Homogeneity and Identity in Thermodynamics

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1   Introduction

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. To illustrate, consider this example: "Let (M, g_{ab}) be a temporally orientable spacetime" may be an assumption to prove some theorem in general relativity. In this proposition, both 'spacetime' and 'temporally orientable' are concepts which are given mathematically precise definitions in the formalism of general relativity. Without such definitions, the proposition wouldn't have quantitative meaning in the theory, even if we may have intuitive grasps on what it means to be temporally orientable. Although much of physics seems to naturally respect this practice, some of thermodynamics does not.

I will argue that the terms 'identical', 'different' and 'mixture' are examples of concepts that are often used without any formal definition, and yet are still used in stating or deriving propositions in thermodynamics. Thus, statements such as "Let A and B be two different gases" or "Consider a mixture of two ideal gases A and B" are often given only qualitative meaning drawn from extra-theoretic considerations. There is nothing inherently wrong with doing this; physicists often proceed with reasoning without fully defining certain concepts, relying on intuitive or extra-theoretic understanding of the terms. This is often necessary when new physics is being formulated and new paths of discovery being forged. However, it is important that they should be given clear thermodynamic meaning in applications where certain quantitative judgments are needed, in particular regarding subtle facts about entropy of mixing. It is also important for philosophers of physics who are interested in understanding the conceptual foundations of a theory in clear and rigorous terms. The dangers of not precisely defining concepts in theoretical reasoning are illustrated in this particular case by the existence of a purported paradox in deriving the entropy of mixing: Gibbs' paradox. Roughly speaking, (one version of) the paradox is that we can apparently derive a non-zero entropy of mixing when the gases are identical, contradicting the view that there should be no entropy of mixing in this case.

This is not to say that these terms have eluded definition entirely. Both physicists and philosophers who comment on the paradox mostly do take care to define these terms; in fact, most see these terms' definition (rightly, in my view) as the heart of the problem and the key to the solution. Rather, my point is that existing definitions do not respect the good practice described above: they are not thermodynamic, but extra-theoretic, appealing to concepts and ideas outside the realm of thermodynamics. This is often

heuristically useful and helps us muddle through abstract reasoning by latching on to more familiar situations. But I am interested in those investigations where taking care in this regard is to avoid paradoxical conclusions. Gibbs' paradox is a case in point.

My thesis is that it is possible to provide thermodynamic explications of 'identity', 'difference' and 'mixture' using the powerful but less commonly used geometric formulation of thermodynamics[1]. This leads to a new perspective on mixing, identity, and the conceptual and formal structure of thermodynamics that is free from Gibbs' paradox.

In Section 2, I introduce Gibbs' paradox in thermodynamics and explain how it is driven by a lack of a clear understanding of what it means for thermodynamic systems to be 'identical' or 'different' and what it means to form a 'mixture'. Sections 2.1 and 2.2 describe in some detail an early and prominent response to the paradox by van Kampen, seen by many[2] as the authoritative treatment of Gibbs' paradox in thermodynamics, before noting what I see a key difficulty with this response in Section 2.3: the lack of a clear and precise criterion of identity for thermodynamic systems. The rest of the paper is geared towards providing this criterion. Section 3 introduces the powerful geometric formulation of thermodynamics. This provides the necessary formal and conceptual tools to allow us to give a precise definition of "mixture" and "mixing" in Section 4. I argue that the most common definition of mixture in thermodynamics is not a good one, and I propose something better. Finally, in Section 5, I argue for a criterion of identity for thermodynamic systems that is based on the assumption of homogeneity, and I explain how this solves Gibbs' paradox.

2 Gibbs' Paradox in Thermodynamics

The setup for Gibbs' paradox goes as follows. Let two samples of gas at equal temperatures (and equal mole number and volume for simplicity) be separated by a partition. When the partition is removed, do the gases mix? What happens to the entropy of the system: does it increase or stay the same? Standard answers to these questions say that it depends whether the gases are 'identical' or 'different': the gases mix and there is an increase in entropy if the gases are different, known as the 'entropy of mixing'. But they are identical when the samples of gas do not mix and there is no entropy increase. The difference between the two situations is depicted in Figure 1.

Confusions start to arise when we inquire into the precise nature of this identity or difference and how these notions are represented in the thermodynamic formalism. Versions of the paradox exist in both thermodynamics and statistical mechanics. Here we are interested in the thermodynamic version. The statements of the thermodynamic paradox that exist in the literature fall into two categories. The first:

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[1]This formalism has been given detailed mathematical treatments by Hermann (1973) and Arnol'd (1978) who, in fact, attribute the geometric formulation to Gibbs (1878).

[2]See, for example, Saunders (2006, 2013, 2018) whose treatment of the Gibbs paradox in thermodynamics follows van Kampen, van Lith (2018, p. 7) praises van Kampen's analysis and reviews of thermal physics (e.g. Uffink (2007); Frigg (2008)) cite van Kampen as an authoritative treatment of Gibbs' paradox.
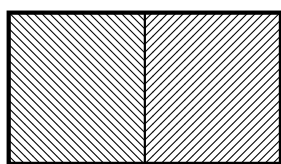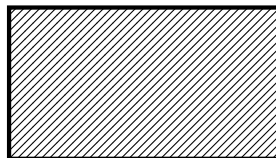
(a) Two different samples of gas separated by a partition.
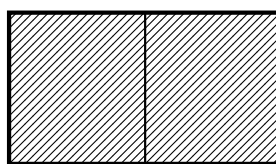
(b) Two identical samples of gas separated by a partition.
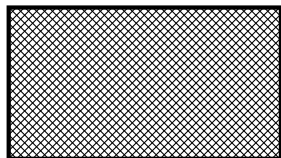
(c) The mixture is formed when the partition is removed.

(d) Nothing happens when the partition is removed.

Figure 1: The Gibbs paradox setup. Intuition dictates that nothing happens to the system when the partition is lifted between two identical samples of gas, while mixing happens when the partition is lifted between different samples of gas.

GP1 On one popular definition, the entropy of mixing does not appear to have any formal component whose value depends on whether the two gases are distinct, thus it seems as though there would still be a non-zero entropy of mixing when the partition is lifted between two identical samples of ideal gas, contradicting the intuition that there is no entropy of mixing for identical gases.([3])

GP1 is driven by two conflicting representations of happens when the partition is lifted. On one representation, the lifting of the partition allows the samples of gas on each side to expand into the other half of the container, inviting us to imagine mixing as two spatially separate expansions occurring independently (see Figure 2).

But if we represent the partition-lifting process in this way, then the result of lifting the partition is completely independent of whether the gases are identical or different, since it is explicitly represented as two spatially separated samples expanding in their own containers; the identity or difference of the substances has no bearing on the result of such independent expansions. This contradicts the result of another representation of mixing depicted in Figure 1 which indicates that the result of removing the partition does depend strongly on the identity of the gases; mixing happens when the partition is lifted between two different samples of gas, while there is no mixing if the gases are identical.

The second version of the paradox is the following:

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

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[3]Bridgman (1961, p. 1698), van Kampen (1984, p. 306), Elwell and Pointon (1972, p. 145), Adkins (1983, p. 217), Fong (1963, pp. 48–49), Partington (1913, p. 274), Fay (1965, p. 218), Pierce (1968, p. 319), Muller (1985, p. 193).
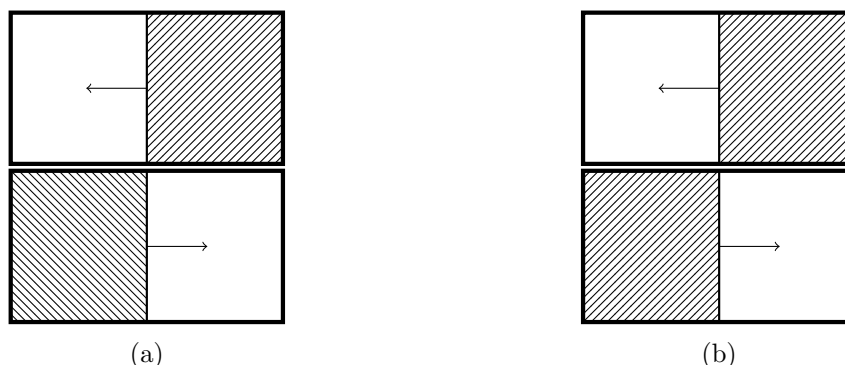
Figure 2: Lifting the partition between two samples of gas on each side of a partition in a container is often modelled as each half of gas undergoing a free expansion in separate containers. Modelling it this way does yield the correct value for the entropy of mixing different gases (Figure 2a), but also results in the same entropy of mixing for identical samples of gas (Figure 2b).

> 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[4] in physical quantities.([5])

GP2 is driven by the intuition that some substances are more similar than others, and that this similarity can be imagined as varying continuously. This similarity and continuous variation, it is argued, should be manifest in a continuous variation of the mixing entropy as the substances go from being different to identical. Commentators who are worried by this version of the paradox aim to remove the discontinuity by demonstrating that the entropy does vary continuously as a function of some variable interpreted as the 'degree of similarity' between the substances. Those who are not worried by this version of the paradox attempt to explain why this discontinuity is not a target of this principle.

These two versions of the paradox identify very different problems. Those concerned with GP2 assume that the mixing entropy for identical gases is zero, seeing the problem to be that the mixing entropy does not vary continuously down to zero as the gases become more similar. By contrast, those concerned by GP1 see the problem precisely in the assumption that GP2 takes for granted: the mixing entropy for identical gases being zero. Since GP1 identifies an issue in something GP2 takes for granted, it is a deeper problem and must be solved first. We will therefore focus our efforts in this paper to

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[4]This principle is seen to originate historically with Leibniz (*Natura non facit saltum*: 'nature does not jump').

[5]Denbigh and Redhead (1989, p. 284), Dieks (2014, p. 1305), Dieks (2011, p. 368), Barsky (2017, p. vii), Denbigh and Denbigh (1985, p. 76), Kondepudi and Prigogine (1998, p. 157), Landsberg (1978, p. 74), Roberts and Miller (1960, p. 379), Sears and Salinger (1975, p. 241), Smith (1952, p. 137), Zemansky and Dittman (1997, p. 391), Swendsen (2018), Dieks (2018), van Lith (2018), Uffink (2007, p. 1000), Klein (1958, p. 80).

solving and understanding GP1.

Needless to say that solutions to GP1 abound and, furthermore, commentators on the paradox agree on the problem and solution. In fact, commentators on Gibbs' paradox universally agree that the thermodynamic paradox has been solved, seeing the interesting and difficult work as articulating and solving the statistical mechanical paradox. My main contention in this paper is that statements of and solutions to the thermodynamic Gibbs paradox suffer from conceptual and mathematical problems, which arise from qualitative extra-theoretic definitions of mixing and identity. Once we clarify these, we end up with a very different, but much more secure, solution.

The strategy typically taken to solve GP1 is to argue somehow that the representation of mixing as two free expansions cannot apply when the gases are identical. In the next Section, I will showcase an extremely popular and oft-cited presentation of this line of reasoning. I will then critically analyse this account and identify mathematical and conceptual problems with it which I will go on to solve.

2.1 Van Kampen's Account

Van Kampen is a frequently cited and highly praised commentator on Gibbs' paradox, who states and gives his own solution. He begins by deriving the entropy as a function $S(p, T)$ of pressure p and temperature T. He leaves the derivation of this function, very typical in standard textbooks on thermodynamics, to the reader, but it is instructive for our purposes to spell it out in detail[6].

We begin by stating what is known as the First Law of thermodynamics for a thermodynamic system consisting of variables for energy U, temperature T, entropy S, pressure p, and volume V:

$$dU = TdS - pdV. \tag{2.1}$$

Now let N be the (constant) mole number and R the ideal gas constant. Adopting the equations of state $U = (3/2)NRT$ and $pV = NRT$ for the ideal gas, and observing that $dU = (3/2)NRdT$, we find that, after some rearrangement, Equation (2.1) becomes,

$$dS = \frac{3NR}{2T}dT + \frac{NR}{V}dV. \tag{2.2}$$

Integrating, we get $S(V, T) = \frac{3}{2}NR\ln T + NR\ln V + K$, and if we substitute $V = NRT/p$, we get van Kampen's expression for $S(p, T)$:

$$S(p, T) = \frac{5}{2}NR\ln T - NR\ln p + C \tag{2.3}$$

where C is a constant of integration absorbing terms containing N and R.

At this point, we depart typical entropy derivations and follow van Kampen's unique argument to calculate the entropy on mixing identical gases and different gases. Van

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[6]The derivation presented in the main text dodges a problem stemming from an inconsistency in van Kampen's presentation, namely: is the number of molecules N a constant or a variable? As I explain in Appendix B.1, he seems to treat it as both. I argue that his expression for $S(p, T)$ can be derived rigorously assuming that N is a variable throughout.

Kampen points out that C cannot be a function of p or T, but may be a function of anything else including N. He then supplies an argument for determining the dependence of C on N (and hence entropy's dependence on N) on the basis of the following two propositions:

> "**Convention 1**. If I have a second system, identical with the first one, I agree to assign to it the same C and therefore the same $S(p, T)$. This is obviously convenient but not logically necessary and by itself contains no information about the physical world.
>
> **Convention 2**. Two separate systems may be regarded as forming together a single system. I agree to take as the entropy of the combined system the sum of the entropies of the two parts. Of course, each part must be in equilibrium but they don't need to be in equilibrium with one another. Hence this convention may serve to define the entropy of systems that are not in equilibrium themselves but can be divided into subsystems that are." (van Kampen, 1984, p. 305)

On the basis of these conventions he argues for the following expressions for the entropy, along with their associated interpretations.

- **The entropy of one gas:**

$$S(p, T, N) = \frac{5}{2} N R \ln T - N R \ln p + cN \qquad \text{(VK1)}$$

where this is just Equation (2.3) with the constant of integration chosen to be such that $C = cN$ for some constant c.

- **The entropy of two gases, A and B:**

$$S(p_A, p_B, T, N_A, N_B) = \frac{5}{2}(N_A + N_B)R \ln T - N_A R \ln p_A - N_B R \ln p_B + c_A N_A + c_B N_B \qquad \text{(VK2)}$$

where $p_A = pN_A/(N_A + N_B)$ and $p_B = pN_B/(N_A + N_B)$ are the 'partial pressures' of the gases A and B.

This equation is derived by calculating $S(p_A, T_A, N_A) + S(p_B, T_B, N_B)$ where each of the summands is given by (VK1) and setting $T = T_A = T_B$.

- **The entropy of two gases, A and B:**

$$S(p_A, p_B, T, N_A, N_B) = \frac{5}{2}(N_A + N_B)R \ln T - (N_A + N_B)R \ln(p_A + p_B) + c(N_A + N_B). \qquad \text{(VK3)}$$

This equation is derived from Equation (VK1) by setting $N = N_A + N_B$ and $p = p_A + p_B$.

We notice immediately that while Equations (VK2) and (VK3) are intended to apply when we have two gases A and B, it is not clear, from what has been said so far, when we apply one and when we apply the other. Van Kampen argues that Equation (VK3) applies when the gases are 'the same' or 'identical' and Equation (VK2) applies when the gases are 'different.' We shall summarise his argument for this shortly, but first we must understand van Kampen's version of the Gibbs paradox.

The paradox stems from the fact that Convention 1 together with Equations (VK2) and (VK3) give rise to a contradiction. Convention 1 may be reasonably interpreted as a necessary condition for two systems to be 'identical': they are assigned the same C. If we apply this to Equation (VK2) by setting[7] $c = c_A = c_B$ then it would seem to give, according to van Kampen's analysis, the entropy for two 'identical' gases A and B. But this entropy is not the same as that given by Equation (VK3), which is also supposed to give the expression for the entropy of two 'identical' gases. The difference between Equation (VK3) with $c = c_A = c_B$ and Equation (VK2) is

$$-N_A R \ln N_A - N_B R \ln N_B + (N_A + N_B) R \ln(N_A + N_B). \qquad \text{(DIF)}$$

The preceding argument is what van Kampen takes to establish the Gibbs paradox:

> "The fact that [Equation (VK2)] does not reduce to [Equation (VK3)] when $A = B$ constitutes the Gibbs paradox. The difference is given in [Equation (DIF)]." (van Kampen, 1984, p. 306)

We are in a situation where we have a valid argument leading to a contradiction. The task, then, is to isolate the false premise.

2.2   Van Kampen's Solution

The logical essence of van Kampen's solution is to block the application of Equation (VK2) to identical gases. This would remove the contradiction. Van Kampen's strategy is to explain why Equation (VK2) applies only when the gases are different and (VK3) only when the gases are identical.

First, regarding identical gases he writes:

> "Consider a set of systems, consisting of identical vessels containing *the same gas* but in different amounts. One is free to represent all possible states obtained in this way in a space with coordinates p, T, N. There is no way, however, to compare entropy values belonging to different N, unless one introduces a new kind of process by which N can be varied in a reversible way. This is done by the familiar device of taking two identical vessels with the same p, T, N and opening up a channel between them. Together with convention 1 this leads to the conclusion that $S(p, T, N)$ must be proportional to N." (van Kampen, 1984, p. 305, original emphasis)

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[7]Despite the fact that van Kampen does not say this explicitly, it is necessary to make the step to get his result.

(a) Allow each gas to undergo a free expansion. (b) Then 'overlap' the containers by applying Gibbs' theorem.
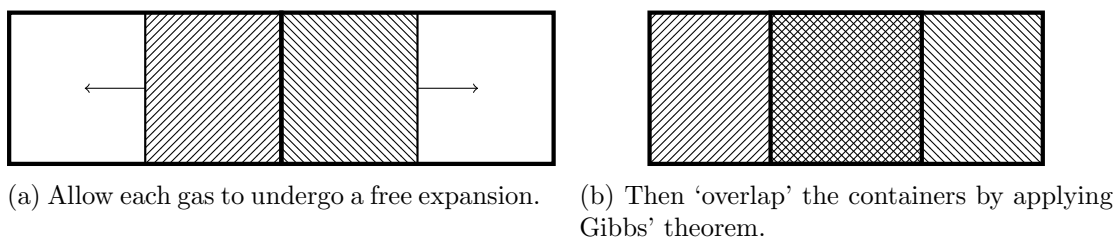
Figure 3: Representing mixing as two free expansions and an application of Gibbs' theorem.

He thus arrives at Equation (VK1). As explained above, this allows the derivation of Equation (VK2) for non-identical gases by substituting $N = N_A + N_B$ and $p = p_A + p_B$. He does not carry out this calculation explicitly, but this step is necessary for deriving his Equation (DIF). He then goes on to consider different types of gases, writing:

> "If two vessels contain *different gases* A, B the entropy of the combined systems is defined by convention 2. When a channel is opened up an irreversible mixing occurs, so that this device cannot be utilised to define the entropy $S(p, T, N_A, N_B)$ of the resulting mixture. In its stead one now uses the familiar reasoning based on semi-permeable walls and obtains for the ideal gas [Equation (VK2)]" (van Kampen, 1984, p. 306, original emphasis)

The 'familiar reasoning' based on semi-permeable membranes is not familiar to all, so let me reconstruct what van Kampen might have meant.

Suppose before the partition is lifted we have gas A on one side and gas B on the other. And suppose, for simplicity of discussion, that the number of moles of each gas is the same, and that each occupy half the total volume of the container, so that the pressure of each gas is the same. We now allow each gas to undergo a free expansion into two separate volumes (see Figure 3a), and then 'overlap' the volumes of gas (Figure 3b). This chain of reasoning is a typical way of representing mixing and calculating the associated entropy increase[8].

The first step is simply two free expansions. The second step is an application of what is sometimes called *Gibbs' theorem*. It states that the entropy of a mixture of ideal gases at temperature T and volume V is the sum of the entropies the individual components would have if they each occupied separate containers of volume V at temperature T. Typical 'proofs' of this theorem[9] make use of the concept of *semi-permeable membranes*. These are membranes which are impermeable to one component of a mixture but permeable to all others. Installing two such membranes in between the containers of gas, one permeable to gas A but impermeable to gas B and another impermeable to gas

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[8]The most explicit example of this reasoning may be found in Adkins (1983, p. 217).

[9]A classic text demonstrating Gibbs' theorem with semipermeable membranes is Planck (1903, pp. 219–220) and other expositions may be found in Buchdahl (1966, pp. 170–171) and Mandl (1988, pp. 129–130).

A but permeable to gas *B*, allows us to overlap the gases in the very same volume and form a mixture without doing any work and while remaining at a constant temperature.

Claiming to have derived equation (VK2) via this reasoning, van Kampen then resolves the paradox by arguing that

> "two different processes had to be chosen for extending the definition of entropy. They are mutually exclusive: the first one cannot be used for two different gases and the second one does not apply to a single one." (van Kampen, 1984, p. 306)

The two processes he is alluding to here are the removal of the partition between the two samples, and the two free expansions plus the 'overlapping' with semipermeable membranes. These, it is argued, are mutually exclusive; the removal of the partition will not work for calculating the entropy of a mixture since this change of state would happen irreversibly under this process. On the other hand, the process of reversible mixing with semi-permeable membranes will not work with identical gases, since there is no differentiating feature which would allow semi-permeable membranes to exist in principle. This means that the step applying Equation (VK2) to identical gases is blocked, since the process used to establish that equation cannot be used on identical gases. This purportedly removes the contradiction at the heart of GP1.

Van Kampen's resolution has been echoed and endorsed in virtually every subsequent treatment of Gibbs' paradox in thermodynamics. His comments have been interpreted as indicating that distinguishability, in the sense that there in principle exist semipermeable membranes which allow the application of Gibbs' theorem, is what is important in resolving Gibbs' paradox. Gases may be different in any sense you like, i.e., there may be a number of properties that the gases do not share, but if there is no process which can reversibly mix or separate the gases in principle, then Equation (VK3) is to be used. Otherwise the gases are distinguishable in that sense, then Equation (VK2) gives the correct value for the entropy of the mixture.

There are variations on this theme of semipermeable membranes. Van Kampen actually ends up articulating a rather strong variation himself, to give the issue a pragmatic dimension: an experimenter dealing with two samples of gas may even know that they are distinguishable, but chooses to ignore this fact and treat them as if they were indistinguishable. In this case, he argues, the experimenter will be led to no contradiction in using (VK3). His solution can be summed up as the view that

> [t]he expression for entropy [...] depends on whether or not [the experimenter] is able an willing to make a distinction. (van Kampen, 1984)

The lesson van Kampen wants us to learn for Gibbs' paradox, is that identity (understood as the sharing or not of intrinsic properties) is not relevant for calculating the entropy of mixing, but rather that the more operational concept of distinguishability is what is important. This operational theme aligns with Bridgman (1961, pp. 168–169) who uses Gibbs' paradox as a case study of how his idea of the 'universe of operations'

to operationally define physical concepts such as distinguishability can be used to solve problems. Another variation is Dieks (2011) who adds another level of justification, ultimately grounding the difference between (VK2) and (VK3) in differences in the physical or chemical properties between the gases, and arguing that this is sufficient to establish the existence in principle of semipermeable membranes for the pair of gases.

In summary, it is widely agreed that distinguishability via semipermeable membranes is what explains the choice between equations (VK2) and (VK3) and therefore solves Gibbs' paradox in thermodynamics.

2.3   The difficulty

It is not clear what criterion of identity van Kampen himself intends to articulate, if any. On my reconstruction, he is giving an operational criterion of identity: two gases are distinguishable if and only if there exist semipermeable membranes which can be used to reversibly separate/mix the gases. But this criterion applies only insofar as we can supplement thermodynamics with a theory of semipermeable membranes. Although it is plausible that we do have this in the context of fluids[10], it is unclear whether it applies to other candidate thermodynamic systems such as elastic bands, magnets, or black holes. This criterion relies on extra-theoretic reasoning which is not clearly generally applicable. If we read van Kampen in this way, the analysis does not go far enough: we still need a fully general criterion of identity which applies to any kind of thermodynamic system.

Aside from not being generally applicable, this criterion of identity falls foul of the physics good practice with which we began this paper: the definition of identity in terms of the existence of semipermeable membranes (or any reversible separation procedure) is extra-theoretic and non-thermodynamic. While they are certainly useful heuristic devices for imagining reversible mixing and separation, semipermeable membranes are not a part of the thermodynamic formalism. In many formulations, this even relies on non-thermodynamic talk of the gases' constituent atoms and their atomic properties. Indeed, it is precisely because the semipermeable membrane mechanism is explicated in terms of the well-known underlying microphysics of the gases that it is so heuristically useful. But this same fact makes its usefulness totally unclear when we do not yet understand a system's microphysics.

We may put the point another way: thermodynamics is an extremely powerful and general theory for when we do not have access to the underlying microphysics of physical systems. As it happens, in the case of gases, we do know about the physics of the micro-constituents and this may be why we are naturally attracted to expressing identity in terms of the properties of those constituents. But, in general, we should not assume that we have access to the microphysics and so we should not let definitions of concepts such as identity to be tied to it. We should strive to explicate identity of thermodynamic systems in purely thermodynamic terms.

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[10]For example, Planck (1903, p. 218), Zemansky and Dittman (1997, p. 387) and Partington (1913, p. 272) mention the separation of hydrogen from air using a palladium or platinum membrane in support of the the theoretical use of semipermeable membranes in thermodynamics.

In spite of its popularity, van Kampen's discussion of the paradox is left wanting. Happily, there is another solution, which I turn to in the following sections.

3 Geometric Thermodynamics

Let me begin by setting out what I will take to be the formal structure of a thermodynamic system.[11] The assumptions we work with are the following.

1. The equilibrium state of a thermodynamic system is represented by a point in the $(k+1)$-dimensional smooth real manifold M with global coordinates $(X_0, ..., X_k)$.

2. These variables are related by a function f such that

$$X_0 = f(X_1, ..., X_k), \tag{3.1}$$

   which is called the *fundamental relation*. This defines a k-dimensional surface in M.

3. f is a homogeneous first-order function of $X_1, ..., X_k$:

$$f(\lambda X_1, ..., \lambda X_k) = \lambda f(X_1, ..., X_k) \tag{3.2}$$

   for every positive real number λ and for all $X_1, \ldots, X_k$.

The variables X_i will be taken to represent thermodynamic properties like energy, entropy, volume and mole number. The function f, when expressed in differential form, turns out to express what is known as the first law of thermodynamics.

We would like to be able to identify a model of thermodynamics with the same precision as we do in classical and quantum mechanics, each of which is equipped with a precise definition of the mathematical structure of their models. For example, a model of Hamiltonian mechanics is a symplectic manifold; and, a model of quantum mechanical system is a Hilbert space with an algebra of observables. This kind of precision inspires the following definition of a thermodynamic system, based on the framework just outlined.

Thermodynamic System. A *thermodynamic system* is a pair (M, f), where:

(i) M is a $(k+1)$-dimensional configuration space given coordinates $X_0, ..., X_k$.

(ii) $X_0 = f(X_1, ..., X_k)$ is the fundamental relation defining a k-dimensional surface in M, where f is first-order homogeneous.

Equivalently, we have a k-dimensional manifold N which is given coordinates $Y_1, ..., Y_k$ and a function $f : N \to \mathbb{R}$, where we can smoothly embed N into a $(k+1)$-dimensional manifold M via the map $\Phi : N \to M$. Then we can think of f as defining a k-dimensional surface in M whose coordinates are given by $X_0, .., X_k$ where $X_i(\Phi(p)) := Y_i(p)$ for $i = 1, ..., k$ and $X_0(\Phi(p)) := f(p)$.

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[11]The presentation here largely follows Callen (1960).

Let me illustrate how this formalism gives rise to the more familiar expressions of thermodynamics using the simple case of the ideal gas. We assume the configuration variables to be S (the entropy), U (the internal energy), V (the volume) and N (the mole number). The fundamental relation in Assumption 2 takes the form

$$S = f(U, V, N) \tag{3.3}$$

and the homogeneity in Assumption 3 takes the form

$$\lambda S = \lambda f(U, V, N) = f(\lambda U, \lambda V, \lambda N) \tag{3.4}$$

Equation (3.4) is often interpreted as the claim that entropy is 'extensive,' a term typically used to describe variables that scale with the 'size' of the system.[12]

To make contact with a more familiar expression of thermodynamics, we write the fundamental relation of the ideal gas in differential form as

$$df = \frac{\partial S}{\partial U} dU + \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial N} dN \tag{3.5}$$

Now adopt the following definitions to denote the partial derivatives occurring in this equation:

$$\frac{\partial f}{\partial U} \equiv \frac{1}{T}; \qquad\qquad \frac{\partial f}{\partial V} \equiv \frac{p}{T}; \qquad\qquad \frac{\partial f}{\partial N} \equiv -\frac{\mu}{T} \tag{3.6}$$

where T, the temperature, p, the pressure and μ, the chemical potential, are known as the system's intensive parameters.[13] These intensive parameters are clearly functions of the extensive parameters U, V, N. Relationships expressing the intensive parameters as functions of the extensive parameters are known as equations of state[14].

We may therefore write the differential form of the fundamental relation, which is commonly referred to as the *first law*,

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN. \tag{3.7}$$

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[12]The geometric framework offers a precise way of defining what extensive variables are in terms of the scaling symmetry of the fundamental relation. In short, we will say that a collection of thermodynamic variables are 'extensive' when we impose the first-order homogeneous property on the fundamental relation. This is explained in further detail in Appendix A.

[13]The intensive parameters are often characterised as those which do not scale with the size of the system. This may be understood more precisely as follows. In the formal setup presented here, the intensive parameters are defined to be the partial derivatives of the fundamental relation with respect to the other extensive parameters. Since they are derivatives of one extensive parameter with respect to another, the intensive parameters are invariant under the scaling of the extensive configuration variables.

[14]It is yet another advantage of this formulation of thermodynamics that it puts the equations of state, familiar to all students of thermodynamics, in their proper conceptual place in the foundations. While important, they are actually derivative from the fundamental relation. An individual equation of state is not sufficient to capture all the thermodynamic information about a system. Taking all the equations of state, however, is equivalent to taking the fundamental relation itself, and hence is sufficient.

It follows from Euler's theorem on homogeneous functions that[15]

$$S = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N.$$ (3.8)

This equation may be used to find the entropy of the ideal gas as a function of the extensive parameters U, V, N provided we know $1/T$, p/T and μ/T each as a function of U, V, N. From our empirical investigations, we know the first two as follows:

$$1/T = 3NR/2U$$ (3.9)

$$p/T = NR/V.$$ (3.10)

These are the familiar equations of state for the ideal gas. We can work out an explicit expression for μ/T from the other two since the three intensive parameters are not independent. This follows from the Gibbs-Duhem relation which is also a consequence of the fundamental relation being first-order homogeneous (see Appendix B.1). The fundamental relation of the ideal gas is thus derived to be

$$S = \left(\frac{3}{2}R\frac{N}{U}\right)U + \left(\frac{NR}{V}\right)V - \left(R\ln\left[\frac{N^{5/2}}{VU^{3/2}}\right] - K\right)N.$$ (3.11)

This equation may be simplified and substitutions of the equations of state may be made to express the entropy as a function of the other variables. I prefer to express the fundamental relation in this form, in order to emphasise the homogeneity of the fundamental relation and to emphasise the conceptual place of the equations of state as the derivatives of S with respect to U, V and N.

4 Mixtures, Equilibration and Mixing

We now use this framework to formulate a precise definition of a mixture as a thermodynamic system. My starting point is to recognise that mixtures are, in some sense, 'composite' systems formed out of individual 'subsystems'. For example, a mixture of hydrogen and helium is, in some sense, a composite system formed out of the individual hydrogen and helium components. I will therefore begin in Section 4.1 with a precise and general definition of composite thermodynamic system before using it to define a thermodynamic mixture in Section 4.2.

While we are analysing mixtures, we cannot avoid giving an analysis of 'mixing'. Mixing is typically described as the process whereby both samples of gas, each initially confined to their half of a container, finally come to occupy the full volume of the container when the partition dividing them is removed. Thus, Dieks writes that mixing is the gases "expanding into the same final volume" (Dieks, 2018) and van Lith writes that we have a mixture when the gases are "spread out over the whole container" (van

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[15]For a proof of this, see Callen (1960, p. 47).

Lith, 2018). It is readily admitted that equilibrium thermodynamics has nothing to say about the process of mixing, because it is obviously a non-equilibrium process. But this provides all the more reason to try to make sense of non-equilibrium talk in an equilibrium theory. To this end, I will describe thermodynamic equilibrium in general terms in Section 4.3 before describing mixing in Section 4.4. Roughly, the strategy I will adopt will be the following. "Removing a partition between two thermodynamic systems", means more formally that we remove a constraint on the thermodynamic variables of a third system, which we call the "mixture" of the original two. Informal heuristic expressions about the "non-equilibrium process" or the "flow" of extensive quantities between two systems are shorthand for the removal of this constraint.

Some readers may note that, despite van Kampen (1984) being the "go-to" reference for modern accounts of Gibbs' paradox in thermodynamics, his account differs from some in a noteworthy respect. In particular, van Kampen identifies the paradox as lurking in Equation (DIF), which is the difference between the entropies of Figures (1c) and (1d), whereas more modern accounts locate the paradox in the difference between the entropies of Figures (1a) and (1c). In other words, van Kampen calculated the entropy difference between a mixture and a pure ideal gas, while modern accounts calculate the entropy difference between the unmixed state of a mixture and the mixed state.

One can formulate this observation as two slightly different puzzles. Van Kampen's puzzle is to try to ground the fundamental relations of ideal gas mixtures and pure ideal gases in some assumption that may be interpreted as difference and identity. The other puzzle is to explain why we do not get an entropy increase when we remove a partition between two identical samples of gas. Both puzzles can be solved. In Section 5, I will give the derivations of the fundamental relations of ideal gas mixtures and pure ideal gases. In this Section I will argue that by clarifying what exactly 'partitions' and 'membranes' are in thermodynamics, and what it means to remove them, we can understand what happens when the partition is removed.

4.1 Subsystems and Composite Systems

Suppose we have k thermodynamic systems $(M^{(1)}, f^{(1)}), ..., (M^{(k)}, f^{(k)})$, whose manifolds are each given coordinates $(U^{(i)}, V^{(i)}, N^{(i)})$ for each $i = 1, ..., k$. Then we may define the composite of these individual thermodynamic systems as follows.

Composite System. Let $(M^{(1)}, f^{(1)}), ..., (M^{(k)}, f^{(k)})$ be k thermodynamic systems where the manifolds $M^{(i)}$ can have different dimensions. Then system i is given coordinates $X_1^{(i)}, ..., X_{\dim(M^{(i)})}^{(i)}$. Then the thermodynamic system (M, f) where $\dim(M) = n$ is a *composite system* of $(M^{(1)}, f^{(1)}), ..., (M^{(k)}, f^{(k)})$ iff M can be given coordinates $X_0, X_1, ..., X_n$ each of which is a function of the coordinates $X_1^{(i)}, ..., X_{\dim(M^{(i)})}^{(i)}$ for all i. For each $i = 1, ..., k$, we say that $(M^{(i)}, f^{(i)})$ is a *subsystem* of (M, f).

Specifying that the coordinates of the composite system must be functions of the coordinates of the subsystems incorporates an important assumption about the relation between the composite system and its subsystems, namely that the composite system

14

supervenes on its subsystems: there may be no change in the composite system without some change in the subsystems. I do not claim that this is the only definition of composite system possible—there may well be others—but I do claim that it relies on a plausible thesis about the relation between composite systems and their subsystems. This definition can help us understand mixtures; my strategy is to understand a thermodynamic mixture to be a thermodynamic system that contains (at least) two subsystems, which represent the components of the mixture.

4.2   What is a mixture?

We all have an intuitive understanding of mixtures: they are made by combining two or more different substances in the very same volume without any chemical reaction happening; if one were to mix two substances which are the same one would not get a mixture, but simply more of the same substance. In Section 5, we will explore the precise sense in which components of a mixture are different, but first we must give a precise definition of a thermodynamic mixture in the geometric framework. In this Section, I will discuss and compare two candidates for such a definition. The first is inspired by many discussions of Gibbs' paradox which follow van Kampen in treating the 'partial pressures' of the gases as *bona fide* thermodynamic variables, i.e. as partial derivatives of the fundamental relation with respect to some extensive variables. I then provide a second definition which I argue should be preferred since it avoids certain difficulties with the first.

For simplicity, let us consider an ideal gas mixture consisting of just two components, denoted 1 and 2. We treat the mixture as a composite system formed out of the individual systems $(M^{(i)}, f^{(i)})$ for $i = 1, 2$ where $M^{(i)}$ is given coordinates $U^{(i)}, V^{(i)}, N^{(i)}$ and $f^{(i)}$ is the fundamental relation for the ideal gas. The first definition of this mixture we consider is the composite thermodynamic system (M_+, f_+) where M_+ given coordinates (U, V_1, V_2, N_1, N_2), where $U := U^{(1)} + U^{(2)}$, $V_1 := V^{(1)}$, $V_2 := V^{(2)}$, $N_1 := N^{(1)}$ and $N_2 := N^{(2)}$, and where the fundamental relation is

$$S = f_+(U, V_1, V_2, N_1, N_2) = \frac{1}{T}U + \frac{p_1}{T}V_1 + \frac{p_2}{T}V_2 - \frac{\mu_1}{T}N_1 - \frac{\mu_2}{T}N_2 \qquad (4.1)$$

with

$$\frac{1}{T} = \frac{3}{2}R\frac{N_1 + N_2}{U}; \qquad (4.2)$$

$$\frac{p_i}{T} = R\frac{N_i}{V_i}; \qquad (4.3)$$

$$\frac{\mu_i}{T} = R\ln\left[\frac{N_i(N_1 + N_2)^{3/2}}{V_i U^{3/2}}\right] + K_i. \qquad (4.4)$$

In this system, the terms p_i/T and the μ_i/T are well-defined intensive thermodynamic variables, because p_i/T is the partial derivative of f_+ with respect to V_i and μ_i/T is the partial derivative of f_+ with respect to N_i for each $i = 1, 2$. If this reconstructed

15

system is supposed to represent a mixture of components 1 and 2 then it has the following unwelcome feature. Although we recover the partial pressures as thermodynamic variables by retaining V_1 and V_2 as extensive variables, we pay a cost: there is no formal representation of "the volume of the mixture", a concept so central to the idea of a mixture that we surely would want to retain it in our formal representation. To solve this problem, we would have to make the *ad hoc* assumption that volumes V_1 and V_2 have the same value and 'overlap', i.e. that they refer to the very same volume in physical space. Now, there does not seem to be anything against doing this, since thermodynamics only says what the values of these volumes are, not "where in space" the volumes are located. At best, thermodynamics does not prohibit the use of this assumption. But the fact that we have to postulate these conditions on the volume variables to make (M_+, f_+) a plausible representation of a mixture should indicate to us that we should seek a better representation. The cost of recovering partial pressures as genuine thermodynamic variables is, I think, too expensive.

I would like to propose an alternative characterisation of mixture which avoids this problem[16]. This second definition represents an ideal gas mixture as the composite system (M_*, f_*), formed out of the individual systems $(M^{(i)}, f^{(i)})$ for $i = 1, 2$, where M_* is given coordinates $(U, V, N_1, ..., N_k)$, where $U := U^{(1)} + U^{(2)}$, $V := V^{(1)} = V^{(2)}$, $N_1 := N^{(1)}$, $N_2 := N^{(2)}$ and the fundamental relation is

$$S = f_*(U, V, N_1, N_2) = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu_1}{T}N_1 - \frac{\mu_2}{T}N_2 \qquad (4.5)$$

where

$$\frac{1}{T} = \frac{3}{2}R\frac{(N_1 + N_2)}{U} \qquad (4.6)$$

$$\frac{p}{T} = R\frac{(N_1 + N_2)}{V} \qquad (4.7)$$

$$\frac{\mu_i}{T} = R\ln\left[\frac{N_i\,(N_1 + N_2)^{3/2}}{VU^{3/2}}\right] + K_i \text{ for } i = 1, 2. \qquad (4.8)$$

Under this characterisation, we must think of an ideal gas mixture as a number of substances, all with the same temperature, occupying the very same volume. This definition eliminates the problem of 'overlapping volumes' by simply having only one volume variable which we may easily interpret as the 'volume of the mixture'. But this means we have to give up the 'partial pressures' as thermodynamic variables and hence give up the typical representation of the mixing process as each gas pushing on a semipermeable membrane with its corresponding partial pressure. We therefore have to develop a different account of mixing. To fill this vacuum I have created, I will describe a representation of mixing based on (M_*, f_*) which makes no reference to semipermeable

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[16]This characterisation is, in fact, the same as Gibbs'. While he did not use the concepts and language of thermodynamic systems and subsystems I am using here, it is clear that he uses the same extensive variables and fundamental relation to define a mixture as I do. For completeness, I reconstruct his discussion of the ideal gas mixture and its fundamental relation in Appendix C.

membranes. But before we can do this, a preliminary step is needed: let me first review the concepts of equilibrium and equilibration.

4.3 Equilibrium and Equilibration

Intuitive grasps on equilibrium and equilibration abound. Roughly characterised, a system is in equilibrium if and only if the macroscopic variables which define the thermodynamic state of the system do not change with time.[17] However, this rough characterisation is problematic when it comes to saying precisely what it means in the thermodynamic formalism, since there is no time parameter in thermodynamics with respect to which to express this constancy. Equilibration is characterised as the process of coming to equilibrium. This invites talk of the flow over time of energy or matter from one subsystem to another. For the same reason, this characterisation poses challenges when formulating it in the concepts and formalism of equilibrium thermodynamics: describing processes mathematically requires changes of quantities with respect to time.

In fact, thermodynamics is equipped with a precise definition of equilibrium which does not rely on any temporal notion. Consider a thermodynamic system with extensive variables $X_0, ..., X_k$. The first key step is to imagine this system to be composed of subsystems such that each subsystem (i) has variables $X_K^{(i)}$ such that $X_K^{(i)} = \lambda^{(i)} X_K$ with $\sum_i \lambda^{(i)} = 1$. This implies that for some K, the $X_K^{(i)}$ for all i may take on any values consistent with $\sum_i X_K^{(i)} = X_K$. This decomposition of the system into subsystems is sufficient for us to say what it means for the system to be in equilibrium.

K-**Equilibrium.** Let (M, f) be a thermodynamic system with variables $X_0, ..., X_k$ which is composed of n subsystems $(M^{(i)}, f^{(i)})$ for $i = 1, .., n$ such that $\sum_i X_K^{(i)} = X_K$ for all $K = 0, ..., k$. Then we say that (M, f) is *in K-equilibrium* if and only if the values of $X_K^{(i)}$ for all i are such that the entropy function $S(X_0^{(1)}, ..., X_k^{(1)}, ..., X_0^{(n)}, ..., X_k^{(n)}) := \sum_i^n S^{(i)}(X_0^{(i)}, ..., X_k^{(i)})$ is at an extremum[18].

Note that the definition is indexed to an extensive variable X_K; we may choose to extremise the entropy with respect to any number of the extensive variables, each of which yields a particular kind of equilibrium. For example, if we choose to extremise the entropy with respect to U, we get a system in thermal equilibrium. Extremising S with respect to V yields mechanical equilibrium and with respect to N, chemical

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[17]See, for example, Adkins (1983, p. 7), Baierlein (1971, p. 4) and Blundell and Blundell (2010, pp. 32–33).

[18]This means that we have equilibrium when $dS = 0$. This definition still leaves open the precise nature of the equilibrium which depends on the sign of d^2S. If the second derivative is negative we have a maximum of the entropy function and we say that the equilibrium is *stable*. If the second derivative is positive or zero, we have extrema other than maxima and we say that the equilibrium is *unstable*.

This characterisation of equilibrium is a variational principle, like the principle of least action in mechanics. For a discussion of this analogy and its connection to the arrow of time see Uffink (2001). Furthermore, this characterisation of equilibrium in terms of a variational principle should be distinguished from the so-called Minus First Law, coined in Brown and Uffink (2001).

equilibrium. In the special case where the system is in equilibrium with respect to all extensive variables then we make the following definition:

Thermodynamic Equilibrium. A system is in *thermodynamic equilibrium* if and only if the system is in K-equilibrium for all K.

Let us illustrate how these definitions work by considering an ideal gas decomposed into two subsystems along the lines outlined above. For the composite system to be in equilibrium, the values of the variables $U^{(1)}, V^{(1)}, N^{(1)}$ and $U^{(2)}, V^{(2)}, N^{(2)}$ must be such that they extremise the entropy of the composite system S which, by the additivity postulate, is given by $S = S^{(1)} + S^{(2)}$. Thus we have that

$$S = S^{(1)} + S^{(2)} = \frac{1}{T^{(1)}}U^{(1)} + \frac{p^{(1)}}{T^{(1)}}V^{(1)} - \frac{\mu^{(1)}}{T^{(1)}}N^{(1)} + \frac{1}{T^{(2)}}U^{(2)} + \frac{p^{(2)}}{T^{(2)}}V^{(2)} - \frac{\mu^{(2)}}{T^{(2)}}N^{(2)}. \quad (4.9)$$

To find the extremum of S we differentiate and set $dS = 0$. If we allow variation in all the extensive variables, then we have, for all $X = U, V, N$, $X^{(1)} + X^{(2)} = X$ where X is constant implying $dX^{(2)} = -dX^{(1)}$. Therefore we find:

$$0 = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} + \left(\frac{p^{(1)}}{T^{(1)}} - \frac{p^{(2)}}{T^{(2)}} \right) dV^{(1)} - \left(\frac{\mu^{(1)}}{T^{(1)}} - \frac{\mu^{(2)}}{T^{(2)}} \right) dN^{(1)}. \quad (4.10)$$

dS must vanish for arbitrary values of $dU^{(1)}$, $dV^{(1)}$ and $dN^{(1)}$ so we find the conditions for thermodynamic equilibrium to be

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}}; \qquad \frac{p^{(1)}}{T^{(1)}} = \frac{p^{(2)}}{T^{(2)}}; \qquad \frac{\mu^{(1)}}{T^{(1)}} = \frac{\mu^{(2)}}{T^{(2)}}. \quad (4.11)$$

Therefore, the ideal gas is at thermodynamic equilibrium when the subsystems have equal temperature, pressure and chemical potential. These conditions allow us to calculate the equilibrium values of the subsystems' extensive variables. For example, substituting the equation of state $U = (3/2)NRT$ into $1/T^{(1)} = 1/T^{(2)}$ yields $U^{(1)}/N^{(1)} = U^{(2)}/N^{(2)}$. Since $U = U^{(1)} + U^{(2)}$, it follows after some rearrangement that $U^{(1)}/N^{(1)} = U^{(2)}/N^{(2)} = U/N$. In the next Section, we will do this for the two representations of mixing.

How do we recover the concept of equilibration in this framework? Since nothing 'happens' in equilibrium thermodynamics, and equilibration is intended to describe some kind of process, it cannot be precisely articulated. The closest thing we can do is compare the states of the system whose values of the subsystems' extensive variables do not extremise the entropy with those which do. We cannot strictly give an account of what happens between these states nor, for that matter, can we even say which state comes 'earlier in time'. Thermodynamics simply does not come with the conceptual and formal resources to articulate such thoughts. It is precisely because of this bare storyline

from non-equilibrium (non-S-extremising) to equilibrium (S-extremising) states that we feel we have to elaborate on it to bring it more into line with everyday experience and language. Thus, we may feel compelled to add that the non-equilibrium state occurs earlier in time than the equilibrium state, and that extensive quantities like energy and matter spontaneously 'flow' between the subsystems in the process of equilibration as a result of the removal of some 'partition' representing a constraint on this flow. It seems that part of what makes equilibrium thermodynamics such a conceptually slippery subject is its very simplicity and sparse conceptual landscape; we have to add so much extra-theoretic, non-equilibrium detail to make intuitive sense of it that, at the end, it becomes difficult to disentangle what is thermodynamics proper and what is not. Having said all this, in the next Sections I will help myself to talk of mixing, equilibration, partitions, and the like for the sake of being concise and readable. If this section serves for anything, it is to remind us of the extra-theoretic and strictly non-thermodynamic status of these concepts.

Having understood the definition and structure of equilibrium, we are now able to bring what we have learnt to bear on mixing and in particular on how to understand the differences between the two representations of mixtures we have so far articulated.

4.4   What is mixing?

Let us begin by understanding the traditional representation of mixing based on the representation of mixture reconstructed in Section 4.2. To represent the mixing equilibration process, we view (M_+, f_+) as being composed out of subsystems $(M_+^{(1)}, f_+^{(1)})$ and $(M_+^{(2)}, f_+^{(2)})$ in the way outlined in the definition of K-equilibrium. Mixing is the transition from the unmixed state (where the values of the subsystems' extensive variables do not extremise the entropy) to the mixed state (where they do) as a result of the removal of a constraint on the flow of the extensive quantities.

In the context of Gibbs' paradox, the temperatures of the samples each side of the partition are equal, leaving only the volume and mole number constraints to be removed. We can think of mixing as removing either the volume constraint or the mole number constraint, but removing one of them will cause both remaining intensive parameters to equalise. The transition from the initial to the final state as a result of the removal of the volume constraint is summarised in Table 1.

This final state may be calculated along the lines explained in Section 4.3. Having decomposed the system into subsystems, we allow the volume to 'flow' between the subsystems, reaching values of $V_1^{(1)}$, $V_1^{(2)}$, $V_2^{(1)}$ and $V_2^{(2)}$ which extremise the entropy:

$$0 = dS = \left(\frac{p_1^{(1)}}{T} - \frac{p_1^{(2)}}{T} \right) dV_1^{(1)} + \left(\frac{p_2^{(1)}}{T} - \frac{p_2^{(2)}}{T} \right) dV_2^{(1)}, \tag{4.12}$$

concluding that the condition for equilibrium is $p_1^{(1)}/T = p_1^{(2)}/T$ and $p_2^{(1)}/T = p_2^{(2)}/T$. Imposing this condition implies that the gases expand to fill the volume of the container,
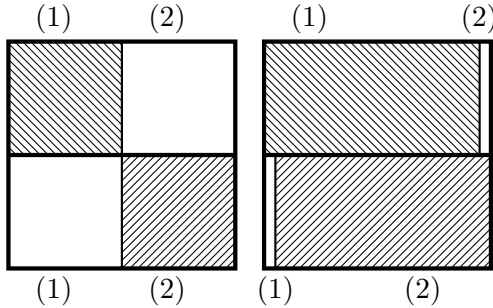
Variable	Initial	Final
$U^{(1)}$	$U/2$	$U/2$
$U^{(2)}$	$U/2$	$U/2$
$V_1^{(1)}$	$V_1/2$	V_1
$V_1^{(2)}$	$V_1/2$	0
$V_2^{(1)}$	$V_2/2$	0
$V_2^{(2)}$	$V_2/2$	V_2
$N_1^{(1)}$	N_1	N_1
$N_1^{(2)}$	0	0
$N_2^{(1)}$	0	0
$N_2^{(2)}$	N_2	N_2

Figure 4: Depiction of mixing represented as two free expansions. In order for this to represent a mixture, we are to imagine that V_1 and V_2 have the same value and 'overlap'.

Table 1: Transition from initial to final state by removal of the volume constraint, when representing mixing on the basis of (M_+, f_+).

with final values[19] as illustrated in Table 1.

We may calculate the entropy change by calculating the difference between the initial and final value of $S_+ = S_+^{(1)} + S_+^{(2)}$. Since it is the volume flowing between the subsystems that generates this entropy increase and there is no flow of energy or mole number between the subsystems, we find that the entropy change is the difference between the initial and final values of the expression

$$R(N_1^{(1)} \ln V_1^{(1)} + N_1^{(2)} \ln V_1^{(2)} + N_2^{(1)} \ln V_2^{(1)} + N_2^{(2)} \ln V_2^{(2)}) \qquad (4.13)$$

where we have used the fundamental relation f_+ in Equation (4.1). Substituting in the initial and final values of these variables taken from Table 1, we can calculate that the entropy change is $2(N_1 + N_2)R \ln 2$.

We now turn to the representation of mixing based on (M_*, f_*). In this case, the mixing process is represented differently, due to the fact that the system has different extensive variables and hence different kinds of internal constraints on the flow of extensive quantities.

We assume that the pressures and temperatures of each subsystem are equal by

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[19]These values are calculated as follows. Substituting in the equation of state $pV = NRT$ for the ideal gas into the conditions of equilibrium $p_i^{(1)}/T = p_i^{(2)}/T$ we get $N_i^{(1)}/V_i^{(1)} = N_i^{(2)}/V_i^{(2)}$. Given that the mole numbers of the subsystems remain constant and the volumes are subject to $V_i = V_i^{(1)} + V_i^{(2)}$, we get $N_i^{(1)}/V_i^{(1)} = N_i^{(2)}/V_i^{(2)} = N_i/V_i$. Rearranging to make V_i^j for $i, j = 1, 2$ the subject, we calculate the values given in Table 1.
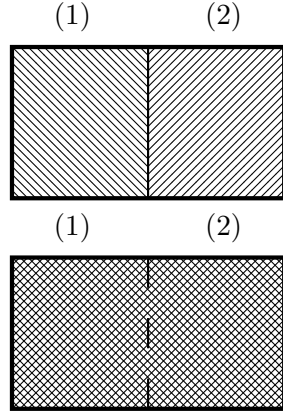
Figure 5: Depiction of mixing based on the thermodynamic system (M_*, f_*).

Variable	Initial	Final
$U^{(1)}$	$U/2$	$U/2$
$U^{(2)}$	$U/2$	$U/2$
$V^{(1)}$	$V/2$	$V/2$
$V^{(2)}$	$V/2$	$V/2$
$N_1^{(1)}$	N	$N/2$
$N_1^{(2)}$	0	$N/2$
$N_2^{(1)}$	0	$N/2$
$N_2^{(2)}$	N	$N/2$

Table 2: Transition from initial to final state by removal of the mole number constraint, when representing mixing on the basis of (M_*, f_*).

removing constraints on the flow of energy and volume. However, we assume the system still has internal constraints on the flow of the mole numbers of the components in place. If we remove the constraint on mole number, the conditions for chemical equilibrium for each component will be satisfied: $\mu_1^{(1)}/T = \mu_1^{(2)}/T$ and $\mu_2^{(1)}/T = \mu_2^{(2)}/T$ as may be easily verified by running a similar calculation to Equation (4.12) to extremise the entropy. From these conditions and the initial values given in Table 2, the final values of $N_1^{(1)}$, $N_1^{(2)}$, $N_2^{(1)}$ and $N_2^{(2)}$ may be calculated. The entropy change is obtained by calculating the initial and final values of $S_* = S_*^{(1)} + S_*^{(2)}$ which, using the fundamental relation f_* in Equation (B.16), is the difference between the initial and final values of the expression

$$R(N_1^{(1)} \ln N_1^{(1)} + N_1^{(2)} \ln N_1^{(2)} + N_2^{(1)} \ln N_2^{(1)} + N_2^{(2)} \ln N_2^{(2)}) \qquad (4.14)$$

where we substitute in the values of the mole numbers from Table 2. We find $\Delta S_* = 2(N_1 + N_2)R \ln 2$.

Comparing the representations of mixing, we see that they represent the process quite differently. In the process based on (M_+, f_+), mixing is initiated by removing the volume constraint, while in the process based on (M_*, f_*), mixing is initiated by removing the mole number constraint. As a result, the calculation of the entropy change is entirely different (the first relies on a flow of volume between the subsystems, while the second relies on the flow of mole number). Both calculations happen to give $2(N_1 + N_2)R \ln 2$. It is interesting to note that one arrives at the very same numerical answer for the entropy increase on mixing despite the systems and processes being entirely different. It is not a coincidence, however, since it follows from Gibbs' theorem (see Section 2.2) that the entropy of a mixture of ideal gases is the sum of the entropies each component would

have if they occupied a container with the same volume and temperature.

In the face of the problems described in Section 4.2, and given that one can recover the standard numerical answer to the entropy increase on mixing on the basis of my preferred representation of a mixture, (M_*, f_*), it seems reasonable to abandon (M_+, f_+) and the overlapping assumption as a representation of mixtures and instead adopt (M_*, f_*) as a better representation.

5 Homogeneity and Identity

Our careful formulation of what it means to be a thermodynamic system and what it means to be a mixture can now be put to work. In this Section, I present a criterion of identity in thermodynamics that is internal to the thermodynamic formalism, instead of relying on qualitative or extra-theoretic concepts. Not only is this discussion of quite general interest, given that similar discussions concerning the identity or equivalence of systems already occur in the context of other physical theories, but it is also of crucial importance in the analysis of Gibbs' paradox.

I will begin by explaining what I take to be the traditional and intuitive view of identity which is often appealed to in thermodynamics and in discussions of Gibbs' paradox. Then I will give new and rigorous derivations of van Kampen's equations (VK2) and (VK3). Doing this will expose certain assumptions which I will go on to interpret as difference and identity respectively.

5.1 The Properties View of Identity

On a traditional and intuitive view, the criterion of identity for physical systems appeals to their physical and chemical properties: two thermodynamic systems are identical if and only if they have the same intrinsic properties. This is often the case, implicitly, in discussions of Gibbs' paradox in thermodynamics. The view is tempting because it seems to capture the intuitions we have when we say that a box of helium is 'of the same kind' as another box of helium but not of the same kind as a box of hydrogen.

The problem is that such a view is in danger of violating the good physics practice discussed in the Introduction: the 'properties' appealed to are often extra-theoretic, non-thermodynamic concepts. So, in order for us to respect the practice, something about the thermodynamic system $(M_{\text{He}}, f_{\text{He}})$ representing the box of helium must be different from the thermodynamic system $(M_{\text{H}}, f_{\text{H}})$ representing the box of hydrogen, and the difference must lie either in the manifolds or the fundamental relation. A difference in the dimension of the manifolds would certainly distinguish two systems. However, this is not plausible in the hydrogen and helium case, since these gases are each described by the same thermodynamic variables. If we are to subscribe to the properties view, any physical and chemical differences between the substances must be found in the fundamental relations.

Specifying that the thermodynamic system has the van der Waals fundamental relation is a natural way to incorporate physical and chemical differences in the thermody-

namic formalism, and to make the intuitive properties view precise. The fundamental relation for a van der Waals gas[20] is

$$S/N = R\ln(V/N - b) + cR\ln(u + aN/V) + k \tag{5.1}$$

where a, b, c are constants that will in general depend on the physical and chemical properties of the gas and k is the constant of integration. The constant a is meant to capture the change in energy due to intermolecular forces, the constant b is meant to capture the volume that each molecule of the gas occupies and c is the specific heat of the substance. The properties which differentiate helium and hydrogen are encoded by the values of the constants. In this case, while both M_{He} and M_{H} are of the same dimension with coordinates U, V and N, the boxes of hydrogen and helium have different fundamental relations in virtue of having different values for the constants (in some fixed system of units) and hence, *qua* van der Waals gas, are different thermodynamic systems.

The problem is that, in practice, boxes of helium and hydrogen at room temperature and pressure can be modelled, to an extremely good approximation, as ideal gases. And the fundamental relation of the ideal gas, as we have seen, is not sensitive to any such constants; it is a function only of U, V and N. Put another way, the ideal gas is only sensitive to how much stuff there is, not what that stuff is. Therefore, *qua* ideal gases, the boxes of hydrogen and helium might appear to be identical since they have the same manifolds and the same fundamental relation.

We can be much more precise here. When we say that (M_{He}, f_{He}) and (M_{H}, f_{H}) have 'the same' manifolds and fundamental relations, we mean that these thermodynamic systems are isomorphic: their manifolds are the same dimension and so we can define a diffeomorphism $\psi : M_{He} \to M_{H}$, and their fundamental relations are all 'the same' in the sense that $f_{H} = \psi_* f_{He}$. Isomorphism is typically held in high regard as a natural standard of equivalence or identity[21], but it leads us to the absurd conclusion that all ideal gases are identical.

I take this as a *reductio* that isomorphism is unsatisfactory as a sufficient criterion of identity since it fails to capture the practice of modelling two ideal gases as non-identical (such as in Gibbs' paradox). Furthermore, appealing to physical and chemical properties of the atomic constituents to differentiate thermodynamic systems is essentially appealing to extra-theoretic considerations when specifying the criterion of identity for thermodynamic systems. Therefore, we should try and find a precise sense in which ideal gases can be different by formulating a general criterion of identity for thermodynamic systems which appeals only to the formalism and concepts of thermodynamics itself.

This strategy I adopt is inspired by considering mixtures. Two different gases combined will form a mixture, while two identical gases combined is just more of the same gas. Thus, the strategy is to change the question. Rather than picking up any two thermodynamic systems and asking whether they are identical, we should instead only be able to ask whether two thermodynamic systems are identical if they are each parts

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[20]Note that this is not the more frequently discussed equation of state of the van der Waals gas: $p = RT/(V - b) - a/V^2$. It may, however, be easily derived from this fundamental relation.

[21]See, for example, Weatherall (2018, p. 331).

of a third system which is the composite of the two. How the composite system is defined yields the answer to the identity question. This Section will execute this strategy in detail. I begin by providing rigorous derivations of van Kampen's equations (VK2) and (VK3). This will expose crucial assumptions in the derivations which I will go on to generalise and interpret as difference and identity. The criterion at which I arrive departs in significant and interesting ways from the traditional and intuitive notion of identity analysed in terms of properties.

5.2 Deriving equations (VK2) and (VK3)

Van Kampen's Equation (VK2) purports to express the entropy of a mixture. In this Section, I will show that Equation (VK2) follows from the definition of mixture as (M_*, f_*). The definitions for the variables for this thermodynamic system, which were first given in Section 4.2, are summarised in Table 3. The physical justification for these definitions are given in Appendix B.2.

Variable	Definition
S	$\sum_i S^{(i)}$
U	$\sum_i U^{(i)}$
V	$V := V^{(1)} = ... = V^{(k)}$
N_i	$\sum_i N^{(i)}$ for $i = 1, ..., k$

Table 3: Definitions of the variables for (M_*, f_*) for deriving Equation (VK2).

Variable	Definition
S	$\sum_i S^{(i)}$
U	$\sum_i U^{(i)}$
V	$\sum_i V^{(i)}$
N	$\sum_i N^{(i)}$

Table 4: Definition of the variables for $(M^{\text{VK3}}, f^{\text{VK3}})$ for deriving Equation (VK3).

With these definitions, the fundamental relation of the ideal gas mixture becomes

$$S = f_*(U, V, N_1, ..., N_k) = \frac{1}{T}U + \frac{p}{T}V - \sum_i \frac{\mu_i}{T}N_i \tag{5.2}$$

where

$$\frac{1}{T} = \sum_i \frac{3}{2}R\frac{N_i}{U} \tag{5.3}$$

$$\frac{p}{T} = \sum_i R\frac{N_i}{V} \tag{5.4}$$

$$\frac{\mu_i}{T} = R\ln\left[\frac{N_i\left(\sum_j N_j\right)^{3/2}}{VU^{3/2}}\right] + K_i \text{ for } i = 1, ..., k \tag{5.5}$$

By eliminating U in favour of T, defining the 'partial pressures' $p_i := N_i/V = pN_i/(\sum_i N_i)$, and absorbing all constants into the K_i, we recover van Kampen's Equation (VK2) for k components in the following form:

$$S = \frac{5}{2}\left(\sum_{i=1}^{k} N_i\right) R\ln T - \sum_{i=1}^{k}\left(N_i R\ln p_i\right) + \left(\sum_{i=1}^{k} N_i K_i\right) \qquad \text{(VK2′)}$$

where the summation indices run over the number of components in the mixture.

We now turn to deriving Equation (VK3). We assume we have k thermodynamic systems $(M^{(1)}, f^{(1)}), ..., (M^{(k)}, f^{(k)})$, whose manifolds are given coordinates or the pure ideal gas. Out of these, we look to define a composite thermodynamic system $(M^{\text{VK3}}, f^{\text{VK3}})$ such that Equation (VK3) may be derived from its fundamental relation and equations of state. This equation is supposed to give the entropy when gases A and B are 'the same'. So it gives the entropy of a system which we create by combining two 'identical' gases A and B to get 'more of the same gas'. Thus the final system is supposed to be the same pure substance as A and B, just more of it, so the coordinates of M^{VK3} are going to be S, U, V, N. The definitions of the variables for $(M^{\text{VK3}}, f^{\text{VK3}})$ are summarised in Table 4 and their physical justification is given in Appendix B.3.

Applying these definitions, we arrive at the fundamental relation

$$S = f^{\text{VK3}}(U, V, N) = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N \qquad (5.6)$$

with the equations of state

$$\frac{1}{T} = \frac{3}{2}R\frac{N}{U}; \qquad (5.7)$$

$$\frac{p}{T} = R\frac{N}{V}; \qquad (5.8)$$

$$\frac{\mu}{T} = R\ln\left[\frac{N^{5/2}}{VU^{3/2}}\right] + K. \qquad (5.9)$$

If we eliminate U in favour of T and V in favour of p, and define $p^{(i)} := N^{(i)}RT/V$ while also writing $N = \sum_i N^{(i)}$ and $p = \sum_i p^{(i)}$ we recover van Kampen's (VK3) in the following form:

$$S = \frac{5}{2}R\left(\sum_{i}^{k} N^{(i)}\right)\ln T - \left(\sum_{i}^{k} N^{(i)}\right)R\ln\left[\sum_{i}^{k} p^{(i)}\right] + \left(\sum_{i}^{k} N^{(i)}\right)K \qquad \text{(VK3′)}$$

At this point, we may compare our Equations (VK2′) and (VK3′) with van Kampen's (VK2) and (VK3) and notice an interesting and important feature of the interpretation of the indices. Van Kampen uses A and B, which are supposed to label the gases, to index the variables in both equations. But what is referred to with 'the gases'? What is the relation of A and B to the composite system in each case?

What we learn from the derivations carried out in this Section, is that use of the indices A and B is ambiguous. It is at least clear that they are meant to be subsystems of the composite in some sense, but in what sense, precisely? Here, I have shown that the

gases can be subsystems of the composite in two different ways. In the next Section, we will investigate to what extent these senses can be interpreted as difference and identity. But at the very least we can note here that van Kampen's use of the same indices in each equation covers up the fact that the indices take on quite different interpretations. Let us start with comparing Equation (VK2$'$) and van Kampen's (VK2). In our (VK2$'$), the subscript indices i run over the components in the mixture. However, while each N_i is a proper thermodynamic variable in the sense that each is a coordinate of M, the so-called 'partial pressures' p_i are not thermodynamic variables in the sense that they are not partial derivatives of f_* with respect to any configuration variable.[22] In (VK3$'$) the indices run over subsystems. In this case, neither the $N^{(i)}$, the mole number of subsystem (i), nor the $p^{(i)}$, the pressure of subsystem (i) is a proper thermodynamic variable since the coordinates of M are U, V, N. Therefore, while van Kampen wrote his entropies as functions of p_A, p_B, T, N_A, N_B for both (VK2) and (VK3) respectively, they really should be written as functions of p, T, N_A, N_B and p, T, N respectively.

In this Section, we have given rigorous derivations of each of van Kampen's equations. This has clarified the status and interpretation of the indices A and B used by van Kampen in his expression of the equations. We have learned that it is not as simple as "letting A and B represent two gases" which may or may not be identical; we have to specify the precise nature of the subsystem-composite system relationship before interpreting the indices. The purpose of examining detailed derivations of these equations is precisely so that we may examine whether any of the assumptions behind the equations may be interpreted as saying that the systems $(M^{(i)}, f^{(i)})$ are 'different' or 'identical' in some sense. We now turn to this issue.

5.3 Criterion of Identity

Here I propose a criterion of identity for thermodynamic systems which does not rely on the traditional and intuitive characterisation in terms of properties, but rather adheres to our mantra by expressing identity in purely thermodynamic terms. Van Kampen's Equation (VK2) purports to be the entropy of a mixture of 'different' substances while (VK3) purports to be the entropy when the substances are 'the same'. With our derivations of Equations (VK2$'$) and (VK3$'$), we have uncovered the assumptions behind these equations and in this section I will argue that these assumptions can be interpreted as 'difference' and 'identity' respectively.

In order to state the precise criterion of identity for thermodynamic systems, we must introduce some formal machinery. Given a chart (U, φ) on M where $U \subseteq M$ and $\varphi : U \to \mathbb{R}^k$, let us adopt the notation $(U, \lambda\varphi)$ to denote the chart that 'scales' each of the coordinate components of $\varphi(U) \in \mathbb{R}^k$ by λ, i.e. $\lambda\varphi$ is defined by $x_i \circ \lambda\varphi(p) := \lambda x_i \circ \varphi(p)$ for each coordinate component $x_i : \mathbb{R}^k \to \mathbb{R}$ for $i = 1, .., k$ and for all $p \in U$.

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[22]Callen (1960, p. 337) emphasised this point. He writes "The partial pressures are purely mathematical constructs with no direct physical meaning." This is a little cryptic, but he may be taken to mean that these pressures are not derivatives of the fundamental relation with respect to any configuration variable.

Identity of Thermodynamic Kinds. Thermodynamic systems (M, f) and (M', f') are of 'identical kinds' iff:

- There exists a diffeomorphism $\psi : M \to M'$ and

- If, for any chart (U, φ) on M, $(\psi(U), \varphi')$ is a chart on M' such that $\varphi' = \lambda \varphi \circ \psi^{-1}$ (that is, φ' is the scaled chart pushed forward to M') then:

$$(f' \circ \varphi'^{-1})(X_1'(\psi(p)), ..., X_k'(\psi(p))) = \lambda(f \circ \varphi^{-1})(X_1(p), ..., X_k(p)) \qquad \text{(ID)}$$

  for all $p \in U$, and where $X_i := x_i \circ \varphi$ and $X_i' := x_i \circ \varphi'$ are the coordinate maps on M and M' respectively.

This criterion of identity for thermodynamic systems is fully general (it does not just apply to ideal gases) and specifies a criterion for each element of the ordered pair. The first criterion requires (at least) that the manifolds be of the same dimension. To understand the second criterion we may abuse notion somewhat and say that for (M, f) and (M', f') to be of 'identical kinds' means that if $X_i' = \lambda X_i$ for some positive real λ then we have that $f'(X_1', ..., X_k') = \lambda f(X_1, ..., X_k)$. Essentially, this criterion of identity says that two thermodynamic systems are identical if and only if, when the coordinates on M are scaled versions of the coordinates on M', then the fundamental relation f on M is a scaled version of the fundamental relation f' on M'. We can see that this criterion relies on f and f' being first-order homogeneous functions of their coordinates: $f'(X_1', ..., X_k') = f'(\lambda X_1, ..., \lambda X_k) = \lambda f(X_1, ..., X_k)$.

The basic idea that this criterion tries to capture is the following: k thermodynamic systems are identical if and only if, when they are composed, the resulting composite system is a scaled version of each of the subsystems. Thus, the criterion of identity is based on the relation between a composite system and its subsystem and the assumption of homogeneity. We will discuss the philosophical implications of this criterion after I show that it does the job: to precisely draw a wedge between Equations (VK2) and (VK3). This directly addresses the contradiction that is at the heart of van Kampen's puzzle. Using this criterion of identity, I will show that the subsystems of the system $(M^{\text{VK2}}, f^{\text{VK2}})$ are all different, and the subsystems of the system $(M^{\text{VK3}}, f^{\text{VK3}})$ are all identical.

We begin by showing that any subsystem $(M^{(i)}, f^{(i)})$ of $(M^{\text{VK3}}, f^{\text{VK3}})$ is identical to $(M^{\text{VK3}}, f^{\text{VK3}})$. We note first that the manifolds $M^{(i)}$ and M^{VK3} are of the same dimension and hence (given also standard smoothness conditions) there exists a diffeomorphism between them. In defining the coordinates of the composite system, we found the relation between them to be $\lambda_i X = X^{(i)}$ for $X = U, V, N$ and where $\lambda_i := N^{(i)} / \sum_i N^{(i)}$. This is just to say that the coordinates of the systems are scaled versions of each other. Therefore, since the fundamental relations are first-order homogeneous, we have $f^{(i)}(U^{(i)}, V^{(i)}, N^{(i)}) = f(\lambda_i U, \lambda_i V, \lambda_i N) = \lambda_i f(U, V, N)$. What we have shown is that each of the subsystems $(M^{(i)}, f^{(i)})$ is identical to the composite system $(M^{\text{VK3}}, f^{\text{VK3}})$. In the case of VK2, the identity condition for the manifold fails: the

dimension of M^{VK3} is not the same as the dimension $M^{(i)}$ so there can be no diffeomorphism between them. Thus, the composite system is not identical to any of the subsystems. We may look at the difference between VK2 and VK3 a different way. For VK2, the mole numbers $N^{(i)}$ of the subsystems were defined to be the mole numbers N_i of the individual components of the composite system. It is essentially this which means that the substances i whose quantities are denoted by the variables N_i are all different: they are independently variable components and hence form a mixture when combined. In contrast, the mole numbers $N^{(i)}$ of the subsystems of $(M^{\mathrm{VK3}}, f^{\mathrm{VK3}})$ were defined to be part of the total mole number $N = \sum_i N^{(i)}$. It is in this sense that the composite system is just "more of the same kind of stuff" as the subsystems $(M^{(i)}, f^{(i)})$.

This criterion defines an identity relation between the subsystems and the composite. One might object that these should not be the relata. Rather, the pertinent question is whether identity holds, not between the subsystem and the composite, but between the subsystems themselves. What we really want is a criterion of identity for thermodynamic systems which will tell us, upon composing these systems, when we get a mixture and when we just get more of the same stuff. This is a natural response and is motivated by a traditional conception of identity where we can just pick up two systems and compare them to determine whether identity holds or not. I respond to this by arguing that it is this kind of thinking that we must avoid when considering identity in thermodynamics. The considerations at the beginning of the Section helped us see this; only by dispensing of this thinking and adopting the criterion of identity can we consider boxes of hydrogen and helium, *qua* ideal gases, to be different. The question of identity between two systems cannot even arise unless they standing in some subsystem-composite relation.

This is not to say that the traditional conception is wrong. Rather, it is the answer to a different question. When we ask whether two things are identical, there are two things we might mean: (1) Are the two physical objects identical? and (2) Are the two representations of the two physical objects identical? The traditional conception in terms of properties would naturally be applied when we are asking the question of physical objects, but in fact we are not concerned with actual physical systems at all. The task we have set ourselves is finding the criterion of identity for representations of our boxes of hydrogen and oxygen *qua* thermodynamic systems. One may well wonder whether we should apply the same criterion to the representations of the systems as to the systems themselves but, as we saw earlier, this leads to some uncomfortable conclusions; if we represent the boxes of hydrogen and oxygen as van der Waals gases, then the criterion of identity as defined above does indeed amount to the same thing as the traditional property view, since the values of the constants a, b and c in the fundamental equation for the van der Waals gas reflect the physical and chemical properties of the gases. The differing properties of hydrogen and oxygen manifest as different values of the constants which results in different fundamental relations. But if we represent the gases as ideal, and if we continue to insist on the traditional conception based on properties, then we arrive at the conclusion that all ideal gases are identical by this criterion. There would then be no such thing as an ideal gas mixture, since all we would get on combining ideal gases is more ideal gas, regardless of the kind of gas the subsystems are meant

to represent. This seems like an unnecessarily radical conclusion, since we want to continue to talk of ideal gas mixtures as composite systems formed from subsystems which themselves are ideal gases but still different from each other in some sense. The criterion I defined provides such a sense, and the difference between van Kampen's equations amounts to the distinction between difference and identity in this sense.

6   Conclusion

In this paper, I have given new definitions of 'identity' and 'mixture' purely in the concepts and formalism of thermodynamics, thereby adhering to the good practice stated at the beginning of this paper. With these definitions, I provided a new perspective on and solution to Gibbs' paradox which arose because we lacked thermodynamic definitions of those terms.

But this paper was about so much more than just Gibbs' paradox. Just like other paradoxes in the history of philosophy, it was worth thinking about, not just for the pleasure of solving a (admittedly niche) problem in the foundations of physics, but because it points to deep, foundational issues which merit investigation. The foundational items that have been highlighted and clarified on our journey to this solution are numerous: the definitions of and distinction between extensive and intensive variables is crisp and precise; a definition of a thermodynamic system was proposed in geometric terms with the fundamental relation taking centre stage; the link between the homogeneity of thermodynamic systems and the scaling symmetry of the fundamental relation played a key role in the definition of identity; the notions of subsystem and composite system received a precise and general analysis, and the role of the entropy extremum postulate in the definition of equilibrium and equilibration was emphasised. Gibbs' paradox has turned out to be surprisingly fruitful.

The philosophical implications of the proposed criterion of identity for thermodynamic systems are particularly interesting. A plausible criterion of identity in terms of isomorphism of the systems' formal structures turned out to lead to unwelcome conclusions. The strategy I developed was to define the 'difference' between the systems as the failure of an identity relation that holds between subsystems of a composite rather than between systems themselves; if two thermodynamic systems are not subsystems of some composite, then the question of their identity cannot even arise.

The traditional conception of identity which appeals to the intrinsic physical and chemical properties of the atomic constituents of the thermodynamic systems is purely heuristic since the properties of atoms are manifestly not in the realm of macroscopic thermodynamics. But there is a stronger reason we should not appeal to such concepts: thermodynamics is an extremely powerful and general theory for when we do not have access to the underlying microphysics of physical systems. As it happens, in the case of gases, we do know about the physics of the micro-constituents and this may be why we are naturally attracted to expressing identity in terms of the properties of those constituents. But, in general, we should not assume that we have access to the microphysics and so we should not let definitions of concepts such as identity to be tied to it. This is why we

strived to explicate identity of thermodynamic systems in purely thermodynamic terms.

Thermodynamics, expressed in the geometric formulation presented here, is an extremely powerful and general theory for modelling and predicting the behaviour of physical systems when the underlying microphysics is unknown, ignored or inaccessible. The full philosophical implications of this formulation have yet to be fully explored but, if this analysis is anything to go by, is sure to be fruitful.

A   Extensive and Intensive Variables

Extensive variables are often described as those thermodynamic variables which scale with the 'size' of the system. While this characterisation does capture an aspect of Equation (3.4), it does not capture its full significance, and is not stated with full mathematical rigour: what does it mean to 'scale'? What is meant by 'size'? Is it the volume? Mole number? Both?

A better way to interpret this property is as expressing that a thermodynamic system is *homogeneous*[23]. Roughly, this means that the system has a symmetry, that it 'looks the same' on all scales. But this is too rough to be able to tell what it is we should scale and what remains invariant under such a symmetry. Here is how to make it more precise.

Use the configuration variables $\{X_0, X_1, ..., X_k\}$ to define a new set obtained by multiplying each by some positive real number λ:

$$\{\lambda X_0, \lambda X_1, ..., \lambda X_k\}. \tag{A.1}$$

If we interpret the variables $\{X_0, X_1, ..., X_k\}$ to be necessary and sufficient for characterising the 'quantity' of a substance, then there is a sense in which the state of the system defined by the variables $\{\lambda X_0, \lambda X_1, ..., \lambda X_k\}$ is 'like' the system defined by variables $\{X_0, X_1, ..., X_k\}$ and yet also 'different.' The variables correspond to a different quantity of the same substance, related to the previous quantity by the scaling parameter λ. The precise sense in which this new system is 'like' the old one is if the fundamental relation is invariant under the transformation $X_i \rightarrow \lambda X_i$. Applying this transformation, Equation (3.1) becomes

$$\lambda X_0 = f(\lambda X_1, ..., \lambda X_k). \tag{A.2}$$

If f is a first-order homogeneous function of the variables $X_1, ..., X_k$, i.e. if it satisfies the homogeneity assumption of Equation (3.2), then we have

$$\lambda X_0 = f(\lambda X_1, ..., \lambda X_k) = \lambda f(X_1, ..., X_k) \implies X_0 = f(X_1, ..., X_k). \tag{A.3}$$

That is, if f is a first-order homogeneous function of the variables $X_1, ..., X_k$, the transformation $X_i \rightarrow \lambda X_i$ is a symmetry of the fundamental relation. It is in this mathematical sense that thermodynamic systems are homogeneous.

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[23]This link between the mathematical sense of homogeneity and the physical sense has been made by Tisza (1966).

This leads us to a precise way to understand what it means for a variable to be extensive. Extensive variables are the configuration variables in terms of which the fundamental relation is defined and whose scaling preserves the functional form of the fundamental relation. This way, we avoid ambiguity in the word 'size' and we also avoid 'brute fact' claims often seen in the discussion of extensivity that volume and mole number are 'obviously' extensive. Extensivity, as characterised here, is a formal notion, independent of what physical interpretation the configuration variables have.

B Deriving Equations (VK1), (VK2) and (VK3)

B.1 Equation (VK1)

Throughout van Kampen's derivation of Equation (2.3) (which provides the base block for deriving Equations (VK1)–(VK3)), he treats N as a constant. We can see this explicitly in his statement of the First Law, Equation (2.1), in which the only variables are U, S, V, T and p. It is also implicit in his derivation since, although he does not write it down explicitly, it is necessary to assume that $dU = (3/2)NRdT$ follows from $U = (3/2)NRT$ in order to derive Equation (2.3). It is again implicit in the derivation of Equation (2.3) where C absorbs terms containing N (this happens in the step from Equation (3.7) to Equation (2.3)).

But he also seems to want to treat N as a variable, for, towards the beginning of his article, he claims that the Gibbs paradox "is a consequence of the way in which the entropy depends on the number of molecules, and I therefore start out in section 2 by sketching how this dependence is established in thermodynamics." (van Kampen, 1984, p. 304). He is therefore clearly engaged in the business of finding entropy as a function of N which is clearly treating N as a variable.

Therefore we can see that he begins his analysis apparently stating forcefully that it is a variable and, indeed, that the whole Gibbs paradox rests on this functional dependence, and yet he carries out his derivation of Equation (2.3) assuming it is a constant, before using his conventions to turn it back into a variable again. Flipping between these interpretations of N is clearly being inconsistent; it cannot be both a constant and a variable. So, which is it? From the point of view of giving a rigorous mathematical derivation of the thermodynamic entropy for the ideal gas, this is a problem.

In this Section, I derive (VK1) by assuming that N is a variable. We begin by assuming that the fundamental relation of the ideal gas takes the form

$$S = f(U, V, N) \tag{B.1}$$

Taking the derivative, we see that this takes on the familiar form of the first law of thermodynamics:

$$T dS = dU + p dV - \mu dN \tag{B.2}$$

This fundamental relation is assumed to be first-order homogeneous and so it follows from Euler's theorem on homogeneous functions that

$$S = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N \tag{B.3}$$

31

We know the following two equations of state from experiment:

$$1/T = 3NR/2U; \qquad\qquad p/T = NRV. \qquad\qquad \text{(B.4)}$$

We may derive an expression for μ/T from these two because the intensive parameters of a first-order homogeneous relation are not independent. We may show this as follows.

Taking the derivative of Equation (B.3), we have:

$$dS = Ud\left(\frac{1}{T}\right) + \frac{1}{T}dU + Vd\left(\frac{p}{T}\right) + \frac{p}{T}dV - Nd\left(\frac{\mu}{T}\right) - \frac{\mu}{T}dN \qquad \text{(B.5)}$$

Subtracting from this Equation (B.2) we get what is known as the *Gibbs-Duhem relation*:

$$0 = Ud\left(\frac{1}{T}\right) + Vd\left(\frac{p}{T}\right) - Nd\left(\frac{\mu}{T}\right) \qquad \text{(B.6)}$$

This equation shows that the intensive parameters are not independent, since it may be integrated to find the third equation of state from the other two. Taking the derivative of Equations (B.4) and substituting into Equation (B.5) we get

$$Nd\left(\frac{\mu}{T}\right) = U\left(\frac{3R}{2U}dN - \frac{3NR}{2U^2}dU\right) + V\left(\frac{R}{V}dN - \frac{NR}{V^2}dV\right) \qquad \text{(B.7)}$$

from which it follows that

$$d\left(\frac{\mu}{T}\right) = \frac{5R}{2N}dN - \frac{3R}{2U}dU - \frac{R}{V}dU. \qquad \text{(B.8)}$$

We may now integrate this to get

$$\frac{\mu}{T} = \frac{5}{2}R\ln N - \frac{3}{2}R\ln U - R\ln V + K = R\ln\left[\frac{N^{5/2}}{U^{3/2}V}\right] + K \qquad \text{(B.9)}$$

where K is the constant of integration.

Substituting the equations of state (B.4) and (B.9) into (B.3) we get the fundamental relation of the ideal gas as a function of U, V, N. It is easy to check that simplifying this equation and eliminating V and U in favour of p and T using the equations of state, we arrive at Equation (VK1).

B.2 Equation (VK2)

In this Appendix, I give detailed physical justifications for the definitions of the variables for (M_*, f_*) which I claim represents the ideal gas mixture.

- S is defined by the additivity postulate to be:

$$S := \sum_i^k S^{(i)} = \sum_{i=1}^k f^{(i)}(U^{(i)}, V^{(i)}, N^{(i)}) \qquad \text{(B.10)}$$

  where each of the $f^{(i)}$ is the fundamental relation of a single ideal gas as given in Equation (3.11).

- U is defined to be:

$$U := \sum_{i=1}^{k} U^{(i)}. \tag{B.11}$$

This definition expresses the physical assumption that the energy of the composite system is the sum of the energies of the individual subsystems. This is a typical physical assumption for the ideal gas mixture which is often motivated by a 'billiard ball' model of an ideal gas in which there are no interactions between the individual molecules. We also impose the condition

$$\partial f^{(1)}/\partial U^{(1)} = ... = \partial f^{(k)}/\partial U^{(k)} \tag{B.12}$$

which expresses the assumption for the simple ideal gas mixture that the temperatures of all the subsystems are the same. This long series of equalities is $U^{(1)}/N^{(1)} = ... = U^{(k)}/N^{(k)}$ where it can be shown that $U^{(i)}/N^{(i)} = U/\sum_i N^{(i)}$ for all i. This assumption does not form part of the definition of the variable U; it is an additional assumption made to incorporate a physical fact about the type of system we are dealing with.

- Variable V is defined to be:

$$V := V^{(1)} = ... = V^{(k)} \tag{B.13}$$

This definition states that the volumes of the subsystems are all equal and that the volume of the mixture V is equal to any one of those. This incorporates part of the definition of mixture which says that the components all occupy the very same volume and, therefore, that the volumes of the components are identical. We also impose the condition

$$\partial f/\partial V := \sum_{i=1}^{k} \partial f^{(i)}/\partial V^{(i)} \tag{B.14}$$

which, together with Equation (B.12), expresses the assumption that the pressure of the mixture is equal to the sum of the pressures of the individual components. This is more familiarly known as Dalton's Law, and is identical to the assumption used by Gibbs in his derivation expressed in Equation (C.3).

- The variables N_i are defined to be:

$$N_i := N^{(i)} \text{ for } i = 1, ..., k \tag{B.15}$$

This definition states that the mole number of component i in the mixture is equal to the mole number of subsystem (i). It also captures precisely the intuition that components of a mixture are subsystems of the mixture.

With these definitions and assumptions the fundamental relation of the ideal gas mixture becomes

$$S = f_*(U, V, N_1, ..., N_k) = \frac{1}{T}U + \frac{p}{T}V - \sum_i \frac{\mu_i}{T}N_i \qquad \text{(B.16)}$$

where

$$\frac{1}{T} = \sum_i \frac{3}{2}R\frac{N_i}{U} \qquad \text{(B.17)}$$

$$\frac{p}{T} = \sum_i R\frac{N_i}{V} \qquad \text{(B.18)}$$

$$\frac{\mu_i}{T} = R\ln\left[\frac{N_i\left(\sum_j N_j\right)^{3/2}}{VU^{3/2}}\right] + K_i \text{ for } i = 1, ..., k \qquad \text{(B.19)}$$

From this explicit fundamental equation, it is easy to see that the pair (M_*, f_*) is a thermodynamic system.

By eliminating U in favour of T, defining the 'partial pressures' $p_i := N_i/V = pN_i/(\sum_i N_i)$, and absorbing all constants into the K_i, we recover van Kampen's Equation (VK2) for k components in the following form:

$$S = \frac{5}{2}\left(\sum_{i=1}^{k} N_i\right)R\ln T - \sum_{i=1}^{k}(N_i R\ln p_i) + \left(\sum_{i=1}^{k} N_i K_i\right) \qquad \text{(VK2')}$$

where the summation indices run over the number of components in the mixture.

B.3 Equation (VK3)

The variables for $(M^{\text{VK3}}, f^{\text{VK3}})$ are defined as follows.

- S is defined, as before, by the additivity postulate:

$$S := \sum_i S^{(i)} = \sum_{i=1}^{k} f^{(i)}(U^{(i)}, V^{(i)}, N^{(i)}). \qquad \text{(B.10)}$$

- As before, U is defined to be:

$$U := \sum_{i=1}^{k} U^{(i)}. \qquad \text{(B.11)}$$

  with

$$\partial f^{(1)}/\partial U^{(1)} = ... = \partial f^{(k)}/\partial U^{(k)} \qquad \text{(B.12)}$$

  which corresponds to equality of temperatures. Again, this long series of equalities is $U^{(1)}/N^{(1)} = ... = U^{(k)}/N^{(k)}$ where it can be shown that $U^{(i)}/N^{(i)} = U/\sum_i N^{(i)}$ for all i. It follows that $U^{(i)} = UN^{(i)}/\sum_i N^{(i)}$.

- V is defined to be:

$$V := \sum_i^k V^{(i)} \tag{B.20}$$

This definition states that the volume of the whole is the sum of the volumes of the subsystems and is thus quite different from the definition expressed in (B.13). We further impose the condition

$$\partial f^{(1)}/\partial V^{(1)} = ... = \partial f^{(k)}/\partial V^{(k)} \tag{B.21}$$

which, together with (B.12), is the assumption of mechanical equilibrium, i.e. that the pressures of the subsystems are equal. The long series of equalities is $N^{(1)}/V^{(1)} = ... = N^{(k)}/V^{(k)}$ where it can be shown that $V^{(i)} = VN^{(i)}/\sum_i N^{(i)}$.

- N is defined to be:

$$N := \sum_{i=1}^k N^{(i)}. \tag{B.22}$$

This assumption states that the mole number of the composite system is the sum of the mole numbers of the subsystems. With this definition, we are no longer considering simple mixtures, which always have more than one configuration variable interpreted as mole number. Here, the composite system has one configuration variable interpreted as mole number and so it is not a mixture.

It follows from the Gibbs-Duhem relation that the intensive variables temperature, pressure and chemical potential are not independent. Therefore, from the previous requirements of equality of temperatures and pressures, it follows that the chemical potentials will be equal. Hence, we have that

$$\partial f^{(1)}/\partial N^{(1)} = ... = \partial f^{(k)}/\partial N^{(k)} \tag{B.23}$$

which, together with (B.12), is the assumption of chemical equilibrium, meaning that there is no transfer of matter from one subsystem to another.

Applying these definitions, we arrive at the fundamental relation

$$S = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N \tag{B.24}$$

with the equations of state

$$\frac{1}{T} = \frac{3}{2}R\frac{N}{U}; \tag{B.25}$$

$$\frac{p}{T} = R\frac{N}{V}; \tag{B.26}$$

$$\frac{\mu}{T} = R\ln\left[\frac{N^{5/2}}{VU^{3/2}}\right] + K. \tag{B.27}$$

If we eliminate U in favour of T and V in favour of p, and define $p^{(i)} := N^{(i)} RT/V$ while also writing $N = \sum_i N^{(i)}$ and $p = \sum_i p^{(i)}$ we recover van Kampen's (VK3) in the following form:

$$S = \frac{5}{2} R \left(\sum_i^k N^{(i)} \right) \ln T - \left(\sum_i^k N^{(i)} \right) R \ln \left[\sum_i^k p^{(i)} \right] + \left(\sum_i^k N^{(i)} \right) K. \qquad \text{(VK3}')$$

C Gibbs' Derivation of the Fundamental Relation of an Ideal Gas Mixture

In this Section, I reconstruct Gibbs' derivation of the fundamental relation of an ideal gas mixture. While he does not explicitly adopt the definition of thermodynamic system I propose, it is clear that he takes (M_*, f_*) to be the definition of an ideal gas mixture. That is, he takes the extensive variables which describe the thermodynamic state of a mixture to be $S, U, V, N_1, ..., N_k$ for a mixture of k components. This may be deduced from the following comment:

> "[I]f we consider the matter in the mass as variable, and write $N_1, ..., N_k$ for the quantities of the various substances $1, ..., k$ of which the mass is composed, U will evidently be a function of S, V, $N_1, ..., N_k$ and we shall have for the complete value of the differential of U
>
> $$dU = TdS - pdV + \mu_1 dN_1 + ... + \mu_k dN_k$$
>
> $\mu_1, ..., \mu_k$ denoting the differential coefficients of U taken with respect to $N_1, ..., N_k$." (Gibbs, 1878, p. 116)

Here, I think it is reasonable to reconstruct Gibbs as stating that the variables for a thermodynamic system of a homogeneous mass consisting of various substances are $S, U, V, N_1, ..., N_k$. It differs from the variables for a pure substance only in the number of variables denoting the quantities of the substances.

Having settled on his choice of variables, he begins his discussion of the ideal gas mixture with the following principle:

> "The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its [chemical] potential." (Gibbs, 1878, p. 215)

He goes on to express this principle in the formalism of thermodynamics as follows. We take the expression for μ/T in Equation (B.9) and write it as a function of pressure and temperature by judicious substitution of the equations of state for the ideal gas. This yields:

$$\frac{\mu}{T} = R \ln p - \frac{5}{2} R \ln T + K \tag{C.1}$$

where K is a constant. We may rearrange this for p to give

$$p = C e^{\mu/T} T^{5/2} \tag{C.2}$$

where C is a constant absorbing all the constant terms that appear in the course of the substitutions. This equation allows us to express the principle Gibbs described. The pressure of an ideal mixture of n components

$$p = \sum_i^n C_i e^{\mu_i/T} T^{5/2}. \tag{C.3}$$

That is, the pressure of the mixture is the sum of the individual pressures each of the gases would have if they were at temperature T and chemical potential μ_i. Gibbs writes:

> "It will be legitimate to assume this equation provisionally as the fundamental equation defining the ideal gas mixture, and afterwards to justify the suitableness of such a definition by the properties which may be deduced from it." (Gibbs, 1878, p. 216)

It is interesting to note Gibbs' claim that Equation (C.3) is a fundamental relation. We have to do a bit more work to understand why, since it does not take the form of the fundamental relation given in Equation (3.1), i.e. it is not expressing a relation between the extensive variables. In fact, all the variables appearing in Equation (C.3) are intensive. Therefore, before we examine Gibbs' conclusions from Equation (C.3), we need to understand why it is a fundamental relation. a';aAA

Let (M, f) be a thermodynamic system with variables $X_0, ..., X_k$ and first-order homogeneous fundamental relation between the extensive variables

$$X_0 = f(X_1, ..., X_k). \tag{C.4}$$

Let us assume that we have an explicit form for this relation. Then we can derive explicit expressions for the intensive parameters, which we denote

$$F_i := \partial f / \partial X_i \text{ for } i = 1, .., k \tag{C.5}$$

as functions of $X_1, ..., X_k$. Let us also consider the expression

$$g(F_1, ..., F_k) := X_0 - \sum_{i=1}^k F_i X_i \tag{C.6}$$

which is the full Legendre transform of the fundamental relation f. Eliminating X_0 from this expression using Equation (C.4) and then eliminating the X_i from that using Equation (C.5), we arrive at a relation between all the intensive parameters. In fact,

because Equation (C.4) is first-order homogeneous, by Euler's theorem it can be written as

$$X_0 = \sum_{i=1}^{k} X_i F_i. \tag{C.7}$$

Substituting Equation (C.7) into (C.6) it follows that

$$g(F_1, ..., F_k) = 0 \tag{C.8}$$

which is the desired explicit relation between the intensive parameters we have been seeking.

The converse is also true: we can find the explicit relation between the extensive parameters assuming we have an explicit relation between the intensive parameters. Therefore, let us assume we have such an explicit relation $g(F_1, ..., F_k) = 0$. X_0 is given by Equation (C.7), so to find X_0 as a function of $X_1, ..., X_k$, we must find each F_i as a function of $X_1, ..., X_k$. To do this, note that the derivative of Equation (C.6) is $dg = dX_0 - \sum_{i=1}^{k} (X_i dF_i + F_i dX_i)$, and note that it follows from Equation (C.4) that $dX_0 = \sum_{i=1}^{k} F_i dX_i$ which means that $dg = -\sum_i X_i dF_i$. From this we deduce

$$-X_i = \frac{\partial g}{\partial F_i} \text{ for } i = 1, ..., k \tag{C.9}$$

which we can then use to eliminate $F_1, ..., F_k$ in favour of $X_1, ..., X_k$ in Equation (C.7), yielding an explicit relation $X_0 = f(X_1, ..., X_k)$ between the extensive variables.

With this clarification, we can better understand and reconstruct Gibbs' reasoning in which he derives certain thermodynamic properties from Equation (C.3) and, even though he does not explicitly do it, I will show how to derive the extensive variable fundamental relation of the ideal gas mixture from Equation (C.3).

The differential of Equation (C.3) is

$$dp = \frac{\partial p}{\partial T} dT + \sum_{i}^{n} \frac{\partial p}{\partial \mu_i} d\mu_i \tag{C.10}$$

The Gibbs-Duhem relation derived from the fundamental relation in the energy representation for the thermodynamic system (M_*, f_*) is

$$0 = SdT - Vdp + \sum_{i}^{n} N_i d\mu_i \tag{C.11}$$

which rearranges to

$$dp = \frac{S}{V} dT + \sum_{i}^{n} \frac{N_i}{V} d\mu_i \tag{C.12}$$

Comparing (C.12) and (C.10) we derive that

$$S/V = \sum_{i}^{n} \left(C_i T^{3/2} e^{\mu_i/T} \left(\frac{5}{2} - \frac{\mu_i}{T} \right) \right) \qquad \text{(C.13)}$$

$$N_i/V = C_i T^{3/2} e^{\mu_i/T} \qquad \text{(C.14)}$$

Substituting (C.14) into (C.3) and (C.14) into (C.13) Gibbs obtains, respectively:

$$p = \sum_{i} \frac{N_i T}{V}; \qquad \text{(C.15)}$$

$$S = \sum_{i} \left(\frac{3}{2} N_i R \ln T - N_i R \ln \frac{N_i}{V} + N_i C_i \right). \qquad \text{(C.16)}$$

None of these preceding equations are fundamental relations between the extensive variables, however. In order to derive the expression for the fundamental relation, we must find an expression for U. This can be done by substituting the expressions for S/V, N_i/V and p into the fundamental relation $S = f(U, V, N_1, .., N_k)$ expressed, according to Euler's theorem, as

$$U = TS - pV + \sum_{i=1}^{k} \mu_i N_i \qquad \text{(C.17)}$$

which yields $U = (3/2)R \left(\sum_i N_i \right) T$. In sum, we have worked out the following equations of state:

$$\frac{1}{T} = \sum_{i} \frac{3}{2} R \frac{N_i}{U} \qquad \frac{p}{T} = \sum_{i} R \frac{N_i}{V} \qquad \frac{\mu_i}{T} = R \ln \left[\frac{N_i \left(\sum_j N_j \right)}{V U^{3/2}} \right] + K_i. \qquad \text{(C.18)}$$

The fundamental relation of the ideal gas mixture may then be derived by substituting these equations of state into:

$$S = f(U, V, N_i, ..., N_k) = \frac{1}{T} U + \frac{p}{T} V - \sum_{i} \frac{\mu_i}{T} N_i. \qquad \text{(C.19)}$$

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