Gibbs' Paradox and Indistinguishability

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- Gas mixing is first analysed by Gibbs in his *Equilibrium of Heterogeneous Substances* but not described as a paradox.
- To my knowledge, first described as a paradox by O. Wiedeburg in a paper titled "The Gibbs Paradox".
- Useful from a philosophical point of view because it forces us to think carefully about identity and indistinguishability.

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- Partly because people thought it was more interesting.
- And partly because people thought the thermodynamic puzzle was already solved.

Views from the literature

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But people tend to feel quite strongly about it...

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> *"After a railway accident, or a fire, or a similar disaster, the authorities are always anxious to answer the question: How could it have happened?" (Schrödinger, Statistical Thermodynamics)*

Gibbs' Paradox in Thermodynamics

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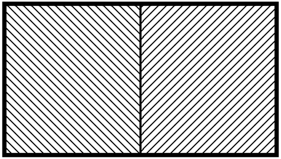
The scenario: two samples of gas, modelled as ideal on either side of partition. Assume pressures and temperatures are equal.



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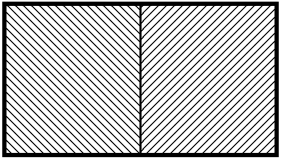
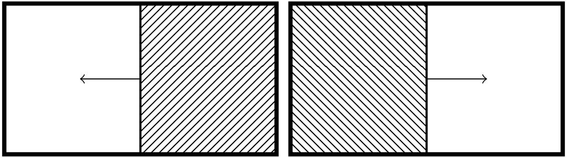


Do the gases mix?

Two Free Expansions



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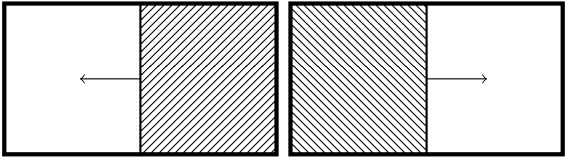

But this way of looking at things does not seem to depend on the indistinguishability of the gases.

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What is this telling us? Two options:

1. There is in fact an entropy of mixing for indistinguishable gases. We have learned something.
2. Indistinguishable gases don't mix. Something has gone wrong.

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- This allows the gases to undergo two free expansions in the very same container.
- There do not exist (in principle) semi-permeable membranes for indistinguishable gases.
- Therefore, indistinguishable gases don't mix, there is no entropy of mixing.

Semi-permeable membranes

"Permeable membranes and semi-permeable membranes do exist in nature, but whether a membrane permeable only to a particular gas exist in nature or not is irrelevant. The existence of some semi-permeable membranes shows the feasibility of such a membrane. Therefore, a membrane permeable only to a particular gas can always be conceived mentally if only for the sake of argument." (Fong, Foundations of Thermodynamics)

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"It depends on the existence of substances exhibiting a selective permeability to gases; such as palladium, platinum, and iron at high temperatures , which are freely permeated by hydrogen, but not by nitrogen.
It is therefore legitimate to postulate, for the purposes of thermo-dynamic reasoning, ideal septa each of which is permeable to one gas but quite impervious to all others. Such septa are called semi-permeable septa." (Partington, A Textbook of Thermodynamics)

Criterion of Indistinguishability

"The entropy of mixing is independent of the exact physical properties of gases A and B. The only thing that plays a role in the calculation and in the final result is that the two gases are <u>different</u>. This difference makes it possible to design—in principle—the semi-permeable membranes that are needed for the reversible mixing process. If the gases are the same, no distinguishing membranes can exist and there is no mixing at all according to thermodynamics: from a thermodynamic point of view nothing happens when the partition is removed in this case." (Dieks, "The Gibbs Paradox Revisited")

Two Gibbs paradoxes

GP1 If there is supposed to be a difference between mixing different gases and 'mixing' two samples of the same kind of gas, then what is this difference and how is it to be represented?

GP2 Given that there is no entropy change when the samples of gas are identical, then the entropy change appears to vary discontinuously from a non-zero value to zero as the gases go from being different to identical. This contradicts a principle, generally held dear by the physics community, that there are no discontinuities in physical quantities.

GP1 and GP2

"But if such considerations explain why the mixture of gas-masses of the same kind stands on a different footing from the mixture of gas-masses of different kinds, the fact is not less significant that the increase of entropy due to the mixture of gases of different kinds, in such a case as we have supposed, is independent of the nature of the gases." (Gibbs)

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"It follows that the entropy of mixing has the same value, $2R \ln 2$, however alike are the two substances, but suddenly collapses to zero when they are the same. It is the absence of any 'warning' of the impending catastrophe, as the substances are made more and more similar, which is the truly paradoxical feature." (Denbigh and Redhead)

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- Are the existence in principle of semi-permeable membranes an adequate criterion of identity?
- Is this criterion sufficiently general?
- What does it mean for them to exist 'in principle'?
- Should we be worried by this apparent discontinuity in the entropy of mixing?

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- What is it that we really want out of all of this anyway?
- We want to derive an entropy of mixing when the gases are different and we want no entropy of mixing when gases are the same.
- But isn't this presupposing what we want to get out?
- Surely, it should be a *result* that there is/is not an entropy of mixing on the basis of an assumption about difference/sameness?

Thermodynamic Argument for Entropy of Mixing

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If this is a thermodynamic argument, purportedly proving a thermodynamic proposition, then the assumptions should be thermodynamic propositions also.

Suggestion: A Methodological Principle

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The concepts used in stating or deriving propositions of a formal theory are only rigorously understood when they are defined in terms of the formalism of that theory. Thus:

- In the assumption ‘Let gases A and B be indistinguishable’, ‘indistinguishability’ should be defined in the thermodynamic formalism.
- Question: does indistinguishability defined in terms of semi-permeable membranes do this?

The View from Geometric thermodynamics

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- First pass: isomorphism?

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- Van der Waals?

The fundamental relation:

$$S/N = R\ln(V/N - b) + cR\ln(u + aN/V) + k,$$

where a, b, c are constants that will in general depend on the physical and chemical properties of the gas.

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- If we want to represent the proposition that k physical systems are indistinguishable, this is to say that when they are composed, the resulting composite system is a scaled version of each of the subsystems.
- Thus, the representation of indistinguishability is based on the relation between a composite system and its subsystem and the assumption of homogeneity.

Prelude to GP in Statistical Mechanics

(a) $s = (1, -1, 2, 1)$.   (b) $\pi(s) = (2, 1, 1, -1)$.

Figure: Two states related by a permutation. In each case, there is one particle with $(r, p) = (1, -1)$ and another with $(2, 1)$ and yet the states are represented by two distinct points in the phase space. The black dot depicts the particle represented by the first factor position and the white dot depicts the particle represented by the second factor position.