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On the absolute entropy of diatomic and polyatomic gases

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The quantum statistics of the monatomic gases were treated by Planck¹ in two papers. In his first paper he considered continuous phase points in the phase space, in the second paper he only assumed definite phase points.

In my paper I generalise Planck's fundamental assumptions. I calculate with simple statistical methods the absolute entropy of the diatomic and polyatomic gases. My assumptions are as follows: The diatomic and polyatomic gas are ideal gases. The molecules are considered to be rigid, the motions of the atoms and electrons are not taken into consideration. By the counting of the phase probability, it is not necessary to treat independently the phase probability referring to the rotational coordinates.

1. Let us consider a gramme molecule of a diatomic gas consisting of N molecules, having volume V and temperature T . To calculate the probability of the given state we divide the 10^N dimensional phase space of the gas — a molecule has 3 translational and 2 rotational coordinates and 5 corresponding momenta — into cells. The cells may be equal or different in volume. To maintain the generality I investigate cells of different size: $P_1 h^{5N}$, $P_2 h^{5N}$, ..., in which h is Planck's constant, P_1, P_2, \dots denote the statistical weight of cells. The thermodynamical behaviour of the gas is determined by the following equation of free energy

$$F = -kT \log \left(\sum P_n e^{-\frac{u_n}{kT}} \right) \quad (1)$$

in which U_n denotes the energy of the n th elemental region. Expressing the energy U_n with the energies of the single molecules we obtain

$$F = -kT \log \sum p_n e^{-kT} \quad (2)$$

where u_n gives the energy of the n th elemental region in the phase space of a molecule. To determine u_n we must consider that in (2) the term number of $\sum_{\text{for states}}$ agrees with the number of the cells in the phase space of a molecule. The total number of the cells in (2) is

$$z = \frac{1}{h^{5N}} \iiint \dots dx_1 dy_1 dz_1 \dots d\vartheta_1 d\varphi_1 \dots dp_{x1} dp_{y1} dp_{z1} \dots dp_{\vartheta1} dp_{\varphi1} \dots \quad (3)$$

in which $x_1, y_1, z_1 \dots$ denote the translational coordinates of the molecule 1, $\dots, \vartheta_1, \varphi_1 \dots$ are the polar coordinates for the determination of the positive direction of the symmetrical axis of the molecule 1, $\dots, p_{x1}, p_{y1}, p_{z1}$ denote the corresponding impulse coordinates, by each molecule the integration has to be extended over all possible values of the coordinates between energy 0 and u . We must divide in equation (3) by $N!$, for with any state fixed by a system of coordinates, there are $N!$ different state points to be considered. Integrating in equation (3) and denoting the moment of inertia with I it is²

$$z = \frac{1}{N! h^{5N}} \frac{V^N (4\pi)^N \pi^{\frac{5N}{2}} I^N (\sqrt{m^3})^N (\sqrt{2u})^{5N}}{\Gamma\left(\frac{5}{2} + 1\right)}. \quad (3a)$$

Using the Stirling approximation for factorial $N!$ and writing $\Gamma\left(\frac{5}{2} + 1\right) = \frac{15\sqrt{\pi}}{8}$, it becomes

$$z = \left(\frac{32\pi^3 e I \sqrt{m^3} \sqrt{(2u)^5} V}{15h^5 N} \right)^N. \quad (3b)$$

2. In the phase space of a molecule the sum of the statistical weights $p_1, p_2, p_3 \dots$ is equal to the number of the cells of size h^5 , i. e.

$$(p_1 + p_2 + \dots + p_n)^N = \left(\frac{32\pi^3 e I \sqrt{m^3} \sqrt{(2u)^5} V}{15h^5 N} \right)^N. \quad (4)$$

For determining the interdependence between the sum of the statistical weights and the number of the cells of different size we can only put forward suggestions. In the following I generalise Planck's assumption referring to the monatomic gases, according to which in the phase space of a molecule the sum of the statistical weights belonging to the cells of different size is equal to the number of cells raised to power of the coordinate number, i. e.

$$p_1 + p_2 + \dots + p_n = n^5. \quad (5)$$

From equations (4) and (5) we find

$$n^5 = \frac{32\pi^3 e I \sqrt{m^3} \sqrt{(2u)^5} V}{15h^5 N} \quad (6)$$

and

$$u = \frac{1}{2} \left(\frac{15h^5 N}{32\pi^3 e I \sqrt{m^3} V} \right)^{2/5} n^2. \quad (7)$$

The quantum energy of the n th cells is generalising Panck's procedure

$$u_n = \frac{1}{2} \left(\frac{15h^5 N}{32\pi^3 e l \sqrt{m^3 V}} \right)^{2/5} (n - \alpha)^2, \quad (8)$$

in which α is a constant, positive, proper fraction. If $\alpha = 0$ the quantum energy gives the extreme energy of cells. The free energy in (2)

$$F = -RT \log \sum_{n=1}^{\infty} [(n+1)^5 - n^5] e^{-\sigma(n-\alpha)^2}, \quad (9)$$

where

$$\sigma = \frac{1}{2kT} \left(\frac{15h^5 N}{32\pi^3 e l \sqrt{m^3 V}} \right)^{2/5}.$$

At high temperatures ($\sigma \ll 1$)

$$F = -RT \log \int_1^{\infty} e^{-\sigma(n-\alpha)^2} dn^5,$$

$$F = -RT \log \left\{ 5 \int_0^{\infty} (x+n_0)^4 e^{-\sigma x^2} dx - 5 \int_0^{1-\alpha} (x+n_0)^4 e^{-\sigma x^2} dx \right\}. \quad (11)$$

The second integral can be neglected and³

$$F = -RT \log \left\{ \frac{5 \cdot 4! \sqrt{\pi}}{\sigma^{5/2} 2^6} + \frac{10\alpha}{\sigma^2} + \frac{10\alpha^2 \sqrt{\pi}}{2\sigma^{3/2}} + \frac{10\alpha^3}{\sigma} + \frac{5\alpha^4 \sqrt{\pi}}{2\sigma^{1/2}} \right\}. \quad (12)$$

Raising out of the first term in logarithm the log. of the second part ($\sigma \ll 1$) can be neglected. Therefore

$$F = -RT \log \frac{8\pi^2 e l \sqrt{(kT)^5} \sqrt{(2m\pi)^3} V}{h^5 N}. \quad (13)$$

Hence

$$S = R \log \frac{8\pi^2 e^{7/2} l \sqrt{(kT)^5} \sqrt{(2m\pi)^3} V}{h^5 N}. \quad (14)$$

This equation agrees with the equation determined by Tetrode⁴, and if we do not take the symmetrical number into consideration, with the value calculated by Ehrenfest⁵ and Trkal. Ehrenfest and Trkal have determined the chemical constant of gases. From this the entropy must be calculated.

3. Let us now investigate a gramme molecule of a polyatomic gas consisting of N molecules, having temperature T , inclosed within the volume V . The total number of cells in (2) is

$$z = \frac{1}{h^{6N} N!} \iint \dots dx_1 dy_1 dz_1 \dots d\vartheta_1 d\varphi_1 d\psi_1 \dots dp_{x_1} dp_{y_1} dp_{z_1} \dots \dots dp_{\vartheta_1} dp_{\varphi_1} dp_{\psi_1} \dots, \quad (15)$$

in which x_1, y_1, z_1 are the translational coordinates of the molecule 1..., ϑ_1, φ_1 respectively $\psi_1 \dots$ denote the angles of the positive direction of the third (L), respectively first (I) principal moment of inertia of the molecule 1..., $p_{x_1}, p_{y_1}, p_{z_1}, p_{\vartheta_1}, p_{\varphi_1}, p_{\psi_1} \dots$ are the corresponding impulse coordinates, the integration by each molecule has to be extended over all possible values of the coordinates bet-

ween energy 0 and u . Denoting the principal moments of inertia of a molecule with I_1, K, L the energy⁶ of a molecule becomes

$$u = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + \frac{1}{2} \{ I (\sin \vartheta \cos \psi \dot{\varphi} - \sin \psi \dot{\vartheta})^2 + \\ + K (-\sin \vartheta \sin \psi \dot{\varphi} - \cos \psi \dot{\vartheta})^2 + L (\cos \vartheta \dot{\varphi} + \dot{\psi})^2 \}, \\ u = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + \frac{1}{2} (Ia^2 + Kb^2 + Lc^2), \quad (16)$$

in which a, b, c are the components of the rotational velocity relating to the principal axes of inertia and

$$a = \sin \vartheta \cos \psi \dot{\varphi} - \sin \psi \dot{\vartheta}, \quad b = -\sin \vartheta \sin \psi \dot{\varphi} - \cos \psi \dot{\vartheta}, \\ c = \cos \vartheta \dot{\varphi} + \dot{\psi}. \quad (17)$$

The interdependence among the impulse coordinates and a, b, c from equations (16), (17) is

$$\left. \begin{aligned} p_{\vartheta} &= -Ia \sin \psi - Kb \cos \psi \\ p_{\varphi} &= Ia \sin \vartheta \cos \psi - Kb \sin \vartheta \sin \psi + Lc \cos \vartheta \\ p_{\psi} &= Lc. \end{aligned} \right\} \quad (18)$$

Introducing in equation (15) $a_1, b_1, c_1 \dots$ instead of $p_{\vartheta_1}, p_{\varphi_1}, p_{\psi_1}, \dots$ we find

$$z = \frac{1}{h^{6N} N!} \iint \dots dx_1, dy_1, dz_1, \dots d\vartheta_1, d\varphi_1, d\psi_1, \dots dp_{x_1}, dp_{y_1}, dp_{z_1}, \dots \\ \dots IKL \sin \vartheta_1 da_1 db_1 dc_1, \dots, \quad (19)$$

integrating

$$z = \left(\frac{4\pi^5 e \sqrt{IKLm^3} \sqrt{(2u)^6 V}}{3h^6 N} \right)^N. \quad (20)$$

The sum of the statistical weights belonging to the cells of different size in the phase space is in agreement with the assumption given by diatomic gases

$$p_1 + p_2 + \dots + p_n = n^6, \quad (21)$$

in which n is the number of the cells of different size. From equations (20) and (21)

$$n^6 = \frac{4\pi^5 e \sqrt{IKLm^3} \sqrt{(2u)^6 V}}{3h^6 N} \quad (22)$$

and

$$u = \frac{1}{2} \left(\frac{3h^6 N}{4\pi^5 e \sqrt{IKLm^3 V}} \right)^{1/6} n^2.$$

The quantum energy of the n th cells is given by

$$u_n = \frac{1}{2} \left(\frac{3h^6 N}{4\pi^5 e \sqrt{IKLm^3 V}} \right)^{1/3} (n - a)^2. \quad (23)$$

The free energy therefore is substituting

$$\sigma = \frac{1}{2kT} \left(\frac{3h^6 N}{4\pi^5 e \sqrt{IKLm^3 V}} \right)^{1/3}$$

$$F = -RT \log \sum_{n=1}^{\infty} [(n+1)^6 - n^6] e^{-\sigma(n-a)^2}. \quad (24)$$

At high temperatures ($\sigma \ll 1$)

$$F = -RT \log \int_0^{\infty} e^{-\sigma(n-\alpha)^2} dn^2, \quad (25)$$

$$F = -RT \log \left\{ 6 \int_0^{\infty} (x+\alpha)^5 e^{-\alpha x^2} dx - 6 \int_0^{1-\alpha} (x+\alpha)^5 e^{-\alpha x^2} dx \right\}. \quad (26)$$

Following the procedure according to equation (11) it becomes

$$S = R \log \frac{8\pi^2 e^{3/2} \sqrt{IKLm^3} \sqrt{(2\pi kT)^6} V}{h^6 N}, \quad (27)$$

which is identical with the equation given by Tetrode⁷, and without considering the symmetrical number, with the value calculated by Ehrenfest⁸ and Trkal.

Summary

The absolute entropy of diatomic and polyatomic gases have been calculated with simple statistical methods on the base of Planck's fundamental assumptions. The obtained results are in agreement with the values determined by Tetrode, Ehrenfest and Trkal.

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$$V = \frac{\sqrt{\pi}^f r^f}{\Gamma\left(\frac{f}{2} + 1\right)}$$

T. H. Schoute: Mehrdimensionale Geometrie, Sammlung Schubert 1905. II. p. 289.

From this the volume of the ellipsoid having different axes can be calculated. In (3) the integration has to be extended by each molecule between energy 0 and

$$u = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + \frac{1}{2I} (p_\phi^2 + \bar{p}_\phi^2) \quad \left(\text{substituting } \bar{p}_\phi = \frac{p_\phi}{\sin \vartheta} \right).$$

$$3 \int_0^{\infty} e^{-tx^2} x^{2n+1} dx = \frac{n!}{2t^{n+1}} \int_0^{\infty} x^{2k} e^{-tx^2} dx = \frac{1}{t^k \sqrt{t}} \frac{(2k)! \sqrt{\pi}}{2^{2k+1} k!}.$$

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