

Substance and time

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**Abstract**

Both the changeability and stability of substances suggests predicates like ‘water’ are dyadic, applying to a quantity of matter at a time. Although this paper will be concerned with matter at equilibrium, the stability this implies obtains while there is constant changing at the microscopic level. Which substance predicates apply to what depends on the length of the time at issue. For longer times, macroscopic substance concepts like ‘water’ apply to mereological sums of what microscopic substance concepts like ‘water molecule’ apply to for much shorter times. This is advanced as an interpretation of Gibbs’ phase rule, which governs the application of permanent substance kinds throughout the lifetime of a mixture, and provides some insight into how the continuous, macroscopic conception of matter (“gunk”) is reconciled with the discrete microscopic conception.

**1. Introduction**

‘Water is  $H_2O$ ’ means, at the very least, that what is water is  $H_2O$ . The converse requires, as we will see, a small step in the direction of modern chemistry and away from what some philosophers understand by what it is to be water. Combining the two claims yields an equivalence: anything is water iff it is  $H_2O$ , to the effect that the two predicates ‘is water’ and ‘is  $H_2O$ ’ hold of exactly the same things. But what are these things?

Since ‘water’ is normally applied to macroscopic quantities of matter, the same applies to the predicate ‘is  $H_2O$ ’, which has a straightforward macroscopic interpretation conforming with the chemist’s use the term ‘ $H_2O$ ’, especially when not further qualified. Being an  $H_2O$  (water) molecule is another matter, applicable to microscopic quantities of matter. It might seem that there is a simple relation between the two kinds of predicate: anything is water iff it is a collection of water ( $H_2O$ ) molecules. But that is

misleading. One problem that has been pointed out by several authors (van Brakel 2000, Needham 2000, 2002a) is that in several states—perhaps not when approaching the ideal gas state at appropriately high temperature and low pressure, but certainly in the liquid and solid state—the particles comprising water are not all water molecules; in fact, hardly any are. But it is not simply a matter of modifying the microscopic interpretation along the lines of ‘is a collection of microparticles’ with an appropriate description of the microparticles.

Substance predicates such as ‘is water’ are two-place predicates, applying to a quantity of matter and a time. Both quantities and times have a mereological structure of parts (Needham 2000, 2002a, 2007), and here I pursue the issue of how the extent of the time governs which predicates apply to which quantities. This bears on the questions of whether a single water molecule is water, and what macroscopic quantities of water consist of. Although what ‘water’ applies to is a mereological sum of quantities to which ‘water molecule’ applies, it is argued that this does not imply that water is a collection of water molecules. On the contrary, the mereological interpretation offered here provides some insight into how the continuous, macroscopic conception of matter (“gunk”) is reconciled with the discrete microscopic conception. Inveterate reductionists are inclined to side step the complexities of the micro-macro relationship and settle for ontological reduction by claiming that what the macro-term applies to is “nothing but” what the micro-term applies to. This already faces the difficulty that the existence of sums is an independent mereological axiom over and above those governing the strictly relational properties of the mereological relations. The difficulty is deepened by an understanding that comes with the temporal perspective of how the sum stands to its parts.

The fact that there is just one substance at the macroscopic level despite water’s diversity at the microscopic level is a consequence of a theorem of thermodynamics known as the Gibbs phase rule. This is a very general theorem applicable to mixtures, and the mereological interpretation will be extended to mixtures as analysed by the phase rule, which, as we will see, might be considered to retain some aspects of ancient conceptions of mixture but certainly goes further and provides a more general view. Considerations of mixtures raise a question about the thesis with which I began, that water is  $H_2O$ , suggesting that whilst it holds for water in isolation, it is sometimes more difficult to apply to water when forming part of a mixture.

## 2. 'Is water'

The time-dependence of the water predicate is connected with the fact that water is, as it is sometimes put, created and destroyed in various chemical processes. Water is produced, for example, in what organic chemists call condensation reactions and in the combustion of hydrocarbons such as methane. It can even be directly generated from its constituent elements by burning, or mixing in the presence of a suitable catalyst. Water is destroyed when sodium reacts with it to produce sodium hydroxide and hydrogen at the expense of the corresponding (in accordance with the laws of chemical proportions) amount of water, and it is directly decomposed into its constitutive elements by electrolysis. A literal interpretation of creation and destruction of quantities of water might seem an attractive metaphysical hypothesis, or a natural interpretation of ordinary ways of speaking about chemical processes. But this doesn't exhaust the possibilities. An interpretation more in line with the fundamental principle, employed in chemists' understanding of chemical reactions since Lavoisier, of the non-destruction of matter<sup>1</sup> underlies the present discussion. According to this interpretation, quantities of matter may bear features of being such-and-such a compound substance at (i.e. during) one time and not at another. Because processes proceed more or less gradually, over a period of time, a quantity won't be all the initial substance after commencement of the transformation, and so won't be the initial substance. It will be partly the initial substance, in the sense that part of it will be the initial substance, and so the process continues until none of the quantity in question is the initial substance. Quantities are permanent. The mereological relations they sustain are the standard ones and not time-dependent in the manner of Thomson (1983). Time-dependence is incorporated in the substance predicate.

The so-called phase properties, the more common ones expressing the conditions of being solid, liquid or gas, are also time-dependent, and expressed by dyadic predicates applying to a quantity and a time. As an ice cube put into a gin and tonic melts, the literal creation and destruction interpretation might again be called upon,<sup>2</sup> but is not obligatory. The quantity initially all ice after some time is only partly ice, the

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<sup>1</sup> As Poincaré (1913, p. 65) puts it, "Lavoisier ... has demonstrated the indestructibility of matter by demonstrating the invariability of mass".

<sup>2</sup> The example of the ice cube is used by Laycock (2006, pp. 21-8, 41-2), who seems to think this interpretation must be called upon.

remainder being liquid. In this case, according to standard chemical theory, the quantity preserves the substance property; both ice and the liquid formed by melting are water. Some philosophers follow Putnam in restricting being the same substance water to being the same liquid, but here we follow elementary scientific practice, which teaches that *water* melts at 0°C. This, of course, is the sense of ‘water’ in which H<sub>2</sub>O is water, and the equivalence mentioned in the introduction holds. In the phase-dependent sense of ‘water’, implying that whatever it is true of is liquid, it doesn’t.

A compound substance predicate such as ‘water’ holds of a quantity but not of all its parts if we think of a quantity of water as being part hydrogen, part oxygen, i.e. of literally containing its component elements as such. But of a quantity for which it does hold, it holds for a time. The reason for the time dependence given above is that the possibility of transformation of substance occurs progressively in temporal sequence. For this purpose, times are usually treated as structureless “instants”. But there is another aspect of the temporal dependence of substance predicates which concerns the length of time they hold and the interplay with the mereological structure of parts of the intervals to which the predicates apply. It may seem natural to think of such predicates as holding of all subintervals of a time to which they apply, at any rate where the intervals are of macroscopic magnitude. The following discussion is largely concerned with whether this view can always be maintained.

### **3. ‘Is H<sub>2</sub>O’ and ‘is a water molecule’**

The expression ‘H<sub>2</sub>O’ is properly understood as a compositional formula, which merely expresses the proportion of the constituent elements in a compound. In this sense, its significance is entirely macroscopic. The gravimetric ratio of hydrogen to oxygen of 1 : 8 is converted into a different scale, reflecting combining power, which can be understood as saying that there is twice as much hydrogen as there is oxygen in water. The analogous compositional formula CO<sub>2</sub> for carbon dioxide expresses on the same scale that there is twice as much oxygen in carbon dioxide as there is in water, despite the gravimetric carbon-to-oxygen ratio of 3 : 8, but just as much oxygen in water as there is carbon in carbon dioxide.

Compositional formulas were elaborated with the discovery of isomers, which are distinct substances with the same composition. Propionaldehyde and acetone, for example, have the same composition, represented by the common compositional formula C<sub>3</sub>H<sub>6</sub>O. They have different physical properties such as melting and boiling

points, and they react differently with chemical reagents. Oxidation of propionaldehyde yields the organic acid propionic acid, whereas reaction of acetone with an oxidant produces acetic and formic acids. This phenomenon of isomerism motivated the development of structural formulas allowing the representation of a distinction between substances with a common compositional formula. Thus, propionaldehyde is written  $\text{CH}_3\text{CH}_2\text{CHO}$ , distinguishing the aldehyde group  $-\text{CHO}$ , and acetone is written  $\text{CH}_3\text{COCH}_3$ , indicating the ketone structure  $\text{RCOR}'$ , where R and R' are alkyl groups such as methyl, ethyl, propyl, and so on. Several kinds of isomerism can be distinguished, but such details needn't concern us here. In the case of water, there are no isomers, and the compositional formula  $\text{H}_2\text{O}$  has no development into a structural formula. But even where needed to distinguish isomers, structural formulas make no direct commitment to microstructure,<sup>3</sup> and can be understood to represent the chemical properties of a substance, i.e. the general lines along which it will react with other substances.

In order to speak of microstructure, it is necessary to go beyond this and offer more specific descriptions. We might be interested in the nature of the microparticles constituting a substance. Particles are entities distinguished by internal bonds holding the parts together significantly more strongly than these parts adhere to adjacent material for an interval of time during which the particle exists. The nineteenth-century understanding of the molecular constitution of substances is still proffered as typical of many organic substances such as hydrocarbons. According to this conception, there is a single species of particle, the individual molecule, which the structural formula of the substance can be held to represent, and the substance can be thought of as a collection of molecules. Although there may be intermolecular interactions, keeping the molecules apart and determining the overall macroscopic density, these modify the molecules rather than forming different kinds of particles from them. Further description would enter into the geometric features of the molecules, the bond strengths, and so forth. But as inorganic chemists in particular point out, what is typical for organic substances is not typical for substances in general. Not only does the principle of fixed valency governing the construction of structural formulas for organic substances not hold in general. If the microstructure is primarily a collection of particles, these particles are not

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<sup>3</sup> As Duhem carefully explained in Duhem (1892 and 1902); see Needham (1996b).

in general molecules in the sense of what a structural formula might be considered to represent, and may well not belong to a single species. Water, in particular, is a substance which doesn't fit the organic substance paradigm at all.

There is a notion of a water molecule—something comprising two hydrogen atoms each bonded with an oxygen atom and having a certain geometric shape, one subject to vibrations and distortions caused by rotations. But these exist as separate units only in the gas phase at sufficiently high temperature and low pressure. We will see something of the way the liquid deviates from the organic paradigm later. Details aside for the moment, the following question suggests itself: Why, if organic substances whose microparticle constitution is essentially that of a collection of molecules are counted as single substances, are substances like water also counted as single substances although their microparticle constitution is not essentially that of a collection of particles of a single kind? Microparticle constitution is not, it seems, a sufficient criterion of substancehood. But without jumping to any conclusions at this stage, let us consider macroscopic criteria, and in particular what thermodynamics has to say on the matter.

### **3. Criteria of purity and the notion of substance**

Having concluded that “*the equilibrium pressure of a two-phase one-component system does not depend on the relative or total amounts of the two phases*”, the authors of a recent textbook note that “[t]his behaviour serves as a criterion of purity, since it is not true of mixtures” (Koningsweld et al. 2001, p. 9; emphasis in original). The system in question is a quantity of matter distinguished from the surroundings by the walls of a container, one of the two phases is the gas in the container and the other is the liquid. The pressure of the matter inside the container depends on the temperature, and is not affected by the amount of matter in each of the phases. If, for example, the container were fitted with a piston, we might try to reduce the pressure by raising it. Were all the matter in the container in a single gas phase, this would reduce the pressure. But it fails to reduce the pressure of the two-phase, one-component system because liquid will go into the gas phase and maintain the pressure, thus complying with the criterion for the behaviour of matter comprising a single substance, that the pressure is dependent on the temperature but independent of the amount of matter in the two phases. Continuing in this way, the liquid will eventually vanish, leaving a single gas phase, the pressure of which is dependent on the amount of matter in the phase.

Water behaves in this way, and so fulfils this criterion of purity, as do paradigm organic substances such as methane and benzene. Quantitative aspects of this pattern of behaviour distinguish them, such as the pressures sustained at given temperatures. The observation that single substances behave in this manner was established experimentally in the nineteenth century. Such evidence confirmed this and similar laws deduced from general principles in the third quarter of that century, which turned out to be special cases of a law first established from thermodynamics by Gibbs. Gibbs' phase rule, as it came to be known, deals with mixtures at equilibrium, comprising heterogeneous quantities of matter containing several substances. The distinct homogeneous parts are called phases; a quantity of water comprising vapour over the liquid, for example, is a two-phase system. Gibbs' phase rule relates the number of phases,  $f$ , to the number of component substances,  $c$ , by

$$\text{Variance} = c - f + 2 \geq 0.$$

The *variance* of a quantity of matter gives a measure of the variety of conditions under which the quantity can sustain  $c$  substances distributed over  $f$  phases at equilibrium in the form of the number of independent variables required to specify the state of the quantity to which it is applied. In order to determine the macroscopic state of the quantity, these variables must determine the temperature, the pressure and the composition of (concentration of each substance in) each phase.

The mixture of liquid water and water vapour, for example, (held at equilibrium) is a univariant system. The vapour can remain in contact with the liquid over a range of temperatures; but since the system is univariant, the vapour pressure has a single value for each temperature within this range, i.e. is a function of temperature only. Any attempt to reduce the pressure by increasing the volume of the quantity (say by drawing out a piston forming a wall of the vessel containing the water) is counteracted by more liquid going into the vapour phase and maintaining the pressure, until all the liquid is used up and the body becomes entirely gaseous. At this point, the entire quantity is a single phase, and it is now a bivariant system. The temperature and pressure can now vary independently. A third variable, the density, cannot; it is fixed for a particular value of temperature and pressure, as required by the familiar Charles-Boyle gas law. The phase rule does allow another circumstance for a single-component system ( $c = 1$ ), namely that the number of phases,  $f$ , is 3. Then the variance is 0, and the conditions under which water sustains three phases simultaneously allow for no variation. This is

called a triple point, and for copresent solid, liquid and gas phases of water at equilibrium, the temperature is  $0.01^{\circ}\text{C}$  and the pressure  $4.58\text{ mm. Hg}$ . This general behaviour is characteristic of matter comprising a single substance, and the specific data (the triple point data, and the function expressing the dependence of vapour pressure on temperature, for example) distinguishes the substance water from others.

By this criterion, what we ordinarily call a quantity of pure water is, indeed, a single substance (by contrast with, say, butter, petrol, smoke, coke, brine, and so on, which may be single substances in some everyday sense, but are not in the chemist's sense). There is no implication that water can't occur as part of a mixture, for example an aqueous solution. The number of substances,  $c$ , in the phase rule is not restricted to one, although the general significance of this number needs, as we will see, to be developed carefully. Note that 'pure' doesn't directly qualify a substance predicate. 'Pure' applies to a quantity, so that a quantity is pure water, for example, if it is not mixed with a quantity of any other substance. A quantity occupying a region containing no other substance than the substance in question is pure. Thus, distilled water in a beaker surrounding a globule of mercury is pure, but it must be understood that the reference is to the quantity occupying the region inside the beaker less that occupied by the globule of mercury. In the same sense, distilled water in a beaker ordinarily said to be "contaminated" by dust particles is pure, the quantity in question occupying a region not including that occupied by the dust particles. The (entire) quantity of matter in the beaker, on the other hand, is not pure water. As we will see, however, the quantity of water in a solution of caustic soda is not pure water, so it not a general tautological truth that substances are always pure in the sense that a quantity of such-and-such a substance comprises just that substance.

The question raised at the end of the last section is thus answered in terms of a criterion supplied by a general theorem of thermodynamics, the phase rule, governing matter at equilibrium. Despite the variety of kinds of microparticle in a quantity of liquid water, it satisfies the phase rule criterion of being a single substance. Some of the reasons why water is thought to have such a complex microstructure will be considered in the section after next. But with a view to saying how this complexity at the microlevel is related to this apparent simplicity at the macrolevel, some further insight into the interpretation of  $c$  in Gibbs' phase rule can first be got by noting how the law is derived and considering some simple examples of its application.

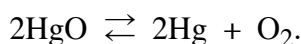
#### 4. Derivation and further illustrations of the phase rule

As the terminology of independent variables in the concept of variance suggests, the derivation of the phase rule is a matter of how many variables are determined by the available relationships expressible as equations.

Altogether there are  $c \times f$  concentrations of each of the  $c$  substances in each of the  $f$  phases, which together with temperature and pressure give a total of  $cf + 2$  variables completely specifying the state. But thermodynamics associates a chemical potential with each substance in each phase, governing its reaction with other substances and its movement to different parts of the system. At equilibrium, when the concentrations in each phase are stationary, thermodynamics requires that the chemical potentials of a given substance are equal across the  $f$  phases. So there are  $f - 1$  equations expressing these equalities for each substance, and so  $c(f - 1)$  equations in all. Further, the concentrations of each substance are specified as fractions,  $x_i$ , of the total mass of each phase, and satisfy an equation  $\sum x_i = 1$ , where the sum is taken over all the substances in the phase. Since there are  $f$  such equations, the total number of independent variables specifying the state of the system is  $(cf + 2) - (c(f - 1) + f) = c + 2 - f$ . This result is the same if some substances are absent from some of the phases. In that case, the number of concentration variables,  $x_i$ , is reduced, but the number of equations expressing equality of chemical potentials across the phases is also reduced by the same number.

The phase rule as stated presupposes that no further constraints are acting on the mixture which would further reduce the number of independent variables. But if there are  $r$  reactions taking place between the substances, then at equilibrium there will be an additional equation ( $\sum \nu_i \mu_i = 0$ , where  $\nu_i$  is the stoichiometric coefficient of the  $i$ th substance in the reaction and  $\mu_i$  is its chemical potential) for each of the  $r$  reactions taking place. These equations reduce the  $c - f + 2$  variables by  $r$ , although this is normally put by saying that it reduces the number of independent substances,  $c$ , by  $r$ . Moreover, chemical reactions may take place in such a way as to render true further equations expressing additional restrictions.

A good illustration is provided by one of Duhem's examples (1910, pp. 175-6). The red oxide of mercury, when heated in a previously emptied closed container, dissociates:



Two phases appear, a solid comprising HgO and a gaseous mixture of oxygen and mercury vapour. There are three species, but one equilibrium constraint and the further constraint that the gas mixture contains equivalent proportions of mercury and oxygen. So there is one independent substance, which means that the two-phase system is univariant: at 520°C, for example, the pressure is fixed at 4176 mm. of Hg. Destroying the equivalent proportions by introducing either a little oxygen or a little mercury removes a constraint and there are two independent substances, making the system bivariant. Fixing the temperature no longer suffices to fix the pressure. Adding sufficient mercury to form a third, liquid, phase, however, returns the system to univariant behaviour. But now the pressure determined by a temperature of 520°C is 8440 mm. of Hg.

Another example Duhem discusses is the classic case of the equilibrium



established when calcium carbonate is introduced into a closed and otherwise empty container and heated. There are three species and one equilibrium, and so just two independent substances. The system seemed to comprise two phases, a white solid and a colourless gas. But this couldn't be reconciled with its variance, which was determined to be one (there is a definite gas pressure for a given temperature). Compliance with the phase rule led chemists to believe there must be three phases—the gas phase, and two distinct solid phases, one containing the CaCO<sub>3</sub> and the other the CaO. A single solid phase would be an intimately mixed solid solution of CaCO<sub>3</sub> and CaO, but they do not form such an intimate mixture.

The calcium carbonate system can be contrasted with that formed by mixing potassium sulphate, ammonium sulphate and insufficient water to dissolve them completely, which is trivariant. Not only can the temperature and pressure vary independently, but also the relative mass of one of the three substances. As might be expected, increasing the mass of one of the salts without changing either temperature or pressure changes the composition of the solution by increasing the concentration of the added salt and decreasing the concentration of the other salt. Since there are no chemical reactions there are three substances, and the number of phases,  $f$ , given by  $3 = 3 - f + 2$ , is 2, so that apart from the liquid solution there is only one solid phase, which, in contrast to the white solid in the previous case, is therefore a homogeneous solid

solution of the two salts. In the case of the calcium carbonate system, the phase rule gives us that  $1 = c - 3 + 2$ , or  $c = 2$ . Since the one solid phase comprises calcium carbonate and the other calcium oxide, it seems we've necessarily used up our quota leaving the gas without a substance composing it! But thermodynamics doesn't select two of the three species as the two substances. It says just that there are two substances, not how they are to be identified with the species. An alternative description, compatible with the phase rule, is that the two substances are CaO and CO<sub>2</sub>, and the remaining species is a combination of these two. Or again, CaCO<sub>3</sub> and CO<sub>2</sub> might be chosen, when the CaO must be understood, as Castellan (1964, p. 247) puts it, as CaCO<sub>3</sub> "minus" CO<sub>2</sub>. But what do "a combination of the two" and "minus" mean here?<sup>4</sup> What is clear, at any rate, is what thermodynamics does and doesn't require, and that it provides a description applicable when processes of change of phase and transformation of substance by chemical reaction have settled down to a state of equilibrium. In order to get a better grip on this somewhat mysterious state of affairs, the situation at the microlevel will be considered in a little more detail before returning to the question of interpretation of the phase-law conception of substance in section 6.

### 5. Microscopic species in water

Variation in microstructure is postulated in the first instance to explain variation in macroscopic features such as melting and boiling points and heat capacities. Our typical organic hydrocarbon, methane, with formula CH<sub>4</sub>, comprises molecular species in

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<sup>4</sup> What he actually says is "If CaCO<sub>3</sub> and CO<sub>2</sub> were chosen as components, the composition of CaO would be described as one mole of CaCO<sub>3</sub> minus one mole of CO<sub>2</sub>." Allusions to algebraic operations, though not uncommon, are rarely explained. Ricci (1951, p. 10) just writes "With CaO and CO<sub>2</sub> [as independent components], the phase CaCO<sub>3</sub> consists of CaO + CO<sub>2</sub>, with CaCO<sub>3</sub> and CaO, the phase CO<sub>2</sub> = CaCO<sub>3</sub> - CaO," leaving the reader to infer the significance of the equations. Zernike (1957, pp. 13-4), discussing the system resulting from mixing CO<sub>2</sub> and NH<sub>3</sub>, which undergo reactions involving ammonium carbamate, urea and water, writes "NH<sub>2</sub>CONH<sub>2</sub> = 2NH<sub>3</sub> + CO<sub>2</sub> - H<sub>2</sub>O", but worries that "again one of the components carries a negative coefficient, ... [which] cannot be [as in a previous case] by the use of ions".

which a carbon atom is strongly bonded to four hydrogen atoms, and these molecules are subject only to weak, so-called van der Waals, forces between the molecules. Such molecules form solids which are soft with low melting points that increase with molecular weight. Methane is a light molecule which is not even a liquid at normal temperature and pressure, but a gas, boiling at  $-161.5^{\circ}\text{C}$ . Pentane, a hydrocarbon of essentially the same kind with formula  $\text{C}_5\text{H}_{12}$ , is liquid at room temperature boiling at  $36.1^{\circ}\text{C}$ , and eicosane, with formula  $\text{C}_{20}\text{H}_{42}$ , is solid at room temperature melting at  $37^{\circ}\text{C}$ . It stands in contrast to substances like common salt ( $\text{NaCl}$ ) and silicon dioxide ( $\text{SiO}_2$ ), which form indefinitely repeating arrays in the solid phase in which no particular pairs, in the case of  $\text{NaCl}$ , or triples, in the case of  $\text{SiO}_2$ , of atoms can be distinguished from their neighbours by virtue of stronger internal bonding between the atoms in putative molecules than between adjacent atoms. A lump of salt consists of an ionically bonded array in which each sodium cation (i.e. a positively charged ion) is surrounded by six chloride anions (i.e. negatively charged ions), and each chloride anion is surrounded by six sodium cations, in a structure which is repeated throughout the whole macroscopic crystal. No particular pairing of a sodium cation with one of its six coordinated chloride anions presents itself as more natural than a pairing with any of the remaining five anions. The formula 'NaCl' simply represents that there are as many equivalents of sodium as there are of chlorine in any sample of salt, which translates into microscopic terms as equal numbers of sodium and chlorine ions. Solid silicon dioxide also takes the form of an array extending over the entire macroscopic crystal in which each Si atom is bonded to four oxygen atoms (covalently, but with considerable ionic character) and each oxygen atom to two silicon atoms. Structures of these kinds are typically hard with high melting points.

Water falls squarely between these two categories, with molecular units distinguished by internal bonding between a single oxygen atom and two hydrogens which is stronger than intermolecular attraction, but where the intermolecular attraction between two water molecules is midway in strength between a van der Waals interaction and an ionic bond. This explains water's unexpectedly high melting and boiling points. Thus, whereas purely on the strength of its molecular weight water would be expected to boil around  $-70^{\circ}\text{C}$ , it doesn't even melt until  $0^{\circ}\text{C}$ , which gives some indication of the strength of the intermolecular force.

The intermolecular forces give rise to an indefinitely repeating crystalline structure in ice analogous to that described for common salt and silicon dioxide. Water has a surprisingly low latent heat of fusion (heat required to change the solid to liquid at the melting point). It is only 15% of the latent heat of evaporation, suggesting that much of the intermolecular structure in the solid is retained in the liquid, and not finally lost until in the gas phase. Moreover, liquid water has a large heat capacity—nearly twice that of ice (at the melting point), and more than twice that of steam (at the boiling point)—enabling the Gulf Stream to convey an enormous amount of energy from the tropics to Northern Europe.<sup>5</sup> Increasing the motion of the molecules accounts for only half of the liquid's heat capacity; there must be a structure in the liquid which the rest is utilised in deforming.

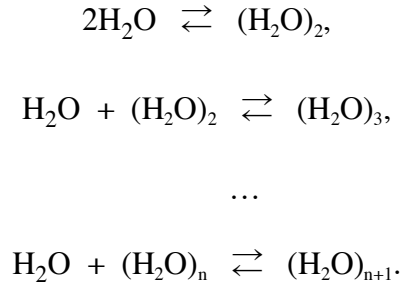
The intermolecular bonding is called hydrogen bonding, and occurs in compounds where hydrogen can lie between two highly electronegative fluorine, oxygen or nitrogen atoms. Its character remains somewhat obscure. Traditionally, writers have been reluctant to ascribe hydrogen two covalent bonds because that would be inconsistent with a fixed valency of one, and it remains controversial whether it is a purely electrostatic interaction due to a build up of positive charge on the hydrogens and negative charge on the electronegative element (oxygen in water), or has a significant covalent contribution. But it is important to understand that hydrogen-bonded water constitutes a cooperative interaction, in which “the interaction of a given water molecule with an already existing cluster of hydrogen-bonded molecules is more favourable, and therefore more probable, than the interaction with another single molecule to form a dimer” (Franks 2000, p. 14). Hydrogen bonding therefore disposes water molecules to amalgamate in very large structures, discouraging the existence of even dimers (i.e. pairs of molecules), and certainly monomers (single, uncombined molecules).

Water molecules therefore aggregate in inter-molecular species which might be represented by  $(\text{H}_2\text{O})_2$ ,  $(\text{H}_2\text{O})_3$ , ...,  $(\text{H}_2\text{O})_n$ , .... But these are not permanent species, nor even stable over nanoseconds. The situation is a dynamic one, in which clusters are continually being formed and broken, reaching equilibrium under stable conditions in

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<sup>5</sup> Delivering energy at a rate that burning all the coal mined in the world in a year could maintain for only 12 hours (Franks 2000, p. 7).

the sense that their concentrations are constant because the rates of formation and destruction are equal. The dynamic equilibria can be represented as follows:

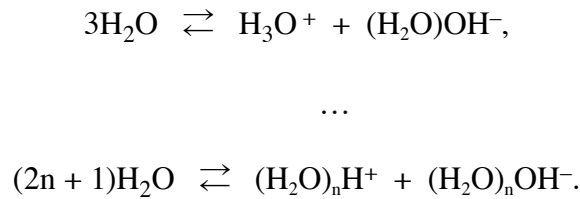


The double arrows indicate that the processes continue in both directions, and the concentrations of the species remain constant by the continual replenishment of disrupted clusters with newly formed ones. It should be stressed, however, that there is great uncertainty about how many such species there are and what their actual structure is. Much of the present view is derived by inference from macrofeatures along the lines indicated above.<sup>6</sup> Even so, enough is known to motivate a modification of this scheme.

A second series of equilibria is established arising from the dissociation of water into ions, positively charged hydrogen cations and negatively charged hydroxyl anions:



These ions are not free particles but attach to the hydrogen-bonded clusters, producing equilibria of the following kinds:




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<sup>6</sup> So if Putnam's stereotypical description of water includes such macrofeatures, the macroscopically indistinguishable twater of twin earth would also be microscopically indistinguishable from water. We will see as the discussion proceeds how the microdescriptions relate to the macroscopic criterion of sameness of substance, leaving no room for an XYZ distinct from H<sub>2</sub>O to satisfy the same criterion.

In pure water the hydrogen and hydroxyl ion concentrations<sup>7</sup> are each very small,  $10^{-7}$  gram ions per litre. It might be thought that such tiny amounts could be ignored. But the dielectric constant of water depends on the existence of these ions and how they are hydrated by attaching to clusters. This concentration determines the neutral pH value (defined as the negative logarithm of the hydrogen ion concentration) of 7. Acidity is the phenomenon of the pH value decreasing (i.e. hydrogen ion concentration increasing) in an aqueous solution (homogeneous mixture of other substance or substances with water). These ionic species, although in very low concentrations, account for some of water's distinctive properties. The pH of the ambient medium controls whether haemoglobin holds onto or releases oxygen, for example, and so is a matter of life and death for us. If microscopic species determine the characteristic features of a substance, then we can't ignore some just because there are relatively few of them (at any given femtosecond).

## 6. Dynamic equilibria and the phase rule

The derivation of the phase rule took no account of the various microparticles present in the components. It is a theorem of classical thermodynamics, which is a purely macroscopic theory, neutral with respect microscopic interpretations. In order to relate macro- and microdescriptions, a standard move in chemical theorising is to consider thermodynamic equilibria, representing stable and macroscopically unchanging states of affairs, to correspond to so-called *dynamic equilibria* on the micro-scale. On the latter conception, there is a continual removal of reactants as they combine to yield products, at the same time as they are continually replenished as the products re-combine to yield the reactants, and a dynamic equilibrium is established when the rate of the forward reaction is the same as the rate of the reverse reaction. Thus, the dissociation of water into hydrogen ions and hydroxyl ions proceeds while the recombination of these ions occurs, removing ions after they have been created. If the forward reaction were allowed to proceed alone, by somehow removing the ions when they are formed, then the reaction would proceed until all the water is dissociated. But this doesn't happen and a balance is reached in which the rate of dissociation equals the rate of association, when the concentration of undissociated species remains constant, despite the continual

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<sup>7</sup> Including all the hydrated hydrogen ion species in the hydrogen ion concentration, and similarly for the hydroxyl ion concentration.

dissociation, because dissociated species are continually replaced. The concentration of dissociated species remains constant for the same reason.

From the point of view of the phase rule, then, the dynamic equilibria between the various cluster species  $\text{H}_2\text{O}$ ,  $(\text{H}_2\text{O})_2$ ,  $(\text{H}_2\text{O})_3$ , ...,  $(\text{H}_2\text{O})_n$ , ... in liquid water involving association by hydrogen bonding are chemical reactions at equilibrium. Accordingly, if there are  $n$  species, whatever  $n$  might be, there are  $n - 1$  equilibria, and therefore just one independent substance. So although chemists are still pursuing unanswered questions about clusters, they are sure that they are in dynamic equilibrium with one another, and the exact number is immaterial to the question of how many substances are present. In the pure liquid, there is just one. The dissociation into ions may seem to present a different case in so far as the equilibrium  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  involves 3 species. But this one reaction yields the further constraint that the concentrations of hydrogen and hydroxyl ions are equal (in molar units), maintaining electrical neutrality. So the three species are matched by two constraints, which brings the number of substances back to one. And as before, the cluster complexes introduce  $2n + 1$  species along with  $2n$  constraints, which again fails to raise the number of independent substances above one. This explains the insensitivity of the thermodynamic criterion of purity based on the phase rule to the variety of particles in water.

## 7. The time of predication

What appears macroscopically as an unchanging state of affairs is the scene of rapid change. Although the changes balance to maintain steady concentrations when dynamic equilibrium is established, the fixed concentrations are not constituted by fixed quantities of matter. How do the rates of the reactions involved in the dynamic equilibria bear on these matters?

The half-life of the dissociation of water (time for half of a given amount of water to decompose) is about 20 microseconds ( $20 \times 10^{-6}$  sec.). So after a very short time on the human scale, say half a second, an appreciable proportion of the water molecules in any given quantity of water will have been dissociated and the ions from any particular molecule will have recombined, though not necessarily with one another. Similarly, each of the steps in the formation and dissociation of polymeric clusters of water species are established in water in the liquid state within intervals of time not exceeding  $10^{-11}$  seconds. Accordingly, the quantity of matter which is such a polymeric species is so for a time of this order of magnitude and no longer. For a significantly longer time,

say of the order of a microsecond ( $10^{-6}$  s.), this quantity is not such a cluster, but a sum whose parts form parts of various such clusters for different subintervals of the time in question. Similarly, a part of such a cluster which is a water molecule, i.e. an  $\text{H}_2\text{O}$  molecule, at some time will not be an  $\text{H}_2\text{O}$  molecule for very long. Given what was said about the dissociation half life of  $\text{H}_2\text{O}$ , the probability of a quantity of matter being an  $\text{H}_2\text{O}$  molecule for as long as, say, 100th of a second is quite small. The two-place predicate 'is an  $\text{H}_2\text{O}$  molecule' doesn't in general hold of any quantity in the liquid state for, say, a whole second. Any quantity which is an  $\text{H}_2\text{O}$  molecule for an appropriately short time will be a sum of disparate and dispersed parts which don't constitute an  $\text{H}_2\text{O}$  molecule for times some factors of 10 longer.

Substance predicates are time dependent, and which substance predicates hold of quantities of matter depends crucially on the order of magnitude of the time at issue. For macroscopic orders of magnitude of tenths or even hundredths of a second and longer, a very small quantity constituting a single entity of some microscopic species for some very short fraction of this time will not, in general, be of the same, or indeed of any other, microscopic species. It will be a mereological sum of various proper parts of many entities of various microscopic kinds for some subinterval of the time in question. Small quantities are microscopic kinds only for very short times. Kinds holding for longer times, of macroscopic orders of magnitude, are macroscopic kinds such as 'water' applying to quantities of macroscopic dimensions. 'Is  $\text{H}_2\text{O}$ ' is such a predicate where the formula is not a proxy for some description of a microspecies such as 'is an  $\text{H}_2\text{O}$  molecule', but understood in macroscopic terms along the lines indicated in section 3. For very short periods, of the order of magnitude of those times for which small quantities can be said to be one or other microscopic species, the concentrations of the various microspecies fluctuate and the equilibrium balance described by formulas such as those given in section 5 and established over longer intervals of time is not realised. If macroscopic criteria based on the phase rule determine the applicability of the substance predicate 'water', then it is applicable to sufficiently large quantities for sufficiently long times over which the microscopic fluctuations are smoothed out, and not to what microdescriptions are true of for much shorter times. A water molecule is not water. For times on the micro scale, descriptions of micro-entities are needed, applicable to micro-quantities. For longer times, however, quantities cannot be partitioned into parts (almost) all of which are definite molecular species for the time in

question. They are mereological sums of small quantities darting between ephemeral microparticles, and the water predicate will apply to such sums for all times longer than the very short periods when fluctuations are significant while equilibrium lasts.

In general, then, larger macroscopic quantities of matter sustain macroscopic kind properties for sufficiently long times, and all their subintervals of a macroscopic order of magnitude, but not shorter, and very small quantities of matter sustain microscopic kind properties for times of a microscopic order of magnitude, but not longer. This is not independent of the prevailing conditions and the kind of substance at issue, however. The molecules in a quantity of water confined entirely to the gas phase under conditions approaching those of an ideal gas (obeying the Charles-Boyle gas law to a very good approximation, requiring a sufficiently high temperature and low pressure) are so thinly distributed that they hardly interact. Under such conditions the molecules have a considerably greater longevity than molecules in the liquid phase. But this is not so if the gas is in contact and at equilibrium with the liquid (in a multiphase system).

The underlying dynamics are also at work in the equilibria between phases in a complex mixture, which undergo exchange of material. The equilibrium between liquid and vapour, for example, involves particles leaving the liquid surface and entering the vapour, but being replaced by other particles from the vapour entering the liquid.<sup>8</sup> Again, in the space of what, on the human time scale is an exceedingly short interval of a fraction of a second, substantial parts of the matter in the liquid have gone into the vapour phase to be replaced by different matter (i.e. different particles) coming in from the vapour phase. There is a continual interchange of material between the two phases. This is often put by saying that water molecules in the vapour phase will enter the liquid phase, be subject to the interactions and become integrated into the microstructure of the liquid. The thought here would be less ambiguously expressed, however, by saying that what are water molecules in the vapour phase will become integrated into the microstructure of the liquid, dropping any suggestion that the molecular units remain intact throughout the course of this process.

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<sup>8</sup> At equilibrium, the total energy of a quantity is distributed over the micro-particles in such a way that not all have the average kinetic energy, but some are extremely energetic, while others are less so. Very energetic particles of the liquid near the liquid-gas interface will enter the gas phase, and less energetic gas-phase particles will enter the liquid phase.

On a macroscopic time scale, what is at one time, say, liquid in a liquid-vapour system, or solid water at the triple point where solid, liquid and gas are all at equilibrium, is in general not all liquid (solid) at another. This raises the question of what it means to say that some quantity is in some particular phase, say liquid, for some time (at some interval). It can't be given the same mereological interpretation suggested above for the macroscopic substance predicate 'water'. If 'is liquid' were distributive, i.e. any part of a quantity which is liquid at a time is liquid at any subinterval of that time, as usually required of mass predicates, then for liquid at equilibrium with another phase, the longer the time, the smaller would be the quantity counted as liquid. In the long run, nothing would be liquid for a time during which all liquid is exchanged with the other phase. But even before reaching this extreme, imposition of the distributive condition would mean that whatever chunk of matter satisfies the condition for a given time is not discernable by perception. Alternatively, perhaps it should be interpreted accumulatively, by analogy with 'occupies'. In order to take account of movement, it is natural to speak of the region that the object sweeps out during the time as that it occupies for that time (Needham 1996a, pp. 216-7). In that case, 'is liquid' would be true of a quantity for time  $t$  iff that quantity were the sum of quantities which are liquid for some subinterval of that time. Just as some part of the region swept out during  $t$  might not be occupied for some subinterval of  $t$ , so some part of the quantity which is liquid for  $t$  would not be liquid for some subinterval of  $t$ . But the longer the time, the greater would be the quantity counted as liquid. The first proposal would count as liquid a quantity of less mass than what apparently is the mass of the liquid from the purely macroscopic perspective, and the longer the time, the smaller the quantity counted liquid. The second proposal would count as liquid a quantity of greater mass than the apparent mass of the liquid from the purely macroscopic perspective, and the longer the time, the greater the quantity counted liquid.

There may well be a certain volume of liquid in the container enclosing the quantity of matter at equilibrium which is fixed over a certain period. From the macroscopic perspective, it seems natural to take it that one and the same thing makes up this volume throughout the period in question. But the above considerations show that there is no such thing. A definite quantity is defined by the accumulation condition, which might serve as a referent of 'the liquid' for certain purposes without detracting from what has just been said. An alternative course of delimiting a definite quantity by reducing the time interval to an instant might suggest itself. But this would take us

further than the limit imposed by statistical fluctuations, beyond the limit set by the time-energy uncertainty principle, and into a realm where scientists hardly dare speculate. This might not deter the metaphysician content to imagine water molecules arranged “waterwise”, but others might be sceptical.

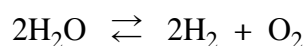
### **8. Aristotle’s conception of a mixt**

Aristotle developed a conception of mixing in *On Generation and Corruption* according to which, when original ingredients are brought together, they interact by virtue of their mutual capacities and susceptibilities to combine and form a homogeneous body: “if combination has taken place, the compound *must* be uniform—any part of such a compound is the same as the whole, just as any part of water is water” (*DG* I.10, 328<sup>a</sup>10f.; Barnes’ trans.). The capacities and susceptibilities driving the interaction are supposed reducible to degrees of the primary qualities of warmth and humidity, and the resulting compound, as this translator puts it, is characterised by degrees of warmth and humidity intermediate between those of the original substances. Since all the parts of the resulting “compound” have the same degree of warmth and humidity, no part exhibits the degrees of warmth and humidity characteristic of the original ingredients, which have therefore given way to a new substance. Reserving the term ‘compound’ for the specific sense it has in modern chemistry, I will follow Duhem (1902) and refer to the Aristotelian conception of a uniform body resulting from such a process of mixing with the antiquated term ‘mixt’. Duhem thought that thermodynamics showed how “chemistry [had] recover[ed] ... the peripatetic notion of a mixt” (1902, p. 183). Provided this is not taken to suggest that it is generally adequate, the Aristotelian conception does, as I will try to show, have a certain affinity with modern theory.

Though he doesn’t say so in as many words, it seems that Aristotle also maintained the converse of the principle just quoted from *DG* I.10, and held that a homogeneous body comprises a single substance. He says, for example, that anyone who adopts “the view of Anaxagoras that all the homoeomerous bodies are elements ... misapprehends the meaning of element. Observation shows that even mixed bodies are often divisible into homoeomerous parts; examples are flesh, bone, wood, and stone” (*Cael* III.4, 302<sup>b</sup>13-7), and flesh, bone, wood, and stone are each treated as single substances. Further, the evaporation of water is treated as a transmutation of one substance into another (water into air), and not a phase transition of the same substance as it is today. If this is right, then Aristotle stands corrected by Gibbs’ conception of a

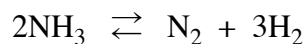
heterogeneous mixture comprising several phases in which several substances are distributed over some or all of the phases, so that even when there are as many substances as phases (and the system is bivariant), they may well not be each uniquely confined to a single phase (unless there happens to be just one substance in one phase). Nevertheless, there is something reminiscent of the Aristotelian notion in applications of the phase rule of the kind exemplified above.

At high temperatures, water begins to dissociate. At around 2000 K (*c.* 1700°C) it is about 1% dissociated (Denbigh 1981, p. 153), and the equilibrium



is established. This is a gas phase reaction in which the number of species present increases from one to three as the temperature rises. At the same time the number of constraints on the whole system increases by two, and the number of substances in the sense of the phase rule remains one. Beginning with water may seem not to conform to Aristotle's conception of a mixt described as bringing different ingredients together. But the Aristotelian idea of attaining intermediate degrees of warmth and humidity suggests the establishment of an equilibrium. And since an equilibrium is at issue in the present case, the same state of affairs results from mixing oxygen and hydrogen in the appropriate proportions and bringing the mixture to the higher temperatures. Note that at lower temperatures, and in the absence of a catalyst, eons could pass before the equilibrium is established and the mixture can be treated as a homogeneous gas comprising two substances.

A similar example is the dissociation of ammonia, where the following equilibrium is established at high temperatures



with the production of nitrogen and hydrogen. These two examples are formally like the dissociation of water into hydrogen and hydroxyl ions, but involve the macroscopically recognisable substances hydrogen and oxygen in addition to water in the one case, and ammonia, nitrogen and hydrogen in the other, rather than transient microscopic species. Nevertheless, it seems that no matter how many species are at chemical equilibrium in a quantity of matter exhibiting a single phase, the quantity comprises just one substance. This is very much like the situation Aristotle describes, if not for quite the same reasons. Even if the proportions of oxygen and hydrogen at any short time, say of the

order of a microsecond, during which the equilibrium is nevertheless established, are low, a substantial part of any quantity of matter in the system will have been through the processes of dissociation and reassociation. In all likelihood, any part of the quantity which is all water at some short initial subinterval of a longer interval of the order of a second will not have remained all water for the second. What the predicate 'is water' applies to under such circumstances for times on the macroscopic scale is mereological sums of quantities which might be hydrogen or oxygen for very much shorter subintervals of this time. The situation is clearly distinguished from the low temperature mixture of hydrogen and oxygen which is not at chemical equilibrium and contains two substances. Mixtures of this latter kind are called solutions—homogeneous mixtures of several substances—a category which was formerly recognised after the law of constant proportions introduced a criterion of compoundhood but receives, apparently, no recognition by Aristotle.

The analogy suggested between the Aristotelian conception of a mixt and a single-substance system breaks down, it seems, with two-substance systems such as the calcium carbonate equilibrium. Unlike the examples just considered, however, this system is heterogeneous. In any case, the analogy was by no means perfect even for single-substance systems, which might consist of several phases. But pursuing an imperfect analogy will give a better idea of what modifications modern chemistry calls for. The fact that the phase rule encompasses these various cases under the same law shows that the same general kind of reasoning applies to the two-substance calcium carbonate equilibrium as it does to the water and ammonia cases, and it would be interesting to see this reflected in a general view of mixture. For this purpose, the phase rule's distinction between phases and substances is crucial.

As with the liquid and vapour phases of the two-phase quantity described at the end of the last section, any part of the quantity which is all part of the calcium carbonate phase at some short initial subinterval of a longer interval of the order of a second will not have remained all calcium carbonate for the whole second. The same applies to the calcium oxide and carbon dioxide phases. There is a continual exchange of matter between calcium carbonate and carbon dioxide phases and calcium oxide and carbon dioxide phases, the carbon dioxide mediating an exchange between calcium carbonate and calcium oxide. None of the predicates 'calcium carbonate phase', 'calcium oxide phase' and 'carbon dioxide (gas) phase' is true of all of any part of the original quantity of matter for times of the order of a microsecond or more. But the tripartite distinction

at issue here is a distinction of three phase properties, although in this exceptional case each phase comprises just one of the three species involved in the equilibrium. The example involving a two-phase mixture of potassium sulphate, ammonium sulphate and water has both salts in the solid phase and all three substances in the liquid phase. Here there is no chemical reaction between the original ingredients, however, and each of the three quantities of each original substance kind remains of that kind throughout the time that the equilibrium is maintained.

In the calcium carbonate equilibrium, the quantity which was originally all calcium carbonate prior to the establishment of the equilibrium must accommodate other substance kinds during the time the equilibrium is maintained. For this time, that quantity is two substances, which may be so described that the quantity can be partitioned into two parts each of which is all of one of the two substances. In the cases of water and ammonia at high temperatures, the quantity originally water and the quantity originally ammonia are each single substances, despite the dissociation. In the present case, what was all calcium carbonate has become two substances, CaO and CO<sub>2</sub>, parts of each combining to form one of the solid phases while other parts of what is this phase dissociate and become part of the gas phase and part of the other solid phase. The partition (division into mutually separate parts whose sum is the quantity partitioned) of the original quantity into independent substances yields quantities all of whose parts are of the particular substance kind throughout (at all subintervals of) the period of equilibrium, whereas the distinction of phases provides no such features of parts of the original quantity holding throughout the equilibrium.

Independent substances may be chosen in other ways, but still represent permanent features of certain parts of the original quantity throughout the duration of the equilibrium. In the present case, the two substances might be taken to be CaCO<sub>3</sub> and CO<sub>2</sub>. Here the parts of the original quantity so described do not form a mereological partition, but overlap, and the substance kinds must be understood in more abstract fashion. The mereological difference<sup>9</sup> of the part taken to be CaCO<sub>3</sub> less the part taken

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<sup>9</sup> The mereological difference,  $X - Y$ , is defined for quantities  $X$  and  $Y$  such that  $X$  is not part of  $Y$ , as the sum of all that is part of  $X$  and separate from  $Y$ . Thus, if  $Y$  is not a part of  $X$ , so that there is a part  $Z$  of  $Y$  separate from  $X$ , then  $Z$  is separate from the difference. And if  $X$  and  $Y$  are separate, the difference is just  $X$ .

to be  $\text{CO}_2$  is identical with the part said to be  $\text{CaO}$  on the other choice of independent substances just mentioned. It cannot be identified with the solid phase called the calcium oxide phase because this phase doesn't have the same parts throughout the duration of the equilibrium. Similarly, the part called  $\text{CO}_2$  in the substance sense of the term, like that on the previous choice of independent substances, cannot be identified with the gas phase for the same reason. But on the choice of  $\text{CaCO}_3$  and  $\text{CO}_2$  as independent substances, this approach provides a mereological interpretation of Castellan's expression " $\text{CaCO}_3$  minus  $\text{CO}_2$ " (see end of section 4), as an account of what the substance predicate 'is  $\text{CaO}$ ' is true of, namely the mereological difference of the  $\text{CaCO}_3$  less the  $\text{CO}_2$ . Just as in water equilibria where the whole original quantity is water, so in this case all the original quantity throughout the duration of the equilibrium is  $\text{CaCO}_3$  in the substance sense of the term, whereas  $\text{CaCO}_3$  in the sense describing one of the solid phases doesn't apply to anything for the entire duration of the equilibrium, and certainly not all the original quantity. ' $\text{CaCO}_3$  phase' applies to parts of the original quantity for shorter intervals of time. This maintains the thermodynamic notion of a substance as not dependent on phase, just as the substance water is not necessarily liquid.

## 9. Generalising Aristotle

If the Aristotelian conception of a mixt is likened to a homogeneous phase, then it doesn't distinguish between those cases which do and those which don't involve a chemical reaction. Where there is no chemical reaction, homogeneous phases can be produced in which original substances are preserved in a solution, such as the solid solution of potassium sulphate and ammonium sulphate, or the liquid solution of potassium sulphate, ammonium sulphate and water, in the example of a trivariant system from section 4. Moreover, as examples like this one well illustrate, where there are several phases, a phase boundary doesn't coincide with a substance boundary. If, on the other hand, the primary notion is compound formation, and the conception of a mixt involves a chemical reaction equilibrium, then in the case where a single phase is involved, Aristotle seems to have hit the nail on the head. At the higher temperatures where water and ammonia dissociate, or equivalently, their elemental components combine, there is just one substance present. What this means is that just one substance term applies to the whole quantity and all its parts for all macroscopic subintervals of

the period of equilibrium. But the Aristotelian conception of a mixt is clearly not going to be generally adequate. Chemical reactions may involve more than one independent substance, and homogeneous bodies may be solutions.

Taking up this latter notion first, there is another ancient conception which can be usefully brought into the picture at this point. The Stoics introduced a notion of mixt which, like Aristotle's, is a homogeneous substance from which the original ingredients can, in principle, be recovered. But they couldn't understand how recovery could be possible unless, in contradistinction to Aristotle's view, it is the separation of substances actually present in the mixt. They avoided conflict with the homogeneity criterion by maintaining, again in contradistinction to Aristotle's view, that two substances can occupy the same place at the same time. The possibility of cooccupancy is rejected outright by Aristotle and by many philosophers in recent times, although it had a powerful advocate in Duhem based on his understanding of thermodynamics (Needham 2002b) and should be taken more seriously (Needham 2007, pp. 40-2). Concerning the predication of quantities and intervals of time on the macroscopic scale, the region occupied by a quantity during such a time is the sum of all the regions occupied by proper parts of the quantity, or at least those of macroscopic dimensions, for subintervals of this time.<sup>10</sup> The trivariant system mentioned above involves a continual exchange of matter between the two phases, although the parts preserve their original substance properties, and the entire quantity of matter is reasonably taken to have parts including two or three of the substances occupying overlapping regions for times within the period of equilibrium. This is not a homogeneous mixture, but for appreciable subintervals of this period, quantities of the two salts will occupy overlapping regions in the same solid phase, and quantities of all three substances will occupy the same place in the same liquid phase.

Turning to the calcium carbonate case, if it were heated in the open, and the gas phase allowed to disperse, the reaction would go to completion, enriching the air with carbon dioxide and leaving a solid residue of calcium oxide. Alternatively, if carbon

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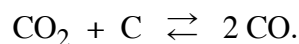
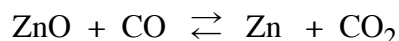
<sup>10</sup> We needn't raise the question what is involved in occupancy by microparticles at extremely short times. But anyone intent on understanding occupying a region in terms of instantaneous occupancy must provide a scientifically based interpretation of occupying at an instant of time, accommodating amongst other things the time-energy uncertainty relations.

dioxide and calcium oxide were brought together at high temperature, and the calcium carbonate phase somehow removed as it forms, the reaction would again go to completion and quantities of carbon dioxide and calcium oxide in stoichiometric proportions would be entirely transformed into the new substance. But as long as the equilibrium holds, the quantity of matter at equilibrium cannot be partitioned, as in the trivariant example, into three parts each all and only one of the substances calcium carbonate, carbon dioxide and calcium oxide throughout the duration of the equilibrium. Unlike the solution formation in the trivariant system to which the Stoic conception of mixing was applied, the number of substances yielding a partition is reduced. This is somewhat like the Aristotelian conception of compound formation. But the number of substances is not reduced to one, and the quantity doesn't become homogeneous.

What seems to be required is a conception of mixture which draws something from each of these ancient views, although both need to be modified. The first point must be that a mixture is not, in general, homogeneous, but comprises several phases, although there are special cases of single-phase mixtures. It is not possible to treat each phase of a multiphase mixture as a homogeneous mixture independent of the other phases. Second, the quantity as a whole can be divided into substances in the sense that there are parts of the quantity which retain the feature of being all and only one of the substances throughout the period of equilibrium and these parts exhaust (their mereological sum is identical with) the quantity. Where there is no chemical reaction, these are the original ingredients in the sense that the quantities of each substance originally brought into contact with the other quantities in the mixture retain their original substance kind throughout the period of equilibrium. Where there is a chemical reaction, the quantities which are all and only one of the substances are not in general identical with quantities which are all and only one of the initial ingredient substances. But in both cases, there is substantial spatial overlapping (cooccupancy of separate parts) of the entire quantity of matter. In the trivariant example, the two salts each occupy the same region as the entire quantity of matter throughout the period of equilibrium, and the water occupies part of this, namely that region which is always occupied by matter which is liquid. In the univariant calcium carbonate equilibrium, the independent substances calcium oxide and carbon dioxide spatially overlap.

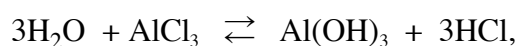
In the calcium carbonate equilibrium it was possible to choose the component substances in such a way that they make a partition of the matter involved, but this may not always be feasible. Consider, for example, the reduction of zinc oxide by carbon.

The reactions can be written as two independent equilibria as follows (Denbigh 1981, pp. 191-3):



This takes no account of possible short-lived intermediates formed in the reaction process, but these would introduce further equilibria and not increase the number of independent substances. The two equations represent all the overall changes involved in five species: ZnO, C, Zn, CO and CO<sub>2</sub>. Since these two equilibria are independent,<sup>11</sup> there are just three component substances. Three substances which partition the quantity of matter involved cannot be chosen from the five species. If we choose the three substances to be C, Zn and CO, then the (quantity which is) C and the (quantity which is) CO overlap. In that case, the CO<sub>2</sub> is the mereological difference of the CO less the C and the ZnO is the mereological difference of the sum the Zn and the CO less the C. (Note that saying CO<sub>2</sub> is the mereological difference of the CO less the C is not to say that there is no carbon in the carbon dioxide. C and CO overlap, but C is not part of CO, so that taking the difference doesn't, as it were, remove all the carbon.) If ZnO, C and CO were chosen, then the Zn would be the mereological difference of the ZnO less the CO, and the CO<sub>2</sub> would be the CO less the C as before. Not all the  $5!/3!(5-3)! = 10$  ways of choosing three substances from five species are options; C, CO and CO<sub>2</sub> are not since neither the Zn nor the ZnO can be derived from them.

The number of independent substances isn't always less than the number of original ingredients mixed. The calcium carbonate case might be considered an example of this. Another is provided by aluminium chloride, AlCl<sub>3</sub>, which, if mixed with water, reacts with the production of aluminium hydroxide, Al(OH)<sub>3</sub>, some of which forms a precipitate. The overall reaction,

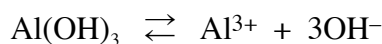


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<sup>11</sup> The number of independent equations is the minimum number sufficient to represent the stoichiometry (not necessarily the kinetics) of the overall reaction. See Denbigh (1981, pp. 169-72).

involves 4 species. If all of the  $\text{Al(OH)}_3$  remained in solution, there would be an additional restricting condition to the effect that the molar concentration of  $\text{Al(OH)}_3$  equals 3 times that of  $\text{HCl}$ . But since some precipitates out of solution, this doesn't hold and the only condition reducing the number of species to independent substances is the equilibrium itself. There are therefore 3 independent substances, which is one more than the number of original ingredients.

Even if there is much more (i.e. many more moles of) water than aluminium chloride, the entire quantity of water is involved at equilibrium. This may be more apparent by taking the ionic dissociations into account:



As we have seen, the first dissociation involves all the water. So if the three independent substances are taken to be  $\text{H}_2\text{O}$ ,  $\text{AlCl}_3$  and  $\text{HCl}$  (the first two being separate and the third overlapping each of the first two), then the sum of the quantities which are these substances exhausts all the material in the system, and the quantity which is the fourth species,  $\text{Al(OH)}_3$ , is the difference of the sum of the water and aluminium chloride less the hydrochloric acid.

The dissociation reactions involve 8 species. The overall reaction is not independent of these dissociation reactions, since adding three times the first dissociation plus the second and subtracting the last two yields the overall reaction, and there are just 4 independent equilibria. As before, there is no additional restricting condition to the effect that the molar concentration of  $\text{Al(OH)}_3$  equals 3 times that of  $\text{HCl}$  since some precipitates out of solution, but there is the further restricting condition on the ionic concentrations expressing the electrical neutrality of the solution:  $3x_{\text{Al}^{3+}} + x_{\text{H}^+} = x_{\text{OH}^-} + x_{\text{Cl}^-}$  (where  $x_{\text{A}}$  is the concentration of A). The 8 species are thus again reduced to 3 independent substances—one more than the number of original ingredients.

Note that the dissociation equilibria show that there are two sources of hydroxyl ions,  $\text{OH}^-$ , namely  $\text{H}_2\text{O}$  and  $\text{Al(OH)}_3$ , and two sources of hydrogen ions,  $\text{H}^+$ , namely

H<sub>2</sub>O and HCl. Because of the dynamic equilibria involved, there is no saying which hydroxyl ions belong to the water and apportioning the remainder to the aluminium hydroxide. The same goes for the hydrogen ions. Rather the hydroxyl ions are common to their two sources. Thus, if the three independent substances are chosen as H<sub>2</sub>O, Al(OH)<sub>3</sub> and HCl, then proceeding as before, the H<sub>2</sub>O and the Al(OH)<sub>3</sub> overlap, as do the H<sub>2</sub>O and HCl, but the Al(OH)<sub>3</sub> and the HCl are separate. The AlCl<sub>3</sub> is the product of the HCl and the Al(OH)<sub>3</sub>, whilst the OH<sup>-</sup> stuff is the product of the H<sub>2</sub>O and the Al(OH)<sub>3</sub>.

To take a simpler example illustrating this point about what exactly is water, consider an aqueous solution of caustic soda (cf. Needham 2000, p. 20). There are two dissociation reactions involving five species:



These two equilibria together with the equation  $x_{\text{Na}^+} + x_{\text{H}^+} = x_{\text{OH}^-}$  expressing the electrical neutrality of the solution total three constraints. The number of independent substances is thus reduced to two, which are naturally chosen as water and sodium hydroxide. The solution was made by dissolving sodium hydroxide in water, which are the two original ingredients. But what these substance predicates apply to is somewhat different before and after making the solution. Before, they apply to separate quantities of matter. After, they apply to overlapping quantities, and the hydroxyl ion stuff is the product of the two. This bears out the point that the distinction between solutions and compounds is not as sharp as it appeared to be at the beginning of the 19th century when Proust's law of constant proportions was accepted as a criterion of compoundhood. In the present example, it is possible to say that the solution comprises a mixture of water and sodium hydroxide, which is perhaps the grounds for calling it a solution. But that doesn't preclude the occurrence of a chemical reaction involving each of these substances in an equilibrium between several species. Moreover, the proportions of hydrogen and oxygen no longer correspond to those given by the compositional formula H<sub>2</sub>O.

Note that this goes further than the idea underlying the Stoic conception of mixture, that quantities of different substances in solution spatially overlap, in fact occupy the same region, during a given interval of time. That view has it that the quantities of the different substances are separate. In the present case, the water and the

sodium hydroxide overlap, and not merely spatially overlap (occupy overlapping regions), in solution.

A second observation is that if water and sodium hydroxide are subsequently separated by boiling the solution and condensing the water, the sum of the resulting quantities is identical with the sum of the initial quantities. But there is no saying whether the white solid and the liquid obtained after separation are identical, respectively, with the white solid and the liquid which were mixed. The mereological criterion of identity requires that there is an answer to this question, and we might well suppose that in all likelihood, they are not identical. But there is no empirical means of ascertaining this.

## **10. Conclusion**

This paper has been concerned with the application of substance predicates to material at equilibrium. Equilibrium implies, as we have seen, that the macroscopic state of the matter is stable, not that there is no underlying change. In particular, there is a continual exchange of matter between the various phases of a heterogeneous quantity of matter. Just as there is no fixed quantity of matter which ‘the ice in this gin and tonic’ refers to when the mixture is not at equilibrium, so at equilibrium ‘the liquid in this container’ doesn’t in general refer to a definite quantity except by some such device as making the time reference explicit and taking ‘the liquid in this container at  $t$ ’ to refer to the mereological sum of quantities which are all liquid throughout some part of  $t$ . But this would allow that some parts of the liquid are not liquid at some subintervals of  $t$ . Even if, unlike the melting ice, the liquid phase has a constant volume, and is confined to the same region of space throughout  $t$ , the phase predicate doesn’t apply to the same quantity throughout  $t$ . Only in specific circumstances is a quantity of material confined to a single phase, as when all the material in a closed container is liquid. Accordingly, contrary to appearances at the macroscopic level (cf. Needham 2007), phase predicates like ‘is liquid’ are not, in general, distributive (hold of all the parts for all the subintervals of a quantity and a time that they relate).

Like phase properties, substance predicates are also time-dependent but specify matter as being another kind of kind rather than being in some particular phase. Some apply to micro-quantities of matter, others to macro-quantities. Often, micro-descriptions are only applicable to very small quantities for very short times, and macro-descriptions are applicable to larger macro-quantities for longer times on the

macro scale. The predicate 'water' is usually taken to be a macro-description, applicable by the phase rule criterion to something whose parts may be undergoing rapid change in microscopic kinds. The term 'H<sub>2</sub>O-molecule' or 'water-molecule' applies to constituents of water which are susceptible to dissociation over very short periods of time. What is ordinarily called a quantity of water for an appropriately long time is a mereological sum of all that is a water molecule for some time during the time in question. But this is not to say that it is a sum of water molecules, at least insofar as this implies that it is a collection of water molecules, since it cannot be partitioned into parts that are water molecules for a macroscopically significant time of, say, a microseconds' duration. Even for any sufficiently short time during which some of this quantity is a water molecule, much of it can't, in all probability, be partitioned into parts which are molecules for this particular time since the dissociations don't occur in step. Thus, the macroscopically significant time is not the sum of a very large number of times when the quantity itself can be partitioned into parts which are molecules.

Unlike phase predicates, however, a substance predicate, applied to a quantity of matter at equilibrium at a time in accordance with the phase rule, is true of that quantity for all subintervals of that time of macroscopic dimension (i.e. at least those of the order of a microsecond and longer). This relative permanence endowed by substance properties distinguishes them from typical phase properties. The restriction means that a macroscopic substance predicate is not applicable to what microscopic predicates are true of only for times shorter than this limit. In particular, what is a water molecule only for such a very short time is not water for that time. The reason for this goes back to the criterion of purity and identification based on the phase rule and relying on general principles of thermodynamics. That itself is not an objection to extending the use of 'water' under specified circumstances to quantities sufficiently small for sufficiently short times when they are water molecules. But what should we say of an immediately succeeding time of the same short duration, when this same quantity is not a water molecule? It is not then water either in virtue of thermodynamic criteria or in virtue of being a water molecule. Should we say that it is water in virtue of having been a water molecule? We wouldn't say that the sum of quantities of hydrogen and oxygen gas produced by electrolytic decomposition of water is water merely because it has been water. But perhaps the context could be elaborated sufficiently to dispel this argument from discontinuity and such small quantities could be reasonably called water. That wouldn't detract from the fact that the substance predicate is standardly applied for

macroscopic times on the basis of macroscopic criteria to macroscopic quantities, in which the microscopic features are smeared out of all recognition.

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