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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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4 **Acidity: Modes of Characterization and Quantification**

5 Klaus Ruthenberg and Hasok Chang

6 [revised version of 11 January 2107]
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11 In only few sections of chemistry there appears a succession of such
12 opposing and contradictory views as in those about acid, alkali and
13 salt. (Kopp 1845, p. 1, our translation)
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17 **Abstract**

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

38 In philosophical discussions of measurement, a great deal of attention has
39 been paid to the process of coordinating a natural property and a mathematical
40 structure. For example, the long tradition of thought culminating in the
41 representational theory of measurement (Krantz et al., 1971) concerns itself
42 with the match between the relational structure holding among physical
43 measurement operations and the formal mathematical structure of the scale on
44 which the measurement results are expressed. The classification of
45 measurement scales by S. S. Stevens (1946) into nominal, ordinal, interval
46 and ratio scales remains cogent and informative. However, not enough
47 attention has been given to what we might consider the pre-history of
48 measurement. For a property to be considered an appropriate subject of
49 measurement in the first place, it must receive a clear, precise and complete
50 enough characterization. Learning to measure something involves, in many
51 cases, a long and difficult process of quantification before something fully
52 recognizable as measurement can be attempted, as exemplified in the classic
53 collection of case studies edited by Harry Woolf (1961).
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1 In this paper we seek to elucidate the pre-history of the measurement of one of
2 the oldest and most important concepts in any branch of science: acidity.¹ We
3 will investigate the characterization and quantification of acidity before the
4 invention of the pH concept and the pH meter, which is commonly considered
5 as the point at which acidity became properly measurable. We will want to put
6 that assumption under scrutiny in Section 4, but for now the sense of it is clear
7 enough: pH is an indication (the log) of the concentration of hydrogen ions in
8 a solution; the latter is a quantity coherently subject to addition and
9 multiplication, so it constitutes a ratio scale. The pH is also a fairly
10 straightforward operational realization of a coherent theoretical concept,
11 namely the Arrhenius definition of acidity (see Table 1). But how was acidity
12 characterized and quantified before this theoretical–metrological articulation
13 of the concept at the turn of the 20th century?
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21 There are several advantages to the choice of acidity as the subject of our
22 case-study. As we have discussed in a previous study (Chang 2012a), acidity
23 is a concept of ancient origin, which has become a quantified scientific
24 concept only through a complex and gradual process of development.² What
25 we will call the *classical* acids here (acetic acid, sulphuric acid, nitric acid,
26 hydrochloric acid, and aqua regia) were among the very first materials to
27 achieve the status of individualized chemical species. Therefore, acidity is a
28 particularly suitable subject for illustrating the processes of concept-formation
29 and quantification that predate straightforward attempts at measurement. The
30 meaning of acidity is still rooted in quotidian operations and experiences, and
31 it will be very instructive to investigate how they formed the basis of later
32 laboratory operations of detection and analysis. With its long history and
33 remarkable durability, acidity has also been a key topic treated in many
34 generations of chemical theory, which means that it is a perfect vehicle for
35 illustrating how theoretical assumptions affect the quantification and
36 measurement of concepts. (In this paper, our main focus will not be on theory,
37 but it would be useful to keep a very rudimentary chronology of major
38 theoretical developments as reference points, as shown in Table 1.) The acid
39 concept is also suitable for illustrating the intersection between classification
40 and measurement, as it began its life as a notion for identifying an important
41 class of substances in relation to other classes of substances, initially with
42 little thought of quantification.
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54 ¹ A previous attempt in a similar vein was our work on the quantification of
55 temperature (Chang 2004).

56 ² For one of the rare philosophical investigations on acidity, see Simon (1980). For a
57 language-centred account of acidity in the 17th and 18th century see Duncan (1981).
58 An emphasis on the link of substances to the “real” world is laid in the excellent book
59 by Klein and Lefèvre (2007).
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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 substance capable of giving up protons
Lewis	1923	Acids as substance capable of receiving electron-pairs

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

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

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).

1 substances commonly identified as salts (sea salt, alum, nitre, etc.)⁵, and then
2 these acids became the starting materials and central conceptual “mother
3 substances” of their compounds: today we call the latter chlorides, sulphates,
4 nitrates, and so forth, and consider them to be stemming from their respective
5 acid. The carbonates, being among the most abundant salt-like minerals in the
6 solid surface of the earth, and their “mother substance”, carbonic acid, do
7 have a particularly intriguing history (Le Grand, 1973, Soentgen, 2010).
8 “Fixed air”, or carbon dioxide (CO₂) as we now call this substance,⁶ was
9 observed early on as it could easily be obtained by heating lime, soda, or
10 potash. And it is a common product in the process of fermentation, though it
11 was not until the middle of the 18th century that Joseph Priestley identified it
12 in breweries. Moreover, some scholars of the principlist schools particularly
13 in the 18th century, tried to identify that gas as the “universal acid” (Le Grand
14 1973).
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21 Many historians and philosophers of science have preferred to address
22 theoretical interpretation when it comes to the understanding of acidity, and
23 tend to neglect the actual manifest knowledge and laboratory achievements.
24 There have been some important exceptions, however. For example, Marie
25 Boas notes: “In the reasonable atmosphere of later eighteenth century science
26 it became customary to define acids empirically: by their characteristic taste,
27 by their attraction or affinity, and by their ability to turn blue vegetable
28 substances red.” (Boas, 1956, pp. 25-26) As characteristic properties of the
29 acids, Lowry, too, lists the same aspects (pp.15-16). The attributes of classical
30 acids all refer to manifest (quotidian) sensual experiences or observations:
31 sour taste, pungent smell, corrosiveness (the disintegration or dissolution of
32 metals), colour-turning of certain dyes (litmus, for example), solubility,
33 distillability, phlogistic (!) impact on human skin, and the mutual “deadening”
34 of acids and bases (which we call neutralization), often recognizable in
35 appearances like heat and foaming.
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43 Following these authors, we want to emphasize the relative independence of
44 the extremely persistent, rich and manifest knowledge about these chemical
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50 ⁵ Paul Walden gives a comprehensive historical overview of the interrelations
51 between salts, acids, and bases in his lectures at Cornell University in 1927-1928
52 (Walden 1929, 27-78).
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54 ⁶ Although the term “carbonic acid” is still to designate CO₂ even in technical
55 applications (see the grey gas cylinders filled with “*Kohlensäure*” in German
56 laboratories and workshops), CO₂ is not an acid, but the *anhydride* to carbonic acid
57 (H₂CO₃), similar as, for example, SO₃ is to H₂SO₄, and N₂O₅ to HNO₃. However, not
58 all such “mother substances” of salts enjoy a proper substantial existence. H₂CO₃, for
59 example, has the character of a merely virtual entity, because it cannot be prepared in
60 pure form.
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1 individuals⁷ from theoretical approaches.⁸ There is good evidence in favour of
 2 the interpretation that early acids inhabited the world for a long time without
 3 specific and elaborated theories about their composition, and had their secure,
 4 almost unchanged, existence due to useful quotidian descriptions.
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6 7 **2.1. Taste**

8 The earliest and most enduring quality associated with acidity has been
 9 sourness.⁹ In contrast to visual experiences, the perception of (sour) taste is
 10 gained only by direct, incorporating contact with samples of certain
 11 substances.¹⁰ Hence, humans do obtain a very intimate and unmediated
 12 impression about specific stuff properties by taste. Particularly as criteria for
 13 classification and individualization of stuff, taste and smell have always
 14 played a significant role in chemistry (and a good nose is still of enormous
 15 help in the laboratories for students and professionals).¹¹ One well-known
 16 outcome of the relation between stuff quality and gustatory experience in the
 17 history of chemistry is the German naming for what is called oxygen in
 18 English: *Sauerstoff*. Now we know that Lavoisier's claim (see Tab. 1) about
 19 oxygen being the essence of acidity is wrong, and moreover oxygen does not
 20 taste sour at all. But classical acids do: Although they do not have (or induce)
 21 the completely same taste in pure form, they taste quite similar when diluted.
 22 By ingestion of certain plants, for example common sorrel in Europe, people
 23 came into contact with the specific sour taste. This quotidian sour taste has
 24 been described from very early on in natural philosophy, and it has been the
 25 origin for the search after the principles lying behind it.
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35 One early example is given by Plato in his late dialogue *Timaeus*. In this more
 36 or less Pythagorean report about contemporary scientific knowledge, the
 37 speaker Timaeus addresses, among other issues, the gustatory sense (65b).
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41 ⁷ For an in-depth investigation of the concept of chemical individual, see Hooykaas
 42 (1958). See also the different, more recent approaches referring to that concept in
 43 Ruthenberg and van Brakel (2008).

44 ⁸ Kopp's opinion about the particular status of "opposing and contradictory views"
 45 on acids, alkali and salt in chemistry, which we use as the epigraph for our paper
 46 (Kopp 1845, p.1), is particularly fascinating in that it hints at the particularly large
 47 gap between empirical knowledge and theoretical interpretation in that field.

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

50 ¹⁰ This aspect can be found in Thomas Nagel's fascinating discussion of the taste
 51 of chocolate, although he follows a different purpose (Nagel, 1987, pp. 20ff).
 52 Note that subjectivity is the obstacle for the quantification and measurement of
 53 that perception.
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55 ¹¹ Lissa Roberts (1995, p. 507) investigates the history of the transition from
 56 sensuous to quantified chemistry in the 18th century and points out "that
 57 unmediated sense evidence played less and less of a public role in the scientific
 58 determination of knowledge, thanks to the 'new' chemist' efforts", that is, the
 59 efforts of Lavoisier, and, we may add, E. F. Geoffroy and J. B. Richter.
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1 Perceptions and phenomena described here are very similar to historical
 2 descriptions like those of Lowry (1915) and of Kopp (1845, p. 8). The acid
 3 “which has been refined by fermentation” was vinegar (cf. the quotation
 4 below).¹² (Note that tropical fruits like oranges and lemons were not known to
 5 the Greek of the fourth century BC.)

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 8 The ancient quotidian description – via taste and other perceptible phenomena
 9 – still served as a basis for some influential proto-theoretical approaches about
 10 2000 years later. For example, Nicolas Lemery (1645-1715) stated:

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 14 “I hope no body will offer to dispute whether an acid has points
 15 or no, seeing every ones experience does demonstrate it, they
 16 need but taste an acid to be satisfied of it, for it pricks the
 17 tongue like any thing keen and finely cut” (Lemery 1686, p. 24;
 18 quoted in Boas 1956, p. 17)

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 22 Even though Lemery’s statement is articulating the mechanist speculation
 23 about acids being made of pointed and sharp particles, it is building on the
 24 knowledge about the particular chemical kind and explicitly connects the
 25 theory to everyday experience, that is, the sour taste.

29 2.2. Effervescence

30 Perhaps less centrally associated with acidity is effervescence, that is the
 31 observation of spontaneous bubbling when, for example, vinegar is poured
 32 over a piece of lime.¹³ In the passage from the *Timaeus* quoted above, we can
 33 find a description of the observation of effervescence, which here serves as an
 34 explanatory device regarding taste and which was later transferred into an
 35 indication in the quantification procedures discussed below: during certain
 36 processes on the tongue “moist capsules” are formed, the films of which
 37 sometimes “are of pure moisture and transparent . . . and the cause of all these
 38 conditions is termed acid”. It requires additional assumptions to understand
 39 why Plato is placing this description here among the presentation and
 40 explanation of human tastes (which are, according to Plato in 65c-66c, the
 41 following: astringent, harsh, bitter, saline, pungent, sour, and sweet¹⁴).

42 Although several translators and commentators have described that section to

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¹² Note that Kopp refers to Caius Plinius Secundus (23/24-79). We find about a dozen entries for vinegar already in the first six books (of 37) of Pliny’s natural history (Plinius, 1881). Thorpe (1909, p. 157) comments: “[F]or a long time all naturally occurring organic acids having a sour taste were regarded as identical with or as forms of vinegar.”

¹³ The modern interpretation of that process is that the stronger acid vinegar is displacing carbonic acid, setting free carbon dioxide from calcium carbonate (cf. our discussion of acid strength in Section 3).

¹⁴ It does not seem correct to ascribe these seven basic tastes to Aristotle; see Ragland (2012).

be unreconstructable (it is one monumental sentence with unclear syntax), the main “chemical” point Plato makes here can be reconstructed as follows:

“Acids are substances which have been refined by fermentation; these, when they enter the mouth, form a combination with the particles of earth and air which are therein, and stir and mix them up in such a way as to produce films of moisture enclosing air, in other words, bubbles: a kind of effervescence in fact is produced by the action on the substance of the tongue.” (Archer-Hind, in Plato 1888, fn p. 242)¹⁵

Plato’s talk of effervescence indeed makes sense, if we imagine a situation like bringing together some acid and pieces of alkaline material (such as lime) in the mouth (cf. children’s effervescence powder). Presumably the observation of similar processes outside of the body inspired Plato (or the authors of his Pythagorean sources). Historians of chemistry do note that such perceptible phenomena were known in antiquity:

“Well known of vinegar, the only known acid at the time of the beginning of our calculation of times, was thus the ability to cause an effervescence with certain substances, and to combine with certain bodies to yield dissolutions.” (Kopp 1845, p. 8, our translation)

About two thousand years later, at the time of Robert Boyle (1627-1691), this typical behaviour of acids was still part of the canonical and active chemical knowledge:¹⁶ “It came to be assumed that, besides taste, the essential characteristic of an acid was that it reacted with an alkali with the production of effervescence.” (Boas 1958, p. 135)

2.3. Colour change

Besides taste and effervescence, the early characterizations of acids also relied on the sense of vision: the change of colour of certain natural materials (e.g.

¹⁵ This comment is a brilliantly unwhiggish attempt to find the central meaning of Plato’s crashed sentence. The explanatory part of that description, however, is of course only fully understandable with good knowledge of the “chemical” theory laid out in the *Timaeus*. According to that theory, the four elements are capable of two main “reaction mechanisms”, namely the “cutting” and the “crushing” processes, respectively. Fire is the most active element and its particles act most effectively as cutting agents; earth is the most passive one, which cannot cut other elements but “crush” them if it is present in excess (when, for example, a fire is extinguished by sand). What is addressed here by the notion of “effervescence” is sharp fire tetrahedra cutting obtuse elementary particles of water or air.

¹⁶ There are even remnants of this quotidian experience in analytical chemistry; see the measurement of the “hardness” of water by the “hydrotimetric” method after Boutron and Boudet from 1855, described by Buswell (1922).

1 plant dyes) on contact with acids and bases. This was perhaps the most
 2 prominent application of the visual sense in early chemistry. In the classical
 3 German kitchen, for example, red cabbage is prepared either with vinegar and
 4 becomes red (*Rotkohl*, customary in Northern Germany), or it is cooked with
 5 some basic sodium bicarbonate, and yields a bluish colour (*Blaukraut*,
 6 customary in Southern Germany). It was only a very small step to transfer this
 7 sort of knowledge from the kitchen into the laboratory.
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 11 Boyle, who is frequently mentioned as one of the pioneers of the development
 12 of chemical indicators (see Baker 1964), considered the change of blue plant
 13 dyes to red as a characteristic property of acids.¹⁷ The first “chymist” to
 14 mention using a dye to differentiate acids and bases, however, was apparently
 15 the Swiss Leonard Thurneisser (1531-1595), who used the oil of violets to
 16 prove that there were two “oils of vitriol” (in modern terms, sulphurous and
 17 sulphuric acid). Whereas the former (H_2SO_3) bleaches the oil of violets, the
 18 latter (H_2SO_4) turns it red (Szabadvary 1966, p. 263). Acid-base indicators
 19 and belonged to the actual realm of experimental and theoretical research in
 20 analytical chemistry until the end of the long 19th century (see Ostwald 1894,
 21 pp. 104-106; Prideaux, 1917; Kolthoff, 1926). Presumably due to the
 22 development of easy-to-handle pH-measurements by glass-electrodes it
 23 appears to have ceased to be a topic for active scientific research.
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31 **3. Quantification before Measurement**

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 35 Once it was recognized that there were many different kinds of acids and
 36 many different instantiations of each kind, it became desirable to bring some
 37 order into the whole field. Overall, the important thing to note is that there
 38 were many ways in which chemical practitioners attempted to discern
 39 quantitative relations among acids. As we will explain further, some of these
 40 attempts generated nominal or ordinal scales as defined by Stevens, but that is
 41 considered by most commentators as insufficient to constitute “measurement”
 42 in the proper sense. We want to restrict the notion of measurement to the
 43 situations where the results of quantification form a ratio or an interval scale.
 44 In a ratio scale, the absolute magnitudes of numbers are physically meaningful
 45 (up to a common constant factor, which would be related to the size of the
 46 chosen unit), and the numbers can meaningfully be added to each other. In an
 47 interval scale, the absolute magnitudes are not physically meaningful but the
 48 difference between two numbers is physically meaningful.¹⁸ Quantification
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 56 ¹⁷ The other criteria according to Boyle are the ability to dissolve substances, the
 57 precipitation of sulphur from alkaline solutions, and the loss of these properties on
 58 contact with alkalies (cf. Walden 1929, p. 36).

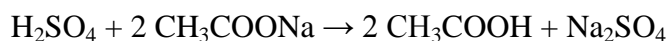
59 ¹⁸ Joel Michell (2004, p. 14) proposes to restrict “measurement” to ratio scales,
 60 but this strikes us as an extreme move, according to which we cannot say, for
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and measurement are often considered quite synonymous, but we think it is useful to distinguish the two terms. In the remainder of this paper we will use “quantification” to mean any successful attempt to introduce order and magnitude into the description of qualities, and reserve “measurement” for a more restrictive class of such attempts as just indicated. None of the quantifications of acidity that will be discussed in this section constituted measurement in this sense.

3.1. Ordering by Affinity

What is meant by the “strength” of an acid? This was a complex notion that emerged gradually. We will trace the various roots of the concept, including the attempts of the late 19th-century physical chemist Wilhelm Ostwald (1853-1932) to quantify it operationally. The connotation of the word “strength” arises metaphorically from our own bodily experience (“one athlete is wrestling down another”). Shaping such an idea into a well-defined scientific concept is not trivial. In a very simple quantitative sense, strength can refer to the concentration of a given acidic substance in a solution. Although that meaning is very clear, it is not very interesting as it does not lead to a comparison between the strengths of different acids. In a comparison of different kinds of acids, the notion of strength may refer to the ability to dissolve various metals, for example. It seems quite plausible to consider that acid the strongest which can dissolve the most noble metals. For example, aqua regia (nitrohydrochloric acid), a mixture of nitric acid and hydrochloric acid, can dissolve gold, which no other acid is capable of. Nitric acid can dissolve copper, which hydrochloric acid and sulphuric acid cannot.

Acid strength can also be discerned in displacement reactions. According to Ostwald (1912, p. 564), the concept of affinity began “with the order in which substances are displaced from analogous compounds.” A strong acid can displace a weak one in that it sets the latter free out of its salts. Sulphuric acid, for example, liberating acetic acid from its salts. Together with its significant smell, this knowledge is still used for the proof of the presence of acetates in analytical tests. In a simplified modern formalism we have, for example:



This kind of acid strength is obviously not referring simply to the concentration of acids (or hydrogen ions). It is not the actual acid concentration, but the *tendency* to dissociate in aqueous solution that characterizes it. The stronger one dissociates more readily and the weaker acid tends to remain in the undissociated form.

example, that we measure temperature on the centigrade or the Fahrenheit scale, in both of which the placement of zero is arbitrary.

This kind of thinking began especially in the context of the affinity theories that dominated 18th-century chemistry.¹⁹ In 1718 Etienne-François Geoffroy (1672-1731) published the *Table des differents rapports observés en Chimie entre differentes substances* (Geoffroy 1718). This table lists relationships of important chemical substances, and it has been considered to be an important turning point for the change from the Peripatetic or Platonic search for principles to the relational description of composed compounds.²⁰ The classical acids played a significant role in Geoffroy's table. Displacement processes were attributed more to acids rather than other substances; acidity and affinity enjoyed a conjoint history for a long time.

TABLE DES DIFFERENTS RAPPORTS
observés entre différentes substances. Mém. de l'Acad. 1718. Pl. 2. page 71.

↪	⊖	⊙	⊕	▽	⊖	⊕	SM	♁	♂	♁	♀	☾	♂	♁	▽
⊖	♁	♂	♁	⊕	⊕	⊕	⊕	⊕	☾	♀	♁	♁	♂	♁	▽
⊕	♁	♀	⊖	⊙	⊙	⊙	⊕	♂	☾	♀	PC	♀	♁	♁	⊕
▽	♀	♁	⊕	⊕	⊕	⊕	♂	♁							
SM	☾	♀	▽		♁	♁	♁	♁	♀						
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			♀					♁	♁						
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	⊙							⊙							

↪ Esprits acides

⊖ Acide du sel marin

⊙ Acide nitreux

⊕ Acide vitriolique

⊕ Sel alcali fixe

⊕ Sel alcali volatil

▽ Terre absorbante

SM Substances metalliques

♁ Mercure

♁ Regule d'Antimoine

⊙ Or

☾ Argent

♀ Cuivre

♂ Fer

♁ Plomb

♁ Etain

♁ Zinc

PC Pierre Calaminaire

♁ Soufre mineral

♁ Principe huileux ou soufre Principe

♁ Esprit de vinaigre

▽ Eau

⊕ Sel

▽ Esprit de vin et Esprit ardens

Geoffroy's Table des Differentes Rapports (1718).

Table 2 Geoffroy's Table des Differentes Rapports (Geoffroy 1718)

If we look at the 6th column in Geoffroy's table (our Table 2), it indicates that "fixed alkali salt" would combine with various acids in the following order of preference: vitriolic (sulphuric) acid, nitric acid, acid of marine salt (hydrochloric acid), and spirit of vinegar (acetic acid). In other words, if

¹⁹ See Duncan (1996), Kim (2003), Klein (1995), and Taylor (2008).

²⁰ Bensaude-Vincent and Stengers state (1996, p. 54): "Since Aristotle's time the properties of a body had been rooted in a 'principle', a substance that acted and explained; now everything took place on the level of relationships."

1 hydrochloric acid is applied to a compound of the alkali salt and acetic acid,
2 hydrochloric acid combines with the alkali salt and displaces the acetic acid,
3 which is freed up. The same ordering is listed in the 5th column under
4 “absorbent earth”, and in the 7th column under “volatile alkali salt.” This
5 established an ordinal scale of acid strength. However, it was no easy matter
6 to combine the orderings under all headings into a single ordering of acids. If
7 we now look at the 8th column under “metallic substances”, we find that the
8 ordering is hydrochloric, sulphuric, nitric, and acetic acid. After Geoffroy
9 many more substances and reactions were added variously to subsequent
10 affinity tables, and the substance categories changed significantly, too. But it
11 was never possible to establish a single consistent order of different kinds of
12 acids according to strength, if strength was defined through replacement
13 reactions.
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19 That is where matters stood for a long time (though there was also a different
20 tradition of affinity-quantification, which we will discuss shortly in Section
21 3.2). In the late 19th century Ostwald made very interesting contributions to
22 the quantification of acid strength, before the advent of the pH concept. His
23 doctoral thesis of 1878, *Volumchemische und optisch-chemische Studien*, was
24 largely dedicated to acid strength. Ostwald gave a two-part motivation for his
25 study. His first aim was the application of volume-chemical measurements on
26 *relative affinity*, which today might be called “reactivity”. The second aim,
27 according to the author even more fundamental, was to underpin
28 investigations about the status of dissolved salts, in relations to the “ionic”
29 chemical processes; Ostwald, Arrhenius, Nernst, and van ’t Hoff, would soon
30 come to be called the “ionists” (cf. Nye 1993).
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37 To obtain a quantified representation of chemical affinity, Ostwald used a
38 dilatometric (or volumetric) approach. Neutralisation reactions of acids with
39 bases result in an increase of volume, as can easily be shown when the
40 reactions are performed in a graduated pipette as reaction vessel. Only the
41 reactions with ammonia yield a volume decrease. The volumetric changes
42 depend on the kind of acid and can be coordinated to acid strength on an
43 ordinal scale. Ostwald calibrated the scale by setting nitric acid as the
44 strongest monobasic acid with the number 100. The resulting scale (see Table
45 3, third column) is very similar to the modern pK_a measures derived from
46 thermochemical and electrochemical determinations (fourth column), with the
47 exception that hydrochloric acid from a modern perspective is stronger than
48 nitric acid.²¹ The reason for the fact that Ostwald’s approach is not entirely in
49 line with later descriptions particularly for the very strong acids might be
50 found in the difficulties of obtaining clear and valid measurements with such
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59 ²¹ In fact, HCl delivers almost five orders of magnitude more hydrogen ions than
60 HNO₃ under equal conditions.
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highly concentrated solutions.²² Correlations with respect to the weaker acids (here acetic acid and its derivatives) are much more conforming to the modern measure.

Acid	Formula	Ostwald's volumetric affinity (1878)	Ostwald's conductivity affinity (1889)	pK _a
nitric	HNO ₃	100	-	-1.37
hydrochloric	HCl	98	-	- 6.1
trichloroacetic	CCl ₃ COOH	80	20(?)	0.89
dichloroacetic	CHCl ₂ COOH	33	5.14	1.30
monochloroacetic	CH ₂ ClCOOH	7.0	0.155	2.81
acetic	CH ₃ COOH	1.2	0.00180	4.76

Table 3 Comparison of affinity (strength) quantifications for selected monobasic acids. Data in the third column are taken from Ostwald (1878, p. 37), and data in the fourth column from Ostwald (1912, p. 566). The pK_a values ($-\log K_a$, where K_a is the equilibrium constant of the acid) are from Christen (1975).

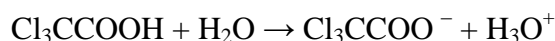
Intriguingly, Ostwald does not explicitly rely on any elaborated theory of acidity and does not try to explain the behaviour of the substances applied in his experiments. We should also keep in mind that it was only in 1887 that Arrhenius published his theory of electrolytic dissociation, on which the modern *protonic* theory of acidity (including the pK_a measure) is based. At the time Ostwald was completing his thesis, the prevailing acidity theory was still that of Liebig (see Table 1). Although his doctoral thesis is not entirely theory-free,²³ it stresses the phenomenological perspective.

In another attempt to quantify (acidic) affinity, Ostwald in 1889 applied the measurement of electrical conductivity. He claims that the dissociation

²² Hydrogen ions of undiluted strong acids, for example, do interfere and diminish their mobility due to their large number, so that the electrical conductivity decreases with elevated concentrations. The “opposite side” of this phenomenon is described in the dilution law.

²³ The interpretation of the phenomena Ostwald used for these inventive measurements is not trivial indeed. Somewhat promising – from a modern perspective – seems to claim that “free” hydrogen (which was “neutralized” in that process) need a larger amount of hydrating water molecules, which were set free during the reaction and thus cause the enlargement of the liquid volume. Obviously, there is no way to explain these phenomena from the point of view of Liebig, which only quite formally connects acidity to the ability to exchange “hydrogen” against “metals”. Hence, Ostwald, as proper empiricist (but not yet energeticist), perhaps just wanted to take precautions with respect to a theoretical explanation.

coefficient is “*the required measure of the chemical affinity*” (cf. Ostwald, 1912, p. 565). The degree of dissociation is equal to the proportion of the molar conductivity and the conductivity at infinite dilution: $a = \mu/\mu_\infty$. Whereas the dilatometric/volumetric quantification method of his thesis is relational in that real chemical reactions must be conducted and affinity numbers be calculated via comparison, the measurement of electrical conductivity can be performed in solutions of simple substances. It looks like a direct measurement (in contrast to a merely theoretical construction) at first sight. However, the situation is not so simple, as made clear by an inspection of dissociation equations like the following:



There are at least two different kinds of ions involved here, which will be transported differently from each other when voltage is applied (in fact working against significant obstructions). Accordingly, what is measured is a resultant of the electrical behaviour of all electrical relevant species involved.²⁴ This measurement leads to reliable results only because the hydrated protons (H_3O^+) are in fact of strongest influence on the conductivity of the solution (which Ostwald could not have known in detail). The conclusion he draws is the one we are still told (or telling) today in introductory chemistry classes: “The influence of the substituent chlorine on the acid properties of acetic acid [sic] is very considerable; we must therefore attribute to it important “acidifying” properties.” (Ostwald, 1912, p. 567)

In modern chemistry, however, these “sour-making” properties would go by the name of *electronegativity*. Due perhaps to the particular instrumental framework of his measurements, Ostwald delivers a precursor of that concept in that he criticizes Berzelius²⁵ and suggests using the terms “positivizing” (*positivierend*) and “negativizing” (*negativierend*). Thus, chlorine acts as *negativizing* part in the derivatives of acetic acid, and the more chlorine is present, the more of this, in modern words, negative-charge-pulling-effect we have, and the more acidic (strong) is the observed species.

²⁴ During his energeticist period, Ostwald struggled with the problem of how to denote aqueous ions in a non-corpuscular framework. For a short critical discussion of this interesting episode, see Ruthenberg 2008. In the cited *Outlines of General Chemistry* from 1912, however, his anti-atomistic attitudes were much less prominent.

²⁵ “Berzelius assumed that the atoms of chlorine were charged with a somewhat large excess of negative electricity and therefore exerted a strong attraction on positively charged bodies, like the metals. This hypothesis is difficult to reconcile with the knowledge we now possess of the behaviour of electricity, since the substances show no free electricity.” (Ostwald, 1912, p. 567)

Ostwald is aware of the historical background of chemical affinity (Ostwald 1912, pp. 563-564). He points out that in the beginning of the construction of affinity tables the emphasis were on salts, because the reactions of these can be observed easily and quickly. According to Ostwald, the tradition of affinity tables began with Georg Ernst Stahl (1660-1734), and comprised other important figures like Geoffroy and Torbern Bergman (1735-1784). After Berthollet's failed attempt to give a mechanical interpretation of affinity ("a larger force overcomes a smaller, with the result that the body moves in the direction of the greater"), "the affinity tables vanished" and "the laws of chemical affinity receded into the background." (Ostwald 1912, p. 565) Quantifying investigations on the affinity (or strength) of acids started again only through the thermochemical investigations (*Thomsen-Berthelot-principle*) by H. P. Thomsen (1826-1909) and the implementation of the law of mass action in 1864.

In their textbook *Intermediate Chemistry* (first published in 1936), Lowry and Cavell give an interesting pertinent comparison of the results of the different approaches to the quantification of the "relative strength" of acids (Lowry and Cavell 1949, p. 616). This comparison, apparently based on measurements at the Cambridge Laboratory of Physical Chemistry (see Tab. 4), comprises results from the measurement of conductivity, the catalytic activity during cane-sugar inversion, and the avidity²⁶ for bases. These approaches become comparable because of the calibrational step to set every solution to the same concentration. Hence, the obvious deviations from the results in Tab. 3 are due to the different sample concentrations.

Acid	Conductivity	Inversion of sugar	Avidity for bases
Hydrochloric	100	100	100
Nitric	100	100	100
Trichloroacetic	88	75	-
Sulphuric	62	54	50 to 60
Formic	2.3	1.5	-
Acetic	0.7	0.4	-

²⁶ The notion of avidity is only rarely used in the early scientific literature and not customary anymore, although it refers well to the relational aspects of chemistry. According to Lowry and Cavell, Thomsen's thermal method and Ostwald's volume method are the "two most important methods for comparing the avidities of two competing acids for a base". According to the authors, the results in column 4 of Tab. 4 refer to both.

Table 4 Strength of acids in half-molar solution (from Lowry and Cavell 1949, p. 616).²⁷

Ostwald seems to have considered his own studies from 1878 onwards as a kind of completion of the search for an appropriate representation of acidic affinity, at least for aqueous solutions: “Thus, the affinity problem for homogeneous equilibrium in electrolytes is really solved, if the coefficients are known” (Ostwald 1912, p.565) He was certainly among those scholars who sought to describe chemical behaviour in an objective and quantitative manner, which commenced with Geoffroy’s table in 1718. However, he did not achieve a full-blown quantitative account of acid strength.

3.2. Titrimetry

Contemporaneously with the early work on affinity-ordering, a very different kind of quantification also developed, focusing on the amounts of materials that combine chemically with each other. Every student of chemistry will remember learning to do titrations. Titrimetry is a basic method of establishing quantitative equivalence in chemistry. If amount a of alkali X neutralizes amount b of acid Y , that establishes an equivalence; if we learn that the same amount of X neutralizes amount c of acid Z , that expands the net of equivalences, this time including an equivalence between the amounts of two acids as well as the alkali–acid equivalence in each case. As the Danish chemist E. Rancke Madsen (1958, p.10) puts it: “By *titrimetry* the component is determined by its ability to participate in a chemical process.”²⁸

The introduction of titrimetry can be traced back at least to the first half of the 18th century and there can hardly be any doubt that the first-ever titrations were performed with respect to acidity. In 1756, for example, the Scottish physician-chemist Francis Home (1719-1813)²⁹ reports the acidimetric titration of potash (potassium carbonate), which was widely used for textile bleaching:³⁰

²⁷ “Since the degree of dissociation increases with dilution, all acids tend to become equal in strength at very high dilutions.” (Lowry and Cavell 1949, p. 617) Note that the same trend is true for the sour taste.

²⁸ Rancke Madsen also identifies two other groups of quantitative analysis: *isolametry* (“the sought component is isolated completely” so that it can be “directly measured”) and *normometry* (“the sought component is determined by comparison with known norms or standards”). Intriguingly, the aspect of standardization/calibration is underestimated here (as in many other pertinent discussions): The characterization of normometry suits any imaginable analytical process, which must involve comparisons with standards.

²⁹ For some biographical and other historical background see Page (2002).

³⁰ In his classic text on the history of analytical chemistry, Ferenc Szabadvary (1966, p. 215) mentions a precursor of that process, namely the following recipe by Glauber (1658, p. 524, our translation with original emphases): “Of this *Liquore Nitri fixi* one shall pour bit by bit dropwise / as much into the overshot *spiritum Nitri* / until the

1 “In order to discover what effect acids would have on these
 2 ashes, and what quantity of the former the latter would destroy;
 3 from which I might be able to form some judgement of the
 4 quantity and strength of the salt they contained....” (quoted in
 5 Rancke Madsen 1958, pp. 34-35)
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10 In this procedure, diluted spirit of nitre (nitric acid, 1:6) was applied spoon-
 11 wise to neutralize a weighed sample of the bleaching material (“blue pearl
 12 ashes”), and the termination of effervescence (caused by carbon dioxide) was
 13 used as the indication that the reaction was complete. The more spoonfuls of
 14 acid were needed, the better was the (bleaching) quality of the potash.
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 18 There were also other acidimetric methods at approximately the same time. In
 19 a small treatise from 1767, the English physician-chemist William Lewis
 20 (1708-1781) addressed Home’s work:
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23 “The quantity of acid, necessary for the saturation of the lye,
 24 should be determined, not by drops or tea-spoonfuls, but by
 25 weight; and the point of saturation, not by ceasing of the
 26 effervescence, which it is extremely difficult, if not
 27 impracticable, to hit with tolerable exactness, but by some effect
 28 less ambiguous and more strongly marked, such as the change of
 29 colour produced in certain vegetable juices, or on paper stained
 30 with them.” (Lewis, 1767, p. 28)
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36 Following such improvements, titrimetry developed into a proper quantitative
 37 procedure step by step by enhancing the practicability and precision of the
 38 measurement (spoon volume vs. weighed portions) and of the indication
 39 (bubbles vs. colour change).³¹ Generally, those improvements of precision
 40 were common in 18th-century chemistry (cf. Golinski 1995). It is also
 41 possible to take the alkalimetric perspective, that is, to use an alkaline
 42 reference substance as titrator to determine an acidic titrand. In 1729, for
 43 example, the French pharmacist Claude-Joseph Geoffroy (1685-1752), the
 44 brother of Etienne-François, applied potassium carbonate (potash) in solid
 45 form as titrator to determine the strength (concentration) of vinegar solutions.
 46 In a similar vein, Guyton de Morveau, Richard Kirwan and others attempted
 47 to quantify affinities in the late 18th century by measuring the different
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54 booming has ended / and both repugnant natures, namely the *Spiritus acidus*, and the
 55 *liquor fixus Nitri*, have killed each other / and the *Spiritus corrosivus* has lost its
 56 *corrosive*, and the *fixed fiery liquor* its spiritedness, and out of the two a natural
 57 saltpeter has been built again, which however is ugly, wherefore one shall put such
 58 liquor into the sand and let steam away the inefficient phlegma...”

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 60 ³¹ Moreover, we learn here that *indicator paper* was already in use in the 18th century.
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amounts of substances that reacted with each other, and of prime importance in these attempts were the neutralization reactions of acids and bases (see Kim 2003, 219-277).

Titrimetry may seem to the modern chemist so straightforward as not to deserve much methodological comment. However, we must not underestimate the amount and level of auxiliary knowledge and skills that were required as underpinnings of titrimetry, rooted in just the sort of qualitative characterization we have discussed in Section 2. In order to be applicable as a titrimetric reaction, a process must be determinable with respect to its completeness. The completeness of chemical reactions, however, is not an easy thing to determine in practice.³² Hence, it is generally subject to pragmatic conventions. The absence of bubble-formation (effervescence) was often interpreted as the end of the reaction (the “deadening”). Claude-Joseph Geoffroy, among others, applied the cessation of effervescence as the indication that the point of neutralization had been reached. In the case of acid–base titrimetry, colour-changing indicators were also commonly employed.³³

Another very important branch of modern chemistry developed mainly out of attempts to quantify acid-base affinity: stoichiometry, whose importance as background to the atomic theory is routinely acknowledged. In his *Anfangsgründe der Stöchiometrie*, Jeremias Benjamin Richter (1762-1807) published material on equivalent ratios. This material was taken up by Ernst Gottfried Fischer (1754-1831), who brought it into a comprehensible table which was published in his translation of Claude-Louis Berthollet’s (1748-1822) *Recherches sur les lois de l’affinité* (Table 5; see Berthollet 1802). That table is a collection of mass-titrimetric data: to neutralize a certain amount of an acid (right column) a certain equivalent amount of a base (left column) is necessary.³⁴

Bases		Acids	
Alumina	525	Hydrofluoric	427
Magnesia	615	Carbonic	577
Ammonia	672	Sebacic	706

³² Or even in theory – according to the modern view of equilibrium phenomena, no chemical reaction is ever “complete” in the sense that nothing further happens.

³³ Among the laboratory skills that are close to quotidian experience we find other rather ingenious practices. Rancke Madsen (1958, p. 50), for example, reports a method to determine the “acidity” of lemon juice described by the Swedish chemist Johan Christian Georgii in 1774. Unusually, Georgii applied a *reversed* titration, by freezing the solutions and removing the ice.

³⁴ For the description of the methodological and historical background, see Szabadvary (1966) and, in particular, Freund (1904).

Lime	793	Muriatic	712
Soda	853	Oxalic	755
Potash	1605	Phosphoric	979
Baryta	2222	Formic	988
		Sulphuric	1000
		Succinic	1209
		Nitric	1405
		Acetic	1480
		Citric	1583
		Tartaric	1694

Table 5 Fischer's representation of Richter's data as incorporated into Berthollet (1802).

4. Has the pH finally rendered acidity measurable?

From the modern perspective, we can see that the most straightforwardly quantifiable acidity concept is the protonic one (especially in the Arrhenius version), according to which the degree of acidity is taken as a simple function of the concentration of hydrogen ions in an aqueous solution, and is duly measured by pH meters. But even this is not as straightforward as it may seem. First of all, note that it is only in the theoretical sense that the pH obviously provides a cogent measurement scale, based on a simple algebraic manipulation of hydrogen-ion concentration. Whether the laboratory methods for measuring pH actually produce cogent measurement scales is a different question. This is a subject that we intend to address in detail in a future paper, but a few details are worth noting here. The standard pH meters only get at hydrogen-ion concentration in a very indirect way. If we determine the pH with a glass electrode, we are only measuring the influence of hydrogen ions on the potential in a specifically constructed electrode. And in order to understand fully such actions of acids in an aqueous environment, we must also acknowledge the inevitable presence and actions of the counter-ion to H^+ in any protonic acid or acidic solution.

Even if we set aside the difficulties of laboratory measurement, it is clear that the pH only gets at acidity in an indirect way. When we say that hydrochloric acid is a protonic acid, that means it has the *capacity* to generate H^+ ions when it is put into water; that capacity is not directly quantifiable. What is more directly quantifiable is the actual H^+ concentration that results from the mutual action of hydrochloric acid and water. If we speak of the "acidity" of the aqueous solution, we are introducing an equivocation regarding what it is that possessed the acidity. Although we can determine something like a "resultant acidity" by pH measurements (or other methods like the neutralization

1 titrations discussed in the previous section), that does not yield any direct
2 information about the source of that “acidity”. The general point is that
3 acidity, even in the most straightforward protonic rendition, is an
4 unobservable quantity. Ostwald, in his *Grundzüge* of general chemistry,
5 emphasizes the downright metaphysical character of the assumption that the
6 affinity properties of substances show fixed relations to their constitution: “A
7 law whose validity has always been assumed is that the affinity of substances
8 stands in regular and unmistakable relation to their composition and
9 constitution.” (Ostwald 1917, p. 563)
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14 Even if we set aside the many-layered indirectness by which pH measurement
15 gets at the acidity concept, it is clear that the protonic concept is too limited in
16 any case, as it only applies to aqueous environments, putting undue limitations
17 on the scope of the concept. If we recall the old quotidian concept, a bundle of
18 observable properties characterizes acids; even if each of those properties
19 (e.g., sourness) may be placed on a one-dimensional scale, there is no such
20 thing as an overall degree of “acidity.” If we take the modern Lewis concept
21 of acidity (see Table 1) its essence is reduced to one property of being a
22 receptor of an electron-pair, but this is a contextual notion depending on what
23 the substance in question is interacting with, and within each context it tends
24 to be an on-off property, rather than one that easily admits of degrees.
25 Accordingly, there is no general laboratory measurement method that gives a
26 quantification of Lewis acidity.
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34 More generally, the point is that the full “stuffy” character of an acid is not
35 measurable by considering just one aspect of it, however important.³⁵ Acids,
36 like all substance kinds, obtain a full-blown representation only by a group or
37 collection of significant criteria. Perhaps the following comparison will be
38 helpful. Consider another substance kind term, “metal.” We could try to
39 define a quantitative notion of “metallicity,” but that would strike anyone as
40 an unnatural and unwise move. The concept of metals came to be introduced
41 with reference to a core group of typical attributes (at normal temperatures):
42 solid state, high electrical conductivity, high thermal conductivity, ductility,
43 gloss. There might be a hierarchy of significance in that list of properties
44 (electrical and thermal conductivity might seem to be necessary conditions,
45 for something to qualify as a metal), but no single attribute is absolutely
46 definitive. If one typical attribute is missing (as in the case of *liquid* mercury),
47 we might not yet be inclined to remove the material from the class. If more
48 are missing (as in the case of silicon, which is solid and glossy, but not
49 ductile, with very small conductivities), we will probably want to class the
50 substance as non-metallic (or perhaps as a “metalloid” or a “semi-metal”).
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59 ³⁵ As to recent discussions of the chemical stuff notion from different perspectives,
60 see Ruthenberg and van Brakel (2008).
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1 The chemical category “acidity”, too, comes with more than just one
2 characteristic.
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5. The Persisting Importance of Qualitative Knowledge

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8 One important theme emerging from the above discussion of the limitations of
9 the pH measure is the lasting significance of qualitative knowledge. If we
10 recognize the importance of the characterization of acids as substances before
11 we can discuss the measurement of acidity, we must return to the quotidian
12 meanings of acidity. There are some existing approaches to early chemistry
13 that support our kind of view. For example, Bruce Moran says: “When viewed
14 as part of the history of alchemy and chemistry, the practices of artisans can
15 tell us a great deal about the variety of opinions concerning how nature
16 operates and what the appropriate means of influencing nature might be.”
17 (Moran 2005, p. 6) For our case, “the appropriate means of influencing
18 nature” is tellingly addressed already by the title of Moran’s impressive book,
19 *Distilling Knowledge*. Acetic acid and the mineral acids have shaped our
20 picture of acids in the first place, and they did so by operational means, first
21 qualitatively, then quantitatively. Surprisingly, very few scholars in the
22 sciences and in the history and philosophy of science have articulated the
23 fundamental importance of the practical and operational part of chemistry.³⁶
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32 This point is related to the basic empiricist view on the priority of experience
33 in science, and the view that reference-fixing is informed by operations and
34 measurements more than by theories (cf. Chang, 2011). Since at least the
35 Middle Ages, strenuous efforts have been made to find a definitive theoretical
36 description of acidity. All these attempts have referred to or relied on the
37 received manifest knowledge, particularly to the knowledge about
38 paradigmatic and persistent epistemic objects. The operational manipulations
39 were developed from and supported by quotidian knowledge were – and still
40 are – crucial for the identification and classification of these historically stable
41 chemical kinds. Moreover, we want to argue for an enlargement of its
42 historical frame such that it would commence with the operational
43 individualization of substances in antiquity – among them the classical acids –
44 up to the present day.
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51 In moving from the quotidian to the more systematic and quantified kind of
52 knowledge, there is one essential step that is still qualitative. We must not lose
53 sight of the fact that in any standard analytical methods the purity of reagents
54 is an essential prerequisite. We may assume, for example, that the nitric acid
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59 ³⁶ The credo of the Bohemian chemist František Wald (1861-1930), for example, was
60 that *all* substances are preparations, cf. (van Brakel, 2013).
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1 used by Home and Lewis as discussed above was available in near pure
2 quality. Purification was an indispensable part of the calibration of all of the
3 quantification methods discussed in Section 3. And in order to avoid
4 methodological circularity, the proof of purity has of course to be performed
5 by a different method, or with standard substances the purity of which is
6 certified otherwise. It is important to see the circularity involved here clearly.
7 In the process of establishing quantification in the first place, ascertaining
8 purity is not a matter of *analysis*, which requires already having access to a
9 method of measuring the pertinent quality of the sample that allows one to say
10 “this sample of X is 98% pure”, etc. Rather, the initial judgement of purity has
11 to take the qualitative form of “quit pure” or “pure enough”.
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16 Synthesis, purification and sample preparation are prerequisites for any
17 analytical method, even those which seem to be kind of sterile and remote
18 from material manipulations, like modern chromatography and spectrometry.
19 Chemically relevant measurement always involves reference and
20 standardisation, which was shown here by the discussion of early acid-base
21 titrations and Ostwald’s affinity research. All applied chemicals were of
22 approximately pure quality; that is, the ability to synthesize pure enough
23 substances was taken for granted in advance of the main experiments. Since at
24 least the Middle Ages, alchemists were able to produce mineral acids (Reti
25 1965). The standard procedure was to heat appropriate salts (for example,
26 kitchen salt, saltpeter, vitriol, or mixtures of these) together with a source of
27 water. During this “dry distillation”, the salts are dismembered and volatile
28 substances are produced, which form acids after reacting with water, by
29 condensation upon cooling. These condensates were purified via (repeated)
30 distillation. Because of its more convenient properties, it appears plausible
31 that nitric acid was preferred in many laboratory procedures, particularly the
32 analytical ones.³⁷ In his *Traité* of 1789, Antoine Lavoisier reports on nitric
33 acid: “It was very anciently known, and its combinations have been more
34 studied by chemists than those of any other acid.” (Lavoisier, 1965, p. 217)
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45 All important properties of the chemical species involved in the analytical
46 procedures also needed to be known, forming an empirically grounded
47 conceptual network. Observations of taste, smell, colour, appearance,
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52 ³⁷ The boiling points (in °C) are: HCl -85; HNO₃ 86; H₂SO₄ 340 (decomposing).
53 Hence, although it must be performed cautiously, the distillation of raw nitric acid is
54 possible at moderate temperatures. Moreover, traces of chloride could be removed
55 simply by precipitation with silver nitrate and filtration. Lavoisier (1965, pp. 214-
56 217) gave a full operational account for the production of nitric acid. In fact, nitric
57 acid was a customary commodity: “In the fifteenth century, nitric acid became
58 widely applied in metallurgy for the separation of gold from silver” (Klein and
59 Lefèvre 2007, p. 16).
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1 solubility, reactivity (cf. effervescence) and specific boiling behaviour,³⁸ are
2 part of the huge relational net of knowledge which specifies and defines a
3 chemical substance. This relational net of substantial characterizations
4 remains stable and the names of its entities usually remain the same, even if a
5 few of its knots were removed, rearranged or newly knitted. Because there is
6 no measurement without standardization, we can conclude that there is “no
7 analysis without synthesis.”³⁹
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11 We also want to counter the notion that true measurement is in the domain of
12 physics, and quantification and measurement in chemistry and other sciences
13 take place most of all by the reduction of various properties to physical
14 quantities. A good characterization of the attitude we want to counter is given
15 in Joachim Schummer’s excellent paper on spectroscopic methods in chemical
16 analysis:
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21 “These physical properties do not describe relations between
22 different chemical substances, but the response of an isolated
23 material sample to electromagnetic fields The success story
24 of instrumentation in chemistry ... is also a success story of
25 physical properties, in the course of which the concept of
26 species identity was modified and adapted to physical properties
27 ... at present, not only the concept of species identity but also
28 the kind of species are changed, from chemical substances to
29 quasi-molecular species.” (Schummer, 2002, p. 196)
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35 The progress of chemistry has often been portrayed as a long reductionist
36 journey starting from an operational science of the behaviour of stuff during
37 the Renaissance, ending with the abstract mathematical physics of the
38 behaviour of outer-shell electrons today. In the history of acidity, too, the
39 methods of measurement changed and became more and more non-relational
40 or “non-chemical” already with the implementation of electroanalytical
41 measurement. Wilhelm Ostwald, a pioneer of physical chemistry, used such
42 approaches very early on. One example is his coordination (the Machian
43 *Zuordnung*) of conductivity to the affinity (strength) of chlorinated acids,
44 which we have discussed briefly above. However, the transition from
45 chemical to physical analysis is not as non-relational as perhaps wished: if the
46 properties of substances are to be quantified and measured, there is no way to
47 bypass the necessity of calibration and standardization by means of reference
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55 ³⁸ Boiling points (quantified and stable boiling temperatures) became analytical
56 properties (“physical constants” or “fixed points”) only after the development of
57 reliable temperature measurement in the 19th century (cf. Chang 2004).

58 ³⁹ A similar insight has been voiced by other authors, including Mi Gyung Kim
59 (2014). Under “synthesis” we here subsume the preparatory steps regarding all
60 substances involved in the “analytical” process.
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1 substances that are *chemically* characterized and prepared, whose physical
2 properties one uses as the basis of the measurement. For example, there is
3 simply no “ab-initio” spectroscopy, which can offer relevant information
4 about *really* unknown material entities: we will always need information
5 about properly prepared samples for comparison, in the form of a spectra
6 catalogue. As Carsten Reinhardt (2006) has observed, modern molecular
7 spectrometry is not so much a part of physics as re-captured chemistry.
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10 11 12 **6. Concluding remarks**

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14 Although most modern chemists may disagree, the qualitative characterization
15 and classification of substances are no less important than quantified
16 descriptions of them. The latter cannot emerge (or exist) without the former.
17 The “conflicting views” about the nature of acids mentioned by Kopp
18 certainly do not concern the operational knowledge with respect to the
19 preparation and identification of substances accumulated over the centuries,
20 which has continued to provide a common basis supporting the shifting
21 theoretical definitions. We have shown some of the significant steps that
22 chemists have taken previous to the modern measurements of acidity,
23 including the qualitative characterization of acids and the quantification of
24 various aspects of the acidity concept. It is a mistake to think that acidity has
25 been reduced to a single quantity called pH (perhaps as much as it is a mistake
26 to think that colour has been reduced to a single quantity called wavelength).
27 At least with respect to the knowledge about the handful of paradigmatic
28 substances discussed here, the concept of acidity is much older and more
29 durable than any of the bold and vaulting theories about it.
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46 Philosophy of Science.
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