Elements, Compounds, and Other Chemical Kinds

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In this article I assess the problems and prospects of a microstructural approach to chemical substances. Saul Kripke and Hilary Putnam famously claimed that to be gold is to have atomic number 79 and to be water is to be H_2O. I relate the first claim to the concept of element in the history of chemistry, arguing that the reference of element names is determined by atomic number. Compounds are more difficult: water is so complex and heterogeneous at the molecular level that 'water is H_2O' seems false under some interpretations. I sketch a response to this problem.

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1. Introduction. Chemical substances are the central kinds of chemistry, as important to understanding that science as the species concept—if there is just one—is to understanding the biological sciences. They are elements, compounds, or mixtures: elements are just those that have no other chemical substances as components. Here are three claims about elements: in the eighteenth century, long before any direct investigation of atomic structure, chemists used element names with determinate extensions; membership of those extensions was conferred by having atoms with particular nuclear charges; and the chemical facts that make all this so were unknown until the twentieth century, so if they are known now they must have been discovered.

The determinate extensions of 'hydrogen', 'oxygen', and other element names were picked out via the intentions with which the element names were used, for substances that could survive chemical change, be components of other substances, and whose presence could explain a com-

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pound's behavior. The only special thing about 'hydrogen' and 'oxygen' was that they were chemical neologisms, introduced by Antoine Lavoisier in the 1780s. This is relevant because other elements like gold, iron, lead, and sulfur had been known and named since ancient times. If an element's name was used without the 'elemental intentions', then either its extension was to some extent indeterminate, as Joseph LaPorte argues (2004), or it was determined in some other way. I do not know when these intentions first appear, but they seem necessary though not sufficient for the emergence of modern chemistry.

The three claims about elements add up to a strong case for microstructuralism. Microstructuralism about a natural kind is the thesis that membership of that kind is conferred by microstructural properties. Kripke and Putnam advanced microstructuralist claims about biological species (tigers and lemons) and chemical substances (gold and water), but biological microstructuralism seems implausible given the wide microstructural variation within biological species. Perhaps membership of biological kinds is conferred instead by historical or causal relations to particular populations of organisms. Or perhaps, as John Dupré argues (1993), different kind-membership conditions are appropriate to different classificatory interests and modes of biological explanation. Now these arguments—against microstructuralism and for pluralism—are local to biology. Chemistry, I argue, is different: the interests that govern its classifications are more unified, and in most cases membership of its kinds is conferred by microstructural properties.

In Section 2, I give a semantic and historical argument for microstructuralism about the elements: since the late eighteenth century, elements have been named within a framework of modal assumptions that, given the laws governing chemical behavior, pick out nuclear charge as determining the application of the name. Compounds are more difficult: I have no general argument for microstructuralism about them, so instead I will respond to some important criticisms of it by Paul Needham (2000, 2002) and Jaap van Brakel (2000). Perhaps arguments for, or against, microstructuralism about compounds ought to be made case by case. In Section 3, I will discuss one famous philosophical example: water.

2. Elements. In 1787, Lavoisier and others proposed a reformed nomenclature for chemistry, in which the names of compound substances would reflect their elemental composition. Phlogistonists complained that the new nomenclature was theoretically laden, embodying substantial compositional claims, illegitimately embedding the reality of oxygen in the very language of chemistry, and excluding phlogiston, its explanatory role usurped jointly by oxygen and caloric, the matter of heat (see Beretta 1993, Chapter 4). The binomial nomenclature survives in modern chemistry, along with key elements from the list of simple substances in Lavoisier's *Traité Elémentaire de Chimie* (1789, 175–176). What conception of element underlay these innovations? Interestingly, there are two quite distinct conceptions: one explicit and one implicit.

In the preface to the *Traité*, Lavoisier proposed an analytical definition of 'simple substance' to supplant a priori metaphysical speculation about the ultimate principles of which things are made: he undertook to treat substances as simple until 'experiment and observation' prove otherwise (1789, xxiv). While it is widely associated with Lavoisier's name, this definition of element was not original to him. Nor is it what motivated his uses of the names of particular elements like oxygen in chemical explanation. Furthermore, he applied the analytical criterion only patchily. He excluded many substances that had not been decomposed in the laboratory from his list of simple substances: some (like soda and potash) because by chemical analogy he suspected them of being compounds; others because he thought they contained as components one or more of his hypothetical elements (caloric, the ether, the fluoric radical) and, hence, must be compounds (see Hendry 2005, Section 2).

The new compositional nomenclature embodied another, implicit notion of element, which is also at work in Lavoisier's thinking about chemical substances: only this second notion can explain the role of oxygen in Lavoisier's theory of acidity. Lavoisier had noted in the 1770s that air is absorbed in the formation of nitric, sulfuric, and phosphoric acids. By the time of the *Traité* he had concluded that acids are a chemical genus whose characteristic component is oxygen, and whose differentiae are various acidifiable 'principles' like azote (nitrogen), sulfur, and phosphorus. When oxygenated to a higher degree, the principles form stronger acids: compare sulfurous and sulfuric acids, phosphorous and phosphoric acids, and nitrous and nitric acids. In the *Traité* Lavoisier provided a summary table of oxygen's compounds with various other elements (1789, facing page 185). If oxygen can be the common component of a range of different substances, it must be capable of surviving chemical change. If it can bestow acidity on its compounds, it must at least partly determine their behavior. Hence Lavoisier's implicit notion of element, embodied in his use of the names of particular elements in chemical explanation, is the notion of a substance that (i) is a component of other substances, (ii) can survive chemical change, and (iii) whose presence can explain the chemical and physical behavior of its compounds. Oxygen was not unique in being the subject of these assumptions: Lavoisier thought caloric to be the characteristic chemical component of 'aëriform fluids', or gases (1789, 15).

Moving on to the nineteenth century, D. I. Mendeleev made Lavoisier's implicit notion of element quite explicit, distinguishing between the two different notions that we have already seen in use by Lavoisier: on the one hand, there is chlorine the poisonous green gas that F. A. Paneth (1962) called a 'simple substance'; on the other hand is chlorine the component of common salt and hydrogen chloride (Paneth's 'basic substance'). Chlorine the green gas is not present in salt but is used up in its formation. Mendeleev also noted that basic substances, rather than simple substances, occupy the places in the periodic table, because those places are allotted on the basis of properties of the compounds as well as of the free elements (i.e., simple substances). Mendeleev noted the explanatory requirements on basic substances and reasoned that they must carry from their simple substances to their compounds some property that determines their behavior in the different contexts. He identified the property in question as atomic, or elemental, weight (see Hendry 2005, Section 3).

In 1923, the International Union of Pure and Applied Chemistry (IUPAC) proposed to redefine 'element' in the light of isotopy: the existence of atoms with the same atomic number, but different atomic weights (see Kragh 2000, Section 3). Paneth had earlier (in 1916) argued for nuclear charge as the defining property of the elements, pointing out that even though isotopes are not identical in their behavior—there are thermodynamic differences consequent on their different masses—they are chemically *interchangeable*, in the sense that they undergo the same chemical reactions. The redefinition was the subject of prolonged debate: before the fundamental relationship between nuclear charge, electronic structure, and chemical behavior was understood, nuclear charge seemed to some chemists more of a physicists' property, of little relevance to chemistry. Furthermore, the redefinition broke with the idea, handed down from Dalton, that elements are composed of identical atoms. Nor did the discussion end with the IUPAC decision. In the 1930s, when the different isotopes of hydrogen were discovered, Ida Noddack argued that, since they can be separated by electrolysis, protium (^{1}H) and deuterium (^{2}D) are not chemically identical. Now, once it is realized that atoms that were once counted as being of the same element (like ^{35}Cl and ^{37}Cl) have different masses, it is obvious that the 'atomic weights' measured by nineteenth-century chemists like Mendeleev pertain not to single species of atoms but to populations of atoms: chlorine's atomic weight of about 35.5 is a weighted average dominated by ^{35}Cl (76%) and ^{37}Cl (24%). Given that it makes no sense to classify atoms according to the statistical properties of heterogeneous ensembles to which they happen to belong, to argue for the retention of atomic weight as the basis of the periodic table is a radical stance, not a conservative one, requiring wholesale reform of the periodic system. Hence Noddack proposed a system of some 260 isotope-elements (Kragh 2000, 442–443). Ironically, it seems that Mendeleev's periodic table, with its clear presentation of chemical trends and analogies, could be preserved in 1923 only by changing the property that defined each place in it.

Joseph LaPorte (2004, 103–110) puts isotopy to good use in a thought experiment that turns the philosophical lesson of Putnam's 'Twin Earth' on its head. LaPorte considers a group of scientists, trained before the discovery of isotopy, who travel to a planet where heavy water (^2D_2O) fills the rivers and lakes. Observing (among other differences) that Earth fish soon die when placed in the Twin Earth 'water', the scientists conclude that it is a different substance from water. Isotopy is discovered back on Earth while they are away, but the scientists who stayed at home decide that deuterium *is* hydrogen and that heavy water is water. Do the traveling scientists make a mistake? LaPorte argues not: regarding heavy water as falling within the extension of 'water' was a decision that was taken when isotopy was discovered. Prior usage was indeterminate.

Now the differences in behavior between isotopes are subtle and quantitative—thermodynamic and kinetic—rather than gross and qualitative. These differences can be magnified in striking ways and underlie the processes of their separation. For instance, heavy water is mildly toxic because, compared with protium oxide, it slows down various metabolic processes by a factor of 6 or 7. This is enough to kill fish, which cling to life within a narrow band of kinetic viability. The kinetic differences shown by hydrogen's isotopes are far more marked than those for other elements, however, because isotope variations are marginal effects, determined by percentage differences between their atomic weights: adding a neutron to a heavier nucleus makes a smaller proportional difference. In fact, isotope effects diminish rapidly as atomic weight increases. Thus, for instance, reactions involving ^{37}Cl are slowed down only by a modest factor of 1.01 or so with respect to ^{35}Cl. So the isotope effect in hydrogen is an extreme case: a monster, not a paradigm. In other cases, atomic charge is the overwhelming determinant of chemical behavior, and atomic weight is a negligible factor. Now this establishes only that, given the global facts about isotopic variation, IUPAC's decision to count deuterium as hydrogen was by far the most natural one. A response to LaPorte's argument, however, must show more: that prior usage of 'hydrogen' picked out a determinate extension, that membership of the extension was earned by having a particular nuclear charge, and that atomic weight was irrelevant. The scientific realist's view of the matter, that these things were discovered rather than stipulated, is tenable only if this prior determinacy can be established. That argument I will now supply.

Consider again Lavoisier. He had the ability to prepare samples of hydrogen in the laboratory. His preparation methods gathered populations of atoms with a nuclear charge of 1, regardless of their atomic weights. As a matter of fact his atomic populations would have consisted overwhelmingly of ^1H, but that reflected his starting materials, not his methods of preparation. Lavoisier intended element names to refer indifferently to their different states of chemical combination and assumed that the presence of an element in a compound explained the chemical properties of the compound. His theories of acidity and the gaseous state both make these assumptions, about oxygen and caloric respectively. Finally, of the candidate properties that survive chemical change, it is nuclear charge, and not atomic weight, that overwhelmingly determines the chemical behavior of both elements and compounds, via the electronic structure of free and bound atoms. Hence Lavoisier's intentions uniquely pick out sameness of nuclear charge as the important similarity relation for elements, given the laws that govern the causal processes he was interested in explaining. LaPorte's semantic indeterminacy does not arise for the names of the elements because they were given in a semantic context that was structured by implicit modal assumptions about the elements. Of course, 'heavy water' names a compound rather than an element, but the same factors that make isotopic differences irrelevant to element identity apply also to compounds. As long as the same interests govern the extension of compound names, if deuterium is hydrogen then heavy water is water.

3. Compounds. If elemental composition were sufficient to determine chemical-kind membership for compounds, extending my argument for microstructuralism to compounds would be simple, though nontrivial. However, isomerism makes elemental composition insufficient. Isomers are distinct compounds with distinct chemical and physical properties that contain the same elements in the same proportions. For instance, ethanol (CH_3CH_2OH), the active ingredient of whisky, boils at 78.4°C. Methoxymethane (dimethyl ether, CH_3OCH_3) is sometimes used as an aerosol propellant and boils at -24.9°C. Clearly the distinctness of ethanol and methoxymethane as substances must lie in their different molecular structures, but the appeal to structure is vague and problematic in a number of ways, as Needham (2000, 2002) and van Brakel (2000) have pointed out. First, sameness of molecular structure is a vague relation, and this vagueness will be inherited by criteria of sameness of substance that depend on it. Second, some compound substances are heterogeneous at the molecular level: even when pure they are complex mixtures of different microscopic species.

Molecular structure is defined in terms of continuous variables like internuclear distances and angles between bonds. Therefore the similarity of one molecular geometry to another is a vague, and so an intransitive relation. Hence it is not an equivalence relation between molecular structures, dividing them into mutually exclusive and jointly exhaustive extensions for chemical kinds. Interatomic geometry will instead group molecules into vague-bounded, overlapping clusters of similar structures.

Though vague at their edges, these molecular kinds will typically center on the low-energy equilibrium geometries that characterize stable chemical substances. This need not always be so: chemists often give systematic names to unstable species. For instance, carbonium ions are reactive intermediates formed in organic reactions, whose structures and relative stabilities are important in explaining the mechanisms and products of additions to alkenes (see, e.g., Roberts and Caserio 1965, 182–184). The obvious response to this problem of vagueness, then, is to embrace it, for it presents no antinomy. In any case, given the vast numbers of molecules involved, vagueness will inevitably infect the relationship between molecular species and macroscopic substances.

Turning now to molecular heterogeneity, the slogan 'water is H_2O' might tempt one to think of bodies of water as mere assemblages of H_2O molecules. That identification is challenged by the recognition that real water is far from homogeneous at the molecular level (Needham 2000). First, a small but characteristic proportion of the H_2O molecules in any body of pure water—a proportion that varies with temperature—dissociates via the following equilibrium:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-.$$

Second, undissociated H_2O molecules are polar: they display permanent electric dipoles, amounting to partial charges centred on the hydrogen and oxygen nuclei. Strong interactions between the permanent electric dipoles of H_2O molecules greatly increase the melting and boiling points of water in comparison to the hydrides of other elements in its group (H_2S, H_2Se, and H_2Te). The polarity also gives rise to oligomolecular species in which H_2O molecules are linked by hydrogen bonds between centers of opposite partial charge. These polymeric species are similar in structure to ice and affect water's physical properties, like its viscosity, right up to its boiling point. In short, macroscopic bodies of water are complex and dynamic congeries of different molecular species, in which there is a constant dissociation of individual molecules, reassociation of ions, and formation, growth, and dissociation of oligomers. Being H_2O, if understood as a molecular condition, cannot capture the molecular complexity of water.

One might defend the identification of bodies of water with mere assemblages of H_2O molecules by regarding the ions and oligomers as something other than water, natural impurities that arise from chemical interactions between H_2O molecules. On this view, however, bodies of water have a short, and necessarily impure, existence. What we thought was a persisting sample of water we now see as a series of fleeting existences, causally connected. Leaving aside that unsavory consequence, it is quite unnatural to view the ions and oligomers as impurities. The transport properties of H_3O^+ and OH^- ions are responsible for the electrical conductivity of water, so if they are impurities in water then what is normally called the electrical conductivity of water (and measured as such) is not a property of *water*, but of an aqueous solution of its ionic dissociation products. Conversely, if the electrical conductivity is a property of the water, the dissociation products must be part of the water. The transport story is complex: hydrated protons display anomalously high mobility in water because protons themselves need not move very far through the liquid. Instead there is a coordinated process of structural diffusion (the Grotthus mechanism). A proton migrates from one H_2O molecule to its neighbor, which releases a proton to *its* neighbor, and so on, so that the excess positive charge of hydronium ions is transported through the water, but not the ions. This transport mechanism makes it even less plausible to view the protons as anything but integral parts of the water and of the mechanism underlying its electrical conductivity. Now turn to the oligomers: these are similar in structure to ice (one might regard them as microscopic nascent ice crystals). If the formation of ice is to be a phase change rather than a change of chemical substance, the oligomers must be water too. Ice *is* water in the chemists' phase-unqualified usage of 'water' in which one can ask how much water there is on Mars. Hence the oligomers are water. I conclude then that samples of water are not mere assemblages of H_2O molecules. But then what are they?

Needham (2000) and van Brakel (2000) see bodies of water as macroscopic objects whose microstructure may be investigated empirically. The microstructure may even explain some properties of water, but according to Needham and van Brakel, it does not follow from this that water's microstructure is what makes it water. I agree that water is a macroscopic substance and that the molecular complexity issue shows that samples of water are complex and dynamic entities, heterogeneous at the molecular level, and relatively independent of the water molecules they contain. Nevertheless, being water should be understood in terms of composition by H_2O molecules. After all, how else can we make some water except by creating, or bringing together, some H_2O molecules? We must be careful, however, in how we interpret 'composition'. Composite objects may bear different relations to their parts. Some composites are mere assemblages. Even some bodies of water are mere assemblages: consider, for instance, a very diffuse cloud of H_2O molecules strung out in empty space between two distant stars. In other cases, the composition involves dynamic causal interaction. Consider some H_2O molecules brought together at standard temperature and pressure, interacting spontaneously. They form liquid water, and as we have seen, some of them dissociate, new ones form, and so on. Some H_2O molecules are 'used up' in the process, like the eggs in a cake. Now distinguish between two kinds of part: *com-*

ponents persist in the composite, while *ingredients* need not persist—they may be used up in forming the composite. Components and ingredients participate in the structure of a composite in different ways: components by persisting, ingredients by offering their parts. Water, then, is the substance that has H_2O molecules as its ingredients, though many of them will in fact live on in the water. Turning back to the elements for a moment, it is easy to see the relationship between water and its constituent elements, hydrogen and oxygen. Considered as simple substances, hydrogen and oxygen are ingredients. As basic substances they are components, their persistence underwritten by the continued existence of the nuclei and their charges.

We may allow that composition be reflexive, so that single H_2O molecules count as water. For Needham and van Brakel, only macroscopic bodies of stuff can be water, because only macroscopic bodies can bear the thermodynamic properties—melting point, boiling point, and so on—that are normally used to identify water. However, even if thermodynamic properties are used to identify water, it does not follow that they are what makes it water, and when we ask, for instance, how much of the human body is water, the answer is independent of the display of any thermodynamic properties in vivo. If so, the possession of macroscopic properties cannot be necessary. It also seems natural for the extension of 'water' to include individual H_2O molecules, because general claims about water ought to apply to them. If they do count as water, individual H_2O molecules are the smallest items that can qualify as water on their own account. Hydroxyl ions and protons, in contrast, qualify as water only as part of a larger body.

My proposal, then, is that water is the substance formed by bringing together H_2O molecules and allowing them to interact spontaneously. One constraint should be emphasized, however. Consider the following decay chain, beginning when ^{16}O absorbs two protons:

$$^{1}H_2{}^{16}O \rightarrow {}^{18}Ne \rightarrow {}^{18}F \rightarrow {}^{18}O.$$

This reaction seems to be a theoretical possibility: Coulombic repulsion between the protons and the oxygen nucleus normally provides a formidable energy barrier, but resonances between excited states of $^{1}H_2{}^{16}O$ and ^{18}Ne allow for nonvanishing transition probabilities. Experiments to see whether the theoretical possibility is realized are inconclusive (see Belyaev et al. 2001), but the mere possibility is, at first glance, a problem for my account of water's identity if it is to have any counternomic robustness. The exotic isotope ^{18}Ne is formed from an H_2O molecule through a spontaneous internal interaction. Is it water, then, on my account? No: sameness of elemental composition provides a necessary, though insufficient, condition for sameness of substance. It is necessary because elements survive in their compounds, their survival underwritten by the survival of the nuclei, as we saw in Section 2. It is insufficient because isomers exist: different substances with the same elemental composition. The ^{18}Ne is not water, then, because the *basic* substances hydrogen and oxygen are used up in making it. The elemental composition condition on substance identity requires that elements be components of substances, not mere ingredients.

I have spent a lot of time on one case: water. This is not only because Putnam chose it as a widely cited example but also because, as Needham and van Brakel make clear, its molecular heterogeneity poses important questions to the microstructuralist. Also, an informed debate can proceed because extremely detailed information on the structure of water has been gathered (Franks 1972–1982), perhaps because of the ubiquity and importance of water as a solvent. I have attempted to square the thought that the H_2O molecule is characteristic of water with the fact that samples of water survive the destruction of individual H_2O molecules. My strategy has been to focus on dynamic composition, that is, how samples of water are brought into being. My proposal may be too broad: I have placed no limits on what proportion of the characteristic molecules must survive. Maybe an ad hoc restriction is required. Alternatively, there may be another way of identifying the characteristic molecule that does not rely on dynamic composition.

Other compound substances present fewer problems to the microstructuralist. Some are simply more uniform as collections of molecules, while others are typically encountered as components of mixtures, rather than as (relatively) pure macroscopic samples. In either case there is less opportunity for the extensions of the substance terms to come apart from the extensions of the names of their characteristic molecular species.

4. Conclusion. The microstructuralist case for the elements seems strong. A single microstructural property, nuclear charge, persists through the various manifestations of an element and is central to explaining the behavior that historical figures like Lavoisier used to classify substances and then name them. Compounds, as we have seen, are more problematic and complex, so that microstructuralism about compounds will need to be assessed case by case, and water is only one. I have two further comments to make about the scope of the microstructuralist claim.

First, chemistry names kinds at different mereological and logical levels. Apart from individual compounds and substances, it names kinds of atoms, ions, molecules, elements, and compounds, as we have seen, and also higher kinds like metals and acids. Microstructuralism clearly fails for one higher kind, the acids. As Ian Hacking (1983, 84–85) and Kyle Stanford and Philip Kitcher (2000, Section V) point out, no microstructural feature unites the acids and the bases; instead there has been a succession of definitions of acidity that do not corefer, though they do agree on certain core cases. Hacking is right to argue that the question, "Is it an acid?" cannot be answered without qualification. We can ask, 'Is it a Lewis acid?' or, 'Is it a Brønsted-Lowry acid?' and so on, answering to nothing deeper than relevant definitions. While this discontinuity is an interesting phenomenon and shows that not all kind terms can be understood in the same way, it does not reflect on other chemical kinds. When speaking of elements, chemists do not need to distinguish Lavoisier-oxygen from Dalton-oxygen, Mendeleev-oxygen, or IUPAC-oxygen. There is just oxygen, and a history of hypotheses about what characterizes the substance. These hypotheses *do* answer to something deeper: oxygen. The existence of syndrome kinds is no refutation of microstructural accounts of the elements.

What about 'water' and 'gold'? Remember that 'oxygen' was a special case, an antiphlogistic neologism. In contrast, 'water' and 'gold' were used independently of chemistry, which brings us to a second scope issue: discipline specificity. My argument concerning the elements relies on the presence of modal intentions that are characteristic of the epistemic interests of chemistry. Many substance terms are used in contexts that are not governed by these interests. It is well known that the extension of 'jade' is not determined by microstructural similarities alone but also by various manifest properties (e.g., LaPorte 2004, 100). That may be so, but then the term does not name a *chemical* substance. This is not a question-begging move but a substantial claim. The classificatory practices of a scientific discipline reflect its particular theoretical and explanatory interests. In chemical company, I bet that every chemist will disambiguate 'jade' between jadeite and nephrite.

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