and k and is certainly the most famous paper by Max Planck. The other paper on Annalen der Physik [4], is the second part of the 1900 presentation. Two days, 7, January, 1901 and 9, January, 1901, is the difference between the submission dates.

The second paper has the title, *Uber die Elementarquanta der Materie und der Elektrizitat* or in english *About the elementary quanta of matter and the electricity.* This paper opens an opportunity to study the history of some fundamental constants, especially those of interest in chemistry.

What were the constants known by Planck in 1900? Was he aware of the gas constant, the Drude's constant, the number of particle in a cubic centimeter, the number

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of particle in a mole, the charge of electron and, consequently, the Faraday constant? The Drude constant, as to be discussed, is proportional to the what is known today as the Boltzmann constant. The present work is a step to answer and clarify this question. In this second paper, a four pages paper, Planck managed to redefine the concept of entropy and to recalculate three universal constant.

Two words of caution about terminology have to be said: 1) The term, Boltzmann's constant, appears only in 1906 with the work of Ehrenfest [5]. Before this date it was known as Drude-Boltzmann constant, as in the Planck's paper; 2) The term, Avogadro's constant, was also a latter denomination, made by Perrin in 1909 [6, 7]. Until 1909 the term, Avogadro's constant, did not appear in the literature. Nevertheless, because of the objective of the present work, the Avogadro's constant terminology is to be used.

2. *R*, The Ideal Gas Constant

While discussing the entropy, Planck says in 1900, *... R being the well known gas constant...* . This constant also appears in his 1897 book entitled "Treatise on Thermodynamics". The gas constant was certainly well known by the end of XIX century. For example, W. Nernst in 1895, on page 40 of his book *Theoretical Chemistry from the Standpoint of Avogadro's Rule* [8],

"By the help of Avogadro's rule, the laws of gases can be summed up in the following form ...,

$$pv = \frac{p_0 v_0}{273} T = RT$$

in which the factor R is only conditioned by the unit of measure chosen, but is independent of the chemical composition of the gases in question" , making it explicit that R is an universal constant for ideal gases. Although the expression $pv = RT$ appeared before, as in the work of É. Clapeyron and R. Clausius [9] the quantity R was not yet to be considered an universal constant because it depended on the gas being used. Nernst attributes to Horstmann [10] the use of Avogadro's rule to make this conclusion about the gas constant [11, 12].

3. The Loschmidt Number

The number of particles in 1cm^3 was first estimated by Josef Loschmidt in 1865 and published in 1866 under the title *Zur Grosser der Luftmolecule*, or *On the Size of Air Molecules* [13]. From the original publication: *It is the purpouse of this communication to obtain with the help of this theory, a value for yet another constant – namely the magnitude of the diameter of the air molecules.*

Using the mean free path value, viscosity and data about condensation, Loschmidt estimated the diameter, s of the air as,

$$s = 0,000000969\text{mm} = 9,69 \times 10^{-8}\text{cm} \tag{1}$$

or, $s \approx 10$ Å, a result within the correct order of magnitude. For the main component of the air, N_2, one has $s \approx 2$ Å [14]. The number of particles in a cubic centimeter was known by Loschmidt,

$$N_L = \frac{1}{\frac{4}{3}\pi l s^2} \tag{2}$$

a result obtained from kinetic theory [15]. Inserting the value of s and $l = 0,000140\text{mm}=1,4 \times 10^{-5}\text{cm}$, it can be calculated as,

$$N_L = 1.83 \times 10^{18}\text{cm}^{-3} \tag{3}$$

The tabulated result for the Loschmidt number is taken today to be, $N_L = 2,6868 \times 10^{19}\text{cm}^{-3}$, indicating, again, a fair estimate made by Josef Loschmidt in 1865.

4. The Drude Constant

Planck also wrote $f = \omega R = k$ with $\omega = \frac{k}{R}$. Was the constant k also known by Planck? Again yes, and it was called described by him as a second constant of nature [3]. It was calculated dy Drude [16] in 1900. From kinetic theory, Drude wrote the equations,

$$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2 = \cdots = \alpha T \tag{4}$$

with T the absolute temperature and α *eine universelle Constante* an universal constant, and

$$p = \frac{2}{3}\alpha \mathfrak{N} T \tag{5}$$

The quantity $\mathfrak{N}$ was defined to be the number of molecules for 1 cm^3. Therefore,

$$pV = \frac{2}{3}\alpha N T \tag{6}$$

and $\frac{2}{3}\alpha = k$, another constant. By using Loschmidt number and the ideal gas equation,

$$1.013 \times 10^6 = \frac{2}{3}\alpha \times 10^{20} \times 273 \tag{7}$$

Drude calculates $\alpha = 0.56 \times 10^{-16}$ erg K^{-1}.

In another approach, with the theory of the free mean path and heat diffusion,

$$\frac{\alpha}{e} = 4.42 \times 10^{-7}\text{erg K}^{-1}\text{esu}^{-1} \tag{8}$$

J.J. Thomson [17] has experimentally determined several values of the electronic charge. With 6.0×10^{-10}esu, as one of the values calculated by Thomson, Drude was able to calculate,

$$\alpha = 2.65 \times \times 10^{-16}\text{erg K}^{-1} \tag{9}$$

or,

$$k = \frac{2}{3}\alpha = 1.76 \times \times 10^{-16}\text{erg K}^{-1} \tag{10}$$

Observe the excellent value calculated by Thomson (15% of error), since 6.0×10^{-10}esu $= 2.00 \times 10^{-19}$C.

It has to be noted that the numerical value of the Boltzmann constant was never calculated by Boltzmann. Planck was aware of that and named the k constant as the Drude-Boltzmann constant. Unfortunately, Drude's name has disappeared from the constant denomination. In a paper of 1906 [5], Paul Ehrenfest made it explicitily, *Boltzmann constant*, unlike Planck. That is possible the first reference in which Drude's name was missing. Paul Ehrenfest completed his doctoral studies under Boltzmann in 1904. There is no mention to *Boltzmann constant* in his thesis [18]. Also, the denomination *Boltzmann constant* was not a tribute to Boltzmann after his death. Submission date for Ehrenfest's paper is June, 28, 1906. Boltzmann died in September, 5, 1906 [19].

5. Planck or Boltzmann?

An analysis of the paper, *On the Relationship between the Second Fundamental Theorem of the Mechanical Theory of Heat and Probability Calculations Regarding the Conditions for Thermal Equilibrium* by L. Boltzmann [20] is necessary to understand the final step made by Planck to calculate Avogadro's constant.

There are four basic equations in Boltzmann's paper to be discussed here. From his equation number (63), $dQ = NdT + pdV$ one must conclude $N = C_V$. From his equation (64), $pV = \frac{2}{3}NT$, one obtains $pV = RT$, in which $C_V = \frac{3}{2}R$ was used. From equation (65) and one unnumbered equation between equation (64) and (65),

$$\Omega = R\ln(T^{\frac{3}{2}}V) + C \tag{11}$$

This is the expression for the entropy, since $W = C'T^{\frac{3}{2}}V$ [21, 22], or proportional to it. Boltzmann defines the entropy as $\frac{2}{3}\Omega$ as in his equation (65). Boltzmann approach was based on distinguishable particles, calculating averages over a probability distribution and treating the states as continuous. From this framework he was able to establish Ω.

On the other hand, considering indistinguishable particles and discrete states, Planck established the density of states, corresponding to the distribution of the particles in these states. Planck also wrote $S = R\ln P$ in his 1900 paper, but he made a step further, considering individual quantities and rewriting [23],

$$S = k\ln W \tag{12}$$

Comparing the two equations he defined,

$$wR = k \tag{13}$$

with w a porportionality constant. In writing expression (13), Planck implicitly assumes that the two definitions of entropy are equivalent, differing by a constant of proportionality. That is what $wR = k$ means. The two scientists had the same physical concept about entropy.

6. Max Planck Determination of the Avogadro Constant

From equation (13) one may conclude, $\frac{1}{w} = N_A$ with N_A the Avogadro number. It seems that Max Planck was the first to write

$$R = N_Ak \tag{14}$$

The final step was straighforward,

$$N_A = \frac{1}{w} = \frac{R}{k} = \frac{8.314}{1.34 \times 10^{-23}} = 6.174 \times 10^{23}\ \mathrm{mol}^{-1} \tag{15}$$

In Planck's words, ... *since H = 1.01, or, in a mole of any substance there are* $1/\omega = 6.175 \times 10^{23}$ *real molecules.* The concept of mol was clear to Planck, since equation of state and gas constant were well established. Avogadro's constant was well know by Planck.

Planck compared this result with those from Meyer. In his book of kinetic theory [24] states that in a one cubic centimeter ... *there are about 640 trillions of hydrogen molecules in 1 milligram*, that is Planck took Loschmidt number as $N_L = 640 \times 1000000000000$. Converting this number to cubic meter and grams, he calculated

$$\begin{aligned} N_A &= 640 \times 1000000000000 \times 10^6 \times 1000 \\ &= 6.4 \times 10^{23}\ \mathrm{mol}^{-1} \end{aligned} \tag{16}$$

per mol of hydrogen. Again, Avogadro's constant was known even before Planck, in 1899. Before that, scientist prefer to talk about the Loschmidt number. Meyer was probably the first scientist to mention number of particles per mol.

7. Loschmidt's Number by Planck

In another approach, in the same paper, Planck calculates the Loschmidt number, ... *Loschmidt's number L, that is, the number of gas molecules in 1 cm*^{3} *at* ^0C *and 1 atm*, using the equation of state,

$$L = \frac{1013200}{R \times 273 \times \omega} = 2.76 \times 10^{19}\ \mathrm{cm}^{-3} \tag{17}$$

an excellent result if compared with the accepted value. Planck's calculation is just the usage of the equation of state, $L = \frac{p}{kT}$ in CGS units, that is $L = \frac{1013200}{1.34\times10^{-16}\times273}\ \mathrm{cm}^{-3}$.

8. The Electronic Charge

Planck does not mention a reference for the Faraday constant used in his work. He wrote $e = \epsilon w$, or in modern language, $N_Ae = F$, uses $\epsilon = 3.2223 \times 10^{-5}$ esu mol^{-1}= 96603 C mol^{-1} with no reference, to calculate the electronic charge,

$$e = \epsilon w = 4.69 \times 10^{-10}\mathrm{esu} \tag{18}$$

Tabela 1: Constant known and calculate by Planck in 1900. Significant figures as in the original work.

Constants	As know by Planck	As calculated by Planck	Accepted values
R	8.31×10^7 erg K^{-1} mol^{-1} (0.05%)	Not calculated by Planck	8.314×10^7 erg K^{-1} mol^{-1}
F	96603 C mol^{-1} (0.1%)	Not calculated by Planck	96485 C mol^{-1}
L	$1.83 \times 10^{18}cm^{-3}$ (93 %)	2.76×10^{19} cm^{-3} (3%)	$2.687 \times 10^{19}cm^{-3}$
k	1.76×10^{-16}erg K^{-1}(27%)	1.346×10^{-16}erg K^{-1} (3%)	1.381×10^{-16} erg K^{-1}
N_A	6.4×10^{23} mol^{-1}(6 %)	6.174×10^{23} mol^{-1} (3%)	6.022×10^{23} mol^{-1}
e	2.168×10^{-19}C (36%)	1.5644×10^{-19}C (3%)	1.602×10^{-19} C
h	Did not exist	6.55×10^{-27} erg s (1%)	6.626×10^{-27} erg s

This is also an excellent result since 4.69×10^{-10}esu $= 1.5644 \times 10^{-19}$C, with an error of 3%, if compared with the tabulated value, 1.602×10^{-19} C. The result 18 was compared to the previous result, 2.186×10^{-19} C, as obtained by J.J. Thomson [17]. The Faraday constant used by Planck was also very precise for the year 1900, with an error of 0.1%. The accepted value today is $F = 96485$ C mol^{-1}.

Faraday's constant was well established by the end of XIX century. The precise measurement of the Faraday's constant was made by Lord Rayleigh and Mrs. H. Sidgwick, in the paper *On the electro-chemical equivalent of silver*, at *Phil. Trans.*, page 411, in 1884, [25]. On page 439 it is mentioned that they obtained $m = 1.11794 \times 10^{-3}$g as the amount of silver deposited at the electrodes. Therefore,

$$1.11794 \times 10^{-3} = \frac{107.93}{1}\frac{1}{F} \tag{19}$$

or,

$$F = \frac{107.93}{1.11794 \times 10^{-3}} = 96.544 \text{ C mol}^{-1} \tag{20}$$

with an impressive error of 0.07 %. Planck chose to use F=96603 C mol^{-1}, but this will affect his value of electronic charge at the third siginificant place. He would have obtained $e = 1.5635 \times 10^{-19}$C, instead.

The first measurement of the electronic charge goes back to 1874 and was made by George Johnstone Stony, on the paper, On the Physical Units of Nature. Phil. Mag. 11,384(1881). The value $\frac{1}{XX} = 10^{-20}$ appears on page 388 of the paper. Several measurements were performed after this. Planck used the most precise value at his time, as made by J.J. Thomson.

9. Conclusions

The lecture given by Planck at the German Physical Society is unique in physics. In the same talk, Planck gives the energy discretization, the Planck's constant (within an error of 1%) and the Drude-Boltzmann constant(within an error of 3%). But part of this talk, the second published paper, is also fascinating and much can be learned from it, specially about the constant at the end of the XIX century.

By 1900, Max Planck was aware of several important constants in chemistry and physics. The ideal gas constant, R, was known to three significant figures. Planck does not cite the reference to the value of $R = 8.31 \times 10^7$ used in the work, but the value was well known, for example from Walther Nernst's Theoretical Chemistry book.

The Loschmidt number was established by Planck with an accuracy of 3%. Using the ideal gas equation of state and the conditions for calculating this number Planck calculated 2.76×10^{19} cm^{-3}. The value tabulated today is $2,687 \times 10^{19}cm^{-3}$.

In a crucial step, Planck writes $R = N_A k$. With the values of R and k already obtained, it was able to set Avogadro's constant to $6,174 \times 10^{23}$ mol^{-1}, again a very accurate value for the XIX century, representing an error below 3 %, compared to the tabulated result 6.022×10^{23} mol^{-1}.

Using Faraday's constant, also known in 1900, Planck calculates the charge on the electron as 4.69×10^{-10}esu $= 1.5644 \times 10^{-19}$C, an excellent value if compared to the tabulated one, 1.602×10^{-19} C.

A summary of the constants know by Planck, calculated by him together with today accepeted values is given in Tabela 1. Except for the Planck's constant, which is in percentual error of about 1%, all the other constants calculated by Planck are in error of about 3%. Faraday's constant was not calculated by Planck, but he used a value within 0.1% of error, although a more precise value was available.

The first paper written by Planck is certainly very important for energy quantization was introduced, together with the constant h, the Planck constant. Also, the Drude-Boltzmann was recalculated in this first paper. However, in his second article, in addition to showing that his definition of entropy is conceptually equivalent to the one defined by Boltzmann, much can be learned about the constant, R, k, N_A, L, e and F at the end of the XIX century.

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