What is water?

Paul Needham

Putnam's writings have established as philosophical orthodoxy the idea that substance kinds are identified by microscopic structure. The precise nature of the claim is difficult to pin down to a concise quotable formulation, however, and seems to rest on assumptions about how chemical kinds, typified by water, are understood by scientists and laymen which have not been clearly stated. Not only have the scientific details been severely rationed. Putnam is too quick on the dots in exemplifying the features forming his stereotypes, given the poor general characterisation offered of the layman's conception. Any attempt to fill out the list soon runs into the problem of discerning how the line is supposedly drawn between ordinary and scientific descriptions. I suggest that microstructure does not play the leading role in individuating chemical kinds that recent discussions presuppose; rather, there is a complexity and variety at the microlevel which is unified only if seen in relation to single macroscopically distinguished kinds. Some aspects of the systematic role macroscopic features of matter play in determining chemical kinds, in particular thermodynamic criteria for sameness of kind, are outlined in section 1. Section 2 addresses the problem of providing a construal of 'water is H_2O' and relating micro- to macrodescriptions.

1. There is an ambiguity in the modern use of the term 'water' which it is important to be clear about. Consider whether ice is water. In one sense, it is not. This is the sense in which water is taken actually to be a liquid – a sense in which 'water' resembles kind terms like 'diamond', 'graphite', 'quartz' and 'steam', which specify a substance as a chemical kind (carbon, silicon dioxide, water) in a particular form (a particular crystalline form, gas) generally known as a *phase* in physical chemistry. In the sense in which ice is water, water is understood as chemical kinds are understood in contemporary science, independent of any particular phase property. The two senses seem to be blurred in the *Shorter Oxford English Dictionary*, which defines water as 'the liquid … which forms the main constituent of seas, lakes, rivers and rain …; it is a compound of hydrogen and oxygen (formula H_2O), and was formerly regarded as one of the four elements'. Although the phase-qualified sense of 'water' as liquid water seems to have been maintained from Aristotle until comparatively recently,[1] it was definitely abandoned with the establishment of the law of constant proportions at the beginning of the eighteenth century. Water was then

characterised in terms of its composition – the proportion of hydrogen to oxygen as indicated by its compositional formula, which eventually came to be written H_2O.

Dalton is renowned for his atomic interpretation of compositional formulas, but few of his contemporaries thought that the mere proportions of the constituent elements necessitated any such move. Considerably more was required to motivate the atomic theory. The gravimetric proportions of hydrogen to oxygen in water are 1:8, and the compositional formula H_2O represents this ratio in accordance with a convention that provides a sense to saying that hydrogen sulphide, with compositional formula H_2S, contains just as much hydrogen as does water, although its composition comprises 1 part by weight of hydrogen to 16 of sulphur.

It soon emerged that composition provides only a necessary condition for sameness of kind. Compounds were discovered standing to one another as isomers – substances with the same composition but different chemical properties and different physical properties such as melting points and densities. The systematisation of these variants led to refinements in the notion of chemical constitution which called for the development of structural formulas. The compositional formula C_2H_6O, for example, is common to ethyl alcohol, C_2H_5OH, and dimethyl ether, $(CH_3)_2O$. (But in the special case of water, which has no isomers, composition suffices to distinguish it from other compounds.) The notion of a structural formula was elaborated throughout the nineteenth century, and today loosely covers a variety of kinds of expression representing various aspects of structure. In the first decades of the twentieth century, variants of substances with all their chemical properties in common (i.e. participating in the same kinds of chemical reaction) but differing in the substitution of an element with an isotopic variant of the same element became well known. Thus, there is heavy water, in which hydrogen is replaced by its isotope deuterium, and there is water in which oxygen with atomic weight 16 is substituted by radioactive oxygen 18. But by this time a different approach to the notion of kind of matter had emerged from classical thermodynamics as developed by Willard Gibbs towards the end of the nineteenth century.

One of Gibbs' most striking results was the phase rule, in which the *number of chemical kinds* actually figures as one of the terms. The rule applies to heterogeneous systems, the homogeneous parts being called

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[1] Joseph Black, whose discovery around 1760 that warming a body doesn't always result in a rise in the body's temperature led him to introduce the notion of latent heat, understood the heating of ice at 0°C, which converts the ice to water at the same temperature, to involve a chemical change of substance by the reaction of ice with caloric to produce water.

phases, over which several substances are distributed. It states that the number of independent variables required to specify the state of a system with f distinct phases, its *variance,* is given by

$$c - f + 2,$$

where c is the number of kinds. The variables at issue cover intensive properties of temperature, pressure and concentration of substances in each phase. The variance is always non-negative for any system which can be sustained at equilibrium, and the higher the variance, the greater the variety of conditions under which the system can sustain c kinds of substance distributed over f phases.

The application of the rule can be illustrated by considering whether solid, liquid and gaseous water can occur together in stable equilibrium. In this situation there are three phases and one component kind, and $1 - 3 + 2 = 0$. Accordingly, the solid, liquid and gas phases of water can all be present in equilibrium, but only under unique circumstances – a specific temperature (0.01°C) and a specific pressure (4.58 mm. of Hg), the so-called triple point of water. When just two phases are present, the system is univariant. For example, water vapour comes to equilibrium with the liquid over a range of temperatures; but for any particular temperature the vapour pressure always has the same value, and cannot vary independently of temperature. For a single phase, say water vapour, the temperature and pressure can vary independently. On the other hand, the phase rule precludes four phases of sulphur – gas, liquid, and the two solid forms rhombic and monoclinic – all being present at equilibrium with one another. This general kind of behaviour is characteristic of a quantity of material comprising a single kind of substance. The specific data – such as the correlation of specific pressures with specific temperatures for the single vapour phase – distinguish one substance from another.

The identification of the number of kinds in a system is not in general as straightforward as the above account would suggest. The derivation of the phase rule takes account of the number of relations between the intensive variables describing the state of each phase when the whole system is at equilibrium. The temperatures of any two spatial parts of the system at equilibrium with one another are equal, as are the pressures and each substance's chemical potential (governing its concentration), giving a total of $c + 2$ variables. These variables are not independent, however, because a thermodynamic relation (the Gibbs-Duhem equation) holds between them for each phase, reducing the number of independent variables to $c - f + 2$, as stated above. But any additional constraint on a particular system that can be described by an equation relating some of these variables and rendering one dependent on the others further reduces the total number of independ-

ent variables, and any application of the phase rule must take this into account.

To illustrate, the industrial production of zinc by the reduction of zinc oxide with carbon, producing carbon monoxide and carbon dioxide, involves the chemical reactions

$$ZnO + C \rightleftharpoons Zn + CO$$
$$2CO \rightleftharpoons C + CO_2.$$
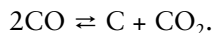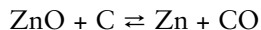
When equilibrium is established between reactants and products, these two processes provide two constraints so that of the five substances involved, only three are independent kinds in the system under consideration. Solid zinc and carbon are immiscible, and therefore constitute two phases. The third, vapour, phase is constituted of CO, CO_2 and zinc vapour (gases are always miscible). This would suggest that the system should be bivariant, having three independent kinds and three phases. In fact, it is univariant, so that at any temperature there is a single, definite pressure and composition of the vapour phase. Only one variable is independent. This is explained by a further relationship between the concentrations of the substances in the vapour phase, all of which derives from the zinc oxide and carbon in the solid phase.

Another of Gibbs' remarkable results, often referred to as 'Gibbs' paradox', provides a criterion of sameness of kind in terms of a definite physical magnitude, unfortunately of a somewhat abstract character, namely the entropy of mixing. The law in question is usually presented as a feature of a mixture of two or more noble gases, the point being that even where no chemical reactions occur (providing an additional source of entropy change), there is still a definite amount of entropy associated with the mixing of different substances depending only on the relative amounts of the substances involved. What is felt to be the paradoxical character of Gibbs' law is expressed in one textbook as follows:

> The application of mathematics to the macroscopic processes of nature usually gives rise to continuous results. Our experience suggests that, as the two diffusing gases become more and more alike, the entropy change due to diffusion should get smaller and smaller, approaching zero as the gases become identical. The fact that this is not the case is known as *Gibbs' paradox*. (Zemansky and Dittman 1981, p. 362)

Quantities of matter which are not miscible in the liquid state but constitute distinct phases are different kinds of substance. An entropy of mixing – traceable in the final analysis to a definite amount of heating upon separation – is otherwise associated with any two quantities of material of

different kinds, no matter how similar. Quantities of deuterium oxide and radioactive water, when mixed with each other or with 'ordinary' water (protium oxide), exhibit the entropy change specified by Gibbs; but no two quantities of 'ordinary' water do so.[2]

In specifying the heat of separation, no method of actually achieving the separation is actually indicated by the law, and a suitable procedure must be determined from case to case. But this doesn't detract from the theoretical significance of the principle, which permeates the macrotheory of substances. The energy and entropy of a system are fundamental thermodynamic magnitudes which are treated as functions of variables specifying, among other things, the amount of each substance kind present in the system. It is only to be expected that this should issue in laws which can be considered to provide criteria for distinguishing substance kinds.

2. What bearing do the thermodynamic criteria of sameness of kind have on the familiar claim that 'water is H_2O'? In order to make any headway, some clarification of the logical form of the claim is needed. The claim is often described as an identity, and written 'water = H_2O'. But how, on that view, are the corresponding terms to be understood? Which thing could water, or the world's water, be? Water is continually being consumed in chemical reactions and created in others. It is combined with carbon dioxide in the photosynthesis of carbohydrates, for example, and produced in the neutralisation of acids by hydroxides and alcohols. Accordingly, some of what is water at one time is not so at another, and some of what isn't is. Delimiting a definite quantity of matter as water therefore requires fixing a time. It is far from clear what could be meant by fixing on what is water at a particular instant, literally conceived, however. It will transpire that, understood as a macroscopic term, 'water' can only be applied to a body for a sizeable interval.

What the other term of the putative identity, 'H_2O', is supposed to denote is even more difficult to glean. It is often taken to denote a single molecule. Questions of the time dimension arise even in this case, although on a different scale of magnitude. It is unclear what a molecular structure is at extremely short intervals of time which, in view of the uncertainty principle, render the 'uncertainty' in its energy very large. In any case, a particular structure of a water molecule frozen by what Eisenberg and Kauzmann (1969: 152) call an instantaneous snapshot (with a notional shutter speed short compared with the periods of vibration) will in general be different from that at another, given that water molecules move, shudder and gyrate.

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[2] Naturally occurring water is a mixture containing proportions of these isotopic variants too small to have any noticeable effect on standard applications of the phase rule.

But before getting too heavily involved in these details, it must be pointed out that a single water molecule can't be identified with a quantity of matter of macroscopic proportions. In fact, a water molecule is not water – it doesn't quench thirst, and can't be said to exhibit a triple point; it can't even be ascribed a temperature. So the single molecule interpretation can't be at issue in the putative identity. The expression 'H_2O' must be understood to stand in a logically coherent relation to 'water', and it is clear from what has just been said that the latter is to be understood in terms of a two-place predicate 'is water' applying to a quantity of matter and a time. 'H_2O' must be understood in corresponding fashion, as a predicate 'is H_2O', however that is then elaborated. Proponents of the view that predicates refer may see in this a relation of property-sameness, though perhaps not a relation of identity. Not everyone shares this view, however, and I don't want to make the discussion dependent on any particular view of predicate ontology. Presumably all will agree that the truth of 'water is H_2O' requires coextension of the predicates, even if this is not sufficient for the property-sameness sought by some. Accordingly, it must at least be clear what the predicates are true of and that they are true of the same (identical) things.

The claim that water is H_2O seems to be regarded in such a way that 'is water' is to be understood on the basis of ordinary, everyday features which are observable and macroscopic – terms often taken to be two ways of saying the same thing – and which stand in contrast to a deep scientific description represented by 'is H_2O'. How is this contrast drawn? There is an unfortunate ambiguity in the modal connotation of 'observable'. The term might be used as Alexander (1985) uses it in distinguishing Locke's primary qualities as observable and secondary qualities as unobservable. A property is observable in this sense if some of its instantiations are observable (by someone appropriately positioned). A stricter use would require any instantiation to be observable. The macroscopic property of being a liquid is observable in the first sense though not in the second, as the following situation illustrates. When small quantities of lead (melting point 327°C) are slowly added to antimony (melting point 631°C) at 300°C,

> All the added lead melts and the molten lead dissolves enough of the solid antimony to bring the liquid to the composition [indicated in the phase diagram]. … [T]he relative amount of liquid present … is quite small, so the liquid may not be visible; nevertheless it is present at equilibrium. (Castellan 1964: 298)

Accepting that macroscopic terms are observable precludes the stronger reading. But the question remains whether the more abstruse notions of energy and entropy, and notions like enthalpy defined in terms of them, are to be excluded by dint of failing even the weaker criterion of observability

or are to be included because they are macroscopic. Observing the body which carries a particular property is not necessarily to observe an instantiation of the property, even though the property is, unlike 'is a molecule', applicable to a clearly visible body. The transformation of ice to water has been observed many times without the associated increase in entropy being noticed.

This prompts the question of whether lawlike features are to be included in the characterisation of being water. Putnam expressly states in his 1992 paper (p. 434) that 'low-level' laws are to be included. Perhaps he has in mind something like the fact that if a particular freezing point, for example, is to be recognised as the characteristic feature of water that it is, then it has to be understood with qualifications adequate to render it a reproducible feature. As Duhem (1982, pp. 165-79) makes very clear, however, recasting everyday truisms into testable claims requires the imposition of a certain conceptual precision which brings yet further laws into the picture, raising the question of the principle on which any delimitation of laws might be based. Is there a way of characterising the distinction between deep and low-level laws which provides a clear criterion for differentiating features appropriate to 'is water' and 'is H_2O'? Where, in particular, does it leave macroscopic features like energy and entropy and their derivatives, which are quite abstract and considerably less easily classified as observable than 'is liquid', as well as featuring in very general laws?

As already remarked, H_2O is the compositional formula of water whose interpretation makes no call on the atomic theory. It should be clear from what has been said that if 'is H_2O' alludes merely to a scientific account, a description in macroscopic terms fits the bill, and no good sense has been given to demoting this as shallow or 'low-level'; it is just not the whole the story about water. Let us put aside the question of how ordinary and scientific descriptions are to be distinguished and consider the idea that it is in virtue of structure at the microscopic level, for the description of which 'is H_2O' goes proxy, that water possesses macroscopic features underlying the 'is water' predicate.

If 'is water' and 'is H_2O' are to be true of the same things, the microstructure interpretation of 'is H_2O' must be to the general effect 'consists of corpuscles of such and such a kind'. As van Brakel (1986, p. 299) has stressed, however, the molecular species in quantities of water are not confined to corpuscles with two hydrogen atoms and one oxygen atom. Water's relatively high freezing and boiling points, in relation to other substances of comparable molecular weight, indicate substantial structure above this level, and there are hydrogen-bonded polymers of the simple monomer molecule. There are also ions derived from these molecular species, such as positively charged hydrogen ions and negatively charged

hydroxyl ions, together with their polymeric forms. The character and amount of these structures varies with the prevailing macroscopic conditions. Moreover, water is not confined to quantities of pure water, but occurs in solutions – homogeneous mixtures distinguished from single substances called compounds. The relative concentrations of these various ionic species differ from solution to solution. (In fact, in a caustic soda solution both the water and the sodium hydroxide are sources of the hydroxyl ions, although there is no saying which are water's. This creates something of a problem for determining what our predicates do and don't apply to, and challenges the basic coextensivity claim; but let us overlook this here.) Although the concentrations of molecular and ionic species remain fixed (on a suitable time scale) under fixed conditions, there is a constant dissociation which is compensated by an appropriate rate of association. These corpuscular species have quite complex internal motions (ranges of quantum states), and their wholesale movements make the intermolecular structure particularly difficult to model in the liquid and vapour states. In view of the sensitivity of the distribution of particular determinate forms of the many determinable features to prevailing conditions, the actual description of the relevant microscopic structure – which must be sufficiently relaxed to accommodate all these variations without including too much – would be a truly daunting task. It would be instructive to enquire about the source of such microstructure descriptions as we do have. But first and foremost, it should be asked why this vast range of microscopic structures is associated with one and the same substance kind, rather than a genus of related substances. I suggest it is because macroscopic criteria determine sameness of substance kind, whose variable microstructure is then made the subject of scientific investigation.

This is one reason why the contention that something which couldn't be distinguished from water by ordinary systematic macroscopic features might nevertheless possess a radically different microstructure which couldn't be incorporated into the variability of water's actual microstructure is altogether implausible. Of course, substances alike in non-systematically applied criteria may well differ radically in microstructure – a cursory glance may fail to distinguish two kinds of substance where half a minute's more careful inspection does the trick. Sometimes we might have to go so far as to measure a boiling point, or ride into the nearest town to find a drop of acid to test for fool's gold. Stubborn cases have involved quantities of matter whose mixed character has proved very difficult to discern. The extreme case is ortho- and parahydrogen; but it is precisely their similarity in microstructure that gives rise to Gibbs' paradox.

A comparison with temperature is apposite. So far from being the average kinetic energy of the constituent corpuscles (a result derived specifically

for ideal gases), the absolute temperature can, under special conditions, even (unlike kinetic energy) be negative (Zemansky and Dittman 1981, pp. 505-14), or ascribed to radiation which doesn't even consist of any sort of corpuscles. Temperature can certainly be related to microstructure, by accounts which vary from one range of temperature to another and from one kind of bearer of temperature to another. What unifies these treatments is the *classical* (thermodynamic) principle that equates temperature with $\partial U/\partial S$ (the rate of change of energy with respect to entropy). This principle is assumed, and not derived, in applications of statistical mechanics.

A macroscopically oriented account of sameness of kind doesn't challenge the claim that quantities of water have some appropriate range of microfeatures under specified conditions. But recognising microproperties is not to favour them as more essential than others. If water is necessarily H_2O, it necessarily has its characteristic density too, characteristically reaching a local maximum at 4°C, it necessarily freezes at 0°C under normal atmospheric pressure, freezing at lower temperatures under higher pressures (in systematic fashion, explaining, for example, the movement of glaciers), and so on for what science counts as water's essential macroscopic features. The distinction between macro- and microfeatures doesn't coincide with accidental and necessary ones.[3]

University of Stockholm
S-106 91 Stockholm, Sweden
Paul.Needham@philosophy.su.se

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