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Acidity: Modes of characterization and quantification

Klaus Ruthenberg^{b,*}, Hasok Chang^a^a Department of History and Philosophy of Science, University of Cambridge, Free School Lane, Cambridge CB2 3RH, United Kingdom^b Faculty of Science & Centre for Science and Culture, Coburg University of Applied Sciences and Arts, Friedrich-Streib-Str. 2, 96450 Coburg, Germany

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ABSTRACT

This paper provides an account of early historical developments in the characterization and quantification of acidity, which may be considered preliminary steps leading to the measurement of acidity. In this “pre-history” of acidity measurement, emphasis is laid on the relative independence of the rich empirical knowledge about acids from theories of acidity. Many attempts were made to compare and assess the strengths of various acids, based on concrete laboratory operations. However, at least until the arrival of the pH measure, the quantification attempts failed to produce anything qualifying as a measurement scale of a recognizable type. It is doubtful whether even pH qualifies as a true measure of acidity, when the full meaning of acidity is taken into account.

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In only few sections of chemistry there appears a succession of such opposing and contradictory views as in those about acid, alkali and salt (Kopp (1845), p. 1, our translation).

1. Introduction

In philosophical discussions of measurement, a great deal of attention has been paid to the process of coordinating a natural property and a mathematical structure. For example, the long tradition of thought culminating in the representational theory of measurement (Krantz, Luce, Suppes, & Tversky, 1971) concerns itself with the match between the relational structure holding among physical measurement operations and the formal mathematical structure of the scale on which the measurement results are expressed. The classification of measurement scales by S. S. Stevens (1946) into nominal, ordinal, interval and ratio scales remains cogent and informative. However, not enough attention has been given to what we might consider the pre-history of measurement. For a property to be considered an appropriate subject of measurement in the first place, it must receive a clear, precise and complete enough characterization. Learning to measure something involves, in many cases, a long and difficult process of quantification before something fully recognizable as measurement can be attempted, as exemplified in the classic collection of case studies edited by Harry Woolf (1961).

In this paper we seek to elucidate the pre-history of the measurement of one of the oldest and most important concepts in any branch of science: acidity.¹ We will investigate the characterization and quantification of acidity before the invention of the pH concept and the pH meter, which is commonly considered as the point at which acidity became properly measurable. We will want to put that assumption under scrutiny in Section 4, but for now the sense of it is clear enough: pH is an indication (the log) of the concentration of hydrogen ions in a solution; the latter is a quantity coherently subject to addition and multiplication, so it constitutes a ratio scale. The pH is also a fairly straightforward operational realization of a coherent theoretical concept, namely the Arrhenius definition of acidity (see Table 1). But how was acidity characterized and quantified before this theoretical–metrological articulation of the concept at the turn of the 20th century?

There are several advantages to the choice of acidity as the subject of our case-study. As we have discussed in a previous study (Chang, 2012), acidity is a concept of ancient origin, which has become a quantified scientific concept only through a complex and gradual process of development.² What we will call the *classical* acids here (acetic acid, sulphuric acid, nitric acid, hydrochloric acid, and aqua regia) were among the very first materials to achieve the

¹ A previous attempt in a similar vein was our work on the quantification of temperature (Chang, 2004).

² For one of the rare philosophical investigations on acidity, see Simon (1980). For a language-centred account of acidity in the 17th and 18th century see Duncan (1981). An emphasis on the link of substances to the “real” world is laid in the excellent book by Klein and Lefèvre (2007).

* Corresponding author.

E-mail address: klaus.ruthenberg@hs-coburg.de (K. Ruthenberg).

Table 1
Major approaches in the theories of acidity. Selected from Walden (1929), Luder and Zuffanti (1946), Simon (1980), and Finston and Rychtman (1982).

Scholar	Year	Theoretical Approach
Lavoisier	1780s	Oxygen as the acidifying element
Davy	1810	Hydrogen, not oxygen as the determinant of acids
Liebig	1838	Acids as hydrogen compounds in which the hydrogen may be replaced by metals
Arrhenius	1887	Dissociation theory of aqueous solutions: acids as donors of hydrogen ions
Brønsted; Lowry	1923	Acids as substances capable of giving up protons
Lewis	1923	Acids as substance capable of receiving electron-pairs

status of individualized chemical species. Therefore, acidity is a particularly suitable subject for illustrating the processes of concept-formation and quantification that predate straightforward attempts at measurement. The meaning of acidity is still rooted in quotidian operations and experiences, and it will be very instructive to investigate how these formed the basis of later laboratory operations of detection and analysis. With its long history and remarkable durability, acidity has also been a key topic treated in many generations of chemical theory, which means that it is a perfect vehicle for illustrating how theoretical assumptions affect the quantification and measurement of concepts. (In this paper, our main focus will not be on theory, but it would be useful to keep a very rudimentary chronology of major theoretical developments as reference points, as shown in Table 1.) The acid concept is also suitable for illustrating the intersection between classification and measurement, as it began its life as a notion for identifying an important class of substances in relation to other classes of substances, initially with little thought of quantification.

2. Qualitative characterizations of acids

It is important to remember the origins of the notion of acidity clearly. The English chemist Thomas Martin Lowry (1874–1936) published his *Historical Introduction to Chemistry* (1915) before he became renowned as one of the originators of the modern protonic acid–base theory (the “Brønsted–Lowry theory”). In chapter 2 of this book, he gives a brief account of the “discovery of the common acids” which can still be considered authoritative.³ Vinegar, of vegetable origin, was the earliest known acid. Citric acid and other organic acids would have been present in foodstuffs without being clearly identified. The so-called mineral acids, including sulphuric acid (oil of vitriol, vitriolic acid), hydrochloric acid (muriatic acid, spirit of salt), nitric acid (aqua fortis), and nitrohydrochloric acid (aqua regia) were synthesized much later, when distillation techniques were improved: “The first of these to be prepared was undoubtedly oil of vitriol, which Geber (800 A.D.) described as obtained by the distillation of alum.” (p. 13). Because at the outset the mineral acids were prepared by heating of salts (together with a source of water, which usually was gained just by moisture) followed by the cooling and condensing of the gaseous products,⁴ a close relationship between acids and salts was easily assumed: “One result of the discovery of the acids was to add very greatly to the number of ‘salts’ which were known” (Lowry, 1915, p. 16). With respect to the materials involved, hence, the operational procedures in the early workshops were cyclic: In the first place, acids

were produced from substances commonly identified as salts (sea salt, alum, nitre, etc.)⁵, and then these acids became the starting materials and central conceptual “mother substances” of their compounds: today we call the latter chlorides, sulphates, nitrates, and so forth, and consider them to be stemming from their respective acid. The carbonates, being among the most abundant salt-like minerals in the solid surface of the earth, and their “mother substance”, carbonic acid, do have a particularly intriguing history (Le Grand, 1973; Soentgen, 2010). “Fixed air”, or carbon dioxide (CO₂) as we now call this substance,⁶ was observed early on as it could easily be obtained by heating lime, soda, or potash. And it is a common product in the process of fermentation, though it was not until the middle of the 18th century that Joseph Priestley identified it in breweries. Moreover, some scholars of the principlist schools particularly in the 18th century, tried to identify that gas as the “universal acid” (Le Grand, 1973).

Many historians and philosophers of science have preferred to address theoretical interpretation when it comes to the understanding of acidity, and tend to neglect the actual manifest knowledge and laboratory achievements. There have been some important exceptions, however. For example, Marie Boas notes: “In the reasonable atmosphere of later eighteenth century science it became customary to define acids empirically: by their characteristic taste, by their attraction or affinity, and by their ability to turn blue vegetable substances red” (1956, pp. 25–26). As characteristic properties of the acids, Lowry, too, lists the same aspects (1915, pp.15–16). The attributes of classical acids all refer to manifest (quotidian) sensual experiences or observations: sour taste, pungent smell, corrosiveness (the disintegration or dissolution of metals), colour-turning of certain dyes (litmus, for example), solubility, distillability, “phlogistic” impact on human skin, and the mutual “deadening” of acids and bases (which we call neutralization), often recognizable in appearances like heat and foaming.

Following these authors, we want to emphasize the relative independence of the extremely persistent, rich and manifest knowledge about these chemical individuals⁷ from theoretical approaches.⁸ There is good evidence in favour of the interpretation that early acids inhabited the world for a long time without specific and elaborated theories about their composition, and had their secure, almost unchanged, existence due to useful quotidian descriptions.

2.1. Taste

The earliest and most enduring quality associated with acidity has been sourness.⁹ In contrast to visual experiences, the perception of (sour) taste is gained only by direct, incorporating contact

⁵ Paul Walden gives a comprehensive historical overview of the interrelations between salts, acids, and bases in his lectures at Cornell University in 1927–1928 (1929), pp. 27–78.

⁶ Although the term “carbonic acid” is still used to designate CO₂ even in technical applications (see the grey gas cylinders filled with “Kohlensäure” in German laboratories and workshops), CO₂ is not an acid, but the *anhydride* to carbonic acid (H₂CO₃), similar to, for example, SO₃ is to H₂SO₄, and N₂O₅ to HNO₃. However, not all such “mother substances” of salts enjoy a proper substantial existence. H₂CO₃, for example, has the character of a merely virtual entity, because it cannot be prepared in pure form.

⁷ For an in-depth investigation of the concept of chemical individual, see Hooykaas (1958). See also the different, more recent approaches referring to that concept in Ruthenberg and van Brakel (2008).

⁸ Kopp’s opinion about the particular status of “opposing and contradictory views” on acids, alkali and salt in chemistry, which we use as the epigraph for our paper, is particularly fascinating in that it hints at the particularly large gap between empirical knowledge and theoretical interpretation in that field.

⁹ We will not discuss the sense of smell here. Whereas the classical acids do indeed have very different smells, the sour taste in diluted state is similar in many of them.

³ Kopp (1845), pp. 8–13, gives a similar account of the early history of acidity in his still valuable and reliable history of chemistry.

⁴ For an interesting inter-cultural comparison of early distillation vessels see Butler and Needham (1980).

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