Influence of the Distribution of Gas Molecules by Temperature on The Rate of Gas-Forming Reactions

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Abstract

A method is proposed for calculating the temperature distribution of gas molecules depending on the gas temperature T . The method consists of determining the mean free path of molecules that characterizes the gas temperature, at which the maximum number of molecules with temperature $\tau = T$, and then the desired distribution. The results show that at a given gas temperature, the total mass of molecules contains a large number of molecules whose temperatures are much different from the total gas temperature. From this, it follows that the ceramic technology of synthesis in principle does not allow us to obtain highly pure substances.

Keywords: gas-forming reactions, reaction rate, the temperature distribution of molecules, molecule temperature, mean free path.

1. Introduction

In [1-5], by extrapolating the temperature of a gas as a large collection of molecules, a substantiation of the concept of the temperature of a molecule is given to an individual molecule.

It is generally accepted that the inverse of the derivative of the entropy of a body by its energy is called *the absolute temperature* or simply the temperature *T*:

$$\frac{dT}{dE} = \frac{1}{T} \qquad (1)$$

The main disadvantage of such a formal definition is that (like entropy) the temperature should be a purely statistical quantity, meaning only for macroscopic bodies. This definition of temperature is not essential, it does not reveal the physical meaning of temperature but plays a role only as a tool for constructing theories of statistical physics, which gave the parameter "temperature" the meaning of the characteristic of the distribution of the statistical ensemble over possible states. In fact, she just used it as such a characteristic. This application created the illusion that temperature alone is the characteristic of the distribution of the statistical ensemble over possible states. This misleading brought enormous damage to physics and, above all, physics itself. In fact, the concept of temperature, as characteristics of an individual particle, of several particles and even of a large number of particles, if their velocity distribution does not correspond to a stationary distribution, formally, ceased to make sense. As a result, this has caused difficulties in theories where the concept of temperature is required. It was necessary to adapt and reconstruct these theories in such a way that the temperature either was involved in some indirect way, when instead of it the kinetic energy or velocities of the particles are used.

The concept of temperature is the primary one that arose on the basis of experience, long before the emergence of the concept of entropy, as a thermodynamic function of the state of a statistical ensemble, and the emergence of statistical physics itself. However, in practice, indirect measurement of the temperature as a quantity characterizing the direction of heat exchange is often used, so that the amount of heat (as energy transferred by heat exchange) is transferred from a body with a higher temperature to a body with a lower temperature. But the essential definition is also used*: "Temperature is a quantity characterizing the average kinetic energy of the translational motion of molecules of an ideal gas".* It is easy to see that from this point of view the concept of the temperature of a molecule has a completely definite meaning: for one molecule, its average kinetic energy is equal to the kinetic energy of this molecule. The fact that when using the definition of the concept of temperature (1), the temperature of a single particle or even groups of particles is devoid of physical meaning, is a failure of the probabilistic approach in statistical physics.

It was noted in [2, 3] that thermal radiation plays an important role in the interaction between gas molecules, the curve of frequency dependence on the temperature of which has a domed shape, as well as the Maxwell distribution curve. The relaxation of this distribution from the resulting fluctuations can be provided by photons of this radiation, whose velocity far exceeds the velocity of the gas molecules. Based on this, it was concluded that during the free path of the i-molecule ϑ_i, it will have its own temperature τ_i:

$$\tau_i = \frac{0{,}289776829}{\lambda_i^{max}} \text{ K,} \qquad (2)$$

where 0.289776829 cm·K is the Wine constant (K is the Kelvin degree), λ_i^{max} — the wavelength of the maximum intensity in the spectrum of the corresponding gas cell. Since the temperature of a particular molecule in the gas composition is considered, in addition to the thermal radiation surrounding the molecule, it must be determined by the interactions of a given molecule with other gas molecules.

Since the temperature of a particular molecule in the gas composition is considered, in addition to the thermal radiation surrounding the molecule, it must be determined by the interactions of a given molecule with other gas molecules. Such a volume is the gas cell in which the test molecule is located, and other molecules of the surrounding gas environment, which collide with the given gas molecule, act as the walls of a given volume.

The concept of temperature is often associated with the kinetic energy of particles, and sometimes even the temperature is measured not in degrees, but in energy units. Formula (2) formally allows us to determine the temperature of the molecule, and most importantly, to show that each molecule can have and has its temperature, but the physical meaning of this temperature remains unclear. The intrinsic definition of the temperature is qualitative, and its extrapolation to the temperature of one molecule is not formally made. The purpose of this paper is to reveal the physical meaning of the concept of the temperature of gas and separate molecule.

In contrast to [2, 3], under a gas cell we mean a cylinder with an area πr^2 (r is the radius of the molecule) at the base and a height l equal to the mean free path of the molecule being analyzed. This value is not equal to the mean free path of the molecules of the gas under investigation, but is inherent only in the particular molecule chosen and over a specific time interval ϑ . Accordingly, the free path ϑ of this molecule is equal to

$$\vartheta = \frac{l}{v}, \qquad (3)$$

where v is the velocity of the molecule moving in the direction of the counter molecule, with which the nearest collision will occur? The volume W of a gas cell will be determined, respectively, by formula

$$W = \pi r^2 l. \qquad (4)$$

If the gas is strongly rarefied and the value of l is relatively large, then during the time other molecules can enter the cell, which will either cross it, or move along the same trajectory as the molecule being analyzed. To determine the temperature of the molecule under analysis by formula (2), it is necessary that there be no other molecules in the time interval $\Delta\vartheta \leq \vartheta$ in the gas cell in which the molecule being analyzed. If they are present, (for example, molecules that intersect the cell at an angle to the generatrix of the corresponding cylinder or following it at some distance), then the temperature of the gas cell itself, in which there are already several molecules, will be fixed. The entire space of the gaseous medium consists of a mosaic of various gas cells, in each of which there is a corresponding molecule or more than one, but not colliding with each other within a time ϑ.

For definiteness, we shall assume that the gas consists of monatomic molecules of radius r and mass m. The equation of state of such a gas is described by the Clapeyron formula

$$PV = nRT, \qquad (5)$$

where $P -$ the gas pressure, $n -$ the number of moles of gas in the volume V, $T -$ the temperature, $R = 8{,}3144 \cdot 10^7$ erg /mole·K. For one mole of gas from formula (5) we have:

$$PV = RT = N\frac{R}{N}T = NkT, \qquad (6)$$

where $N = 6,02 \cdot 10^{23} -$ the Avogadro number, where $k = 1,3807 \cdot 10^{-16}$ *erg / mole·*K is the Boltzmann constant. Let us denote the fraction of the pressure per molecule that is among other molecules, when it strikes the end wall of the gas cell through

$$P_1 = \frac{P}{N}. \qquad (7)$$

Dividing equation (6) by *N*, we obtain

$$P_1 V = kT \qquad (8)$$

If in the last equation we choose the gas volume equal to the volume of the gas cell *V* = *W*, in which there is only one gas molecule, then the gas temperature in this cell will obviously be equal to the temperature of this molecule *T* = τ , and equality (6) can now be written in the form

$$P_1 W = k\tau . \qquad (9)$$

Equation (9) allows us to give a formal definition of the temperature of an individual molecule. The wall of the gas cell in question is a molecule from the surrounding gaseous medium, with which the molecule under analysis is located inside this gas cell. The mechanism of interaction of colliding molecules lies in the fact that the molecules must first extinguish their velocities to zero and only then the exchange of velocities with the corresponding dissipation coefficient will occur in the next stage of the interaction. Therefore, the change in the velocity of the colliding molecules is

$$\Delta v = v, \qquad (10)$$

and the impact force, respectively:

$$F = \frac{m\Delta v}{\Delta t} = \frac{mv}{\Delta t}, \qquad (11)$$

where $\Delta t -$ the time of collision of a molecule with another molecule, which is counted from the moment of their contact to the point of their collision in a plane normal to the trajectory of the motion of the colliding molecules, coinciding with the end plane of the cylinder of the gas cell:

$$\Delta t = \frac{2r}{v}. \qquad (12)$$

Substituting (12) into (11), we obtain:

$$F = \frac{mv^2}{2r}, \qquad (13)$$

then:

$$P_1 = \frac{F}{S} = \frac{F}{\pi r^2}, \qquad (14)$$

where $S -$ the area of the end plane of the gas cell. Substituting (13) into (14), we obtain:

$$P_1 = \frac{mv^2}{2\pi r^3}. \qquad (15)$$

Substituting expressions (4) and (15) into formula (9), finally for the temperature of the molecule we obtain:

$$\tau = \frac{l}{kr} \cdot \frac{mv^2}{2} \qquad (16)$$

or

$$\tau = \frac{l}{kr} E, \qquad (17)$$

where $E = mv^2/2 -$ kinetic energy of the molecule. Thus, as expected, the temperature of the molecule is directly proportional to its kinetic energy. But it still differs from it still by the dependence on the mean free path and the size of the molecule. The presence of this dependence makes the temperature of the molecule,

unlike energy, a nonadditive function. Formula (16) additionally indicates the dependence of the temperature of the molecule on its mass and velocity.

Knowledge of the temperature τ_i of the gas molecules makes it possible to estimate their distribution at a gas temperature T. Thus, if the temperature of the thermal decomposition of the chemical compound is T_0, and the synthesis is annealed by ceramic technologies at a temperature $T < T_0$, then at the same temperature in the gas phase will be contained along with molecules in which $\tau \le T_0$, molecules whose temperatures are higher T_0 .

It is these molecules that collide with the formed phase and will disintegrate it. It immediately follows that ceramic technologies, regardless of the duration of the annealing time and the degree of quenching, in principle, do not give a guarantee of obtaining high-purity chemicals. However, knowledge of the distribution of gas molecules over their temperatures, as shown in [2, 3], makes it possible in principle to estimate the qualitative chemical composition and the amount of gas that can not be eliminated at a chosen temperature in accordance with the phase composition of this chemical impurity system. The form of such a distribution was found in [2-4], but it was made on the basis of the erroneous assumption that the energy of the thermal radiation of a gas molecule is equal to its kinetic energy. It was found in [6, 7] that this is not so, and the corresponding formula for this dependence is derived. It follows from the foregoing that the formulas presented earlier in [2-4] for the distribution of gas molecules according to their temperatures are erroneous.

The purpose of this paper is to create an algorithm for obtaining the temperature distribution of ideal gas molecules as a function of the total gas temperature.

2. Derivation of the Basic Formula and Algorithm of the Method

From the formula (17) we obtain the following equalities:

$$E = \frac{kr\tau}{l}; \quad dE = \frac{kr}{l}d\tau; \quad \sqrt{E} = \sqrt{\frac{kr\tau}{l}}; \quad e^{-\frac{E}{kT}} = e^{-\frac{r\tau}{lT}} \tag{18}$$

Substituting (18) into the formula for the kinetic energy distribution of gas molecules as a function of the gas temperature [8]

$$dn_E = n\frac{2}{\sqrt{\pi(kT)^3}}e^{-\frac{E}{kT}}\sqrt{E}\,dE , \tag{19}$$

we obtain the required distribution allowing us to estimate the fraction of the number of molecules dn_τ at a temperature τ in the range $d\tau$ of the total number of molecules n at the total gas temperature T:

$$dn_\tau = 2n\sqrt{\frac{\tau}{\pi}\left(\frac{r}{lT}\right)^3}\,e^{-\frac{r\tau}{lT}}d\tau . \tag{20}$$

If we divide formula (20) by n and multiply the result by 100%, then a formula will be obtained to estimate the percentages of the number of molecules:

$$\frac{100dn_\tau}{n} = 200\sqrt{\frac{\tau}{\pi}\left(\frac{r}{lT}\right)^3}\,e^{-\frac{r\tau}{lT}}d\tau\,\% . \tag{21}$$

The resulting free-path lengths are used in the obtained formulas (20, 21). This indicates that each free path corresponds to a different molecular temperature distribution. Of all the possible values of l, the greatest interest is of the length free path l_s characterizing the total gas temperature is T, at which the number of gas molecules with $\tau = T$ is a maximum. Formula (21) will look

$$\frac{100dn_\tau}{n} = 200\sqrt{\frac{\tau}{\pi}\left(\frac{r}{l_sT}\right)^3}\,e^{-\frac{r\tau}{l_sT}}d\tau\,\% . \tag{22}$$

It is obvious that with $\tau \neq T$ the formula (22) will give, respectively, different results. To find the value l_s , we calculate the values $\frac{100dn_\tau}{n}$ for different values l for the gas temperature T of interest by formula (21), we construct either a graphical dependence l on $\frac{100dn_\tau}{n}$ in ordinary or logarithmic coordinates or a corresponding table and from these data we find a value l_s corresponding to the extremum of this dependence. The choice of the range of values l_s for constructing the dependence on $\frac{100dn_\tau}{n}$ is determined by the condition that a set of these values fall into the region that captures the above-mentioned extremum. The very distribution of the temperature of gas molecules at its temperature T is calculated by formula (22).

3. Example Calculation of Distribution

To find the value l_s, we calculate, using formula (5), the values l for different values $\frac{100dn_\tau}{n}$ at $\tau = T =$ 1000 K for oxygen, whose molecule radius is taken to be $1{,}21 \cdot 10^{-8}$ cm [8]. We choose an interval $d\tau = \pm 100^0 \sim 200^0$. The results of the calculations are tab. 1. It can be seen from this table that the maximum number of gas molecules equal to 9% with the temperature of the molecule 1000 K at 1000 K is observed at the mean free path $l = l_s = 10^{-8}$ cm. Choosing this value as characterizing the mean free path by formula (22), we find the quantitative content of molecules in percent, having the appropriate temperature. The results of the calculation of the temperature distribution of oxygen molecules at 1000 K are presented in Table. 2. In [1, 5], a formula is given for estimating the gas temperature as a function of the temperatures of the molecules that make up the gas. In accordance with this formula, the temperature of the gas is determined by the sum of the contributions of the temperatures of its constituent molecules, referred to their total quantity:

$$T = \frac{\sum \tau_i \left(\frac{100dn_\tau}{n} \right)}{\sum \frac{100dn_\tau}{n}} . \qquad (23)$$

This makes it possible to verify the correctness of the distribution obtained.

Table 1. Dependence of the number of gas molecules on their mean free path at 1000 K

$\frac{100dn_\tau}{n}$ %	l cm
$3 \cdot 10^{-8}$	10^{-2}
10^{-6}	10^{-3}
$3 \cdot 10^{-5}$	10^{-4}
10^{-3}	10^{-5}
$3 \cdot 10^{-2}$	10^{-6}
1	10^{-7}
$3{,}6$	$10^{-7,5}$
9	10^{-8}
$3{,}4$	$10^{-8,5}$
$5 \cdot 10^{-3}$	10^{-9}
10^{-48}	10^{-10}

Table 2. Dependence of the number of gas molecules on their temperatures and their contribution to the gas temperature

τ K	$\dfrac{100dn_\tau}{n}$ %	$\dfrac{100\tau dn_\tau}{n}$	τ K	$\dfrac{100dn_\tau}{n}$ %	$\dfrac{100\tau dn_\tau}{n}$	τ K	$\dfrac{100dn_\tau}{n}$ %	$\dfrac{100\tau dn_\tau}{n}$
200	10,5	2100	1200	7,7	9240	2200	3,1	6820
400	11.7	4680	1400	6,5	9100	2400	2,7	6480
600	11,2	6720	1600	5,5	8800	2600	2,1	5460
800	10,2	8160	1800	4,5	8100	2800	1,7	4760
1000	9,0	9000	2000	3,8	7600	3000	1,4	4200

Table 2 shows the values of the molecular temperature contributions $\dfrac{100\tau dn_\tau}{n}\%$ as a function of their temperatures. From formula (23) it follows that the gas temperature in our example should be equal to 1000 K. The calculation carried out by this formula yields a close value of 1067 K. To obtain more accurate results, it is necessary to calculate at lower values dn_τ. From Table. 2 it follows that at 1000 ± 200 K the largest number of molecules do not have temperatures lying in this interval. The maximum content of molecules in this temperature range is at a rather low temperature of 400 ± 200 K. The high average temperature of the gas is thus provided by molecules with high temperatures.

The rates of oxidation-reduction gas-phase reactions depend on the concentration in the gas phase of molecules (in particular, oxygen) with the corresponding molecular temperatures. As shown by calculations of the distribution of gas molecules from their temperatures at a given gas temperature, a relatively large number of molecules are contained in the total mass of molecules whose temperatures differ much from the total gas temperature. In accordance with the thermodynamic equilibrium at such temperatures, the phase composition of the system can be different, i.e. not corresponding to the phase composition of the synthesis temperature of the substance of interest. In the reaction mixture there will already be impurities not only, respectively, oxidized or reduced phases, but in general phases of another stoichiometric composition, with a different ratio of the base components, and these impurities can not be eliminated by increasing the annealing time. Attempts to change the annealing temperature, the gas pressure or the total pressure on the reaction mixture can also fail, since under the new conditions the temperature spread of the gas molecules does not guarantee that under these changed conditions the thermodynamic equilibrium will correspond to the single-phase nature of the reaction product. From what has been said, it follows that ceramic synthesis technologies do not in principle allow obtaining highly pure substances, although in practice, in most cases, it is possible to obtain functional materials of acceptable purity. But it is important here, to know that this is not always possible.

Conclusions

1. A method is proposed for calculating the temperature distribution of gas molecules as a function of the total gas temperature.

2. An example is given of calculating the temperature distribution of oxygen molecules at 1000 K. The maximum content of molecules in this temperature range is at a rather low temperatur of 400 ± 200 K. The high average temperature of the gas is thus provided by molecules with high temperatures.

3. The correctness of the obtained distribution is confirmed by the additive formula for the total gas temperature in terms of the sum of the fractional contents of the temperatures of individual molecules.

4. Ceramic synthesis technologies do not in principle allow obtaining highly pure substances.

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