# GIBBS PARADOX IS A CONSEQUENCE OF NON-ADDICTION ENTROPIES OF IDEAL GAS FOR A CONSTANT VOLUME [1]


**V. Ihnatovych**

Department of Philosophy, National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”, Kyiv, Ukraine

e-mail: v.ihnatovych@kpi.ua



**Abstract**

The entropy of the *i*-th ideal gas $S_i$ in thermodynamics is expressed by a formula that contains the term $-Rn_i \ln n_i$ ($n_i$ — the number of moles of a gas). So that entropy is not an additive quantity, as for constant volume $S(n_1+n_2) \neq S(n_1)+S(n_2)$. Assuming that entropy of a mixture of different ideal gases is equal to the sum of entropy of its components, physics get the following formula for a mixture of $n_1$ and $n_2$ gas moles, which contains the term $R[(n_1+n_2)\ln(n_1+n_2)-(n_1 \ln n_1 + n_2 \ln n_2)]$. This term is equal to the difference $S(n_1)+S(n_2)-S(n_1+n_2)$. The same term is present in the formula for the entropy change in consequence of a mixing process of two ideal gases, initially separated by an impenetrable septum. When passing to a mixture (mixing) of identical gases, the indicated term “disappears”. The inexplicable within the framework of the physics the appearance and the “disappearance” of this term due to the nonadditivity of the entropy of ideal gas is the essence of various formulations of the Gibbs paradox, whose physical explanation search lasts more than 100 years.



**Keywords**: Gibbs paradox, entropy, ideal gases, additive properties.


## 1. Introduction

The Gibbs paradox arises in the theoretical consideration of the problem of entropy change when two ideal gases initially separated by an impenetrable septum are mixed. The value of the entropy of mixing process does not depend on the properties of the gases being mixed, as long as they are different, but it jumps to zero when it comes to a mixing of

---

[1] Proceedings of Eighteenth International Scientific Mykhailo Kravchuk Conference, October 7–10, 2017, Kyiv: Vol. 2. — Kyiv: NTUU “KPI”, 2017. — P. 262-266 [In Russian]. URL: http://matan.kpi.ua/public/files/2017/kravchuk-conf2017/Kravchuk2017-vol2.pdf

There is no breakdown of paragraphs in the original.

identical gases. This behavior of entropy of mixing process is paradoxical. Attempts to explain the Gibbs paradox have been undertaken for more than a hundred years (Khaytun, 2010).

At one time, the author analyzed the arguments that lead to the Gibbs paradox and showed that the conclusion about a paradoxical jump in the entropy of mixing process is a consequence of two premises: “the formula for the entropy of a pure ideal gas contains the term $-Rn_i \ln n_i$” and “the entropy of a mixture of ideal gases is equal to the sum of entropies of components of the mixture” (Ihnatovych, 2010). In this communication, the author intends to show that the two premises are logically incompatible: a function that is expressed by a formula containing the summand $an \ln n$ is not additive.

## 2. On the additivity of quantities and properties

“ADDITIVITY is a property of quantities, consisting in the fact that the value of a quantity corresponding to an entire object is equal to the sum of the values of the quantities corresponding to its parts for any division of the object into parts” (Mathematical encyclopedia, Vol. 1 1977, p. 94).

$$A = \sum_i A_i \,, \tag{1}$$

where $A$ is the value of some additive quantity corresponding to the whole object, $A_i$ are values of the quantities corresponding to its parts.

Now let us clarify which properties in physics are called additive.

“When the numerical value $x$ of a value representing a given property can be calculated by the mixing rule from numerical values $x$ of the same value taken for the component parts, then this property is called additive. In this case

$$mx = \sum m_i x_i \,,$$

where $m_i$ — the masses ... of the constituent parts and $m = \sum m_i$” (Khvolson, 1933, p. 59). ($x$ — specific value of the value — *V. I.*)

The values of specific property are determined by:

$$a_i = \frac{A_i}{m_i} \,. \tag{2a}$$

$$a_c = \frac{A_c}{m_c} \,. \tag{2b}$$

where $a_i$ are values of specific property of the components of the mixture, $m_i$ are the masses of the components of the mixture, $a_c$ — the values of specific property of the mixtures, and $m_c$ is the mass of the mixture.

$$m_c = \sum_i m_i \,. \tag{3}$$

The mass fraction of the mixture component $x_i$ is determined by:

$$x_i = \frac{m_i}{m_c} = \frac{m_i}{\sum_i m_i} \,. \tag{4}$$

The formula expressing values of specific additive properties of mixtures through values of specific properties of components follows from (1) — (4):

$$a_c = \sum_i x_i a_i \,. \tag{5}$$

If we assume that $a_i$ are not specific, but the, $x_i$ molar fractions of the components, then the average molar parameters of the mixture will be determined by formula (5).

For the calculation of molar parameters, $x_i$ are found by the formula:

$$x_i = \frac{n_i}{n_c} = \frac{n_i}{\sum_i n_i} = \frac{N_i}{N_c} = \frac{N_i}{\sum_i N_i} \,. \tag{6}$$

where $n_i$ — the number of moles of components, $n_c$- the total number of moles in the mixture, $N_i$ — the number of molecules of the components, $N_c$ — total number of molecules in the mixture.

It follows from formula (5) that specific (molar) additive properties of the mixture depend on specific (molar) properties and specific (molar) fractions of components of the mixture, but do not depend on the mass of the mixture. From this it follows that such properties of substances whose specific (molar) values do not depend on their quantity, that is, those properties whose values for a certain amount of matter are directly proportional to the amount of matter, i.e., parameters $m_i, n_i, N_i$, can be additive. It also follows from formula (5) that the specific properties of mixtures of identical components are equal to specific properties of components.

### 3. On the additive properties of ideal gases

The additive properties of mixtures of ideal gases are (see, for example, (Belyaev, 1987)): mass, weight, heat capacity, internal energy, and also — if different parts have the same pressure — volume, and — if different parts have the same volume — density and pressure. It is easy to see that all these properties are directly proportional to the amounts of gases. We draw attention to the fact that the pressure and density are additive properties of the mixture under the condition that its volume is constant, and the volume of the mixture is an additive property under the condition of constant pressure: only under such conditions, these properties of an ideal gas are directly proportional to its quantity (parameters $m, n, N$ ).

The pressure, temperature and volume of an ideal gas are related to each other by the thermal equations of the state of an ideal gas:

$$p_i V_i = \frac{m_i}{M_i} RT = n_i RT = N_i kT \ . \tag{7}$$

where $p_i$ — pressure, $V_i$ — volume, $T$ — thermodynamic (absolute) temperature, $M_i$ — molecular mass of gas, $R$ — universal gas constant, $k$ — Boltzmann constant.

The same equation relates the corresponding properties of mixtures of ideal gases. If we derive from formula (7) formulas expressing some additive property of the gas ( $p_i$, $V_i$, $m_i$, $M_i$) through other properties of gases, then these formulas will be valid for additive properties of mixtures of ideal gases. And other formulas connecting some additive properties of pure gases are valid for the corresponding additive properties of mixtures. This follows from formula (5) and from the proportionality of additive properties to the quantities of gases.

### 4. On the additivity of the entropy of ideal gases and the Gibbs paradox

The entropy of an ideal gas in thermodynamics is expressed by the formula:

$$S_i = n_i \left( c_{Vi} \ln T + R \ln \frac{V}{n_i} + S_{0i} \right) . \tag{8}$$

where $c_{Vi}$ is the molar heat capacity of a gas at a constant volume, $S_{0i}$ is a constant that depends only on the nature of the gas.

According to (8), the entropy is not a quantity proportional to the amount of gas, respectively, is not an additive quantity. As a consequence, for a two-component mixture from the formula (8) the next formula follows (see (Ihnatovych, 2010)):

$$S_1 + S_2 = S_c + R\left[(n_1 + n_2)\ln(n_1 + n_2) - (n_1 \ln n_1 + n_2 \ln n_2)\right] = \\ = S_c - n_c R\left(x_1 \ln x_1 + x_2 \ln x_2\right) \quad . \tag{9}$$

where $S_c$ is the expression obtained on the basis of the formula (8) when corresponding parameters of the mixture are substituted into it.

It is assumed that the entropy of a mixture of ideal gases is equal to the sum of the entropies of the components of the mixture, and a formula of the form (9) expresses the entropy of the mixture. Therefore, the appearance of the second term in this formula is not attributed to the nonadditivity of the entropy function of an ideal gas, and for over 100 years it has been attempted to explain by some specific properties of the mixtures in comparison with pure gases, which constitutes one of the directions for finding the solution of the Gibbs paradox.

For the case of mixing of two different ideal gases with the same initial temperatures and pressures, it follows from formula (9) (and a number of others) that the value of entropy of mixing is equal to the second term in formula (9). Since in the case of the identity of the components formula (9) does not become to the formula (8), it becomes a necessary to explain the «disappearance» of the second term in formula (9) when changing from a mixture (mixing) of different ideal gases to a mixture (mixing) of identical ideal gases. This is the content of other formulations of the Gibbs paradox.

Gel’fer, Lyuboshits, Podgoretskij (1975) derived the formula for the entropy of an ideal gas is containing a term of the form $kN\ln(V/N)$ on the basis of the requirement «the additivity of entropy with respect to the separation of the system into subsystems» (Gel’fer et al., 1975, p.16), where the subsystems are formed by dividing the volume of the gas into parts. In other words, an additive quantity whose value for an integer is equal to the sum of the values for parts not for any partitioning of the system into parts, but only if the pressures in the parts are equal, is called additive. The fact that a function defined under this condition turns out to be non-additive if the volume is constant is further considering by other authors as a paradox, to the solution of which they make a lot of efforts.

Terletsky (1975) obtains an expression for the entropy of an ideal gas containing a term $kN\ln V$ and asserts that it does not satisfy the additivity principle, since entropy does not increase by a $\alpha$ factor with a simultaneous increase of $N$ and $V$ in $\alpha$ time (Terletsky, 1984, P. 3). For the entropy has this property (additivity when the pressures in parts are equal), the author introduces the term $kN\ln(V/N)$ into the formula, and then begins to discuss the paradox caused by the nonadditivity of the function obtained by him, when the volumes are equal.

## 5. Conclusion

Thus, the underlying paradox of Gibbs is a glaring contradiction. The formula for the entropy of an ideal gas is obtained on the basis of the requirement that the entropy of an ideal gas be additive under the condition that pressures of the parts are equal, that leads to nonadditivity of the entropy provided that volumes of the parts are equal. The entropy of the mixture is found on the assumption of its additivity, provided that volumes of the parts are equal. A rational explanation of the results obtained on the basis of these logically incompatible premises is sought for more than 100 years.

## References

Belyaev, N.M. (1987) *Thermodynamics*. Kiev: Vishcha school. [Russian]

Gel’fer, J. M., Lyuboshits, V. L., Podgoretskij, M. I. (1975) Gibbs Paradox and identity of particles in quantum mechanics. Moscow: Nauka Publishers [Russian]

Ihnatovych, V. M. (2010) *Gibbs' paradox from the point of view of the mathematician*. Kyiv: Publishing Group «ATOPOL» [Russian]

Khaytun, S. D. (2010) *The History of the Gibbs' Paradox* (Ed. 3rd) Moscow: Nauka Publishers [Russian]

Khvolson O.D. (1933) *Course of Physics*. (Vol.1 / Ed. 7th, add.) Moscow-Leningrad: State technical and theoretical Publ. [Russian]

*Mathematical encyclopedia. Vol. 1* (1977) Chief editor I. M. Vinogradov. Moscow, Soviet encyclopedia [Russian].

Terletsky, Ya.P. (1984) *The Gibbs paradox in classical statistical mechanics* // Thermophysical properties of metastable systems. Sverdlovsk, UNSC of the USSR Academy of Sciences. [Russian]