

Definite Integral and the Gibbs Paradox

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Abstract: The Gibbs paradox does not exist at all. Entropy is an additive quantity but not an extensive quantity. Neither entropy nor the increment of entropy is an extensive quantity. When T denotes thermodynamic temperature, $\ln T$ does not make sense. The correctness of dimension is a necessary condition for proper formulas. The definite integral is preferable to the indefinite integral; it should be used in science instead of the latter. The Gibbs correction factor is not only cumbersome but also erroneous; it causes some contradictions in statistical mechanics. Entropy is not a quantity that can be measured, but the increment of entropy can be measured. So what the experiment can check is not entropy but the increment of entropy.

Keywords: Gibbs paradox; entropy; extensive; additive; definite integral

1 Introduction

In many textbooks on thermodynamics and statistical physics, there are some erroneous formulas. The causes are: 1. The dimension is not correct; 2. When the definite integral should be used on all terms of a differential equation, some terms are integrated definitely but others not; 3. The basic notion is wrong; 4. The argumentation is illogical. This article solves these problems exemplarily.

2 Does $\ln T$ Make Sense?

Symbol explanation : “ \equiv ” denotes identity; $\frac{\partial f(x, y)}{\partial x} \equiv f_x \equiv \left(\frac{\partial f}{\partial x} \right)_y \equiv f_{x|y}$.

As is well known, the argument of $\ln x$ is a pure number, either a real number or a complex number. So when T denotes a pure number, $\ln T$ makes sense; when T denotes thermodynamic temperature, $\ln T$ does not make sense, nor does $\ln V$ when V denotes thermodynamic volume. If a quantity x is not a pure number, neither $\ln x$ nor e^x makes sense. Only when we specify the unit of quantity x so that x denotes a pure number can $\ln x$ or e^x make sense.

2.1 There Are Two Erroneous Formulas in Literature [1, p. 53]

$$S = nC_{V,m} \ln T + nR \ln V + S_0 \quad <1.15.4>$$

$$S_0 = n(S_{m0} - R \ln n) \quad <1.15.5>$$

Because $\ln T$, $\ln V$, $\ln n$ do not make sense, the above formulas are wrong. Let C_V be the heat capacity of ideal gas at constant volume, N the number of molecules of the gas, and let k denote Boltzmann's constant. $dU = TdS - pdV$, $pV = NkT$, so the correct formulas are as follows:

$$dS = \frac{C_V}{T} dT + \frac{p}{T} dV = \frac{C_V}{T} dT + \frac{Nk}{V} dV \quad (1)$$

$$\int_{S_0}^S dS = \int_{T_0}^T \frac{C_V}{T} dT + \int_{V_0}^V \frac{p}{T} dV = \int_{T_0}^T \frac{C_V}{T} dT + \int_{V_0}^V \frac{Nk}{V} dV \quad (2)$$

$$\therefore S - S_0 = \int_{T_0}^T \frac{C_V}{T} dT + \int_{V_0}^V \frac{Nk}{V} dV \quad (3)$$

For monatomic ideal gas : $C_V = \frac{3}{2} Nk$

$$\therefore S - S_0 = \frac{3}{2} Nk \ln \frac{T}{T_0} + Nk \ln \frac{V}{V_0} = Nk \ln \left[\frac{V}{V_0} \left(\frac{T}{T_0} \right)^{\frac{3}{2}} \right] = Nk \ln \left[\frac{p_0}{p} \left(\frac{T}{T_0} \right)^{\frac{5}{2}} \right] \quad (4)$$

2.2 There Are The Following Two Formulas in Literature [1, p. 81]

$$dS = \frac{C_V}{T} dT + p_{TV} dV \quad <2.4.4>$$

$$S = \int \frac{C_V}{T} dT + p_{TV} dV + S_0 \quad <2.4.5>$$

Formula <2.4.5> is wrong because when equation <2.4.4> is integrated, some terms use the definite integral but others not. The correct method is that all terms should use the definite integral as follows:

$$\int_{S_0}^S dS = \int_{T_0}^T \frac{C_V}{T} dT + \int_{V_0}^V p_{TV} dV \quad (5)$$

$$S = S_0 + \int_{T_0}^T \frac{C_V}{T} dT + \int_{V_0}^V p_{TV} dV \quad (6)$$

The merit of the definite integral is clear and explicit. The indefinite integral has an arbitrary constant; it causes misunderstanding and erroneous argumentation easily, so it should only be used as a training method in calculus. In order to avoid ambiguity, the definite integral should be used in science instead of the indefinite integral.

2.3 There Are The Following Two Formulas in Literature [1, p. 346]

$$S = k \ln \Omega = Nk \ln \left[\frac{V}{Nh^3} \left(\frac{4\pi mE}{3N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} Nk + k \left(\ln \frac{3N}{2} + \ln \frac{\Delta E}{E} \right)$$

$$S = Nk \ln \left[\frac{V}{Nh^3} \left(\frac{4\pi mE}{3N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} Nk \quad \langle 9.3.26 \rangle$$

Apparently formula $\langle 9.3.26 \rangle$ is wrong because when $\Delta E \rightarrow 0+$, $\ln \frac{\Delta E}{E} \rightarrow -\infty$, we cannot get it from the former formula. This kind of error is

illogical argumentation. It is an exemplary case of omitting some terms unreasonably. It shows that an ideal isolated system which does not exchange mass and energy with its surroundings does not exist. Furthermore, the micro-canonical ensemble should not be used in the case in question.

3 Is Entropy an Extensive Quantity?

Many textbooks [2-4] classify thermodynamic quantities as two classes: extensive or intensive. The following is a typical definition [3]:

The quantities we use to describe the macroscopic behavior of a system in equilibrium are called properties, the observable characteristics of a system. Other names are thermodynamic variables or thermodynamic coordinates. An extremely important concept is that of a state variable, a property whose differential is exact.

Properties are extensive or intensive. An extensive is proportional to the mass. An example is the volume V ; if the mass is doubled, the volume is doubled (assuming that the density remains constant). An intensive property is independent of the mass. Temperature T is an intensive property; its value is not affected by a change of mass. Pressure p and density ρ are further examples of intensive properties.

In other words, extensive quantities are ones that are proportional to the number of molecules and are additive; intensive quantities are ones that are got by an extensive quantity divided by another extensive quantity and are non-additive. But this kind of classification is not complete. The complete classification is as follows:

$$\text{scalar} \left\{ \begin{array}{l} \text{additive scalar} \left\{ \begin{array}{l} \text{extensive and additive (mass, volume,} \\ \text{number of particles etc.)} \\ \text{non-extensive but additive (time, entropy,} \\ \text{probability etc.)} \end{array} \right. \\ \\ \text{non-additive scalar} \left\{ \begin{array}{l} \text{intensive and non-additive (temperature,} \\ \text{density etc.)} \\ \text{nonintensive and nonadditive (speed,} \\ \text{rate of increase etc.)} \end{array} \right. \end{array} \right.$$

From Boltzmann entropy $S = k \ln \Omega = k \ln(N! \prod_{i=1}^l \frac{g_i^{n_i}}{n_i!})$ and Gibbs entropy

$$[4] \quad S = -k \sum_j P_j \ln P_j, \text{ we can know that entropy is not an extensive quantity.}$$

A system is an entity which consists of many particles and has a definite volume and temperature. The equation for the entropy of a monatomic gas is:

$$S = Nk \left\{ \frac{3}{2} + \ln \left[\frac{V}{h^3} (2\pi mkT)^{\frac{3}{2}} \right] \right\} \quad (7)$$

It follows that entropy is a systematic quantity, a measure of disorder of the system.

Let Ω be the number of microstates for a system in equilibrium. If the system is composed of two independent subsystems, then $\Omega = \Omega_1 \Omega_2$, $S = k \ln \Omega = k \ln(\Omega_1 \Omega_2) = k \ln \Omega_1 + k \ln \Omega_2 = S_1 + S_2$, so entropy is an additive quantity. For a system in equilibrium, all the extensives are accumulations of the corresponding quantity of a particle and are proportional to the number of particles. A particle has mass but not entropy, so mass is extensive but entropy is not. If entropy S were extensive, then $\frac{S}{N}$ would be the entropy of a particle, which (like the temperature of a particle) is meaningless.

Some people confuse additive quantity with extensive quantity, others confuse

entropy with the increment of entropy, which brings about some erroneous notions in thermodynamics and statistical mechanics. Correcting these wrong notions is one of the main reasons why I have written this article.

4 Is the Gibbs Correction Factor Right?

There is the following problem in literature [5]:

There are two ideal monatomic gases in an adiabatic container with volume V . The number of molecules are N_1 and N_2 respectively. The temperature of the system in equilibrium is T . Find the equation of state, internal energy and entropy of the system, starting with canonical ensemble.

Solution: Let m_1 and m_2 be the molecular mass of the two gases respectively,

$$\text{the energy of the system is } E = \sum_{i=1}^{3N_1} \frac{p_{1i}^2}{2m_1} + \sum_{j=1}^{3N_2} \frac{p_{1j}^2}{2m_2} \quad (8).$$

$$\begin{aligned} \text{Partion function is : } Z &= \frac{1}{N_1! N_2! h^{3N_1} h^{3N_2}} \int e^{-\beta E} d\Gamma_A d\Gamma_B \\ &= \frac{V^{N_1}}{N_1! h^{3N_1}} \left(\frac{2\pi m_1}{\beta} \right)^{\frac{3N_1}{2}} \frac{V^{N_2}}{N_2! h^{3N_2}} \left(\frac{2\pi m_2}{\beta} \right)^{\frac{3N_2}{2}} = Z_1 Z_2 \quad (9) \end{aligned}$$

The pressure of the mixed ideal gases is:

$$p = \frac{1}{\beta} (\ln Z)_V = \frac{N_1 kT}{V} + \frac{N_2 kT}{V} = \frac{(N_1 + N_2) kT}{V} \quad (10)$$

$$\text{The equation of state is: } pV = (N_1 + N_2) kT \quad (11)$$

The pressure of the mixed ideal gases is equal to the sum of the pressures generated by all the constituent gases; this is Dalton's law of partial pressures. When the molecules are of the same kind, formula (10) still holds, which means that the pressure of the ideal gas is equal to the sum of the pressures generated by all the constituent subsystems.

$$U = -(\ln Z)_\beta = \frac{3}{2} (N_1 + N_2) kT \quad (12)$$

The internal energy of the mixed ideal gases is equal to the sum of the internal energies of all the constituent gases. When the molecules are of the same kind, formula (12) still holds, which means that the internal energy of the ideal gas is equal to the sum of the internal energies of all the constituent subsystems.

$$S = k[\ln Z - \beta(\ln Z)_\beta] = N_1 k \ln \left[\frac{V}{N_1 h^3} (2\pi m_1 kT)^{\frac{3}{2}} \right] + \frac{5}{2} N_1 k$$

$$+ N_2 k \ln \left[\frac{V}{N_2 h^3} (2\pi m_2 kT)^{\frac{3}{2}} \right] + \frac{5}{2} N_2 k \quad (13)$$

The entropy of the mixed ideal gases is equal to the sum of the entropies of all the constituent gases. When the molecules are of the same kind, it follows from formula (13):

$$S = N_1 k \ln \left[\frac{V}{N_1 h^3} (2\pi m kT)^{\frac{3}{2}} \right] + \frac{5}{2} N_1 k + N_2 k \ln \left[\frac{V}{N_2 h^3} (2\pi m kT)^{\frac{3}{2}} \right] + \frac{5}{2} N_2 k \quad (14)$$

According to the Sackur-Tetrode formula, the entropy of monatomic ideal gas is:

$$S' = Nk \ln \left[\frac{V}{Nh^3} (2\pi mkT)^{\frac{3}{2}} \right] + \frac{5}{2} Nk$$

$$= (N_1 + N_2)k \ln \left[\frac{V}{Nh^3} (2\pi mkT)^{\frac{3}{2}} \right] + \frac{5}{2} (N_1 + N_2)k \quad (15)$$

$$S - S' = (N \ln N - N_1 \ln N_1 - N_2 \ln N_2)k = Nk \left(\frac{N_1}{N} \ln \frac{N}{N_1} + \frac{N_2}{N} \ln \frac{N}{N_2} \right) > 0$$

Apparently $S \neq S'$, which means that the entropy of the ideal gas is not equal to the sum of the entropies of all the constituent subsystems. This is contradictory to the additive quality of entropy. The cause that makes the error is introducing the

Gibbs correction factor $\frac{1}{N!}$ to the partition function of canonical ensemble. The

introduction of the Gibbs correction factor $\frac{1}{N!}$ to the partition function is not

only cumbersome, in that it does not change the probability distribution of the system in question; but it is also erroneous: in that it is based on the wrong notion that entropy is an extensive quantity, it leads to some contradictions in statistical mechanics [6-9]. It may be justified in the grand canonical ensemble as an ad hoc

prescription [8]: *the statistical weight of a state (l) must be weighted by $\frac{1}{N_l!}$.*

The correct calculation for the entropy is by using formula (7):

$$S_1 = N_1 k \left\{ \frac{3}{2} + \ln \left[\frac{V}{h^3} (2\pi m_1 k T)^{\frac{3}{2}} \right] \right\}; S_2 = N_2 k \left\{ \frac{3}{2} + \ln \left[\frac{V}{h^3} (2\pi m_2 k T)^{\frac{3}{2}} \right] \right\};$$

$$S = S_1 + S_2 = N_1 k \ln \left[\frac{V}{h^3} (2\pi m_1 k T)^{\frac{3}{2}} \right] + \frac{3}{2} N k + N_2 k \ln \left[\frac{V}{h^3} (2\pi m_2 k T)^{\frac{3}{2}} \right] \quad (13')$$

The entropy of the mixed ideal gases is equal to the sum of the entropies of all the constituent gases. When the molecules are of the same kind, formula (13') still holds, which means that the entropy of the ideal gas is equal to the sum of the entropies of all the constituent subsystems.

5 Does the Gibbs Paradox Exist?

There are two different, classical, ideal monatomic gases initially in the two compartments (volumes V_1 and V_2 , $V_1 + V_2 = V$) of a rigid adiabatic container, separated by a diathermal diaphragm. They have the same pressure and temperature, the number of molecules of each compartment are N_1 and N_2 respectively, $N_1 + N_2 = N$. If the diaphragm is removed, calculate the increment of entropy of the system.

Solution 1(thermodynamic method): Let m_1 and m_2 be the molecular mass of the two gases respectively.

Initial state: system $N_1 \rightarrow V_1, T_0, P_0$; system $N_2 \rightarrow V_2, T_0, P_0$

Final state: system $N_1 \rightarrow V, T, P_1$; system $N_2 \rightarrow V, T, P_2$.

Because there is no energy, heat introducing and chemical reaction, the temperature of the system remains constant, i.e. $T = T_0$. Using Dalton's law of partial pressure, we know:

$$p_1 = \frac{N_1 k T}{V}; p_2 = \frac{N_2 k T}{V}$$

$$\therefore p = p_1 + p_2 = \frac{(N_1 + N_2) k T}{V} = \frac{N k T}{V} = p_0 = \frac{N_1 k T}{V_1} = \frac{N_2 k T}{V_2}$$

From formula (4), we have:

$$\Delta S_1 = S_1 - S_{10} = N_1 k \ln \left[\frac{V}{V_1} \left(\frac{T}{T_0} \right)^{\frac{3}{2}} \right] = N_1 k \ln \left(\frac{V}{V_1} \right) = N_1 k \ln \left(\frac{N}{N_1} \right)$$

$$\Delta S_2 = S_2 - S_{20} = N_2 k \ln \left[\frac{V}{V_2} \left(\frac{T}{T_0} \right)^{\frac{3}{2}} \right] = N_2 k \ln \left(\frac{V}{V_2} \right) = N_2 k \ln \left(\frac{N}{N_2} \right)$$

So the increment of entropy after mixing is:

$$\Delta S = \Delta S_1 + \Delta S_2 = N_1 k \ln \left(\frac{V}{V_1} \right) + N_2 k \ln \left(\frac{V}{V_2} \right) = N_1 k \ln \left(\frac{N}{N_1} \right) + N_2 k \ln \left(\frac{N}{N_2} \right) > 0 \quad (16)$$

Apparently the increment of entropy after mixing is the same whether the two gases are different or not, because the two gases will occupy the total volume finally and homogeneously. Meanwhile, from formula (16) we can see that the increment of entropy is not an extensive quantity.

Solution 2(statistical mechanics method): From formula (7) we have:

$$S_{10} = N_1 k \left\{ \frac{3}{2} + \ln \left[\frac{V_1}{h^3} (2\pi m_1 k T)^{\frac{3}{2}} \right] \right\}; S_1 = N_1 k \left\{ \frac{3}{2} + \ln \left[\frac{V}{h^3} (2\pi m_1 k T)^{\frac{3}{2}} \right] \right\}$$

$$\therefore \Delta S_1 = S_1 - S_{10} = N_1 k \ln \left(\frac{V}{V_1} \right). \text{ Similarly, } \Delta S_2 = S_2 - S_{20} = N_2 k \ln \left(\frac{V}{V_2} \right).$$

$$\therefore \Delta S = \Delta S_1 + \Delta S_2 = N_1 k \ln \left(\frac{V}{V_1} \right) + N_2 k \ln \left(\frac{V}{V_2} \right). \text{ The result is the same as}$$

solution 1.

Some people think that if the two gases are identical, there can be no change in entropy when the diaphragm is removed ($\Delta S = 0$). This is the so-called Gibbs paradox.

Firstly, neither entropy nor the increase of entropy is an extensive quantity. Based on the wrong notion that entropy is an extensive quantity, some people argue that $\Delta S = 0$.

Secondly, after the diaphragm is removed, each gas moves into the other, and a new equilibrium state is obtained in which both gases occupy the total volume. It is clear that the process of mixing is irreversible: once the mixing is done, the two gases, whether they are different or not, will not return spontaneously to their initial compartments. The final state is more disordered than the initial one.

According to the second law of thermodynamics, $dS \geq \frac{dQ}{T} = \frac{dU + pdV}{T}$. For

adiabatic process, $dQ = 0$. For irreversible adiabatic process, $dS > 0$.

Thirdly, if we re-install the diaphragm, we will not regain the initial state. The number of molecules in V_1 may not be exactly N_1 , let alone they are the same initial N_1 molecules. The reason why mixing takes place is that molecules move randomly and forever.

Fourthly, the above two solutions give the same result whether the gases are different or not. For the mixing of two identical gases, literature [3] gives the third solution. Before the diaphragm is removed, there are N_1, N_2 molecules in V_1, V_2 respectively. This is only one method of arranging the N molecules with N_1 in one container and N_2 in the other, but arranging the N molecules with N_1 in one container and N_2 in the other has $\frac{N!}{N_1!N_2!}$ methods, so the increment of entropy after the diaphragm is removed is: $\Delta S = k \ln \Omega - k \ln \Omega_0 = k \ln \frac{\Omega}{\Omega_0} = k \ln \frac{N!}{N_1!N_2!}$.

Using Stirling's approximation, $\ln N! = N \ln N - N$, we obtain:

$$\Delta S = k \ln \frac{N!}{N_1!N_2!} = N_1 k \ln \left(\frac{N}{N_1} \right) + N_2 k \ln \left(\frac{N}{N_2} \right) = N_1 k \ln \left(\frac{V}{V_1} \right) + N_2 k \ln \left(\frac{V}{V_2} \right)$$

Lastly, classical particles are distinguishable by their positions in the phase lattice and may be traced by their trajectory. They obey the Maxwell-Boltzmann distribution [3]. The total number of microstates corresponding to an allowable configuration is $\Omega_{MB} = N! \sum_{i=1}^l \frac{g_i^{n_i}}{n_i!}$. Quantum particles, both bosons and

fermions, are indistinguishable. The total number of microstates obeying the Bose-Einstein distribution is $\Omega_{BE} = \sum_{i=1}^l \frac{(g_i + n_i - 1)!}{n_i! (g_i - 1)!}$; while those obeying the

Fermi-Dirac distribution is $\Omega_{FD} = \sum_{i=1}^l \frac{g_i!}{n_i! (g_i - n_i)!}$. Apparently

$$\Omega_{MB} > \Omega_{BE} > \frac{\Omega_{MB}}{N!} > \Omega_{FD}. \text{ Because } S = k \ln \Omega,$$

$$S_{MB} > S_{BE}; S_{MB} > S_{FD}.$$

A particle cannot be distinguishable and indistinguishable simultaneously, so it cannot obey the Maxwell-Boltzmann distribution and quantum distribution (either the Bose-Einstein distribution or the Fermi-Dirac distribution) simultaneously.

Therefore the classic Maxwell-Boltzmann distribution is not the limit case of quantum distributions. They have their respective ranges of applicability. Different particles obey different distribution. Under standard temperature and pressure [8], the ideal gases obey the Maxwell-Boltzmann distribution. They are distinguishable and within the classical regime.

Conclusions

In all, the Gibbs paradox does not exist at all. Entropy is additive but not extensive. Neither entropy nor the increment of entropy is extensive. Some people confuse entropy with the increment of entropy, others confuse additive quality with extensive quality. Based on a wrong notion that entropy is extensive, the Gibbs

correction factor $\frac{1}{N!}$ is added to the partition function of canonical ensemble.

This is not only cumbersome but also erroneous. Entropy is not a quantity that can be measured, but the increment of entropy can be measured. So what the experiment can check is not entropy but the increment of entropy.

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