A Mereological Interpretation of the Phase Rule

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Gibbs's phase rule treats mixtures by relating the number of independent variables governing their state to the numbers of phases and independent substances. For the case of a single substance, it provides a criterion of purity. But where more substances are involved, the notion of independent substance is less readily understood. Textbook writers sometimes use algebraic terminology in ways that are suggestive but cannot be taken as literally accurate. I suggest that a mereological interpretation applies to these cases, as it captures more concisely the insights underlying the use of algebraic terminology and illuminates the general notion of substance.

1. The Phase Rule and the Criterion of Purity. As the notion of substance developed after Lavoisier, it became clear that it had to be understood independently of the state of aggregation since it makes no sense to speak of the composition of, for example, water as comprising hydrogen and oxygen gas.[1] Gibbs introduced the general term "phase" for states of aggregation, which he systematically distinguished from substances in his phase rule. This is a general theorem of thermodynamics, applicable to mixtures in the sense of quantities of matter exhibiting one or more phases over which one or more substances are distributed. In the case of a single substance, it is used as a criterion of purity (that a quantity of matter comprises one substance) and provides some insights into the relation between microscopic descriptions of matter at the molecular level and macroscopic descriptions that phase and substance properties exemplify.

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1. At normal pressure, water might well be solid or liquid at temperatures when hydrogen and oxygen are gases. This point is elaborated in Needham (2002, 208–9).

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But where cases involve several independent substances, as the rule has it, the notion of substance becomes perplexing. Textbook writers sometimes seek to clarify what is at issue by resorting to algebraic terminology. This is suggestive but not entirely clear. A mereological interpretation is put forward here, which generalizes the interpretation of the single-substance case and provides a concise interpretation of the algebraic terminology that does shed light on the copresence of several substances.

In a nutshell, the phase rule says that the *variance*—that is, the number of independent variables governing the temperature, pressure, and composition of (concentration of each substance in) each phase—is given by

$$c - f + 2 \geq 0,$$

where c is the number of substances distributed over f phases at equilibrium. For example, a two-phase system comprising a single substance is, according to this law, univariant. Thus, the state of a system that comprises water in the form of liquid in contact with the vapor enclosed in a container fitted with a piston that allows change of volume is governed by just one independent variable. At a given temperature, the pressure is fixed. Any attempt to vary it, for example, by reducing the volume with the piston, will only result in material being transferred from the vapor to the liquid, maintaining the pressure—as long as two phases remain. Similarly, attempting to reduce the pressure by withdrawing the piston and increasing the volume will only result in material being transferred from the liquid to the vapor, again maintaining the pressure. Eventually, only a single phase will remain, and then the system will be bivariant, when pressure and temperature can vary independently, as allowed by the familiar gas law. This behavior is characteristic of a single substance, without recourse to the microconstitution of matter.

The derivation of the phase rule proceeds by reducing the $cf + 2$ variables (cf concentrations of each of the c substances in each of the f phases, together with temperature and pressure). First, $c(f - 1)$ equations from thermodynamics express the equalities of the chemical potentials of each substance across each of the f phases. Then an equation of the kind $\sum x_i = 1$ holds for each of the f phases, where x_i is the concentration of the ith substance in the phase concerned. The total number of independent variables is therefore $(cf + 2) - [c(f - 1) + f] = c + 2 - f$. This presupposes that no other constraints on the mixture further reduce the number of independent variables. But where chemical reactions are proceeding, there will be an equation involving chemical potentials that expresses an equilibrium between reactants and products for each independent reaction. Moreover, chemical reactions often take place under conditions that introduce additional restrictions in the form of equations that further reduce the number of independent variables (usually described as reducing

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the number of independent substances). Applications of the phase rule in the interpretation of the behavior of complex mixtures must take into account the possibility of such factors reducing the variance beyond what is given by the general $c - f + 2$ formula.

The characteristic phase-rule behavior of single substances just described has some bearing on the relation between micro- and macrostructure. The development of chemical formulas in the nineteenth century is sometimes taken to carry with it the so-called molecular conception of the microconstitution of substances as simply a collection of particles or molecules of a single kind that the chemical formula supposedly represents. Clearly, it cannot be the whole story about the microstructure because it makes no distinction between the various phases that a single substance can exhibit. Nevertheless, something along these lines does seem to hold for many substances, especially organic substances, with weak intermolecular forces insufficient to bind molecules into significant units. But many substances fail to comply with this picture, typically inorganic substances. Water, in particular, diverges markedly from this paradigm conception of substances as molecular. Much of the indefinitely extended, interlinked microstructure of ice is retained in the liquid phase, only to be relinquished in the gas phase with the input of a latent heat of vaporization considerably higher than the latent heat of fusion. Moreover, the boiling point is some 250 kelvin higher than that of methane, a molecular substance with comparable molecular weight. In the liquid phase, water molecules are predisposed to link up by the formulation of hydrogen bonds that are considerably stronger than the intermolecular forces at work between methane molecules, if not quite as strong as typical covalent bonds. At the same time, there is a tendency to dissociate, with the resulting hydrogen and hydroxyl ions becoming associated with the larger hydrogen-bonded conglomerates of water molecules.

This suffices, without pursuing the details of the microstructure of water and other substances further, to raise the question of why substances that do not consist essentially of a collection of similar particles nevertheless comprise single substances, given that other substances consisting essentially of a collection of molecules do. Clearly, whether a quantity of matter comprises a single substance or several is not a simple matter of whether it comprises distinguishable particles of a single or several kinds. The phase rule determines the issue, specifying a range of behavior (some aspects of which were illustrated above) typical of single-component quantities of matter.

2. The Calcium Carbonate Case. A classic case involving two substances is provided by the results of heating calcium carbonate. Joseph Black first recognized the reduction in weight when limestone is heated, and he de-

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scribed it as due to the loss of air, later understood to be carbon dioxide. Performed in a closed container, the carbon dioxide gas cannot disperse, and the decomposition of the limestone does not go to completion but reaches equilibrium, represented by

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

This equilibrium perplexed chemists toward the end of the nineteenth century. There are three substances—calcium carbonate, calcium oxide, and carbon dioxide—but one equilibrium and so, in accordance with the above reasoning in connection with the derivation of the phase rule, just two independent substances. Apparently, there are two phases, a white solid and a colorless gas, which would suggest a variance of two. But the experimentally determined variance is one (there is a definite gas pressure for a given temperature). The phase rule thus led chemists to believe that there must be two solid phases, even though the phases could not be discerned in the apparently homogeneous white solid. They concluded that the calcium oxide does not form an intimately mixed solid solution with the calcium carbonate but that there must be distinct calcium carbonate and calcium oxide phases. Subsequently, new methods of analysis of the crystal structure were able to show that the calcium oxide is confined to isolated "islands" within the surrounding calcium carbonate, much as oil forms droplets in water when a vinaigrette dressing is shaken.

Now, if there are only two substances, and the white solid comprises a calcium carbonate and a calcium oxide phase, it seems that we have used up our quota of substances, leaving the gas without a substance composing it! But the gas is definitely matter, and we might look for a way of construing the carbon dioxide as the calcium carbonate less, or "minus," the calcium oxide. Something like this is suggested by Castellan (1964, 247) when he says, "If $CaCO_3$ and CO_2 were chosen as components, the composition of CaO would be described as one mole of $CaCO_3$ minus one mole of CO_2." Here Castellan has "chosen" $CaCO_3$ and CO_2 as component substances and speaks of the CaO as the difference between them. The phase rule says only that there are two independent substances, and Castellan follows the usual textbook procedure of showing how the two independent substances can be chosen in alternative ways from all the substances (he says "species") present. In the present case, there are three alternatives: calcium carbonate and calcium oxide, calcium carbonate and carbon dioxide, or calcium oxide and carbon dioxide. The suggestion is that the third remaining substance can in each case be recovered by an algebraic operation on the two chosen independent substances. Castellan's statement is not entirely accurate because the phase rule applies to any amounts of calcium carbonate subjected to the conditions of this equilibrium and not just one mole. Speaking of a measure of one mole might,

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misleadingly, be taken to suggest that the algebraic operations are the familiar ones on numbers, whereas what is required is mereological operations on quantities of matter.

It is not uncommon for writers on the phase rule to make allusions to algebraic operations, although they are rarely explained. Ricci (1951, 10) just writes, "With CaO and CO_2 [as independent components], the phase $CaCO_3$ consists of CaO + CO_2, with $CaCO_3$ and CaO [as independent components], the phase $CO_2 = CaCO_3 - CaO$," leaving the reader to infer the significance of the equations. Again, it seems to me that this statement is not accurate, and in giving a more definite and explicit mereological interpretation of the algebraic operations, phase and substance properties must be distinguished.

3. Ensuring the Applicability of Mereological Operations. The two solid phases are, it seems, mereologically separate. This, at any rate, is what the confinement of calcium oxide to isolated "islands" would seem to suggest. And by the same line of thought, each of the solid phases is separate from the gas (CO_2) phase. But in that case, Castellan's application of his "minus" operation, when considering $CaCO_3$ minus one mole of CO_2, will not yield the CaO as intended, at least if the operation is mereological difference. The mereological difference of X less Y is defined for quantities X and Y such that X is not part of Y, for which it is the sum of all that is part of X and separate from Y. If X and Y are separate, then the difference is just X. Accordingly, if the CO_2 is separate from the $CaCO_3$, the mereological difference of $CaCO_3$ less CO_2 is just $CaCO_3$. Similarly, the mereological difference of $CaCO_3$ less CaO is again $CaCO_3$ and not CO_2. So if the operations are applied to the phases, as Ricci clearly suggests, it seems there is no matter constituting the gas phase! Similarly, the $CaCO_3$ phase will not consist of the CaO phase + the CO_2 phase if "+" is mereological summation.

For a fresh approach with a view to finding a viable interpretation of the mereological operations, I take it that if the calcium carbonate equilibrium involves two independent substances and these may be chosen in different ways, then the alternative choices must divide the total quantity of matter into substances in essentially the same way. All three substances stand in certain mereological relations to one another, and any two can be related to a third in terms of their relationship to one another. On the first choice of independent substances, calcium carbonate and calcium oxide, the suggestion was that carbon dioxide can be taken as the calcium carbonate less the calcium oxide. If "less" is to be understood as mereological difference, and the carbon dioxide is not a null entity but some definite quantity of matter distinct from both the calcium carbonate and the calcium oxide, we are naturally led to the following interpretation.

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The entire quantity of matter in the equilibrium is all calcium carbonate, and the calcium oxide is a proper part of this. The mereological difference between the calcium carbonate and the calcium oxide is then defined and is another proper part of the calcium carbonate separate from the calcium oxide, which we may call carbon dioxide.

An alternative choice of independent substances would be calcium carbonate and carbon dioxide, taking the calcium oxide to be the calcium carbonate less the carbon dioxide and recovering the same overall mereological structure as before. The calcium oxide, like the carbon dioxide, is a proper part of the calcium carbonate, which is the entire quantity of matter in the system. A third choice of independent substances makes a mereological partition of the entire quantity of matter, the calcium oxide and the carbon dioxide being separate, and their sum is the entire quantity. In this case, the calcium carbonate is the mereological sum of the calcium oxide and the carbon dioxide, which gives us a mereological interpretation of the "+" in the above quotation from Ricci. But for the reasons just explained, it is not, as Ricci says, the calcium carbonate phase that is this sum, but the calcium carbonate substance.

4. The Distinction between Phase and Substance. Arriving at a reasonable interpretation of the algebraic operations—one that makes sense of the possibility of alternative choices of independent substances—has led to the drawing of a sharp distinction between "calcium carbonate substance" and "calcium carbonate phase." One is a substance predicate, which alongside "calcium oxide substance" and "carbon dioxide substance" is related to the number c in the phase rule, and the other is a phase predicate, which alongside "calcium oxide phase" and "carbon dioxide phase" is counted by the number f in the phase rule. The two predicates "calcium carbonate substance" and "calcium carbonate phase" are not coextensive. The former applies to the entire quantity of matter, and the latter apparently does not, since what it applies to is apparently separate from both the calcium oxide phase and the carbon dioxide phase.

The situation can be compared in certain respects with a single-substance system where, for example, a container encloses a quantity of water exhibiting a liquid and a gas phase. The entire quantity of matter is the substance water, but within this quantity, distinctions of phase are drawn. The calcium carbonate case resembles this insofar as the entire quantity of matter exhibits several phases, even though it differs insofar as the entire quantity, which is calcium carbonate substance, can be partitioned into two other substances. In the water case, the pressure is fixed at constant temperature, when the volumes of liquid and gas remain constant. But this does not imply that the matter comprising the liquid phase or the gas phase remains the same. Although, from the macroscopic view-

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point, the equilibrium between the two phases implies constancy of the macroscopic variables, there is continual movement at the microlevel. According to the general principle connecting macro- and microphenomena introduced by Van 't Hoff at the end of the nineteenth century, corresponding to a static equilibrium at the macrolevel there is a dynamic equilibrium at the microlevel in which a balance obtains between the rates of counteracting processes. As elaborated since Van 't Hoff's time, there is a distribution of energy over all the particles, and the more energetic ones near the surface of the liquid enter the gas phase, while some of the gas particles close to the interface enter the liquid phase. A dynamic equilibrium between the phases obtains when the rate of matter entering the gas phase from the liquid equals the rate of matter entering the liquid phase from the gas. A quantity of matter that is all liquid throughout an interval of time will in general be smaller than (i.e., be a proper part of) a quantity that is all liquid throughout a proper subinterval of that time. In the extreme case, there is no quantity of matter that is all liquid throughout very long intervals of time.[2]

Time enters the picture from the macroscopic point of view insofar as the phase rule concerns matter at equilibrium, which takes time to become established after a change and which does not apply to intervals short enough that statistical fluctuations are significant. Over an interval of time of macroscopic magnitude for which features governed by the phase rule can be considered to apply, the dynamic equilibrium between the liquid and gas phases entails that their fixed volumes are not volumes of particular quantities of matter. It is a property of the entire quantity of matter that it exhibits liquid and gas phases of specific volumes, but the volumes of each phase are not borne by particular quantities of matter. The expression "the liquid" (or, in general, "the phases") is therefore something of a misnomer. There is no such object as the liquid in the two-phase system described in the preceding paragraph. There are objects like the quantity of matter that is all liquid throughout some specific interval of time (provided the interval is not too long). But it is unclear whether this kind of object can be ascribed a volume at all; it certainly cannot be ascribed the mass or volume of the liquid exhibited by the entire quantity of water in the container for the interval of time at issue.

The three phases in the calcium carbonate equilibrium are to be considered in the same fashion. That is, there are no such things. Rather, there is the entire quantity of matter, which, as in the water case, is all one substance (here, calcium carbonate substance), and this quantity exhibits three phases. The predicate "calcium carbonate phase" is dyadic,

2. For further discussion of the understanding of these relations, as expressed by mass predicates, see Needham (2007).

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applying to a quantity of matter for an interval of time, and if it is distributive, it applies to what is all calcium carbonate phase throughout that interval. (Since this quantity is smaller, the longer the interval of time, this means that for sufficiently long times, there may be no such quantity satisfying the predicate, even though the quantity as a whole exhibits the three phases for such times. This may be taken to argue for a nondistributive interpretation of the predicate.) Matter falling under the three phase predicates is in dynamic equilibrium, as matter is interchanged between the calcium carbonate phase, the calcium oxide phase, and the gas phase while decomposition and combination proceed. The substance predicates, by contrast, are permanently applicable (while the equilibrium lasts). What is all calcium carbonate substance (has the calcium carbonate substance property) is the whole quantity of matter in the system for the duration of the equilibrium, and what is all calcium oxide substance is a proper part of this latter quantity for the same duration. Parts of the calcium oxide substance are sometimes calcium carbonate phase and sometimes calcium oxide phase; similarly, some of what is all carbon dioxide substance throughout the duration of the equilibrium is sometimes calcium carbonate phase and sometimes gas phase.

Again there is an analogy to be drawn with the water case. From the microscopic perspective, the fact that there is a fixed quantity of matter that bears the water substance property throughout the duration of the equilibrium does not imply that there are no processes of change going on within this quantity. There are many reactions under way involving the particles ("microscopic species") in the water. One involves a dissociation of water molecules into hydrogen and hydroxyl ions. Although the hydrogen ion and hydroxyl ion concentrations are extremely low, there is a dynamic equilibrium in which the rate of dissociation of water molecules into hydrogen and hydroxyl ions equals the rate of association of hydrogen and hydroxyl ions into water molecules. Because of this, it would be the wrong mereological interpretation to say that only a very small part of any given quantity of water comprises hydrogen ions. Like phase predicates, substance predicates are binary, applying to a quantity of matter at an interval of time. The rates of the reactions at the microlevel are so fast that during what on the macroscale is a relatively short period of, say, a microsecond (10^{-6} seconds), a considerable proportion of a given quantity of water will have gone through the dissociation process. What is a single water molecule for a short fraction of this time may have parts associated with and subsequently dissociated from many other parts of the given quantity of water during the course of this time. The given quantity is a sum of such sometime bits of water molecules, and this sum cannot be mereologically partitioned into a collection of water molecules for a macroscopically significant length of time. Since the dissociations

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of distinct molecules do not occur in step, there will not, in general, be a mereological partition of the quantity into molecules even for intervals of microscopic dimensions.

Much the same can be said of the calcium carbonate equilibrium. In the isolated state at room temperature and pressure, calcium carbonate is an ionic substance comprising calcium and carbonate ions. But the calcium carbonate substance in the equilibrium case is not simply a collection of calcium and carbonate ions. These are involved in the dynamic equilibrium in which calcium oxide and carbon dioxide is generated at a rate equal to the rate of association of calcium oxide and carbon dioxide to yield calcium carbonate (calcium and carbonate ions). The quantity of matter that is calcium carbonate substance throughout the duration of the equilibrium is a sum taken over this time of the various bits of matter that go to make up microscopic entities such as carbonate ions for much shorter times. These sometime bits of entities of various microscopic species continually associate, dissociate, and reassociate, though not necessarily with their previous partners. So the calcium carbonate substance is a quantity that cannot be partitioned into particles of the various microscopic species involved in the dynamic equilibria.

Modified versions of the phase rule have been put forward, sometimes adopted and adapted by later authors, with a view to avoiding obscurities in identifying the number of independent components. Bowden (1938, 331) bemoans the fact that in the form given above, the term c "has to bear the brunt of the matter and assume a responsibility not shouldered by the equation itself," which it would not if, as he later says, it denoted "the *total* number of chemical constituents (that is, actual chemical substances) present in the system" (Bowden 1960, 288). He therefore suggests writing the phase rule in the form

$$\text{Variance} = c - R - r - f + 2 \geq 0,$$

where R is the number of reversible chemical reactions and r is a restriction term equal to the number of pairs of phases having the same concentrations of substances. But as the two cases considered here illustrate, it is not true that this equation can be applied "without recourse to any process of counting or choosing components, since every chemical individual is taken into consideration" (Bowden 1960, 288). There is no saying how many reactions are involved in the formation of hydrogen-bonded clusters in water, but for each new cluster species, there is a distinct reaction, and, as we saw, phase-rule behavior is the criterion by which water is taken to comprise a single substance. I suggest that the obscure concept is what Bowden calls a chemical individual.

5. Conclusion. Gibbs's phase rule might be casually expressed as a re-

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lation between the substances and the phases in a mixture. The fundamental distinction between phase and substance as explicated here, however, raises some doubts about this manner of speaking. While there are things that are substances, it is doubtful whether there are things that are phases. Although the volume of liquid under a gas in an enclosed container may remain unchanged throughout a period of equilibrium, there is reason to question whether there is any single quantity of matter that is the liquid throughout this time. If we understand the phase property of being a liquid to be a mass relation holding between a quantity and an interval of time expressed by the two-place predicate "is a liquid," it will hold of all (every part) of whatever quantity it applies to for every subinterval of whatever interval it holds at. Then for a given quantity of matter and interval of time for which that quantity is liquid, the "is a liquid" predicate will hold of successive proper parts of this quantity for successively more inclusive intervals. Conversely, for shorter times, larger quantities of matter will be all liquid. In this sense, phase properties such as being liquid are not permanent features of matter in mixtures at equilibrium. The property of exhibiting such and such a volume of liquid throughout the duration of the equilibrium is a property of the entire quantity of matter involved in the equilibrium and not of some proper part of it.

Substance properties, by contrast, are permanent features of matter in a mixture for the duration of the equilibrium. That is, a quantity of matter is all such and such a substance kind throughout the time equilibrium is maintained. It then makes sense to talk about *the* matter of such and such a substance kind in the mixture—namely, the largest quantity of matter in the mixture that is all of that substance kind throughout the duration of the equilibrium. Definite quantities of this sort are the subject of the mereological operations at issue in the interpretation of the notion of independent substances as it appears in applications of the phase rule. Where several independent substances are present, there is no question of their being the only substances present. This is already suggested by the possibility of choosing the independent substances in different ways. Substances mentioned in one such choice can be recovered under an alternative choice in terms of mereological operations on the substances featuring in the alternative choice.

When just one substance is present, there is no alternative choice of independent substances and no scope for the application of mereological operations, save to say that what is this single substance is the sum of all the parts of the matter in the mixture. This need not be quite the trivial claim it seems to be when the sum, which is taken over a period of time, cannot be partitioned into parts each bearing the property of being some molecular species throughout the time in question. The substance of a single-substance quantity may be confined to a single phase (when it is

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bivariant), may be distributed over two phases (as in the case of the univariant liquid-gas mixtures discussed in sec. 1), or may be distributed over three phases at the triple point (with zero variance). This is the behavior of a substance in isolation.

The calcium carbonate equilibrium provides a case where several substances are present. On the mereological analysis offered here, the calcium carbonate substance is distributed over the three phases present in the univariant mixture. Unlike the isolated substance case, however, if a sample of the gas phase were extracted from the apparatus and the material subjected to an analysis, it would have the properties exhibited by carbon dioxide in isolation and not those of calcium carbonate in isolation. If the properties actually exhibited in isolation are taken to be definitive of elements and compounds, then the substances in the calcium carbonate equilibrium system should not be called calcium carbonate, calcium oxide, and carbon dioxide. The phase rule is noncommittal on this point, saying merely that there are two independent substances, and they might be called, say, calcium carbonate* and calcium oxide*. If elements and compounds are understood to be characterized by properties actually exhibited in isolation, however, then we cannot go on to speak of them occurring in mixtures involving several substances, which must be considered to be new substances. To this extent, we would be following the Aristotelian conception of mixture, according to which the original ingredients do not occur in the mixture. But clearly the further Aristotelian claim that only one substance occurs in what results from the mixing is not justified by phase-rule considerations. The understanding in question says nothing about the composition of quantities of matter under conditions when they do not fulfill criteria for comprising a single substance and requires that new names be introduced for substances not occurring in isolation.

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