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EARLY INDUSTRIAL pH MEASUREMENT AND CONTROL

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Being used for sales pitches for cosmetics and the like, the term "pH" has become part of our everyday language. The importance of pH ("hydrogen ion concentration" in the older literature), and hence of its measurement and control, is therefore readily accepted.

Nowadays, the glass-electrode pH meter is a very common instrument. Although the glass electrode was described in

1909 (1), its high electrical resistance delayed its routine use until the development of suitable electronics nearly three decades later. Accordingly, pH measurements were made in the laboratory by the use of chemical indicators, or by low-resistance potentiometric indicators such as the hydrogen, antimony-antimony oxide, or quinhydrone electrodes (2).

Adaptions of these systems filled some important industrial needs until glass-electrode technology reached a state of maturity. For example, a rather complicated system for the control of water-softening by the lime-soda process was patented in 1906 (3). Dosing was regulated by photometrically monitoring the color change of phenolphthalein. Concerning potentiometric systems, the hydrogen electrode has a long and interesting history (4). One of its earliest industrial applications was to the estimation of the acidity of tanning liquors (5).

Earl A. Keeler was greatly involved in the development and use of the industrial hydrogen electrode. He was born in 1892, joined Leeds & Northrup in 1913, and remained with this instrument-making firm until the end of 1922. Judging by the gentle fun poked at him by the editor of the firm's house journal *The Recorder*, Keeler was a popular staff member. Apart from his activities in connection with pH, he was a leading figure in the industrial applications of electrolytic conductance. Keeler later joined the Brown Instrument Company, but was then concerned mainly with humidity measurement, furnace-gas

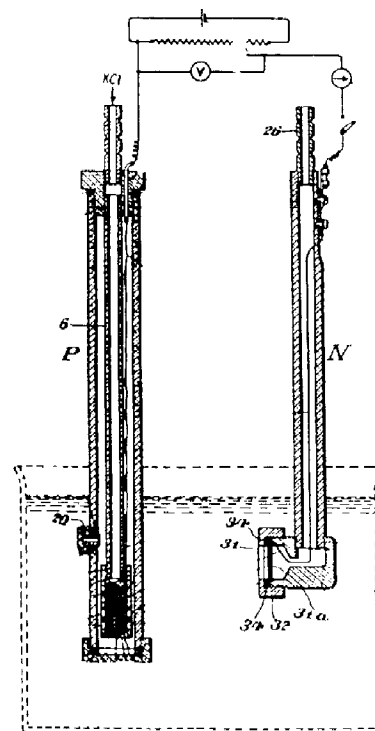


Figure 1. Keeler's 1923 design for a "robust" Bakelite-embedded hydrogen-calomel electrode system for use in industrial pH determinations (7).

Figure 2. An alternative electrode design from Keeler's 1923 patent with both the cathode and anode embedded in a single Bakelite rod (7).

analysis, and temperature control.

Keeler's patent, applied for in 1920, described circuitry to modify the signal from a hydrogen-calomel electrode combination so that a voltmeter could be made to read directly in pH units. This patent was not granted until 1926 (6). By then he had filed, and had been granted, another patent concerned with a robust industrial-type hydrogen-calomel electrode system (7). This is shown in Figures 1 and 2. Structurally, hydrogen electrode N and calomel electrode P were based on hard rubber, Bakelite, or the like. One of the problems with any kind of hydrogen electrode is that the platinized platinum element which forms the actual electrode is easily deactivated by sludge deposition or by "poisoning". In Keeler's design, a platinum gauze disk 31, retained by screwcap 32 and gasket 34, was used. The disk could be readily removed for cleaning, replatinization, or replacement. Hydrogen, supplied through tube 26, passed through the gauze and out into the solution. As with hydrogen electrodes for laboratory use, the flow of gas was so slow that there was no danger of a fire hazard.

A platinum gauze rectangle coated with mercury(I) chloride-mercury paste, rolled up, and placed in a silk bag, was the basis of the calomel electrode P. Decinormal potassium chloride solution flowed from a reservoir down through central tube 6, through the bag, then out into the test solution. The capillary orifice in plug 20 kept the flow rate very

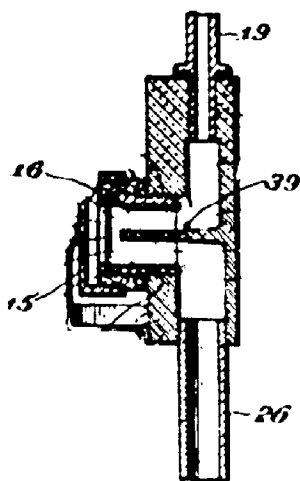
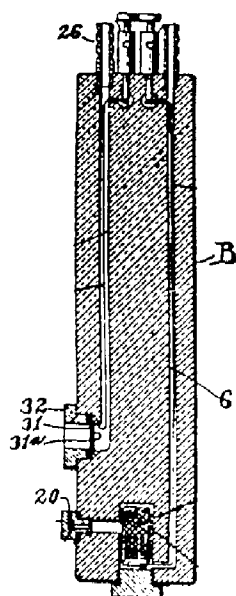


Figure 3. A detail from Keeler's 1923 patent for the monitoring of pH in flow systems (8).



low. An obvious extension, also shown, was to make a single unit that contained both indicator and reference electrodes.

Similar principles were used in a system for flowing streams. Figures 3 and 4, reproduced from the patent (8), show the arrangement. A feature was presaturation of the stream with hydrogen before reaching the indicator electrode. The stream, which might be raw water with a pressure head of about 10 feet, entered glass-wool filter 25 through tube 23. Emerging from jet 20, the stream entrained electrolytically-generated hydrogen entering through tube 22. Deflected horizontally, the stream passed through the platinum gauze disk, over the dam 16 formed in cap 15, into chamber 5, and then left by discharge pipe 26. The body of the system also contained the flow-type calomel electrode. A capillary opening 39 connected this with chamber 5.

Keeler stated that, in determining the acidity of water, air

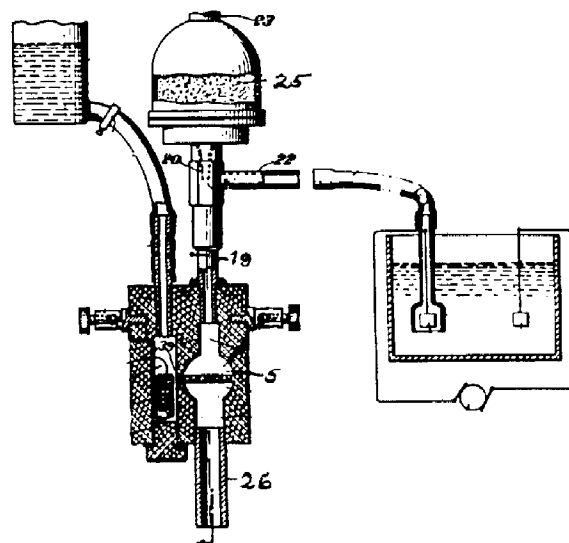


Figure 4. A detail from Keeler's 1923 patent for the monitoring of pH in flow systems (8).

proved satisfactory as the gas. Apparently, the action was then that of an oxygen electrode, so that the calibration of the system had to be suitably adjusted.

The next steps were the recording of pH and, if necessary, its control. In 1922, Irving B. Smith and Keeler filed a description of equipment for the performance of these steps. The patent, which included the diagram shown in Figure 5, was not issued until 1928 (9). The complicated appearance of the diagram is largely due to "known art", i.e., the mechanism of a chart recorder that was patented in 1915. An excellent description of the principles of this type of recorder is available (10).

A hydrogen-calomel electrode system developed a potential dependent upon the pH of the solution flowing into vessel A. This potential shifted the pointer of galvanometer G, which is part of the recorder mechanism, causing pen 40 to indicate

the pH on the motor-driven chart. The overflow tube, *m*, of vessel *C* kept constant the rate of flow into *A*, which had its own overflow tube.

Suppose that an acidic flowing stream has to be brought to a desired pH by the addition of sodium hydroxide solution, delivered at constant head from vessel *D* through valve *V*. The degree of opening of this valve, controlled by wheel *W*, a part of the recorder mechanism, suitably adjusted the flow of alkali to produce the desired pH. This was selected by appropriately setting wiper, *i*, of potentiometer *R*. If pH adjustment was possible by mere dilution, then sodium hydroxide solution was replaced by water.

The inevitable delay after filing patent specifications did not hinder Keeler from publicizing some of the industrial applications of his inventions. He pointed out that potentiometric alkalinity control in the carbonation of sugar juices was not affected by color differences (11). Electrode systems similar to those shown in Figure 1 were illustrated in two articles on potentiometric control of industrial processes. The first referred to the processing of beet and pineapple juices, water purification, wool scouring, leather tanning, and sewage disposal (12). Boiler feed control was the main concern of the second article (13). This topic was treated more extensively in an article co-authored by a power station engineer (14).

It is well known that the quinhydrone electrode is not precise if the pH is greater than about 8 (2). An additional objection from the industrial point of view is that quinhydrone must be added to the sample. In 1931, Charles C. Coons examined two methods for dosing flowing sample streams (15). One involved passage of the stream through solid quinhydrone, either retained in a cloth sack or in pellet form. He concluded that the other method, addition of quinhydrone

solution to the stream, was simpler and more effective.

To test the efficiency of the "solution" method, runs that lasted several days were made with continuously-flowing tap water. At intervals, the flow was switched to one of slightly acidified water and then back to the original stream. Uniform response to these switchings was obtained. Also writing in 1931, George A. Perley referred to the use of the quinhydrone solution-feed technique in waterworks practice (10).

The literature concerning the antimony-antimony oxide electrode is extensive (16). In 1939, Perley examined the industrial possibilities of this electrode, where

a limit of error of 0.1 to 0.2 pH was acceptable (17). The recommended form of electrode, merely a stick cast from high-purity antimony, was very robust. The addition of antimony oxide was not necessary, because this sparingly soluble compound forms on the surface when antimony comes in contact with air-containing aqueous solutions. A rubber-coated stick, the exposed end of which is ground and polished, was found to be superior to other forms. In the same 1939 article, Perley stated that over 500 industrial pH installations were using the molded rubber-coated antimony electrode (17). Satisfactory performance was obtained in a wide variety of applications, such as in

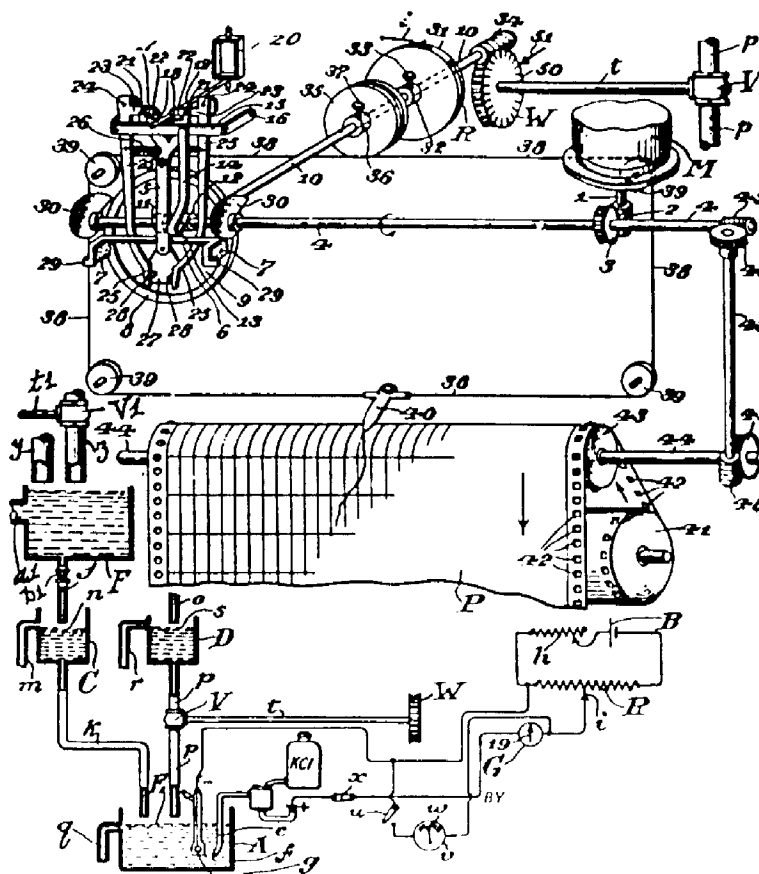


Figure 5. Keeler and Smith's 1928 design for the automatic recording and control of pH in industrial processes (9).

beer, alum solutions, paper-mill liquors, water treatment systems, clay suspensions, and the like (18).

When used in conjunction with a low-resistance reference electrode, the pH electrodes discussed could supply the small current needed to operate the galvanometer-type recorders then in use. With the discovery and development of the triode and later vacuum tubes, the need for these low-resistance electrode systems began to disappear. pH meters and recorders having a high input impedance could be made, so that the electrical resistance of the electrode system no longer re-

mained an important consideration. The flow-type calomel electrode could be replaced by one designed to give an almost negligible flow of potassium chloride solution. One of the most successful designs, described in 1947, made use of a controlled-crack junction tube (19). Pyrex glass was used for the body of the tube. A hole 5 to 10 mm in diameter was blown in the bottom and the hole was closed by sealing in a plug of glass having a high coefficient of expansion. After proper annealing, a permanent crack of controlled dimensions was obtained. A typical leak rate was 0.006 mL/hr.

Because of improvements in instrumentation, the high resistance of the glass electrode ceased to be a handicap, and it became the pH electrode of choice. Once this had occurred, highly-specialized glasses that provided a stable, much improved performance were discovered and exploited (20-22).

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OLD CHEMISTRIES

James Tytler's "A System of Chemistry"

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In the year 1791, the United States was slowly becoming a nation. George Washington was in the third year of his presidency. Vermont became the 14th state. The Bill of Rights amendments to the Constitution went into effect. And Philadelphia publisher Thomas Dobson marketed *A System of Chemistry* (1). This volume was the second full-size chemistry book published in America (2) and the first American imprint to introduce the new chemistry of Lavoisier and his French colleagues (3).

A year earlier, Dobson had begun the ambitious task of publishing an American edition of the 18-volume *Encyclopaedia Britannica*. He was pirating the third Edinburgh edition of *Britannica*, which was issued in 300 parts from 1788 to 1797. As each part reached America, Dobson would have a few of the articles edited by Americans and issue half-volume sections every ten weeks. The American title, *Encyclopaedia; or Dictionary of Arts, Sciences and Miscellaneous Literature*, merely omitted the word "Britannica" from that of the Edinburgh edition. Title pages bear the date 1798 because front