

# A Basic History of Acid— From Aristotle to Arnold

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## The rise of acid/base theory and its associated instruments transformed chemistry.

Originally, our concepts of acidity came from the ancient Greeks who defined “sour-tasting” substances as *oxein*, which mutated into the Latin word for vinegar, *acetum*, which became anglicized to our own “acid”. Acid substances were eventually found not only to taste sour, but also to change the color of litmus paper and corrode metals. In contrast, bases were typically defined and studied by their ability to counteract acids—and thus followed behind the acids in their chemical characterization. Their more rigid terminology (alkaline) is derived from an Arabic root word associated with “roasting” because of the fact that the first bases were characterized from the soap-making substances obtained from roasting ashes and treating them with water and slaked lime.

It was not until French chemist Antoine Laurent Lavoisier (1743–1796) turned his attention to the classification of acids and bases that a theoretical structuring of these compounds began. His idea was that all acids contained more or less of a particular “essence” that was responsible for their acidity and were not uniquely different. Unfortunately, he wrongly thought oxein-genic substance was, as he called it, oxygen. By the early 19th century, English chemist Humphry Davy (1778–1829) demonstrated that oxygen could not be responsible for acidity, because there were numerous acids that did not contain oxygen. But it was decades later that the idea of acidity being associated with the presence of hydrogen was proposed by the German chemist Justus von Liebig (1803–1873).

Clarity was brought to the field when, in the 1890s, Svante August Arrhenius (1859–1927) finally defined acids as “substances delivering hydrogen cations to the solution” and bases as “substances delivering hydroxyl anions to the solution”. He also proposed that the mechanism by which acids and bases interacted to neutralize one another was by forming water and the appropriate salt. Later, Danish chemist Johannes

Brønsted and English chemist Thomas Lowry would independently propose a modification of the definitions, retaining the connection of the proton release to acids, but defining bases more broadly as any substance capable of binding protons. Thus, meas-



Arnold Beckman with the “acidimeter” he constructed in 1934.

urements of the hydrogen ion became key to defining the level of acidity, and bases truly were relegated to the mirror-companion of acids as simply receptors.

The above definitions, relying on protons and hydroxyl ions as it did, generally related to reactions in water solution. Gilbert Lewis (1875–1946) refined the acid and base concept to include dissolution events in nonaqueous solvents, where free protons are not involved. Developing along with these theoretical considerations, the practical measurement of acidity has a long history, and this practice is at the foundation of analytical chemistry and ultimately of the analytical instrument business. The concept of pH was perhaps the most important in facilitating this evolution.

It was the work of Hermann Walther Nernst (1864–1941) that, in 1889, gave

the theoretical foundation for the use of electrode potential to measure the concentration of an ion in solution. With Arrhenius’s definition of acidity as the result of hydrogen ion concentration, it was a small step to create a scale of acidity based on the results of electrode potential

In his 1909 paper in *Biochemische Zeitschrift*, S. P. L. Sørensen developed a new colorimetric assay for acidity. But more importantly, he defined the concept of expressing acidity as the negative logarithm of the hydrogen ion concentration, which he termed pH. And he was one of the first to attempt to use electrostatic methods to discern pH. His method involved a hydrogen electrode in combination with a calomel reference electrode. It was sufficiently inconvenient that it did not replace the use of indicator methods.

Additionally, the usefulness of his pH concept was first relatively ignored except in the field of enzymology. Leonor Michaelis (of Michaelis/Menten enzyme kinetics fame) published a monograph, *Die Wasserstoffionkonzentration*, that helped to convince biochemists and later, chemists in general, of the critical importance of pH to analytical research. From then on, measurement of pH, especially in the life sciences, became considered of greater and greater importance.

Despite Sørensen’s attempts at electrode measurements, at that time, acid/base determinations relied primarily on titration experiments. Known concentrations of colored indicator dyes were caused to lose or change color by drop-wise addition of the test solution, thereby allowing standardized measurements to be determined. Ever finer grades of litmus paper and other dye-impregnated indicator strips were also used, with color comparisons against printed standards the key to determining pH.

But the truly modern measurement of pH was revolutionized by two major innovations. The first was the 1930 development by Duncan McInnes and Malcolm Dole of a superior glass electrode capable of responding to hydrogen ions. The second occurred in 1934, when Arnold O. Beckman invented the acidimeter based on the request of

an old friend, Glen Joseph, who worked for the California Fruit Growers Association ([www.geocities.com/bioelectrochemistry/beckman.htm](http://www.geocities.com/bioelectrochemistry/beckman.htm)). The citrus growers needed a way of monitoring fruit acidity during the production of pectin and citric acid—sulfur dioxide used as a preservative made standard methods of testing unusable. Beckman designed a sensitive and sturdy instrument that he called an acidimeter that used a pair of vacuum-tube signal amplifiers and glass electrodes to measure pH easily.

Mainly because of its cost (\$195 in Depression-era America), Beckman's acidimeter received a lukewarm reception when presented at the September 1935 ACS meeting in San Francisco. But after being assured by advisers at the University of Pennsylvania that it was a good product, the Arthur H. Thomas Co. became one of the first major suppliers of the Beckman acidimeter, selling more than 100 in the first year ([www.thomasci.com/history.htm](http://www.thomasci.com/history.htm)). This helped Beckman's own company, NTL, flourish despite the bad economic times, and ultimately led to the formation of the company that bears his name. The device earned him a place in the National Inventors Hall of Fame in 1987.

From its first unveiling, the original Beckman acidimeter became the inspiration for a host of improvements and adaptations in what would universally be known as the pH meter, giving profound impetus to the rise of the international instrument business. For example, Swiss engineer Bertold Suhner developed one of the first European pH meters for Metrohm, only a few years after Beckman introduced his device. And the company followed in 1950 with the first combined pH electrodes ([www.metrohm.com/company/profile\\_e.html](http://www.metrohm.com/company/profile_e.html)).

In another example, soon after World War II ended, Masao Horiba, a student at Kyoto University, abandoned his thesis research when the university cyclotron he was using was destroyed in accordance with the U.S. policy to eliminate all nuclear physics capabilities in Japan. He established a "wireless" research company (then the term for what would become electronics) and discovered that the most important aspect of the process that he used to construct capacitors for his equipment was ensuring a consistent pH in the solution used to make oxide film. According to Horiba, "The market for pH meters was dominated by American products, which were not only very expensive, but not suited to the humid Japanese climate." With the

## From Super to Magic

Not only has the concept of acids evolved over time, the ultimate possible "strength" of acids has evolved, too. The simple, natural product juices and fermentation products such as vinegar and the lactic acid in buttermilk gave way to the mineral acids of alchemists and the Enlightenment chemists. But in 1927, James Bryant Conant, a Harvard chemist, coined the term "superacid" when he developed an acid from mixing sulfuric acid with fluorosulfuric acid to create a solution literally a million times stronger than earlier acids. In the 1960s, Case Western Reserve University's George Olah developed an even more powerful "Magic Acid"—a mix of antimony pentafluoride ( $\text{SbF}_5$ ) and fluorosulfuric acid ( $\text{HSO}_3\text{F}$ ), named for its magical ability to dissolve candle wax—forcing hydrocarbons to accept protons in an unheard-of manner. "Super-bases" that remove hydrogen from almost anything have existed since the 1850s, but the term itself is modern.

cooperation of two university professors from Kyoto, Horiba developed a suitable pH meter, which was named the "Alligator". By 1950, he was producing glass electrodes, and by 1953, he established Horiba, Ltd., based on the success of a series of his pH meter designs (<http://global.horiba.com>).

Throughout the postwar years to the present, other corporations followed in the wake of Beckman with their own pH meters, tailored to every sensitivity, size, task, and price. Monitoring acidity has, over the years, become a major business, as well as a research mainstay of the analytical instrument industry—all from the tartness of vinegar and the initial curiosity of the ancient world.

### Suggested Reading

BBC, *The History of Acids and Bases*; [www.bbc.co.uk/dna/h2g2/A708257](http://www.bbc.co.uk/dna/h2g2/A708257).

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Szabadvary, F. *History of Analytical Chemistry*, Pergamon Press: New York, 1966.

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