

Entropy Calculation of Reversible Mixing of Ideal Gases Shows Absence of Gibbs Paradox

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Abstract: We consider the work of reversible mixing of ideal gases using a real process. New assumptions were made concerning infinite shifts, infinite number of cycles and infinite work to provide an accurate calculation of entropy resulting from reversible mixing of ideal gases. We derived an equation showing the dependence of this entropy on the difference in potential of mixed gases, which is evidence for the absence of Gibbs' paradox.

Keywords: Gibbs paradox; entropy of mixing; distinguishability, half-penetrable membrane.

Introduction

The problem of ideal gases mixing entropy was solved by J. W. Gibbs in 1876 [1]. The result of this solution was known as Gibbs' paradox and has existed for more than 120 years due to an annoying misunderstanding caused by this solution. Up to now, hundreds of attempts have been made to explain the independence of mixing entropy from the difference in physical properties between the gases to be

mixed. We shall not consider all of these attempts, but shall use the main results of these attempts in order to derive our new equation.

The existence of Gibbs' paradox is strange in classic thermodynamics, because the named paradox does not arise from experimental data, but from equations that contradict the Gibbs' equation.

In our article, the work of the reversible mixing of ideal gases is calculated. This result allows us to show both the absence of Gibbs' paradox and some thermodynamic limitations that imply the impossible existence of pure substances, absolute vacuum, and half-penetrable membranes.

The Description of the Problem

We consider the work of mixing ideal gases satisfying the Equations found by J. W. Gibbs [1] in the following manner:

$$P = \sum_i \frac{M_i \cdot R \cdot T}{m_i \cdot V}, \quad (1)$$

$$S = \sum_i \left(M_i \cdot H_i + M_i \cdot C_i \cdot \ln T + \frac{M_i}{m_i} \cdot \ln \frac{V}{m_i} \right), \quad (2)$$

where P - pressure of the gas mixture, M_i - mass of i component of the gas mixture, R - universal gas constant, T - absolute temperature, m_i - molal mass of i component of the gas mixture, V - volume of gas mixture, S - entropy of gas mixture, H_i , C_i - constants.

Equation (1) expresses Dalton's law experimentally, while equation (2) is a consequence from this law, found by J. W. Gibbs [1]. Let us note that volume V in these equations is common to all components of the mixture and has no indexes i , therefore it is constant when the mixture volume is not changed. In other words, changing V corresponds to a real change of mixture volume and of each component.

Taking the above concepts into consideration it is really strange that Gibbs derived an equation for the entropy of mixing diffusable gases and marked the volumes occupied by the different gases with indices as shown in the equation below. According to this equation, a certain amount of entropy was produced during the mixing of 1 mole (total) of two different gases taken in the quantity of 1/2 mole each.

$$\Delta S = \frac{R \cdot M_1}{m_1} \cdot \ln V + \frac{R \cdot M_2}{m_2} \cdot \ln V - \frac{R \cdot M_1}{m_1} \cdot \ln \frac{V}{2} - \frac{R \cdot M_2}{m_2} \cdot \ln \frac{V}{2} = R \cdot \ln 2. \quad (3)$$

This result is really strange, because Gibbs established that the entropy of the gas mixture is equal to the sum of the entropies of the components, if they separately occupied the entire volume at the temperature of the mixture.

So, equation (3) should be written in the following way

$$\Delta S = \frac{R \cdot M_1}{m_1} \cdot \ln V + \frac{R \cdot M_2}{m_2} \cdot \ln V - \frac{R \cdot M_1}{m_1} \cdot \ln V - \frac{R \cdot M_2}{m_2} \cdot \ln V \equiv 0, \quad (4)$$

which corresponds to Gibbs' law. This equation assumes that: 1) these few gases are in contact with each other and are separated only by moving thermoconductive membranes, 2) that the values of pressure and temperature are common for all gases, and 3) that their volumes are $V / \left(\sum_i 1 \right)$, because we consider equal parts of gases. If so, any change in the full volume dV of such a composite shall correspond to the change in volume of each component $dV / \left(\sum_i 1 \right)$, and the differential of the composite entropy may be written

$$(dS)_T = \sum_i \frac{R \cdot M_i}{m_i} \cdot \frac{1}{\left(\sum_i 1 \right)} \cdot \frac{dV}{\left(\sum_i 1 \right)} \equiv \sum_i \frac{R \cdot M_i}{m_i} \cdot \frac{dV}{V}. \quad (5)$$

This last equation means that in a composite, each gas has the property as if it occupied the entire volume. Further on, it is clear that the entropy of such a composite is equal to the sum of its component entropies, so equation (4) is right in this case. But, if the membranes separating the gases are taken out, then equation (4) is correct for the case of identical gases only. In the case of mixing different gases with no membranes to separate them, this process is not reversible. We cannot use equation (4) in this case because it expresses the reversible situation, where gases were mixed in the considered volume. Therefore, for the process of diffusion during gas mixing, we can say only that

$$\Delta S > 0, \quad (6)$$

according to the second law of thermodynamics. So, we determined that the entropy of identical gases mixing was equal to zero. There have been many attempts to calculate the work of separating or mixing of different gases [2], but most of them showed that entropy mixing is independent of the gas difference.

So, we are wondering why the problem of the increasing entropy still exists? Let us consider the known solutions of the Gibbs' paradox. According to the purposes of this article we shall divide the known solutions into two main groups – thermodynamics and statistical solutions. The reason for this separation is in the approach to the problem. In the thermodynamics solutions, the work or heat obtained either during mixing or separating different substances, are calculated. In the statistical solution, entropy of the mixture is calculated directly and is based on the certain model of the substance. Here we shall find that a common place thermodynamics solution of the Gibbs' paradox allows us to avoid the Gibbs' paradox in order to find the right solution.

Similarly, the first attempt to find the work of mixing two different gases belongs to the Lord Rayleigh [3]. Rayleigh suggested using the gravitational field for separating two different gases from a mixture. Using this technique, these gases could not be completely separated because of the limited height of the apparatus. It was suggested that an infinite number of cycles would have to be used to separate the pure gases from a mixture. Certainly, in the result of this process, the value of $R \cdot \ln 2$ was obtained for mixing entropy of different gases taken in the quantity of 1/2 mole each. We cannot agree with the possibility that this is a reversible process, where an infinite number of cycles were used. This theory would actually require that, each reversible process be infinitely long. If we have to make an infinite number of the infinitely long processes then this would not provide a reversible condition of this process at all. G. Lorenz made a similar attempt [4] in 1907. He suggested using an infinitely long tube situated in the gravitational field to separate out the different gases from a mixture. According to his calculation it appeared that the mixing entropy was constant for different gases and equal to zero for identical gases. However, we cannot accept a hypothesis allowing a real process with infinite shifts. Actually, a limited speed of any shift of the substance is an experimentally proven fact. That is why the process of using infinite shifts of the substance could not be realized, either. To tell the truth, we have never found any valid suggestion for this process using an infinitely strong gravitational field for separating different gases in a limited long tube. Also, modern understanding of nature prohibits such a process. We should note here that an infinite difference of the gravitational potential could not be used because it contradicts the general relativity theory.

Having marked the impossibility of the reversible process at an infinite difference in the gravitational potentials of different gases, we shall now consider solutions of the Gibbs' paradox, which are based on separating different gases with half-penetrable membranes. As far as we know, according to [2], the first attempt to use half-penetrable membranes for mixing two different gases was made by Wiedeburg [5]. In this article, the work of the isothermal mixing of the two different gases, taken in quantity of one mole each, was determined to be equal to $R \cdot T \cdot \ln 2$, while work of the mixing of the identical gases was equal to zero. It is interesting, that A. Einstein [6] expressed considerable doubts in the possible existence of ideal half-penetrable membranes. However, he also states, that the existence of such membranes did not contradict the second law of the thermodynamics and could therefore be accepted. This same idea was expressed very clearly by von Neumann [6], who suggested that any conceivable process could be used for deriving thermodynamics theorems. It seems

to us, that both of the mentioned scientists (Einstein and Neumann) had considerable doubts in this approach and we do not understand why they used it. It is clear to us, that the ideal half-penetrable membrane should provide, in some way, an infinite difference of the potentials for different substances. It was shown above that such an infinite difference in the potentials could not result from a gravitational field, so we have to decide if this infinite difference could be created by other means.

This approach to the problem is known as the so-called operational solution of the Gibbs' paradox [2]. This solution covers both thermodynamics solutions and statistical solutions of the paradox. Here, we shall consider only the thermodynamics part of this solution, because the statistic part of this solution shall be apparent at the end of the present article. We shall not consider the historical development of these solutions, because it has already been covered in the book by Khaytun [2]. So, the interaction between measurement apparatus and mixing gases is considered in this case. The concept of partly separated gases is the main idea of the operational solution [7]. And according to Khaytun et al [7], any half-penetrable membrane (treated as a gas-separating apparatus) cannot be ideal for similar gases. This means that the said entropy difference could not exist for similar gases as an experimentally measured value. This fact removes Gibbs' paradox according to the operational solution. However, this approach is not generally accepted [8]. Even more, it has been shown by Zraiskii [8], that separating different substances with a non-ideal apparatus leads to new paradoxes. In reality, this hypothesis contradicts the existence of the equal molecules, because in order to determine if the molecules are identical, a gas-separating apparatus without errors is needed which is impossible according to operational theory. The drawback of this theory according to Zraiskii [8] is the dependence of the physical processes on the observer's point of view. In reality, changes in entropy in this case depend on the gas-distinguishing apparatus quality. In other words, a different final entropy is obtained by mixing the same gases by various apparatuses even though all other parameters are held constant. It looks strange. However, such operational approach was developed further. And it is interesting, that in the works by Lin [9,10] results were consistent with the paradoxes found by Zraiskii [8], i.e. entropy mixing is maximal at mixing the same substances and is minimal at mixing different substances. We cannot accept this approach to the problem because these results contradict the second law of the thermodynamics, due to the fact that mixing of the same gas is a reversible process which means that no change in entropy can occur at all. We shall not analyze the statistical part of these works here. Also, we simply cannot understand why the author of these articles [9,10] made the conclusion that the entropy of mixing oil and water is equal to zero which was deduced from the fact that their liquid phases do not mix self-willed. From our point of view, such behavior of liquids means that their chemical potentials would be higher inside other liquids only. This example is similar to the case where gases with different molal weights do not mix in a vertically oriented tube placed in a gravitational field because the mixing entropy is equal to zero. It is clear in this case, that such mixing corresponds to increasing mixture free energy and therefore cannot be made self-willed. However, the vapors of oil and water can mix in any alignment. So, this example does not demonstrate anything.

The approach, which is the closest to ours, is expressed by Blumenfeld et al. [11]. There are specific requirements that need to be met in order for a gas-separating apparatus to completely separate similar substances. The authors showed that a gas-separating apparatus must be absolutely solid (which corresponds to creating an infinite difference in the potentials of the substances according to our opinion) or must be at a temperature of absolute zero to allow complete separation of different substances. However, we know that the third law of the thermodynamics prohibits the existence of temperatures equal to absolute zero [12], and special relativity theory prohibits the existence of the substances that are completely solid. Therefore, we found that all known thermodynamics solutions of the Gibbs paradox use the processes prohibited either by thermodynamics or by the relativity theory.

In this article, we consider gases with equal potentials in all conditions as identical. Thus, to obtain an accurate value of the ideal gases mixing entropy, it is necessary to calculate the entropy of a reversible process of mixing or separating the ideal gases. We consider only reversible processes, where an infinite number of cycles, infinite shifts, infinite potentials, infinite work or heats are not allowed. In other words, we state that reversible processes that use infinite shifts, infinite value of work or heat for limited quantities of substance cannot exist.

Entropy Calculation of the Reversible Separating of Ideal Gases

Let us find the work A_1 of separating two different gases using a reversible isothermal process, which allows us to find the entropy of the reversible mixing of these gases in the following way

$$\Delta S = \frac{A_1}{T}, \quad (7)$$

because we consider ideal gases, assuming that their specific molal heats are constant, and therefore any quantity of heat obtained or spent in our isothermal process has to be transformed into work.

To separate different gases, a vertically oriented tube with length $2h$ is placed in a gravitational field with acceleration g . A mixture of equal molal parts of two ideal gases is injected into the central part of the tube at pressure P_0 with volume V_0 . The work A_0 is spent per mole of mixture

$$A_0 = -P_0 \cdot V_0 = -R \cdot T \quad (8)$$

The work A_+ of taking out 1/2 mole of the gas mixture from the top of the tube and the work A_- of taking out 1/2 mole of the gas mixture from the bottom of the tube are

$$A_+ = A_- = P_+ \cdot V_+ = P_- \cdot V_- = \frac{1}{2} \cdot R \cdot T, \quad (9)$$

where P_+ - mixture pressure at height h , V_+ - volume of 1/2 mole of ideal gas at pressure P_+ , P_- - mixture pressure at deep h , V_- - volume of 1/2 mole of ideal gas at pressure P_- .

To find pressures P_+ and P_- let us use Dalton's law (1) and barometric law. So

$$\begin{aligned} P_+ &= \frac{1}{2} \cdot P_0 \cdot \left(\exp\left(-\frac{m_1 \cdot g \cdot h}{R \cdot T}\right) + \exp\left(-\frac{m_2 \cdot g \cdot h}{R \cdot T}\right) \right), \\ P_- &= \frac{1}{2} \cdot P_0 \cdot \left(\exp\left(\frac{m_1 \cdot g \cdot h}{R \cdot T}\right) + \exp\left(\frac{m_2 \cdot g \cdot h}{R \cdot T}\right) \right), \end{aligned} \quad (10)$$

where m_1 - molal mass of gas 1, m_2 - molal mass of gas 2.

At isothermal compression V_+ to $V_0/2$ at pressure P_0 the work A_{p+} has to be spent and at isothermal expansion V_- to $V_0/2$ at pressure P_0 , the work A_{p-} has to be obtained in the following quantities

$$\begin{aligned} A_{p+} &= -\frac{1}{2} \cdot R \cdot T \cdot \ln \left(\frac{2}{\exp\left(-\frac{m_1 \cdot g \cdot h}{R \cdot T}\right) + \exp\left(-\frac{m_2 \cdot g \cdot h}{R \cdot T}\right)} \right), \\ A_{p-} &= -\frac{1}{2} \cdot R \cdot T \cdot \ln \left(\frac{2}{\exp\left(\frac{m_1 \cdot g \cdot h}{R \cdot T}\right) + \exp\left(\frac{m_2 \cdot g \cdot h}{R \cdot T}\right)} \right). \end{aligned} \quad (11)$$

To calculate mechanic work A_{m+} obtained by descending the gas in volume V_+ at depth h and mechanic work A_{m-} spent by lifting the gas in volume V_+ to height h , let us calculate the masses of these mixtures, defining them as M_+ and M_- respectively.

$$\text{Since } M_+ = (\mathbf{r}_{1+} + \mathbf{r}_{2+}) \cdot V_+ \text{ and } M_- = (\mathbf{r}_{1-} + \mathbf{r}_{2-}) \cdot V_-$$

where \mathbf{r}_{1+} - density of gas 1 at height h , \mathbf{r}_{2+} - density of gas 2 at height h , \mathbf{r}_{1-} - density of gas 1 at deep h , \mathbf{r}_{2-} - density of gas 2 at deep h ,

$$\text{and } \mathbf{r} = \frac{P}{R \cdot T}, \quad (12)$$

then, using the barometric law, we obtain,

$$M_+ = \frac{m_1 \cdot \exp\left(-\frac{m_1 \cdot g \cdot h}{R \cdot T}\right) + m_2 \cdot \exp\left(-\frac{m_2 \cdot g \cdot h}{R \cdot T}\right)}{\exp\left(-\frac{m_1 \cdot g \cdot h}{R \cdot T}\right) + \exp\left(-\frac{m_2 \cdot g \cdot h}{R \cdot T}\right)} \text{ and}$$

$$M_- = \frac{m_1 \cdot \exp\left(\frac{m_1 \cdot g \cdot h}{R \cdot T}\right) + m_2 \cdot \exp\left(\frac{m_2 \cdot g \cdot h}{R \cdot T}\right)}{\exp\left(\frac{m_1 \cdot g \cdot h}{R \cdot T}\right) + \exp\left(\frac{m_2 \cdot g \cdot h}{R \cdot T}\right)}.$$

Therefore, the sought quantities of mechanical work are

$$A_{m+} = M_+ \cdot g \cdot h,$$

$$A_{m-} = -M_- \cdot g \cdot h.$$

Then the following work A_1 is spent on separating 1 mole of mixture into 2 different volumes of mixtures with the different concentrations of components:

$$A_1 = A_0 + A_+ + A_- + A_{p+} + A_{p-} + A_{m+} + A_{m-} =$$

$$-(m_1 - m_2) \cdot g \cdot h \cdot \frac{\exp\left(\frac{(m_1 - m_2) \cdot g \cdot h}{R \cdot T}\right)}{1 + \exp\left(\frac{(m_1 - m_2) \cdot g \cdot h}{R \cdot T}\right)} + R \cdot T \cdot \ln \left(\frac{1 + \exp\left(\frac{(m_1 - m_2) \cdot g \cdot h}{R \cdot T}\right)}{2} \right). \quad (13)$$

However, we obtained mixtures of the separated gases again. If we indicate as y the relative difference in potentials of the gases:

$$y = \frac{(m_1 - m_2) \cdot g \cdot h}{R \cdot T}, \quad (14)$$

then we can find the molal fraction of gases in volumes V_+ and V_- using (10) and (12) as

$$x_{1+} = 1/(1 + \exp y),$$

$$x_{2+} = 1/(1 + \exp(-y)),$$

$$x_{1-} = 1/(1 + \exp(-y)),$$

$$x_{2-} = 1/(1 + \exp y). \quad (15)$$

where x_{1+} - molal fraction of gas 1 in volume V_+ , x_{2+} - molal fraction of gas 2 in volume V_+ , x_{1-} - molal fraction of gas 1 in volume V_- , x_{2-} - molal fraction of gas 2 in volume V_- .

So the entropy of mixing two different gases taken in quantity 1/2 mole each according to (7) is

$$\Delta S = R \cdot \left(\frac{y \cdot \exp y}{1 + \exp y} - \ln \frac{1 + \exp y}{2} \right). \quad (16)$$

The Analysis of Results

Now we can find the entropy of separating similar gases, for which $y \rightarrow 0$ at any h.

$$\lim_{y \rightarrow 0} \Delta S = 0$$

which means that the entropy of separating or mixing identical gases is equal to zero. Thus we can see that the entropy of separating gases from their mixture depends on the relative difference of their potentials to temperature. We should indicate that pure gases are not obtained as a result of such separating, but their mixtures with component fractions are given in equation (15). Hence, in order to completely separate gases at temperatures different from zero, a process with an infinite difference of gas potentials, an infinite number of cycles, or an infinite work or heat would be required. But we have already stated that such a reversible process as explained in the previous sentence is impossible.

As the quantity of heat or work which is spent in an unreversible processes is more than in a reversible processes, (according to the second law of thermodynamics), therefore, obtaining a completely pure substances at temperatures different from zero is impossible. The consequence of this result is that a complete vacuum in final volume cannot exist and that ideal half-penetrable membranes cannot be created, because in order to exist there must be an infinite difference in potentials between the different gases. Having determined that different gases may reversibly mix only at definite potential differences which is dependent on the fractions of mixing gases, we can now calculate the entropy of mixing gases as a function of their molal fraction before mixing. We shall define y from (14) as a function of x_{1+} in the following way

$$y = \ln \frac{1 - x_{1+}}{x_{1+}}.$$

After substituting it in (16) we can see that the entropy of reversible mixing of the ideal gases in two volumes containing 1/2 mole of mixture each with main component concentration $x_{1+} = x_{2-}$ is accordingly

$$\Delta S = R \cdot (\ln 2 + (1 - x_{1+}) \ln(1 - x_{1+}) + x_{1+} \cdot \ln x_{1+}) \quad (17)$$

This equation shows the absence of Gibbs' paradox. In reality, for identical gases, while, $m_1 = m_2$ we can find

$$\lim_{m_1 \rightarrow m_2} \Delta S = \lim_{y \rightarrow 0} \Delta S = \lim_{x_{1+} \rightarrow \frac{1}{2}} \Delta S = 0.$$

And for different gases

$$\lim_{y \rightarrow \infty} \Delta S = \lim_{x_{1+} \rightarrow 1} \Delta S \Rightarrow R \cdot \ln 2.$$

However, having determined the impossibility of the existence of pure substances, we can say that the entropy of mixing ideal gases will always be less than for pure substances and depends on the difference in potentials between the gases in the mixture. This dependency expresses the possibility in principle of obtaining more clean substances when the substances in the mixture are more different. So, the mixing entropy for these substances shall be higher than for mixing similar substances that cannot be cleanly separated one from another.

We should note here, that equation (17) was known years ago ([12], for example). However, this equation was not considered as solution of the Gibbs' paradox, because it seemed that the entropy of mixing pure gases was independent of their difference in potential. We determined in our article that obtaining a pure substance was totally impossible, so only equation (17) has a physical sense.

It is interesting that equation (17) coincides with the final expression of the operational theory of the Gibbs' paradox (equation 9.7 in [2]):

$$\Delta S = R \cdot (\ln 2 + w \cdot \ln w + (1 - w) \cdot \ln(1 - w)),$$

where w is probability of separating the different gases by the separating apparatus. However we consider our result as new for the following reasons:

1. We showed that the existence of pure gases was a wrong model of the real situation.
2. Having determined impossibility of the existence of pure substances in general, we can see why statistical approaches cannot be used to find solution to the Gibbs' paradox. In reality, all of these approaches are based on the assumption that pure gases are being mixed. Certainly, any further correct calculations that start from these assumptions should lead to the fact, that entropy mixing does not depend on the difference between mixing gases.
3. We showed that entropy mixing does indeed depend on the difference in conditions (such as molal fractions) of the mixed substances during mixing process only.

Conclusions

1. The calculation of the ideal gases mixing entropy is a classic thermodynamic problem, which can be solved by methods of classic thermodynamics supplemented with postulates about the impossibility of reversible processes using infinite shifts, infinite values of work or heat involved in processes with limited quantities of substance.
2. Calculation of the ideal gases reversible mixing work shows the absence of the Gibbs' paradox.
3. Entropy of ideal gases mixing is determined by Equation (17), where gas molal fraction corresponds to the difference between gases.
4. Obtaining finite volumes of pure substances or complete vacuum is impossible.
5. Half-penetrable membranes that are not completely penetrable to some substances cannot be created.

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