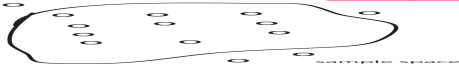


Gibbs Paradox



PHY 4523 Statistical Mechanics

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1. Introduction

Josiah Willard Gibbs lived a prolific career in terms of producing astonishing, revolutionary ideas that eventually formed the basis for statistical mechanics, quantum theory, biophysics, etc. Because Gibbs had an innumerable amount of scientific contributions, only the Gibbs Paradox will be thoroughly discussed here in order to keep the paper clear and concise.

2. Gibbs Paradox

a. The Problem

In statistical mechanics, the Gibbs paradox suggests that the entropy of a closed system may decrease, thereby violating the second law of thermodynamics [1]. In particular, consider two types of ideal gases, one with an n_1 amount of moles and another with n_2 amount of moles. The two types of gases are unable to interact and are confined in two volumes V_1 and V_2 , respectively, and they are separated by a diaphragm [1]. The initial conditions are that $\frac{V_1}{V_2} = \frac{n_1}{n_2}$, the temperatures are equal or $T_1 = T_2$, and the pressures are equal or $P_1 = P_2 = n_1RT/V_1$. When the diaphragm is removed, the two gasses diffuse through each other and a new equilibrium state is formed with $n = n_1 + n_2$ moles of a gas mixture, $V = V_1 + V_2$ as the total volume, and the total energy, pressure, and temperature all being the same as in the initial state. The situation is shown in figure 1 on the following page.

Since the gases are different, the entropy change from the diffusion is,

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = nR \log V - (n_1R \log V_1 + n_2R \log V_2)$$

or,

$$S = -nR[f \log f + (1 - f) \log(1 - f)]$$

where $f = n_1/n = V_1/V$ is the mole fraction of component 1 [1]. In a simpler form, Gibbs assumed the particular case in which $f = 1/2$, leading to

$$\Delta S = nR \log 2 \quad [1].$$

Figure 1. Shows two different gasses initially separated by a partition then combined after the removal of the partition.



It should be noted that the entropy is independent of the nature of the gases. In other words, when one mixes two different types of gases, their entropy will increase.

In another case, two identical gases are placed under the same conditions as the previous experiment (with their volumes, pressures, temperatures, all being equal) [2]. After removing the diaphragm in this scenario, and then calculating the resulting entropy, one would find that the entropy is

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = 0$$

The situation is portrayed in figure 2.

Figure 2. Shows the result of combining two identical gases after the partition is removed. The total entropy change is equal to zero.



According to Ben-Naim, two other types of paradoxes occur when examining the two experiments (besides explicitly seeing the second law of thermodynamics being violated). The

first arises from treating the particles classically, not recognizing the indistinguishability of the particles, while the other paradox arises from the idea that the indistinguishability of the particles is a property that can be changed continuously [2].

The first paradox arises when the classical partition function is used, gives the correct equation of state, the correct heat capacity and other correct properties of an ideal gas. It does not, however, give the correct entropy because the entropy of the system does not have the additive property, i.e. the entropy is not an extensive function of the variables E , V , and N [2]. But in order to fix this, one must simply correct the classical partition function by adding in the indistinguishability of the particles, which allows the entropy to become an extensive function [2].

The second paradox, the one being demonstrated by figures 1 and 2, is called the entropy of mixing paradox [2]. The paradox in this case is often stated by supposing that one could have changed the extent of the indistinguishability of the particle continuously, say linearly from the distinguishable particles to the indistinguishable [2]. If one does that, one should expect ΔS to change continuously from ΔS_1 , when the particles are distinguishable, to ΔS_2 , when they become indistinguishable; however, it is impossible to observe any intermediary value between ΔS_1 and ΔS_2 [2]. Seeing ΔS change discontinuously is the paradox.

b. Explanation

To sum up the results, mixing two dissimilar gases results in an increase in entropy independent of the nature of the gases. Mixing two identical gases, however, results in no increase in entropy. For clarification, when two unlike gases mix and their entropy increases, that means the gases could be separated again and brought back to their original states (reversible change) by means that would leave changes in external bodies, such as the lowering of the weight, or a transfer of heat from a hot body to a cold one [1]. The “original state”, moreover, simply means that the original thermodynamic state, defined for example by specifying only the chemical composition, total energy, volume, and number of moles of a gas [1]. Thus, taking the system as a whole to represent the state is what is being evaluated. The same exact individual particles do not have to return to their initial states. The thermodynamic state may be replicated as long as the larger specifications such as total energy, volume, etc. are matched. Since changes

in the external bodies occur in order to reconstruct the original thermodynamic state, entropy of the system is increased. In complete contrast, when mixing two identical gases and causing no change in entropy, the original thermodynamic state can be recovered without any external change by simply reinserting the diaphragm, keeping the macroscopic properties identical as the initial state. In short, since there has been no change in the thermodynamic state, it follows that there can be no change in the entropy or in any other thermodynamic function [1].

c. Violation of the Second Law of Thermodynamics

To see how the Gibbs Paradox violates the second law of thermodynamics, one must first consider two samples of a certain gas, for example argon, denoted by A1 and A2. The two gases are identical except that A2 reacts with an imaginary superkalic element called Whifnium [1]. Specifically, Whifnium has the property that it is permeable to A2 but not A1. Samples of pure A1 and A2 would be created. The initial conditions would be for $n_1 = fn$ moles of A1 in the volume $V_1 = fV$, and $n_2 = (1-f)n$ moles of A2 in $V_2 = (1-f)V$. With this knowledge of the Whifnium, the entropy increase of the diffusion of the two gases is described as:

$$\Delta S = \Delta S_1 + \Delta S_2$$

where

$$\Delta S_1 = -nRf \log f$$

$$\Delta S_2 = -nR(1-f) \log(1-f) \quad [1].$$

Based on the increase in entropy, one can observe the change in work that one can extract from the process:

$$W = -\Delta F = T\Delta S$$

A movable piston of Whifnium is placed beside the diaphragm and when the diaphragm is removed, A2 will diffuse through this piston until its partial pressure is the same on both sides, after which the piston is slowly moved in the direction of increasing V_1 [1]. The work from A1 should be

$$W_1 = \int_{V_1}^V P_1 dV = n_1 RT \log(V/V_1)$$

or

$$W_1 = T \Delta S_1 \quad [1].$$

Furthermore, another imaginary superkalic element called Whafnium is used that has the opposite effect of Whifnium, i.e. it is permeable to A1 but not to A2. Then we can make an apparatus with two superkalic pistons; the Whifnium moves to the right, giving the work $W_1 = T \Delta S_1$, while the Whafnium moves to the left, yielding $W_2 = T \Delta S_2$ [1].

With this in mind, let us perform two experiments using the gases A1 and A2. In experiment 1, mixing of a volume V_1 of A1 and V_2 of A2 takes place spontaneously, without superkalic pistons, from an initial thermodynamic state X_i to a final one X_f without any change of temperature, pressure, or internal energy and without doing any work; so it causes no heat flow between the diffusion cell and a surrounding heat bath of temperature T [1]. In short, because the initial and final states are the same, nothing happens.

However, in experiment 2, we insert the superkalic pistons and perform the same mixing reversibly starting at X_i . The final state has X_f , but now work has been done, thereby meaning that heat $Q = W$ flows into the diffusion cell from the heat bath [1]. Thus, the initial and final states are now different. To an observer unaware of the properties of the superkalic elements, all the heat has been entirely converted into work and the entropy of the system has decreased spontaneously by: $S = -\Delta Q/T$. And so, the second law of thermodynamics has been violated. To an observer aware of the properties of the superkalic elements, however, the increase in entropy of the argon is compensated by the decrease in entropy of the heat bath; thus, there is no change in the total entropy. The paradox is answered by changing the wording of the second law. The correct statement of the second law is not that an entropy decrease is impossible in principle, or even improbable; rather that it cannot be achieved reproducibly by manipulating the macrovariables $\{X_1, \dots, X_n\}$ that we have chosen to define our macrostate [1].

d. Discussion on the Other Two Interpretations of the Gibbs Paradox

There were two types of paradoxes that were mentioned earlier in part (a). The first arose from the fact that the classical partition function did not take into account the indistinguishability of the particles. According to Ben-Naim, this scenario should not even be considered a form of the Gibbs paradox because in order to solve it, one must simply add the corrections for the indistinguishability of the particles to allow the entropy to become an extensive function [2]. In regards to the second paradox, Ben-Naim states that it is an illusion arising from our mental imaging, in which particles are assigned mental coordinates and mental projectories [2]. The flaw arises when we think we can mentally reverse the process by placing each particle back to its original position, which is a process that scientists deem impossible in modern times [2]. And so, to solve the paradox, he states that one must think of the particles as indistinguishable from the outset, thereby rendering the question of whether or not one can bring each particle to its original position meaningless [2]. There would be no need to look at the continuity or discontinuity of the entropy in this case.

e. Applications

The Gibbs paradox has led to a number of useful applications in chemistry. One application consists of inventing a general technique for facile organic synthesis. Substances of dissimilar properties will separate with the result that substances of really indistinguishable properties will self-aggregate driven by the entropy effect, thereby leading to self-organizational patterns that can be controlled by changing property similarities of the constituent individuals [3]. When rejecting the Gibbs paradox of entropy of mixing, another application arises as some scientists can now explain the hydrophobic effect, which states that fluids of identical or very similar properties will mix spontaneously, while fluids of different properties will separate [3]. As stated by Shu-kun, a theory in contrast to the results of the Gibbs paradox can answer the phenomena of the hydrophobic effect. By rejecting the Gibbs paradox once again, an explanation for the resonance theory can be supplied. After the rejection, one can believe that the second law of thermodynamics can be perfectly applied to quantum systems to judge the structural stability and process spontaneity [3].

f. Additional Thoughts on the Gibbs Paradox

The Gibbs paradox is a puzzle that involves determining whether entropy is an extensive quantity, how the entropy changes when identical particles are mixed, and the proper way to count states in systems of identical particles [4]. To solve this problem, a few other scientists claim that it is the perception of the system by the observer that must change. By looking at the paradox from an information theory perspective, one can create a precise definition of the terms system and state that will help answer the problem. Specifically, the misconception for these terms arise when people think of entropy as a real physical quantity that one can justify in talking about the entropy of the system [4]. The entropy, however, is not a property of the description of the system but a property of the macrostate – it is a function of the macroscopic variables used to define the macrostate [4]. Having specified the macrostate, an entropy can be interpreted as the amount of additional information required to specify the microstate [4]. And so, with these changes, the paradox is resolved once it is realized that there is no such thing as the entropy of a system, that there are many entropies, and that the choice between treating particles as being distinguishable or not depends on the resolution of the experiment [4].

4. Conclusions

The Gibbs paradox arises when the mixing of entropy is in question. It arises because of the different arguments on how to treat particles (whether distinguishable or indistinguishable) and whether entropy is extensive or not. A major consequence of the paradox can be seen when the second law of thermodynamics seems to be broken. By rejecting the Gibbs paradox, one may find useful applications when trying to explain phenomena such as the hydrophobic effect or resonance theory.

5. References

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