Acidity: The Persistence of the Everyday in the Scientific

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Acidity provides an interesting example of an everyday concept that developed fully into a scientific one; it is one of the oldest concepts in chemistry and remains an important one. However, up to now there has been no unity to it. Currently two standard theoretical definitions coexist (Brønsted and Lowry's and Lewis's); the standard laboratory measure of acidity, namely the pH, only corresponds directly to the Brønsted-Lowry concept. The lasting identity of the acidity concept in modern chemistry is based on the persistence of the quotidian concept. This is suggestive for considerations of other scientific concepts.

1. The Long and Winding History of the Acidity Concept. Acidity is one of the oldest and most important concepts in chemistry. It was known at the everyday level as soon as people produced vinegar, and sour taste has been associated with acidity ever since then. Before the arrival of the so-called mineral acids (sulfuric, hydrochloric, and nitric) through the work of alchemists in the middle ages,[1] vinegar was the archetypal acid. This early centrality of vinegar is inscribed in the name of its active chemical ingredient, acetic acid, which is really a piece of circular nonsense—the "acidic acid" since "acetic" and "acidic" share the same Latin root.

By the early modern era the concept of acidity had established itself very solidly in the quotidian realm, its operational meaning bolstered by the use of various indicators (e.g., litmus) and the neutralization reactions with bases

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[1] On that development, see Multhauf (1996), 243.

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(see Lowry 1936, chap. 2). But the familiarity of acids and bases should not mislead us into thinking that they are not interesting or complicated. It is scandalous that school chemistry tends to render the lesson on acidity so dull, giving no indication of how fascinating and puzzling the concept of acidity is. The latter sense is the least I hope to convey in this article. Just a little knowledge of the history of science should be sufficient to remind us that there have been a plethora of conflicting theoretical definitions of acidity, and the basic[2] identity of the acidity concept has been maintained due to the quotidian operational meaning, rather than any unifying consensus in the realm of high theory or precise measurement.

It is interesting to start with a glimpse of the complex interplay of concepts in Dr. Johnson's dictionary (1755), where he takes the definition of "acid" from John Quincy's *Lexicon Physico-Medicum* published in 1719, as follows: "A'CID. *adj. [acidus, Lat. Acide, Fr.] Sour; sharp.* Liquours and substances are called *acids*, which, being composed of pointed particles, affect the taste in a sharp and piercing manner. The common way of trying, whether any particular liquor hath in it any particles of this kind, is by mixing it with syrup of violets, when it will turn of a red colour; but if it contains alkaline or lixivial particles, it changes that syrup green." This definition is an interesting mix of the everyday concept of acidity and a mechanistic metaphysical notion, advanced by the likes of Pierre Gassendi in the seventeenth century, that acids were corrosive because they were made up of sharp particles. Starting from that picture, we witness many interesting twists and turns in the theory of acids.

Turning away from the empirically groundless mechanistic fantasies, many chemists tried to identify a chemical essence of acidity and made various attempts that bore complicated, sometimes contradictory, relationships with one another. It is interesting to note John Stuart Mill's retrospective account given in the late nineteenth century, in which he used the fluctuations in the theoretical concepts of acidity as "a striking instance" illustrating the general point that "since the classifications in any science are continually modified as scientific knowledge advances, the definitions in the sciences are also constantly varying" (1884, 91).[3]

In the eighteenth century the notion of a "universal acid" as the root of all acids became popular; the universal acid was vitriolic (sulfuric) acid to some and fixed air (carbon dioxide) to some others. Antoine-Laurent Lavoisier's famous identification of oxygen (literally, acid generator) as the "principle" of acidity needs to be understood in the same vein, and it was only a mirror image of the contemporary phlogistonist notion that acidity was caused by

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[2] This is an unfortunate word choice for a discussion of acids but curiously difficult to improve on.

[3] I think Allan Olley for drawing my attention to this passage in Mill.

dephlogistication, which was upheld by Richard Kirwan among others (see Brock 1992, 112–13).

Even though the term "oxygen" somehow survived, the Lavoisierian acid theory behind it was decisively refuted by the early years of the nineteenth century. Lavoisier and his contemporaries were well aware that there was no evidence of oxygen in certain acids, including muriatic acid (in modern terms, hydrochloric acid, HCl) and prussic acid (hydrocyanic acid, HCN), yet they had persisted in their hope that oxygen would eventually be found in them; Lavoisier was so optimistic about this that he included in his list of chemical elements the hypothetical "muriatic radical," which combined with oxygen to form muriatic acid. The eventual downfall of Lavoisier's theory of acids came in the work of Humphry Davy, who recognized chlorine as an element and muriatic acid as the compound of chlorine and hydrogen, with neither oxygen nor the muriatic radical among its constituents (see Gray, Coates, and Åkesson 2007 and references therein). Davy had no decisive view about the general nature of acids. However, through his work on chlorine he raised the profile of hydrochloric acid as a paradigmatic acid and suggested the idea that hydrogen rather than oxygen might be the key ingredient of acids, which was developed further by others including Auguste Laurent and Justus Liebig (see Lowry 1936, 248–50).

To what extent the idea of "hydracids" prefigured modern conceptions of acidity is debatable, but there is at least one clear link, through the work of Svante Arrhenius in the late nineteenth century.[4] The famous part of Arrhenius's work was to recognize that water molecules could (spontaneously) dissociate into two ions, namely H^+ and OH^-. In pure water there would be equal numbers of these two ion species. Arrhenius recognized that in typical acidic solutions there was a preponderance of H^+ ions in comparison to OH^- ions; he identified acidity with the ability of a substance to produce an excess of H^+ ions in an aqueous solution and alkalinity with the ability to produce an excess of OH^- ions. So the essence of acid-alkali reaction was the production of water by the combination of H^+ and OH^- ions. This notion of acidity built nicely on Liebig's emphasis on the essential place of hydrogen in acids. By 1923 Arrhenius's conception was generalized, in theories advanced independently by Johannes Nicolaus Brønsted in Denmark and Thomas Martin Lowry in England, into the notion that acids were H^+ donors and bases were H^+ acceptors. In the Brønsted-Lowry theory, OH^- becomes merely one type of H^+ acceptor, and the definition of acids and bases is no longer confined to aqueous solutions; the Brønsted-Lowry theory encompasses substances such as ammonia (NH_3), which does not obviously have any OH^- ions to give and which can also react in a gaseous form without the help of water to generate OH^-. Curiously, in the very same year a very

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[4] On Arrhenius's ionic theory and related developments, see Brock (1992), chap. 10.

different theory of acidity was proposed by the American chemist Gilbert Newton Lewis, who defined an acid as the acceptor of a lone pair of electrons. For example, here is his representation of the reaction of a silver ion and an ammonia molecule:

$$Ag^{+} + 2{:}NH_3 \rightarrow [H_3N{:}Ag{:}NH_3]^{+}.$$

There the silver is acting as an acid, by accepting a pair of electrons (represented as “:”) from each of the ammonia molecules. I will say more about the Lewis theory below.

2. The Disunity of the Current Acidity Concept. Now, the point is not just that there have been historical fluctuations in the concept of acidity. The messiness still persists. For example, if you ask what it is that possesses acidity, you get a variety of answers from current chemistry textbooks. There is a quite wonderful textbook of organic chemistry that implies five different answers almost in one breath. The authors ask “why some *molecules* are acidic and others basic” (Clayden et al. 2001, 181). But sometimes acidity is said to be possessed by freestanding ions, not the molecules that produce those ions (“the hydronium ion, H_3O^{+}, is the conjugate acid of water”; 183); this goes well with the Lewis theory. Subtly different from that is the idea that acidity can be possessed by an ion within a molecule, which underlies the question of “which protons in more complex molecules are more acidic” (181). Different yet again is the idea that an atom or a group of atoms within a molecule can be acidic or not: “pK_a tells us how acidic (or not) a given hydrogen atom in a compound is” (181); “amino acids . . . have separate acidic and basic groups built into the same molecule” (183). Finally, there is the notion, consonant with early and quotidian conceptions, that a solution possesses acidity: “The pH of a solution is only a measure of the acidity of the solution” (183).

Perhaps all of that is just philosophical hairsplitting, and there is no incompatibility in acidity being possessed simultaneously and variously by solutions, molecules, ions, and various components of molecules. Hairsplitting, however, may be effective in countering certain philosophical arguments. The multiplicity of scientific views about what kinds of objects can possess acidity would create a problem for those who want to argue that the term “acid” picks out a set of objects sharing the same essential “inner constitution”—for example, Kyle Stanford and Philip Kitcher (2000, 114–20), who give one of the few extended discussions of the acidity concept available in the philosophical literature.

Even more serious is the fact that there are two accepted definitions of “acid” (due to Brønsted-Lowry and Lewis) and that various textbooks do not exactly agree about the relation between these two definitions. Perhaps the most popular story told by good chemists is that the Lewis definition encompasses the Brønsted-Lowry definition, that it is a generalization of the latter, because a proton donor is also capable of accepting an electron pair (while not all electron-pair acceptors have protons to give). But I have my doubts about this. Consider the reaction of hydrochloric acid and sodium hydroxide to produce an aqueous solution of common salt, which is very simple and almost a paradigmatic case of acid-base neutralization:

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{NaCl} + \mathrm{H_2O}.$$

It is clear how the Brønsted-Lowry account of this reaction should go:

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{Cl^-} + (\mathrm{H^+} + \mathrm{NaOH}) \rightarrow \mathrm{Cl^-} + \mathrm{H_2O} + \mathrm{Na^+}.$$

But how would the same reaction be understood from the Lewis point of view? Does HCl accept a pair of electrons from NaOH? That is not obvious since the HCl molecule does not have an empty orbital into which to accept an electron pair. At any rate, nearly all of the HCl in an aqueous solution will be dissociated into H^+ and Cl^- ions, so what must happen is that the H^+ ion (or, to be physically more realistic, the H_3O^+ ion) accepts the electron pair from the OH^- ion. But then what is acidic is the H^+ ion, not HCl as a substance or a molecule, which is contrary to the Brønsted-Lowry concept (and to common parlance). And if we consider the reaction of HCl in its pure gas phase (not in aqueous solution), for example, with ammonia, we cannot think in terms of the dissociated form of HCl. The standard explanation in that case seems to be that HCl is a polar molecule, with the electron density heavily distributed around the chlorine nucleus rather than the hydrogen nucleus, allowing the hydrogen end of the molecule to act as an electron-pair acceptor. So in that case the HCl molecule would first accept a pair of electrons from the NH_3 molecule, and then it breaks up as a result.

So the Lewis account works out only if we accept that HCl is an acid in its gaseous state but not in an aqueous solution (in the latter case, only H^+ is). In contrast, in the Brønsted-Lowry account HCl is an acid only in an aqueous solution (or some similar situation) and not in its gaseous state. At least in this case, we do not seem to have a straightforward reduction of the Brønsted-Lowry theory of acids to the Lewis theory of acids. I am almost inclined to say that the two concepts are incommensurable. It might be sufficient, for present purposes, to say that the Lewis and the Brønsted-Lowry definitions refer to two different sets of chemical substances; there is an overlap between the two sets, but one is not a subset of the other. The more ambitious theorists might want to reduce both definitions to a common fundamental theoretical basis, but I think that is going to be difficult to achieve—just imagine trying to pull out the concept of acidity from ab initio quantum computations.

And whichever definition we take, it seems that different acids do their acidic things for different reasons. Consider the fact that acids have the power of dissolving metals—surely one of the most distinctive and interesting properties of acids. For example, in the sort of experiment that Henry Cavendish first published in 1766, zinc is dissolved in sulfuric acid, releasing bubbles of hydrogen gas. And here is the story that the Brønsted-Lowry theory tells about the acid-metal reaction, taken from a standard textbook (Stoker 2005, 563): "the metal dissolves and hydrogen gas (H_2) is liberated. In the reaction the metal atoms lose electrons and become metal ions. The lost electrons are taken up by the hydrogen ions (protons) of the acid; the hydrogen atoms become electrically neutral, combine into molecules, and emerge from the reaction mixture as hydrogen gas." This may seem absolutely straightforward, as do the equations given in the same text:

$$\text{molecular equation: } Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$
$$\text{net ionic equation: } Zn + 2H^+ \rightarrow Zn^{2+} + H_2.$$

But we only have to consider the action of another mineral acid, to realize that the above account cannot be the universal story. Nitric acid, HNO_3, is seemingly a perfectly good Brønsted-Lowry acid. But drop a piece of copper into nitric acid: while it dissolves and bubbles up as expected, what emerges from the solution is not hydrogen, but a brown fume. The fume is nitrogen dioxide (NO_2), a secondary product formed by the reaction between the oxygen in the atmosphere and the nitric oxide (NO), which is the gas that initially emerges from the solution of copper in nitric acid. No hydrogen gas is produced. What is going on? Here is Lowry's own account (1936, 91): "The preparation of the gas [nitric oxide, NO] from copper and nitric acid is often represented by the equation $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$, but many other products are formed at the same time." So, even for Lowry himself it was clear that the action of acids on metals was not always the simple Brønsted-Lowry conversion of $2H^+$ into H_2 by the transfer of electrons from the metal.[5]

3. pH: A Floating Measure of Acidity. At this point there may be a strong temptation to get back to something more certain and sensible like measurement to anchor the meaning of acidity, rather than seeking security in ever-changing theories. But in this case the only credible measurement method we have available provides more complications, rather than conceptual stability or clarity. We do have a widely used measure of acidity in the form of pH, but I will argue that it is not a measure entirely fit for grounding the con-

[5] It would be interesting to investigate how Brønsted, and Lewis, considered the reaction between copper and nitric acid.

cept of acidity in its theoretical or empirical aspect. (This is reminiscent of Heinz Post's notion of "floating models," which are not connected convincingly either to theory or to experiment.)[6]

It is widely accepted that pH measures the concentration of H^+ (or H_3O^+) ions, expressing the number on a logarithmic scale. Two things are immediately obvious from that. First, it only applies to the acidity of solutions, not of any of the other entities mentioned earlier that can be said to possess acidity at least theoretically. It is also worth noting that the pH scale is based on the dissociation constant of water—a very narrow operational basis of a concept that has, theoretically, become extremely general, especially in Lewis's hands. Second, pH only measures Brønsted-Lowry acidity and has no clear connection to Lewis acidity. This is of course understandable, given that the definition and measurement of pH by Søren Sørensen (the head of Carlsberg Laboratory's chemical department) dates back to 1909, more than a decade before Lewis articulated his theory of acids. Actually pH also predates Brønsted's and Lowry's theory of acidity, but at least there is a close enough link between the latter and the Arrhenius theory, on which the original pH concept and measure were based.

History aside, this situation raises a scientific and philosophical difficulty: even if we assume that all Brønsted-Lowry acids are Lewis acids, it is certainly not the case that all Lewis acids are Brønsted-Lowry acids; therefore, there are Lewis acids that lack any precise quantitative measure empirically. And even for Lewis acids that are Brønsted-Lowry acids, can we safely consider the measure of H^+ concentration as the measure of Lewis acidity? What does the degree of Lewis acidity mean, even theoretically? It would have to be something like the propensity to accept electron pairs, but there would be several different theoretical ways of making that notion properly quantitative, not to mention linking those ways to performable measurement operations. This situation is unacceptable, either for the reductionist who would understand all acids as Lewis acids or for the pluralist who would grant independent validity to both the Lewis and the Brønsted-Lowry conceptions.

Even if we just consider the correspondence between Brønsted-Lowry acidity and the laboratory measurement of pH, there are intriguing issues. Roger G. Bates (1973, vi) says in his textbook on pH, "If there is justification for a theoretical section in a book on pH determination, it is because the pH unit lacks precise fundamental definition and because it is essential for users of pH numbers to understand the meaning and limitations of the unit in order to employ pH measurements most advantageously." Bates also comments that the ambiguity in the theory-measurement correspondence here was noticed quite early on: "With the perfection of chemical thermodynamics, it became evident that Sørensen's experimental method did not, in fact, yield hy-

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[6] For an exposition of the notion of floating models, see Redhead (1980), sec. 6.

drogen ion concentration. . . . [The numbers obtained] were not an exact measure of the hydrogen ion activity and, indeed, could never be made so. Thus the door was opened to a plurality of 'theoretical' pH units, none of which could be matched exactly with the experimental number" (v). All in all, the correspondence between the theoretical notions of acidity and the methods of its measurement has been, and continues to be, less than tight.

Nor is it the case that the pH measure corresponds faithfully to the observational criteria by which acidity has been judged. There is certainly no fail-safe correlation between pH values and the characteristic properties of acids such as sourness and corrosiveness. That is perhaps understandable given that the observational properties are not easily quantified and the pH is a precise (albeit ambiguous) quantitative measure. And, as Stanford and Kitcher (2000, 18) argue, it is perfectly legitimate and beneficial that "the acid stereotype is modified in the course of chemical investigation so as to preserve a set of features that can be causally explained in terms of some common underlying structural property." But I believe that the mismatch between pH and observational acidity criteria goes beyond the abandonment of some outdated stereotypic properties. For example, pH as a measure of acidity only makes sense under standard temperature.[7] Neutral solutions can have different pH values since pH only concerns the H^+ concentration without regard to the OH^- concentration. For example, water above 25°C has a higher rate of dissociation than 10^{-14}, so the H^+ concentration as well as the OH^- concentration will be higher than 10^{-7}, which means the pH will be lower than 7, but hot water is just as perfectly neutral as cold water, judged by any reasonable observational measure of acidity.

4. Unity: Scientific versus Quotidian. What do we make of this complex story of the acidity concept, historical and current? We have seen that there is no unified theory of acids, and it is also clear that no single operational definition covers all acids. It may be the case that there is nothing significant and interesting that is shared in common by all the substances that we classify as acids. So we might wonder why chemists even have one word "acid" (or "acidity") to cover all the different meanings. Is it a mere historical accident? If we lost the concept of acidity, would we need to invent it again? Imagine bringing up the next generation of chemists with no preconceived notions of acidity: Would they still come up with a single concept of acidity? The answer is not clear. So why should we not leave acidity aside as a bygone concept that has no place in modern chemistry, in the same way we have left behind the notions of rigid bodies and torque in the transition from classical mechanics to quantum mechanics? In allowing the acidity concept to remain in modern chemistry, have chemists simply been sloppy? Only in some

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[7] See, e.g., the basic discussion in Greenwood and Earnshaw (1997, 48).

ways. Chemists are not thoughtless people—philosophers also need to learn how to make sense of the actual situation in scientific practice as it exists, without giving up our independent judgment.

I would like to defend chemists' retention of the acidity concept. However, I would also like to resist the common reductionist way of making that defense. The succession of acidity concepts that we witness in the history of chemistry does not constitute a straightforward progression of increasing generality, each new concept completely encompassing the previous one. I have argued this point particularly in connection to the relationship between the Brønsted-Lowry concept and the Lewis concept.[8] What we see instead in the long history of acidity is the appropriation of the concept by a whole series of theoretical frameworks, including seventeenth-century mechanical philosophy, the phlogiston theory, Lavoisier's oxygen-based chemistry, Arrhenius's ionic theory, Lewis's electron-pair theory of chemical bonding, and so on. But these theoretical frameworks did not follow on from one another in a cumulative-progressive way; the relationship between them is closer to incommensurability than reduction.

So we return to the question of why chemists working in each and every one of these theoretical systems have felt compelled to appropriate the concept of acidity, rather than rejecting it altogether. We should note that through all the changes to our scientific understanding of acidity, the core of everyday meaning remained, on the basis of a few key operational markers and a few paradigmatic instances. It is difficult to avoid the conclusion that the only good reason for the persistence of acidity concepts in chemistry through the ages is our desire to preserve a reflection of the lasting everyday concept in our science. Here the everyday concept is not a pale and imperfect reflection of a coherent and cogent scientific concept, as the case might be sometimes. In the case of acidity and perhaps in many others, it is the other way around: the everyday concept is the unifying force that holds together a plurality of scientific concepts.

And from this last consideration arises another antireductionist observation, this time regarding the relationship between the everyday concept of acidity and each of the scientific concepts of acidity. The fit between the everyday concept and the scientific concept has never been perfect, and in some cases it has been highly imperfect. It is also not the case that the scientific concept could claim to correct the everyday concept where they differed. If anything, the everyday concept of acidity has so far proved more lasting and robust than most of the scientific concepts of it. A cheap shot, for an initial illustration, is the outcome of the conflict between Lavoisier's

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[8] Despite the actual simultaneity of the rise of these two concepts, it is commonly agreed among those of reductionist inclination that Lewis acidity is both more general and more theoretically advanced than Brønsted-Lowry acidity.

insistence that oxygen was the essence of acidity in all cases and the quotidian intuition that muriatic (hydrochloric) acid was a paradigm case of acidity regardless of chemists' inability to extract oxygen from it. Coming to the twentieth century, we might ask whether Lewis did not generalize the acid concept almost beyond recognition. Lewis did have his own good reasons for spelling out acidity in terms of electron pairs so as to make it fit into his general theory of chemical bonding (see Bogaard 2012, esp. 138). Still, it is extreme to say that being acidic simply means being an acceptor of electron pairs; it is like saying that being smelly comes down to containing a phenyl radical, which is the technical meaning of "aromaticity" in organic chemistry. In both cases, the meaning of the quotidian concept (acidity or smelliness) is clearly different from the scientific concept (electron-pair acceptor-hood or aromaticity); the quotidian concept in each case is broader than the scientific concept and most likely also more lasting. Even for Brønsted-Lowry acidity, there is a clear disconnect from the quotidian concept. For instance, consider the existence of amphoteric substances, namely, those that can act as acids or bases depending on the circumstance. This becomes an interesting question, especially when we realize that "to a certain degree, all compounds are amphoteric" because even a clearly acidic substance can be protonated by an even stronger acid. And in the self-dissociation of water, one molecule of water is said to act as an acid, and another molecule of water acts as a base (Clayden et al. 2001, 183–84). By that point, the scientific concept has clearly departed from the quotidian concept.

I would like to close with a few remarks on the character of the quotidian concept of acidity, which is also not simple. There are a few operational tests of quotidian acidity (e.g., sourness, corrosiveness, and color turning of litmus and other reagents) and a few paradigmatic substances that pass these tests clearly. And then there are various other acids that pass some of these tests but not others. The ability to neutralize alkalis, or bases, is another important quotidian operational test of acidity; however, it would be a mistake to try to elevate this test above all else as a fail-safe criterion, as that only works out if we turn it into a tautology by defining a base as whatever neutralizes an acid. As with many quotidian concepts, what we have here seems to be a Wittgensteinian family-resemblance concept.

But what do we do with the plurality and untidiness of meaning? It is not enough to note that there is no unity to the scientific concept of acidity. Going beyond picking apart universalizing statements to expose their inadequacy, we also need to trace the precise boundaries of the multiple concepts, their uses and misuses, their mutual relations to one another, and the relationship between each of these scientific concepts and the lasting quotidian concept behind all of them. That is a methodological suggestion that we can plausibly attempt to apply more generally, to enrich our understanding of scientific concepts and their places in life outside science.

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