

The original Gibbs paradox is a consequence of a false premise

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The Gibbs Paradox arises when considering rather simple questions concerning the entropy of ideal gases, but remains unresolved for more than a century. There are several formulations of this paradox. In the formulation that J. W. Gibbs himself discussed, we are talking about an inexplicable jump in the entropy of mixing of ideal gases during the transition from mixing of different to mixing of identical ideal gases. Here we show that when obtaining an opinion on the indicated jump, a false premise is used: “a formula that contains the term $-R(n_1 \ln n_1 + n_2 \ln n_2)$ and a formula that contains the term $-R(n_1 + n_2) \ln(n_1 + n_2)$ express different values of the same function”. Without this false premise, the conclusion about an inexplicable jump in the entropy of mixing of ideal gases does not arise.

Introduction

The Gibbs Paradox is one of the most mysterious physical paradoxes. It has been known for over a hundred years. It was explained or discussed by J.W. Gibbs, M. Planck, J.D. van der Waals, A. Sommerfeld and other well-known physicists (see [1–7]). There are several dozens of solutions to this paradox, but there is no such that can be called generally accepted. Various solutions to this paradox are presented in many textbooks (see, e.g., [2,4,10–12]), but papers containing new solutions appear again and again (see, e.g., [6, 13–17]).

There are several formulations (versions, kinds) of the Gibbs paradox. One of them, which was discussed by J. W. Gibbs and which we, by the example of J. van Lith [17], call the original Gibbs paradox, arises when considering the magnitude of the entropy of mixing of two ideal gases separated by an initially impenetrable partition. If different gases have the same temperatures, volumes and pressures, and the number of moles of each gas is equal n , then after removing the partition and mixing the gases, the entropy of the system increases by the entropy of mixing equal to $2nR \ln n$, where R is the universal gas constant. If identical gases with the same temperature and pressure mix, then the entropy of mixing is zero. Thus, during the transition from mixing different gases to mixing identical ideal gases, the entropy of mixing makes a jump, the value of which does not depend on how and how different the gases were. This behavior of the entropy of mixing is paradoxical (see, e.g., [1,2,5,8–11,13,14,16–20]).

A common feature of all works devoted to this formulation of the Gibbs paradox is that authors did not take into account the fact that the conclusion about a paradoxical jump in the entropy of mixing is not based on processing empirical data, but arises by reasoning based on certain premises. They did not analyze this reasoning and did not notice that there is a false premise used in obtaining a conclusion about the paradoxical jump in the entropy of mixing. To discover this premise, let us reproduce and analyze the reasoning that will adhere to this conclusion.

These considerations can be divided into three parts. In the first part, the entropy of mixing of various ideal gases is found. In the second part, the entropy of mixing of identical ideal gases is found. In the third part, a conclusion on the jump in the entropy of mixing during the transition from mixing different gases to mixing identical gases is drawn, based on a comparison of the found values.

Getting formulas for the entropy of mixing ideal gases and conclusions about the paradoxical jump in the entropy of mixing

Among the premises on the basis of which the entropy of mixing of ideal gases is found (see, for example, [1,2,8,10–13,17]), there are formulas that express the entropy of a number of systems.

The entropy of moles of the i -th ideal gas, the volume of which is equal V_i , and the temperature is equal T_i , is expressed by the formula:

$$S_i(n_i, V_i, T) = n_i \left(c_{Vi} \ln T_i + R \ln \frac{V_i}{n_i} + s_{0i} \right), \quad (1)$$

where c_{Vi} is the molar heat capacities of the i -th ideal gas at a constant volume, which depends on the nature of the gas; s_{0i} is constant, which depends on the nature of the gas.

The entropy of a system consisting of two ideal gases separated by an impermeable partition, the quantities of which are equal n_1 and n_2 moles and volumes V_1 and V_2 is expressed by the formula:

$$S(n_1, V_1, n_2, V_2) = S_1(n_1, V_1) + S_2(n_2, V_2), \quad (2)$$

where $S(n_1, V_1)$ and $S(n_2, V_2)$ are entropies of gases.

The entropy of a mixture n_1 and n_2 moles of different ideal gases, the volume of which is equal V , according to the Gibbs theorem, is expressed by the formula:

$$S_m(n_1, n_2, V) = S_1(n_1, V) + S_2(n_2, V), \quad (3)$$

where $S_1(n_1, V)$ и $S_2(n_2, V)$ are entropies of gases.

The change in the entropy of the system during transition from the initial state I to the final state II is expressed by the formula:

$$\Delta S = S_{II} - S_I, \quad (4)$$

where S_I is the entropy of the system in the initial state, S_{II} is the entropy of the system in the final state, p_i is pressure of the i -th ideal gas.

A number of parameters of an ideal gas are related to the equation of state:

$$p_i V_i = n_i R T_i, \quad (5)$$

where p_i is pressure of the i -th ideal gas.

Further on the values related to systems of different gases will be denoted by superscripts d : S_I^d , S_{II}^d , ΔS^d , and the values related to systems of identical ideal gases will be denoted by superscripts i : S_I^i , S_{II}^i , ΔS^i .

Based on the formulas above, we derive formulas for the entropy of mixing of different and identical ideal gases whose temperatures are the same.

Suppose that n_1 and n_2 moles of ideal gases 1 and 2 with equal temperature and pressure are separated by an impermeable partition. Volumes of the gases are equal V_1 and V_2 . From (1) and (2) follows the formula for entropy of this system:

$$S_I^d = S^d(n_1, V_1, n_2, V_2) = (n_1 c_{V1} + n_2 c_{V2}) \ln T + R \left(n_1 \ln \frac{V_1}{n_1} + n_2 \ln \frac{V_2}{n_2} \right) + n_1 s_{01} + n_2 s_{02}. \quad (6)$$

After removing the partition the mixture is formed with of n_1 and n_2 moles of ideal gases 1 and 2 of volume $V_1 + V_2$. From (1) and (3) follows the formula for entropy of this mixture:

$$\begin{aligned} S_{II}^d &= S_m^d(n_1, n_2, V_1 + V_2) = (n_1 c_{V1} + n_2 c_{V2}) \ln T + R \left(n_1 \ln \frac{V_1 + V_2}{n_1} + n_2 \ln \frac{V_1 + V_2}{n_2} \right) + n_1 s_{01} + n_2 s_{02} = \\ &= (n_1 c_{V1} + n_2 c_{V2}) \ln T + R(n_1 + n_2) \ln(V_1 + V_2) - R(n_1 \ln n_1 + n_2 \ln n_2) + n_1 s_{01} + n_2 s_{02} \end{aligned} \quad (7)$$

From (4), (6), (7) follows the formula for ΔS^d the entropy of mixing n_1 and n_2 moles of different ideal gases 1 and 2 with equal temperature and pressure that are separated before mixing by an impermeable partition:

$$\Delta S^d(n_1, n_2) = R(n_1 + n_2) \ln(V_1 + V_2) - R(n_1 \ln n_1 + n_2 \ln n_2) - R \left(n_1 \ln \frac{V_1}{n_1} + n_2 \ln \frac{V_2}{n_2} \right). \quad (8)$$

In the case where the gases that are separated by a partition have not only the same temperature, but also the same pressure value, from (5) follows:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = \frac{V_1 + V_2}{n_1 + n_2}, \quad (9)$$

and from (8) and (9) follows:

$$\Delta S^d(n_1, n_2) = R(n_1 + n_2) \ln(n_1 + n_2) - R(n_1 \ln n_1 + n_2 \ln n_2). \quad (10)$$

If $n_1 = n_2 = n$, then from (10) follows

$$\Delta S^d(n, n) = 2Rn \ln 2. \quad (11)$$

If $n_1 = n_2 = 1$, then from (10) follows

$$\Delta S^d = 2R \ln 2. \quad (12)$$

Now let us consider the case of mixing of identical ideal gases.

Suppose, n_1 and n_2 moles of identical ideal gases (3 and 3), whose temperatures are equal T , and the volumes V_1 and V_2 , are separated by an impenetrable partition. From (1) and (2) follows the formula for entropy of this system:

$$S_I^i = S^i(n_1, V_1, n_2, V_2) = (n_1 + n_2)c_{V3} \ln T + R \left(n_1 \ln \frac{V_1}{n_1} + n_2 \ln \frac{V_2}{n_2} \right) + (n_1 + n_2)s_{03}. \quad (13)$$

After removing the partition, $n_1 + n_2$ moles of pure ideal gas 3 of volume $V_1 + V_2$ are formed, its entropy according to (1) is equal to

$$\begin{aligned} S_{II}^i = S_3(n_1 + n_2, V_1 + V_2) &= (n_1 + n_2)c_{V3} \ln T + R(n_1 + n_2) \ln \frac{V_1 + V_2}{n_1 + n_2} + (n_1 + n_2)s_{03} = \\ &= (n_1 + n_2)c_{V3} \ln T + R(n_1 + n_2) \ln(V_1 + V_2) - R(n_1 + n_2) \ln(n_1 + n_2) + (n_1 + n_2)s_{03} \end{aligned} \quad (14)$$

From (4), (13), (14) follows the formula for ΔS^i the entropy of mixing of n_1 and n_2 moles of identical ideal gases that have equal temperature and pressure values and are separated by an impermeable partition before the mixing:

$$\Delta S^i(n_1, n_2) = R(n_1 + n_2) \ln(V_1 + V_2) - R(n_1 + n_2) \ln(n_1 + n_2) - R \left(n_1 \ln \frac{V_1}{n_1} + n_2 \ln \frac{V_2}{n_2} \right). \quad (15)$$

For the case of mixing identical gases with the same temperatures and pressures from (15) and (9) follows:

$$\Delta S^i(n_1, n_2) = \Delta S^i(n, n) = \Delta S^i(1, 1) = 0. \quad (16)$$

Comparing formulas (10)–(12) with formula (16), we obtain the conclusion on the jump in the entropy of mixing during the transition from mixing different to mixing identical ideal gases.

This conclusion seems absolutely certain. The conclusion about the jump in the entropy of mixing follows from the fact that the value $\Delta S^d(n_1, n_2)$, according to (10)–(12), is not equal to zero, and the entropy value $\Delta S^i(n_1, n_2)$, according to (16), is equal to zero. Each of formulas (10)–(12), (16) is obtained on the basis of the original formulas by means of a mathematical derivation, the correctness of which can be easily verified, since when receiving each intermediate formula, it is indicated from which initial and intermediate formulas it follows.

Why does the conclusion about the paradoxical jump of the entropy of mixing appear

To reveal the error that leads to the conclusion about the jump in the entropy of mixing, we consider the question: what determines the difference between the values of $\Delta S^d(n_1, n_2)$, which is expressed by formulas (10)–(12), and $\Delta S^i(n_1, n_2)$, which is expressed by formula (16)?

If we analyze the derivation of formulas (10)–(12) and (16), we can see that formulas (10)–(12) are special cases of formula (8), formula (16) is a special case of formula (15), and the difference between formulas (10)–(12) and formula (16) is due to the difference between formula (8) and formula (15): formula (8) contains the term $-R(n_1 \ln n_1 + n_2 \ln n_2)$, and formula (15) the term $-R(n_1 + n_2) \ln(n_1 + n_2)$. The value that is called the jump of the entropy of mixing when going from mixing different to mixing identical gases, i.e., the difference in the entropy of mixing $\Delta S^d(n_1, n_2) - \Delta S^i(n_1, n_2)$, is nothing but the difference between these terms equal to $(n_1 + n_2)R \ln(n_1 + n_2) - n_1 R \ln n_1 - n_2 R \ln n_2$.

The difference between the terms $-R(n_1 \ln n_1 + n_2 \ln n_2)$ and $-R(n_1 + n_2) \ln(n_1 + n_2)$ is due to the fact that they are different functions of n_1 and n_2 . Therefore, the difference between formulas (10)–(12) and (16), which express the entropies of mixing of different and identical gases $\Delta S^d(n_1, n_2)$ and $\Delta S^i(n_1, n_2)$, is due to the fact that $\Delta S^d(n_1, n_2)$ and $\Delta S^i(n_1, n_2)$ are different functions of the quantities n_1 and n_2 .

The fact that different functions of quantities n_1 and n_2 have different meanings in the case of identical values n_1 and n_2 , there is nothing paradoxical or inexplicable. However, those who, based on a comparison of formulas (11), (12) and (16), make a conclusion about a paradoxical jump in the entropy of mixing from $2nR \ln n$ or $2R \ln 2$ to zero, proceed from an assumption that $2nR \ln n$, $2R \ln 2$ and 0 are different values of one and the same function — the entropy of mixing ideal gases.

In other words, when obtaining a conclusion about the paradoxical jump in the entropy of mixing under consideration, a false premise is used: “a function $\Delta S^d(n_1, n_2)$, whose formula contains the term $-R(n_1 \ln n_1 + n_2 \ln n_2)$, and a function $\Delta S^i(n_1, n_2)$, whose formula contains the term $-R(n_1 + n_2) \ln(n_1 + n_2)$, are special cases of the same function — the entropy of mixing of ideal gases”. Without using this false premise, one cannot draw a conclusion about a jump in the entropy of mixing. Indeed, if we proceed from the true premise that “ $\Delta S^d(n_1, n_2)$ and $\Delta S^i(n_1, n_2)$ are different functions”, then from a comparison of formulas (10)–(12) and (16), we cannot

conclude that during the transition from mixing different gases to mixing identical gases, some function value jumps.

The value of a single-valued function, which is expressed by some formula, is determined by values of the parameters and arguments that are included in this formula. Since it is generally accepted that formula (16) for the case of identical ideal gases expresses the value of the same function, which for the case of various ideal gases is expressed by formulas (10)–(12), many authors looked for the parameter of ideal gases, due to the difference in values of which the formula (16) differs from formulas (10)–(12). In fact, they tried to solve an insoluble problem: to find a gas parameter that differs from n_1 and n_2 , whose difference in values determines the difference in values of $-R(n_1 \ln n_1 + n_2 \ln n_2)$ and $-R(n_1 + n_2) \ln(n_1 + n_2)$.

Conclusions

The appearance of the Gibbs paradox in the formulation of the conclusion about the entropy jump of the mixing of ideal gases during the transition from mixing of different ideal gases to mixing of identical ideal gases is due to the use of a false premise: “formula that contain the term $-R(n_1 \ln n_1 + n_2 \ln n_2)$ and formula that contain the term $-R(n_1 + n_2) \ln(n_1 + n_2)$ express different values of the same function”. Because this assumption is considered to be true, given the jump is inexplicable. If you remove this false premise, then this formulation of the Gibbs paradox is eliminated.

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References

- [1] Gibbs J W *The Collected works Vol. 1 Thermodynamics* (New York: Longmans, 1928)
- [2] Planck M *Treatise on Thermodynamics* (New York: Longmans, 1903)
- [3] Van der Waals J D and Kohnstamm Ph *Lehrbuch der Thermodynamik. Zweiter Teil* (Leipzig: Verlag von Johann Ambrosius Barth, 1912) (in German)
- [4] Sommerfeld A *Thermodynamics and Statistical Mechanics* (New York: Academic Press, 1956)
- [5] Khaytun S D *The History of the Gibbs Paradox* (Moscow: Nauka, 1986) (in Russian)
- [6] *Gibbs paradox and its resolutions* / Compiled by Shu-Kun Lin. Internet: www.mdpi.org/lin/entropy/gibbs-paradox.htm Last change: 7 November 2009 [cited 2019 Oct 16]

- [7] Darrigol O The Gibbs Paradox: Early History and Solutions *Entropy* **20** 443 (2018)
- [8] Gelfer Ya M and Luboshitz V L and Podgoretskii M I *Gibbs Paradox and Identity of Particles in Quantum Mechanics* (Moscow: Nauka, 1975) (in Russian)
- [9] Denbigh K G and Redhead M L G Gibbs' paradox and non-uniform convergence *Synthese* **81** 283–312 (1989)
- [10] Bazarov I P *Thermodynamics (4th ed., rev. and enl.)* (Moscow: Vysshaya Shkola, 1991) (in Russian)
- [11] Kondepudi, D. and Prigogine I *Modern thermodynamics: From heat engines to dissipative structures* (New York: Wiley, 1998)
- [12] Struchtrup H *Thermodynamics and Energy Conversion* (Heidelberg: Springer, 2014)
- [13] Urusov, V S Gibbs paradox and Symmetrization of a Multicomponent System *Doklady Physical Chemistry* **417** (Part 2) 337–341 (2007)
- [14] Ainsworth P M The Gibbs Paradox and the Definition of Entropy in Statistical Mechanics *Philos. Sci.* **79** 542–560 (2012)
- [15] Etkin V.A. Thermodynamic resolution of “Gibbs paradox” *Preprint* at <https://arxiv.org/abs/1312.7081> (2013)
- [16] Peters H Demonstration and resolution of the Gibbs paradox of the first kind *Eur. J. Phys.* **35** 015023 (2014)
- [17] Van Lith J The Gibbs Paradox Lessons from Thermodynamics *Entropy* **20** 328 (2018)
- [18] Dieks D The Gibbs Paradox and Particle Individuality *Entropy* **20**(6) 466 (2018)
- [19] Saunders S The Gibbs Paradox *Entropy* **20** 552 (2018)
- [20] Swendsen R H Probability, Entropy, and Gibbs' Paradox(es) *Entropy* **20** 450 (2018)