Cremer's Glass Electrode

Max Cremer (1865-1935)

The process of learning about the world involves us building simple mental pictures that we can use to give us understanding. Yet deepening our understanding invariably involves having to unlearn some ideas that are so deeply embedded as to become almost intuitive. At the very least we are forced to let go of some of those certainties as we start to appreciate the complexity of our world. The story of the glass electrode is a curious story of learning and unlearning.

Early in the story of electricity materials were divided into broad classes, conductors and insulators, a distinction established early in the 18th century by the English astronomer Stephen Gray. But almost as soon as the Leyden jar was invented (see CK 116 April 2017), the Dutch physicist van Musschenbroek noticed that not all jars were alike. While some could be charged to deliver whopping charges, others either failed to charge or simply lost their charge with time. Van Musschenbroek speculated that perhaps the glass could conduct electricity; Henry Cavendish later showed that Leyden jars lost their charge spontaneously when heated.

The conductivity of glass was finally demonstrated systematically in 1854 by the German physicist Johann Heinrich Buff a man whose connections extend into being related, by marriage, to both August Hofmann and Justus Liebig (see CK passim). Buff, who had measured electrical conductions in gases and plasmas, extended his studies to glass across a range of temperatures and put paid to the idea that glass was one of the best insulators. His work also attracted others into the field. William Thompson (later Lord Kelvin) was able to make a battery in which a thin sheet of flint glass separated two half-cells. Almost at the same time Wilhelm von Beetz observed that certain types of glass weren't just significant conductors of electricity but that this conduction led to changes in alkalinity at the oppositely polarised surfaces.

It was one of the assistants of the brilliant polymath scientist Hermann von Helmholtz, Wilhelm Giese, who made a critical set of measurements while doing research for his doctorate in 1878. Interested in trying to understand the nature of the charges in a Leyden jar, and suspecting that it was related to surface charges on the glass, Giese built a thin-walled evacuated, mercury-filled tube equipped with an electrode; he sealed this inside a second tube filled an aqueous solution and also equipped with a platinum wire. Giese found that a voltage developed between the electrodes. This potential depended on the nature of the aqueous solution, while the rate at which the voltage was established depended on the thickness of the glass – thin glass responded much faster.

The work may well have influenced his boss, Helmholtz who spoke at a Faraday Discussion meeting in London in 1881. There Helmholtz argued that electrochemistry could only be understood in terms of charged particles. He reported a cell similar to Giese's (see diagram) but with the mercury replaced by copper sulphate, and the other solution with zinc sulphate. This behaved exactly like a Daniell cell (CK 87, Nov 2014) showing that the glass acted like a highly resistive electrolyte. Surprisingly neither Helmholtz, nor Giese (who had was now the head of the German Polar research station on Baffin Island) recognised the potential of their observations even as Ostwald and Arrhenius established the reality of ions in electrolytes and of the dissociation of acids and alkalis.

Twenty five years later it was a physiologist who hit the jackpot. Max Cremer was born in Ürdingen on the banks of the Rhine in the Ruhr, the industrial heartland of German. He studied medicine in Bonn, Würzburg and Berlin, qualifying at age 23. But rather than go into practice he continued to study science for another two years in order to study physiology. Unusually, however, he focused on physics and mathematics, then an unlikely combination for one interested in biology. He obtained his habilitation at the Institute of Physiology in Munich having studied with the great physiologist Carl von Voit and Franz von Soxhlet (see CK1 Sep 2007). Cremer and his contemporaries in Voit's lab studied the metabolism of carbohydrates establishing the relationship between glucose and glycogen, steadily unravelling the biochemical pathways of the livers of rabbits. As his independent career blossomed, Cremer's interest in biophysics came to the fore.

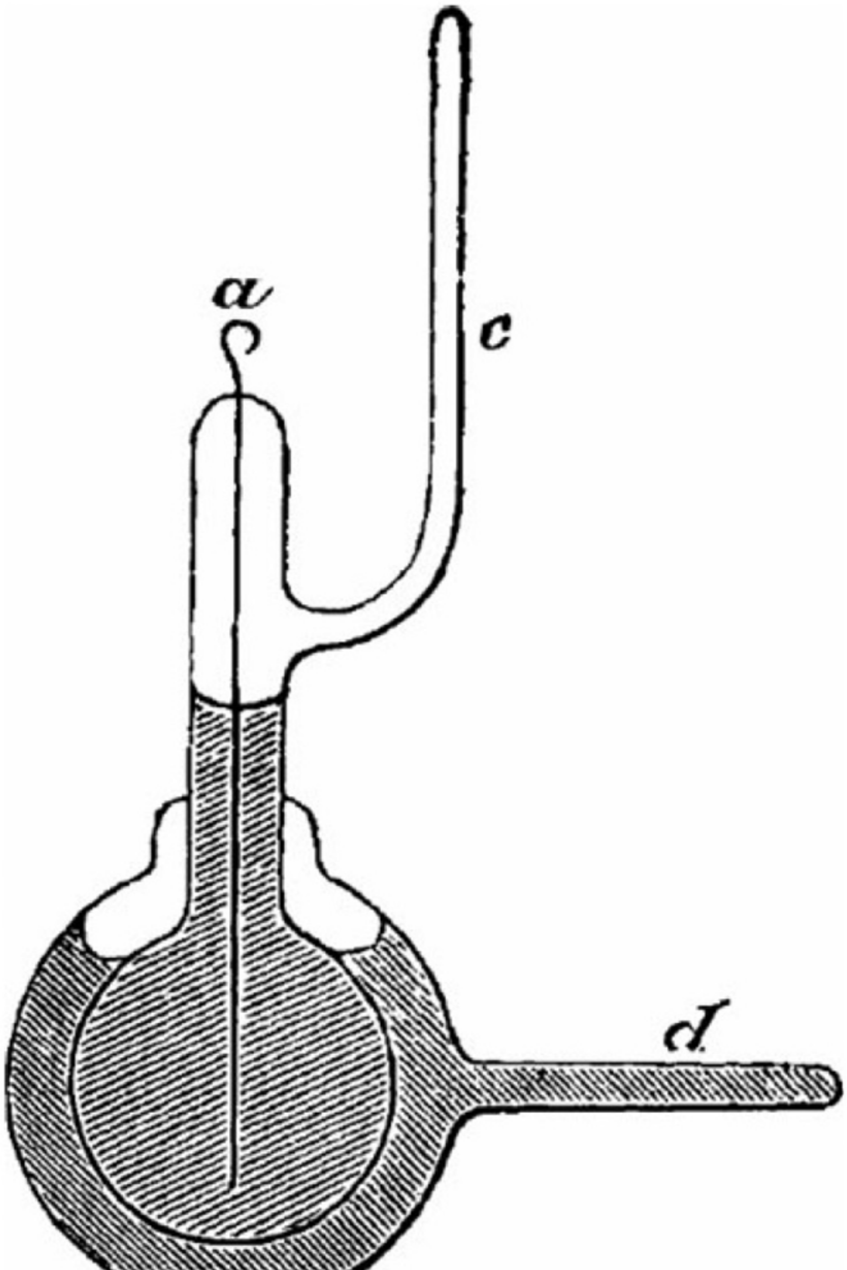
He wanted to understand the role of cell membranes. Aware of the Helmholtz and Giese's work he reasoned that gossamer-thin glass might be a good analogue. Taking a glass tube, he blew a small thin bubble at one end. With a platinum wire and a standard solution inside he placed his bubble tube into a second solution. The emf across the glass bubble varied as he changed the degree of alkalinity and acidity of the solution. It was the birth of what we now call the glass electrode, though the application never occurred to Cremer.

Three years later in 1909, the same year that Sørensen proposed the pH scale, Fritz Haber (see CK59 July 2012) and his student Zigmunt Klemensiewicz conducted an acid-base titration using a variant of Cremer's bulbous electrode, demonstrating that the potential depended on the logarithm of the proton activity. The glass electrode was now a real instrument that could be used to measure Sørensen's pH with ease, and spread rapidly across wide areas of science.

The result is that the concept of pH has become one of those simple ideas that is embedded deep within the psyche of anyone who has studied science. And yet, if you ever find yourself having to teach about pH it's important to remind yourself that an idea that simple, surely, must be too good to be true. Do you dare to dig a little deeper?

References

M. Cremer, *Z. Biologie*, **1906**, *47*, 562
F. Haber and Z. Klemensiewicz 1909) Z Phys Chem, **1909**, *67*, 385


a
c
d
b