Entropy and Chemical Substance

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In this essay I critically examine the role of entropy of mixing in articulating a macroscopic criterion for the sameness and difference of chemical substances. Consider three cases of mixing in which entropy change occurs: isotopic variants, spin isomers, and populations of atoms in different orthogonal quantum states. Using these cases I argue that entropy of mixing tracks differences between physical states, differences that may or may not correspond to a difference of substance. It does not provide a criterion for the sameness and difference of substance that is appropriate to chemistry.

1. Introduction. Since the 1970s it has been widely assumed that the identity of a chemical substance is determined by microstructural properties such as nuclear charge and molecular structure. However, the arguments for microstructuralism presented by Kripke and Putnam in the 1970s have been criticized by philosophers of chemistry on the grounds that they are so lacking in chemical detail that it is difficult to see how they work or what they were supposed to establish (see Needham 2000, 2002, 2010c; van Brakel 2000). Furthermore, there are genuine difficulties for microstructuralism even when it is developed in further detail (for articulation and defense of microstructuralism, see Hendry [2006, 2008, forthcoming]).

Now a balanced debate about microstructuralism requires fully articulated alternatives. What, if not nuclear charge and molecular structure, determines the identity of substances? Opponents of microstructuralism have canvassed two different kinds of approach, drawing on the aims and interests of chemistry as a science and on thermodynamics, respectively. Jaap van Brakel (2000, sec. 3.1) presents chemistry as a "science of stuffs," which, by manipulating and transforming macroscopic samples of substances, investigates their location in a "chemical space" whose coordi-

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nates are dispositional chemical properties. Though of considerable interest, this position has not so far been developed much beyond its initial metaphor, and it is correspondingly difficult to assess. In any case, don't the aims and interests of chemistry lead us back to the microstructural properties in terms of which the discipline explains its central phenomena and differentiates chemical substances? (See Hendry 2006.) The topic of this essay, however, is the thermodynamic perspective on chemical substance. One way to motivate this conception is to focus on substances as separable components of mixtures (see Ostwald 1904). More generally, one might begin with the thought that the thermodynamic behavior of a system is dependent on the number of distinct chemical substances present in it. Metaphorically speaking, nature provides a criterion for when a substance is pure rather than mixed. This, in turn, implies a criterion for sameness and difference for pure substances: if two samples of the same pure substance are mixed, the result will behave as a pure substance; the result of mixing two different substances will behave as a mixture. Given this general criterion, the philosopher of chemistry may then read individual relations of sameness and difference between substances off their behavior when mixed. This, as I understand it, is the general line of thought behind a number of papers by Paul Needham (see Needham [2010a, 2010b] and references therein). In this essay I will investigate one aspect of the thermodynamic conception, entropy of mixing. It seems reasonable that a macroscopic conception of substance should meet two general requirements. First, it should be appropriate to the aims and interests of chemistry. Does it match the kind of compositional thinking that has served chemistry through its development from the eighteenth century to the present day? A criterion may be revisionary to some extent, perhaps requiring us to differentiate between substances we had hitherto regarded as the same. The entropy criterion does do this, as we shall see. But wholesale revision will raise the question of whether the criterion is appropriate not to chemistry but to some other systematic way of thinking about substances. Second, since the thermodynamic conception of chemical substance is motivated by the need for a macroscopic alternative to microstructuralism, it should make no implicit appeal to microstructural information. I will argue that entropy of mixing cannot satisfy both of these requirements.

2. Thermodynamics and Chemical Substance. Textbooks on classical thermodynamics sometimes introduce the theory as describing the physical state of a system without making any assumptions concerning its microscopic structure (see, for instance, Zemansky 1957, 1–3; Denbigh 1966, 3; Vemulapalli 2010). In fact, the thermodynamic behavior of a system depends in a number of ways on the number of substances or components present in it, three of which I consider below. Each of these may give rise

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to a macroscopic criterion of sameness and difference of substance. I leave aside the question of the mutual consistency of the various criteria.

Composition over Phase Change. The practice of separating substances by distillation relies on the fact that a mixture and its vapor typically differ in composition, while a pure substance has the same constitution as its vapor. In distillation, the vapor is collected and cooled, providing a liquid that is enriched in one component. This distillate can successively be redistilled, purifying the relevant component to whatever degree is required. Constancy of composition over phase change might seem to provide a criterion for distinguishing pure substances from mixtures, but an immediate problem concerns azeotropes, which are mixtures of different compounds (like water and ethanol, or water and hydrogen chloride) that, under certain conditions, can be distilled without affecting their composition. One might regard azeotropes as single substances (i.e., compounds); presumably they would be secondary compounds of their components, much as ammonium chloride (NH_4Cl) is a compound of ammonia and hydrogen chloride, but this is not how they are regarded by chemists (see Moore 1963, 140). Arguing for a thermodynamic conception of substance, Ostwald (1904, 514–16) attempted to distinguish between azeotropes and compounds proper on the grounds that azeotrope composition varies with pressure. In fact, altering the pressure at which distillation occurs is one way to separate the components. In this respect azeotropes are more like solutions and other mixtures. The composition of a saturated solution of salt in water, for instance, depends on temperature. In contrast, the composition of most compounds is constant within the range of physical conditions in which they exist. But why does variable composition disqualify an azeotrope from being a compound? Why not regard each compositional ratio as a distinct substance, yielding a whole class of related compounds, each existing within its own (narrowly defined) range of physical conditions? Interestingly, during the first half of the nineteenth century there was an extended debate over whether compounds must have a composition that is fixed and independent of physical conditions, because a range of substances (Berthollides) display variable composition, and not all could be regarded as solutions or mixtures (see Needham 2008, 67–68; 2010c). Constancy of composition over phase transitions therefore seems to fail as a criterion for being a pure substance because it requires appeal to an independent and contentious criterion, one that, moreover, does not clearly disqualify azeotropes.

The Phase Rule. Gibbs' spookily elegant and abstract equation relates the number of components (C) in a multiphase system to the number of phases (P) present in it, and its variance (F), which is the number of in-

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dependent physical variables required to characterize the thermodynamic state of the system:

$$F = C - P + 2.$$

Does the phase rule provide a criterion of sameness and difference for substances? The difficulty is that "components" cannot simply be equated with chemical substances, and in some systems it is a matter of some delicacy how to map one onto the other so as to preserve the truth of the phase rule: Needham (2010a, 2010b) discusses the three-component system of calcium carbonate ($CaCO_3$), carbon dioxide (CO_2), and calcium oxide (CaO). Perhaps the phase rule itself does not tell us how many substances are present in a system but only once a case-by-case matching of phase-rule components to chemical substances has been achieved. If so, then the phase rule itself does not offer a criterion for distinguishing substances and mixtures but only a series of relationships upon which we can impose a carefully constructed interpretation that does so. The question is whether or not such an interpretation amounts to a bookkeeping exercise rather than an autonomous conception of substance.

Entropy of Isothermal Mixing. Whenever samples of two distinct substances in thermal equilibrium are allowed to mix, there is an increase in entropy. In contrast, samples of the very same substance generate no entropy change on isothermal mixing. Since entropy change is described within classical thermodynamics without any reference to microscopic structure, such entropic relations seem to offer a macroscopic criterion for the individuation of chemical substances. In the next two sections I will critically examine this criterion.

3. Entropy of Mixing. Suppose that a number of ideal gases in thermal equilibrium are contained in a series of vessels connected by valves. The valves are opened and the gases allowed to mix. The gases being ideal, there is no interaction between their particles, and so the change in entropy is entirely due to the expansion of each gas into the spaces occupied by the other gases. The total entropy change ΔS_{mix} is just the sum of the change in the partial entropy for each gas:

$$\Delta S_{\text{mix}} = -R \Sigma n_i \ln x_i,$$

where n_i is the number of moles of the ith gas, x_i its mole fraction, R the gas constant.[1]

Where one mole each of two gases mix (i.e., when $n_1 = n_2 = 1$ and $x_1 = x_2 = 1/2$), the formula becomes

1. See Zemansky (1957), 407–8. Denbigh and Denbigh (1985, app. 4.1) apply this also to liquid and solid solutions, provided the ideality assumption holds.

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$$\Delta S_{\text{mix}} = 2R \ln 2.$$

One odd feature of the entropy of mixing is that it is independent of the degree of similarity or dissimilarity. As Denbigh and Denbigh put it: "What is so striking is that, as the two components are made more and more similar, the entropy of mixing *remains constant* at the value $2R \ln 2$. For instance, the entropy of mixing of ortho- and para-hydrogen, which differ from each other only in regard to their nuclear spins, is apparently no smaller than is the entropy of mixing of, say, helium and carbon dioxide" (Denbigh and Denbigh 1985, 76).

A second odd feature is that the entropy change vanishes when the two gases are exactly alike, because the mole fraction is then unity. Together, these two odd features generate what has come to be known as "Gibbs' paradox."

Before we go on to examine the criterion of sameness and difference of substance afforded by entropy of mixing, it is worth considering two provisos. The first concerns the assumption of ideality. The derivation of the expression for entropy of mixing assumes that there is no interaction between the components. But real atoms and molecules do interact, and these interactions will affect the thermodynamic behavior of the system significantly. Does this not mean the entropic criterion has no real application? No. First, the idealization is justified if we wish to consider just that part of the change in thermodynamic state that arises from the expansion of each component into the space occupied by the other. Second, the step change that gives rise to Gibbs' paradox, and therefore the criterion of sameness and difference for substances, remains even if intermolecular interactions are taken into account. When identical gases mix, internal interactions before and after mixing are equal and make no contribution to the entropy change.

The second proviso concerns reversibility. As Denbigh and Denbigh put it:

> Any entropy change $\Delta S (= S_2 - S_1)$ between assigned states 1 and 2 of a system is not directly observable in itself but is a measure of the *disposition* of the system to give rise to a *maximal* heat effect in an external heat reservoir. . . . Thus, whereas in a reversible process the entropy change of the environment is equal in magnitude and opposite in sign to that of the system, in an irreversible process this equality no longer holds; there is a net entropy creation which yet may be unobservable externally. (1985, 78)

In short, the "theoretical" entropy of mixing ($2R \ln 2$) is an upper bound, like the Carnot efficiency of a heat engine. The *actual* heat effect on an external reservoir will be lower. The theoretical entropy is realized only

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when the mixing is achieved via reversible processes, but the reversal of mixing is separation, and the more alike are the two gases being mixed, the more difficult it would be to separate them. Thus, the more alike the two gases being mixed, the greater the difference between the theoretical entropy and the realizable external heat effect. This, essentially, is Denbigh and Denbigh's solution to Gibbs' paradox: although the theoretical entropy change is a step function of the number of different gases being mixed, the physically realizable entropy of mixing decreases continuously as the gases become more alike.[2]

4. Critical Examination: Four Cases of Mixing. So, does entropy of mixing provide a self-contained macroscopic criterion for sameness of substance? On the positive side, the relation defined by zero entropy of isothermal mixing would appear to be a well-behaved similarity relation: it is reflexive, symmetrical, and transitive, and so constitutes an equivalence relation on substances. This gives it an advantage over molecular structure, the standard definiens of substance identity for microstructuralists: a molecule's geometry is defined in terms of continuously varying quantities, like bond lengths and bond angles, so that the similarity of one molecular geometry to another is a vague, and so intransitive, relation and so must fail to be an equivalence relation.[3] On the negative side, entropy fails to offer a self-contained macroscopic criterion that is consistent with the spirit and practice of modern chemical classification. My argument for this involves examination of three "hard cases" of mixing that give rise to entropy change: isotopic variants, spin isomers, and populations of atoms in different quantum states. I also consider a fourth case, nonisothermal mixing, as a contrast whose significance will become clear.

Case 1. Isotopic Variants. Protium (^{1}H) and deuterium (^{2}D) are isotopes of hydrogen, differing in their mass but alike in their nuclear charges. Although there were clear indications of its existence earlier, deuterium was first isolated in 1932, the separation using the differential rates at which ^1H_2O and ^2D_2O are electrolyzed (see Farkas 1935, 115–17). Mixing protium and deuterium involves a positive entropy change, so the entropy criterion counts them as distinct substances, as it does the different isotopes of any element. The same applies to isotopic variants of compounds. Thus, although water is overwhelmingly composed of $^1H_2{}^{16}O$, it typically

2. See Denbigh and Redhead (1989) for a detailed mathematical treatment.

3. One microstructuralist response is to embrace the vagueness (see Hendry 2006). Another is to regard a molecule's structure as defined by its bond topology rather than its geometry.

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contains traces of other isotopic variants and so must be counted as a mixture of several substances on the entropic criterion. As Needham puts it, "Lavoisier thought he had settled the composition of water. But in 1932 Harold Urey showed that what Lavoisier took to be a single substance was a mixture" (2008, 73).

In 1923, following the discovery of isotopy among heavier elements (but before the discovery of deuterium itself), the International Union of Pure and Applied Chemistry (IUPAC) defined elements—and so the extensions of their names—in terms of nuclear charge (see Aston et al. 1923). Hence, under standard chemical nomenclature protium and deuterium both fall within the extension of "hydrogen." Needham (2008, 66) describes the adoption by IUPAC of the coarser-grained classification as a "convention" preserving the periodic table of the elements, and the unity of explanation that comes from regarding isotopes as chemically interchangeable, but this seems too thin a description of the decision. There was a principled discussion among chemists as to the similarities and differences between isotopes (see van der Vet 1979; Kragh 2000), and recognition that, as used by earlier chemists such as Lavoisier and Mendeleev, the extension of element names like "hydrogen," "oxygen," and "chlorine" encompassed heterogeneous populations of atoms that had a range of atomic weights but were alike in their nuclear charge (see Hendry 2006). It therefore seems more accurate to say that what IUPAC decided was to continue this earlier usage while making explicit the determinable property that had always governed the identity of elements. The finer-grained classification offered by the entropy criterion, and the possibility of separating isotopic variants, does show that there are genuine differences among the atomic populations that characterize each element, but this is to recognize a criterion of sameness and difference that was not part of the intellectual context that informed earlier thinking about the elements.

Case 2. Spin Isomers. Ortho-hydrogen (o-H_2) and para-hydrogen (p-H_2) are spin isomers, molecules that differ in respect of the alignment of their nuclear spins: in o-H_2 the spins are parallel, while in p-H_2 they are antiparallel. At standard temperature and pressure, o-H_2 and p-H_2 coexist in a ratio of approximately 3 : 1, while at absolute zero, the equilibrium distribution is 100% p-H_2. However, the activation energy for the transition between the two forms is significant, so liquid hydrogen can be "locked" into a nonequilibrium proportion of the higher-energy ortho form. Since the transition from o-H_2 to p-H_2 is exothermic, the spontaneous (although slow) transition to the low-temperature equilibrium gives rise to heating and the loss of significant amounts of liquid H_2 by evaporation. This can be addressed by catalyzing the transition on cooling.

How does the entropy criterion apply to o-H_2 and p-H_2? Since they

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display a positive entropy of mixing, it seems that they should be counted as distinct substances. Now it is true that the two species interconvert, and one of them, o-H_2, cannot be obtained pure, but this is true of many distinct substances that exist in chemical equilibrium with each other. If one wished to regard o-H_2 and p-H_2 instead as two forms of the same substance, differentiated by their physical states, some principled reason for doing so will need to be identified, one that is consistent with the motivation of the entropy criterion to provide a macroscopic perspective on substance identity. I will consider candidate reasons in the next section, when I discuss the hard cases together.

Case 3. Identical Atoms in Orthogonal Quantum States. Consider one mole each of two populations of atoms that are identical except that they are in different, though degenerate, quantum states ϕ and ψ. If $\alpha = \langle \phi \mid \psi \rangle$ (i.e., α is the "overlap" between ϕ and ψ), the entropy of mixing will be:[4]

$$\Delta S_{\text{mix}}/R = 2\ln 2 - (1+\alpha)\ln(1+\alpha) - (1-\alpha)\ln(1-\alpha).$$

Note that the entropy change on mixing appears to depend continuously on α,[5] and

$$\Delta S_{\text{mix}} = 0 \text{ when } \alpha = 1,$$

$$= 2R \ln 2 \text{ when } \alpha = 0.$$

If the criterion of sameness of substance is that the entropy of mixing is zero, then populations of atoms in orthogonal quantum states, like the different streams of silver atoms in a Stern-Gerlach experiment, are different substances. This, of course, is counterintuitive: surely the recombination of the two Stern-Gerlach streams is a case of mixing the same substance (silver) in different physical states. The question once again is, what principled reasons are there for saying that, drawing only on macroscopic information?

Case 4. Nonisothermal Mixing of Identical Gases. If two samples of hydrogen at different temperatures are allowed to mix, there is also an increase in the overall entropy. They are not, of course, counted as separate substances by the entropy criterion, but that is only because the criterion is restricted explicitly to isothermal mixing. It is perfectly natural, however, to say that the two samples are just the same substance in different physical states.

4. See Denbigh and Denbigh (1985, 84–85), and references therein, the locus classicus being von Neumann (1955).

5. Although see Dieks and van Dijk (1988), who argue that the entropy of mixing is not well defined for nonorthogonal states.

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How do these cases ground an objection to the entropic criterion? Suppose we admit case 1 as an instance of the mixing of different substances. In contrast, case 4 clearly involves mixing the same substance in different states. But cases 2 and 3 are more like case 4 than they are case 1. Entropy of mixing seems to track distinctions between different states rather than different substances and so should be rejected as a criterion of sameness and difference of chemical substance. In the next section I will consider three responses to these cases.

5. Responses to the Hard Cases. We must admit that protium and deuterium are distinct substances, as the entropy criterion requires, though not in quite the same sense of "substance" that informed the development of chemistry from the late eighteenth century. Case 4, by assumption, is not a case of distinct substances mixing, because the entropy change is due to the relaxation of thermal disequilibrium. The hard cases are cases 2 and 3. If one follows the entropy criterion in counting them as different substances (biting the bullet), then the question is why case 4 is different. If cases 2 and 3 are not counted as different substances, some explanation is required of why not (I will consider two such attempts): what principled difference is there between cases 1 and 4, and how does this distinction apply to cases 2 and 3?

5.1. Bullet Biting. Taking inspiration from Needham's acceptance that isotopic variants are different substances (see above), one might simply reject the intuitions that cases 2 and 3 involve the mixing of samples of the same substance in different physical states, embracing the entropic criterion's verdict that cases 1–3 are all cases of substantial difference.[6] There are two objections to this stance. First, one would lose the sense that chemical substances are continuants whose physical state may change. A difference in any physical quantity apart from temperature now seems to constitute a difference of substance, if mixing samples with different values of this quantity gives rise to a positive entropy change. It is simply unclear what relevance such a criterion for the sameness and difference of substances has for chemistry, or what light it could shed upon chemical thinking. Second, the exception for temperature is unmotivated. Why, apart from fiat, does a difference in temperature not constitute a difference of substance?

5.2. Equilibrium. One important difference between cases 1 and 4 is

6. I do not wish to imply that Needham accepts cases 2 and 3 as cases of substantial difference. I merely wish to model the "bullet-biting" response on his approach to isotopic variants.

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that in case 4, the entropy change arises from the relaxation of thermal disequilibrium, while in case 1 it arises from the relaxation of chemical disequilibrium. One might then seek to defend the entropy criterion by saying that two kinds of matter constitute different substances only if, when mixed isothermally, there is an overall entropy change, and this entropy change arises from the relaxation of chemical disequilibrium. But what is chemical equilibrium? In discussing equilibrium generally, textbooks of thermodynamics tend to appeal to the idea of a system lacking a disposition to undergo change. But what is "change"? Presumably, it is when the state at some time is replaced by a different state at some later time. Put this way, the notion of a change already seems to presuppose some idea of sameness and difference. Consider Zemansky, who first introduces mechanical equilibrium as the kind of state in which there is no "unbalanced force in the interior of a system" (Zemansky 1957, 24). He then characterizes chemical equilibrium as follows: "When a system in mechanical equilibrium does not tend to undergo a spontaneous change of internal structure, such as a chemical reaction, or a transfer of matter from one part of the system to another, such as diffusion or solution, however slow, then it is said to be in a state of *chemical equilibrium*. A system not in chemical equilibrium undergoes a change of state that, in some cases, is exceedingly slow. The change ceases when chemical equilibrium is reached" (1957, 24).

Now apply this to the mixing of gases. Suppose we have two identical samples of gas at the same temperature and pressure in two vessels linked by a valve. In fact, some diffusion tends to occur when the valve is opened: some of the gas that was in one vessel will end up in the other vessel. Does this mean that the system overall is not at chemical equilibrium at the instant the valve is opened? No, because the diffusion of sample A into vessel B—which is of course balanced by some of sample B moving into vessel A—does not count as a "spontaneous change of internal structure" because the two gases are identical. Now suppose we have samples of two different gases (again at the same temperature and pressure) in two vessels linked by a valve. At the instant the valve is opened, before any mixing has occurred, the system is not in chemical equilibrium because the diffusion of the two samples through the valve *does* constitute a "spontaneous change of internal structure" in the system. But that change consists precisely in the difference between the two gases. The only difference between the two cases is that in the first the substances being mixed are identical, while in the second they are different. The notion of chemical equilibrium already seems to presuppose a criterion of sameness and difference of substance. Hence, it cannot be used to explicate that notion in a noncircular way.

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5.3. Mechanisms of Relaxation. Consider another important difference between case 1 (isotopic variants) and case 4 (nonisothermal mixing). This requires relaxing the ideality assumption, that is, the assumption that the gases do not interact on mixing (recall that relaxing this assumption does not affect the "step change" underlying Gibbs' paradox and the entropic criterion). In case 1 the nonequilibrium state just prior to mixing relaxes into equilibrium just by intermingling the two samples. None of the protium becomes deuterium, or vice versa, or changes in any other way with regard to the properties that differentiate the two samples. In case 4, in contrast, the system reaches thermal equilibrium via two processes: the hot gas and the cool gas intermingle, but the two bodies of matter also exchange energy, the hot stuff becoming cooler, the cool stuff warmer. This is a salient difference if we wish to regard substances as continuants that are capable of surviving changes to their (nonessential) properties. How does this apply to case 2? In this respect the mixing of *o*-H_2 and *p*-H_2 is closer to nonisothermal mixing: suppose we had pure samples of *p*-H_2 and (*per impossibile*) *o*-H_2, and allowed them to mix. Not only would the mingling occur but some of the *p*-H_2 would become *o*-H_2 (or vice versa, depending on the temperature). The same applies to case 3: as the two streams of silver atoms mix, they will not simply be juxtaposed but will interact in ways that alter their spin states. Hence, one might add the following modification to the entropy criterion: two bodies of matter are different substances if, and only if, they undergo a positive entropy change on isothermal mixing and the two-sample system approaches equilibrium via a mechanism in which there is no change in the individual samples in respect of the properties that differentiate them. With this proviso, the entropy criterion seems defensible, but mechanisms of relaxation seem to be a paradigmatically microstructural consideration, so adding the proviso means that the entropy criterion can no longer be part of a purely macroscopic conception of the sameness and difference of substance.

6. Conclusion. I conclude that there are too many cases of nonzero entropy of mixing for it to provide a criterion for difference of chemical substance. In the case of isotopic variance we saw that entropy marks finer distinctions among substances than were relevant to the eighteenth-century discoverers of the elements, and in 1923 IUPAC considered and rejected an account of the identity of the elements that would have been coextensive with the entropy criterion. Cases 2 and 3 also demonstrate that samples of the same substance in different physical states may display a positive entropy of isothermal mixing, so that one is faced with a choice of either (i) radically revising informed chemical judgment as to which physical differences constitute a difference of chemical substance or (ii)

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providing some further criterion for distinguishing among the hard cases. Since strategy ii appeals to microstructural considerations, entropy of mixing does not provide a criterion for the sameness and difference of substance that is both appropriate to chemistry and independent of microstructure.

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