Glass and Life
The Biochemical Origins of pH

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1 Introduction

In everyday experience glass seems to be a quite stable and almost inert material. It very effectively shelters us from the environment in buildings, aircrafts and submarines, and it serves as container material for almost every chemical. A large amount of practical chemistry takes place in containers made from glass and most theoretical insights of the chemical sciences were achieved just that way.[1] Nevertheless, glass is anything but inert. There is even one particular application of its special dispositions which has led to a kind of "quiet revolution"(Alan Rocke): the measurement of acidity. In a relatively recent monograph on the application of the pH electrode the authors enthusiastically claim: "The glass electrode is to solution chemistry what the silicon chip is to computers – the central component."[2]

Though many experts will agree that modern pH-measurement is of extraordinary relevance in terms of its prevalence and its societal impact (consider, for example, the emergence of "acid rain"), it has not been investigated adequately by historians and philosophers of chemistry. At the most it is just mentioned as important, but when it comes to the narratives of what is sometimes called the "instrumental revolution" or the "material turn", the humble acidity measurement seems not to count as proper instrumental achievement.[3] One task for the present study will be to locate the position of the pH-electrode in the history of chemical measurement in the first half of the 20th century, in a direction quite different from the widely noted moves towards "Big Science".

In the modern scientific common sense, acidity is considered to refer to the "activity", or, the effective concentration of hydrogen ions. The description of aqueous acidity found one culmination with the formulation – or invention – of the pH concept by Søren Sørensen in 1909. Today, this apparently simple number representing acidity is almost a chemical celebrity: we find it as required information on every package of cosmetic articles like shampoo, as well as in the blood analysis results that a physician is perhaps desparately trying to explain to us, not to mention the ubiquitous applications with respect to environmental issues. In his small book on the history of acidity, which is one of the very few attempts to grapple with that concept, the German historian and philosopher of chemistry

Rüdiger Simon repeatedly claims the following: "The dilution law found by Ostwald in 1888 and the introduction of the pH value by Sørensen (1909) facilitated the quantitative registration of the hydrogen ion concentration in aqueous systems."[4] This statement suggests that it has been deeper theoretical findings rather than practical decisions which guided the success of that breathtaking development. We will put that assumption under scrutiny. What exactly was the interrelation between pertinent theories and practices in the context of acidity?

Following this introduction we will give in Section 2 an overview of the first steps of the development of the glass electrode by Max Cremer. Section 3 will give the history of the invention of the pH concept – and its somewhat overestimated relevance. Section 4 will investigate the early technical development and design of measurement. Finally, we will conclude with a discussion of the relevance of the glass electrode in analytical science / chemistry.

2 Biological membranes and electrochemical potential

The glass electrode, which is the key component in pH meters, was in fact developed before the pH concept was created. From a merely conceptual – and modern – point of view, the glass electrode has its origins in two central principles: the electromotive force and the concept of semipermeable membranes. When Max Cremer (1865–1935) in 1906 published his seminal work on the "electromotive properties of tissues"[5] the theory of electromotive forces was well on its way already[6]; and in 1890 Wilhelm Ostwald had published an article on semipermeable membranes, which opened the way for membrane science.[7] As we will see, however, it was rather the ingenious setting of Cremer´s experiments than strict theoretical reasoning that brought about his surprising discovery.

Cremer was a physician (doctorate Munich 1887) and physiologist.[8] He was among the first to apply electrical measurement devices in biology and may be considered one of the founders of modern electrophysiology (*Elektrobiologie*). His long paper is mainly devoted to the electrochemical differences in polyphasic electrochemical cells as a model of electric phenomena in living matter. In electrochemistry a cell is usually analyzed as consisting of two "half cells". One paradigmatic example is the Daniell cell, first invented in 1836 by the English chemist John Frederic Daniell (1790–1845). In the widely adopted configuration of the Daniell cell, a copper electrode in a copper sulphate solution was connected to a zinc electrode in a zinc sulphate solution. The two half-cells were separated by a diaphragm, which was originally an ox gullet,[9] and later a beaker made from porous (unglazed) ceramic. The diaphragm prevented the metal ions from wandering into the other chamber and causing unwanted electrode reactions and

a breakdown of the potential. In such classical setups, one electrode served as a "donor", and the other was the "acceptor". Hence, the Daniell cell is a typical redox system, such that zinc plays the role of the former (and has the tendency to dissolve), copper that of the latter (with a precipitation tendency). In modern standard conditions the Daniell cell provides 1.1 Volts.

In the abovementioned article from 1890, Ostwald suggested a theoretical model for semipermeable membranes:

> As can be inferred from the above, the claim that semipermeable membranes can allow the passage of certain ions but not others throws plenty of light on so many and different areas that a single person can by no means think of finding a solution to all these experimental problems presenting themselves.[10]

In Ostwald's statement we can identify the point of motivation for Cremer, who took up just one out of those "different areas", namely Pfeffer's clay cell, a soaked clay beaker that can be used, for example, to separate sugar from water. Cremer writes:

> Only later one extended this notion of semipermeability as well to such membranes in which single ions were not capable of passing through the membranes. We owe this extension to Ostwald, and it is indeed he who must be considered the founder of the membrane theory for biological currents [*biologische Ströme*].[11]

The notion of membrane stems from the Middle Ages. It became particularly important in the chemical sciences at the end of the 19th century, and it is indispensable in many important modern technological applications. We will come back later to the question of the validity of the membrane theory for the explanation of the mechanism of the glass electrode.

In his study Cremer systematically investigates "*diphasische Flüssigkeitsketten*", that is, two-fluid electrochemical cells. For this purpose, he analyses electrolytes of the same and different kinds in the same and different concentrations. For his measurements he uses galvanometers of the Deprez-d´Arsonval type or the Einthoven type,[12] and in both cases he uses a battery to balance the caused potentials, such that the compensational force equals the electromotive potential he wants to measure. In the "mainly experimental" part of his article he reports the results in which a good fifth of the whole work is devoted to glass membranes. The basic construction he uses is similar to an apparatus used earlier and for different purposes by Helmholtz and Giese.[13] In his Faraday lecture

Zur Elektrode

Zur Elektrode

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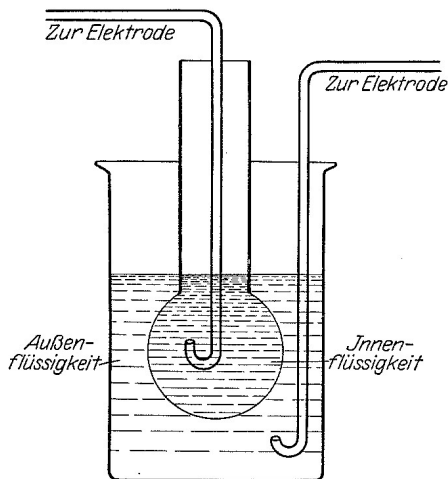flüssigkeit

Innen-
flüssigkeit

Fig. 1: Drawing of the apparatus Cremer used in his study from 1906; From Cremer, "Ursache" (1928) p. 1014; there is no drawing of his apparatus in the original article. The inner and outer liquids are each connected to electrodes, and separated from each other by the glass bulb. The electrodes and the electrometer are not shown in this picture.

from 1881, Hermann von Helmholtz had reported on his and his co-worker Wilhelm Giese´s experiments with a special kind of Daniell cell. What was special about their apparatus was the application of a glass bulb as the diaphragm between the two half-cells.[14] Although he later qualified the impact of the Giese-Helmholtz apparatus on the conception of his experiments, Cremer followed a similar idea and had his laboratory technicians prepare glass balls of 6–10 cm diameter and 0.01 mm thickness (see Fig. 1).

With this apparatus Cremer performed experiments with solutions of different acidity and measured up to several hundred millivolts. He describes his findings as follows:

> It seems as if a very minimal acidifying of one side is sufficient to cause big electromotive forces in comparison to the electromotive forces in physiology. Not only sulphuric acid, but acetic acid also acts this way . . . . As I brought diluted sulphuric acid to the outer side of a bulb to the 0.6 percent kitchen salt solution and caustic soda to the inner, the electromotive force increased . . . to 0.55 Volt.[15]

From this and other statements in the 1906 paper, it is easy to tell that the motivation of the author was not a mainly physico-chemical one as with his predecessors in electrochemistry, such as Ritter, Faraday, Helmholtz, Arrhenius and Nernst.[16] Rather, Cremer used physico-chemical methodology to model biological phenomena in a more quantitative vein, avoiding speculative hypotheses such as the *vis vitalis*, which were alien to him as he stresses in the introduction to his article.

In 1928, perhaps in order to defend his priority for the glass electrode, which in the meantime had become a wider-known successful measurement device,[17] Cremer published a review article about the "causes of electrical phenomena", in which he describes the early story of his achievement as follows:

> I had the correct guess that, if one could somehow make very thin membranes of solid, badly conducting material, they possibly could give noticeable electromotive force in relatively simple cells. For that membrane not to have cracks it should consist of a relatively rigid material, and in that connection I recalled the bulbs which the glassblowers used to fabricate when they join glass tubes; therefore I decided to perform experiments with such glass bulbs.[18]

Only three years after Cremer´s first publication a scientific concept came into being that would turn out to become one of the most frequently measured items in the vast field of the investigations of living or non-living substances. The next section is devoted to this concept, namely the pH. As we will show, like the glass electrode it was developed from a biochemical perspective.

3 The pondus hydrogenii

"Many students believe that there is some mystery to the pH. This is not the case. It is solely a matter of convention and definition."[19] This assessment from a modern popular-scientific introduction to biochemistry by Ernest Baldwin correctly points to the conventional theoretical background of that concept. That assessment was valid in the past, and it remains valid in the present. There are disadvantages to the mathematical definition of pH that are obvious to all those who teach and handle that concept routinely, of which the mystery mentioned by Baldwin is only a minor one. The pH is a convenient representation of a particular type of empirical data, and it contains the risk that humans can face when they try to handle – or understand – logarithms as naturally as ordinal numbers. The difference of pH 2 and pH 5, for example, is easily underestimated intuitively. In fact, it is a factor of three orders of magnitude: in a solution of pH 2, there are 1000 times more hydrogen ions than in that of pH 5.

Rarely can an event of exceptional significance to the history of science be dated so precisely as the "birth" of the pH concept. On 29 May 1909, the Danish scientist Søren Sørensen (1868–1939) submitted the second communication of his "*Enzymstudien*" to the Biochemische Zeitschrift.[20] Sørensen was, like Cremer, a biochemist with a medical background. He was the Director of the chemical department of the Carlsberg Laboratory supported by the famous brewing company. He was working on protein chemistry at the time, and starts his contribution as follows:

"It is a well-known fact that the rate of an enzymatic cleavage is among others dependent on the degree of acidity or alkalinity of the solution under examination."[21]

In the course of the study Sørensen emphasizes the importance of the degree of dissociation, recognizing the fact that not all acids (or bases or salts) dissociate completely when dissolved in water. The momentous introduction of the pH value, however, he gives only after about one half of the almost seventy-page article:

> As to the number p, I suggest the name 'hydrogen ion exponent' [*Wasserstoffionenexponent*] and the notation p_H'. By the hydrogen ion exponent (p_H) then is understood the Briggs logarithm of the reciprocal value of the molar concentration of the solution with respect to hydrogen ions."[22]

The number p is the power of the (molar) concentration of the hydrogen ion, C_p. According to Sørensen, the latter "is smaller than 1 in all cases described in the present essay and can be identified with 10^{-p}." Concentrations higher than one-molar were not relevant for him, because these do not occur in biochemistry (a fact which only later would become obvious, when researchers of a more physico–chemical orientation began to figure out the application range of the pH concept). In the first monograph on the measurement of acidity in biochemistry, the German (later American) Leonor Michaelis (1875-1949) addresses the usefulness of the "*Wasserstoffionenexponent*" as follows:

> It is thus beneficial for the graphic representation to operate with the logarithm instead of the hydrogen number itself. But the method of the concentration cell as well gives only this logarithm in the first place. Hence the suggestion of S.P.L. Sørensen rightly became accepted. . . .[23]

In the second edition of his monograph published in 1922, Michaelis maintains his positive estimation of the pH concept. Hence it becomes clear that already a few years after the introduction of the concept it was widely accepted and began to settle in the basic canon of the biochemical, and then of the physico–chemical sciences. Michaelis´ claim, however, that attempts to measure acidity inevitably result in logarithmic numbers is over-theorized and misleading. Though the Nernst equation claims a logarithmic connection between the electric potential and the concentrations of stuff in a redox or osmotic system, the practical realization of an acidity determination does not necessarily include logarithms, if the calibration of the process is performed properly. The same is true for traditional acidity measurements via titration.

There is another interesting argument in favor of the logarithmic representation. In a later synopsis of the field, Ludwig Kratz, chemist with the Jenaer Glaswerk Schott in Landshut, claims that Sørensen's choice of a logarithmic scale can neither be traced back to mere arbitrariness nor to pure convenience or usefulness. He argues that chemical reactions are influenced rather by large changes of hydrogen ion concentrations, for example one order of magnitude, than by smaller changes like the doubling of concentration. He concludes:

"The pH number is thus representing the correlations of natural laws much better than the concentration."[24]

By "natural laws" Kratz seems to mean something like the Nernst equation, or, more generally, the central thermochemical relation between the change of the Gibbs enthalpy and the equilibrium constant of a chemical process, $\Delta G = RT \ln K$. As to the latter, the logarithm creeps in via the mathematical integration of a term in the form of $1/x$, perhaps an operation that is considered "natural" or "necessary" by most natural scientists. As we will see more clearly in the next section, acidity measurements using the glass electrode were particularly well-suited for connecting with these logarithmic expressions.

However, the coherent linkage between pH, the glass electrode and the above-mentioned lawlike statements is not something that dictates scientific practice absolutely. The pH measure in the end only expresses the molar concentration of hydrogen ions, and there are other ways of getting at that information. There were indeed other acidity-measurement devices competing with the glass electrode, including the hydrogen gas electrode, the quinhydrone electrode, and colored indicators. In addition, pH-measurements with the glass electrode are not entirely self-reliant, as they have to be calibrated by other techniques (which Kratz does mention in his book), often by means of standard solutions.

At this point it will be instructive to have a brief consideration of the competing acidimetric devices. The hydrogen (gas) electrode consists of a piece of platinum streamed with hydrogen gas in an acidic solution. Malcolm Dole states:

> Practically of no great application but theoretically of the utmost importance is the hydrogen-electron [sic] method for determining the pH; this is because the hydrogen electrode gives the standard pH values to which all other methods must be referred and by which all standard solutions, new types of electrodes and new pH methods must be checked.[25]

Known and applied since the later 19th century, the hydrogen electrode is still at the center of electrochemistry. By convention, its electromotive force (emf) is set to zero, and all other reduction potentials are referred to it. As Dole rightly emphasizes, its applicability is restricted to well-defined laboratory settings. Moreover, it is a redox electrode by definition, and therefore other oxidizing or reducing agents must be absent during measurement. Hence, the hydrogen electrode can by no means compete with the glass electrode in everyday practice.

The quinhydrone electrode is an invention of the 20th century.[26] It uses the redox reactions between the organic substances quinone and hydroquinone, which are a function of the hydrogen-ion activity. Disadvantages are the restricted applicable pH-range (8.5 is a critical point), the disturbing impact of oxidizing or reducing chemicals, a "salt error" (the reactivity of quinone and hydroquinone being affected by salts), sensibility to some proteins, and sensibility to higher temperatures. However, the quinhydrone electrode has one main advantage compared to the hydrogen electrode: it is simpler to use as it does not require the mechanism of bubbling hydrogen gas through.

Colored indicators have played an extraordinary role in the practical detection and description of what now is called acidity ever since humans became aware of acids.[27] According to Dole, Friedenthal and Salm made the decisive steps to establish colorimetric determination methods. In one of his early publications in 1904, Friedenthal mentions the other methods known till then (cleavage rates of esters, inversion rates of sugars, and "direct measurement of H^+-ion concentrations with gas electrodes"), and continues:

"None of these methods allows for the immediate measurement of the reaction of a solution in an absolute manner without considerable expenditure of time and apparatus."[28]

This statement shows that the economical side of laboratory work was a strong driving force. There was, by the way, also no sign in those pre-pH papers of the later notion that the logarithmic H^+-concentration would be the more natural way to represent acidity. Friedenthal´s research-economic statement applies of course as well to his own specialty:

Although the p_H value [sic] can be determined colorimetrically with the same precision as with any electrometrical method under suitable conditions, the development has been much more into the direction of the latter [the glass electrode], because the field of application is signifi-

cantly smaller for colorimetric methods, and they are less suitable for in-situ monitoring or even for p$_H$ [sic] process regulation.[29]

But we need to recognize that the glass electrode also had limited applicability, and the same can be said about the pH as a particular representation of the acidity concept. In arguing for the naturalness of the pH concept one may point to the fact that the concentration of hydrogen ions in pure water is something close to 10^{-7} mol/L, and that there is a strong relation between the concentrations of H$^+$ and OH$^-$ in water. However, that fact is true and meaningful only in the normal sort of aqueous solutions, which are of course prevalent in biochemistry but not in all areas of chemistry. Because the pH concept and the glass electrode emerged from bioanalytical perspectives, the interest for the more extreme conditions at the edges of the pH scale or the applicability of the concept and the measurement device to non-aqueous solutions only commenced after a period of settling or "first success". Note that suggestions to extend the acidity-definition to non-aqueous matrices began around 1923.

4 Further developments of an apparently simple measurement device

From the second to the fourth decade of the 20th century the glass electrode passed through its decisive historical period:

> The experiences of almost two decades turned the glass electrode, considered an only occassionally applicable laboratory oddity at the start, to the tool proving itself again and again allowing for the exact determination of one of the most important and informative reference numbers.[30]

Some of the crucial steps of this story, all of them associated with biochemical or biomedical motivations, will be addressed in the following.

4.1 The application perspective

The next important step in the development of the glass electrode following Cremer´s studies was made by the eminent German chemist Fritz Haber (1868–1934) and his Polish Ph.D. student Zygmunt Klemensiewicz (1886–1963), already in the year of the invention of the pH concept.[31] We may assume that Haber is the main if not only author here – the text is mainly written in the first person – and Klemensiewicz his technically skilled assistant[32]:

> The following descriptions show that one can obtain the same success [with respect to acidimetric measurements] with a piece of ordinary Thuringian glass[33] instead of a hydrogen electrode[34]
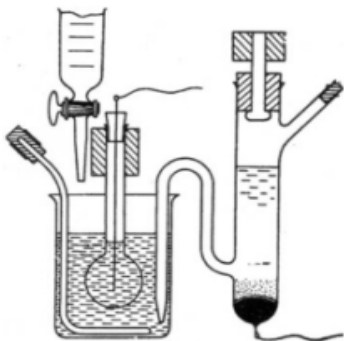
Fig. 2: Scheme of the apparatus used for "acidimetric" measurements, from Haber & Klemensiewicz, "Phasengrenzkräfte".

The "piece of ordinary glass" was nothing else than a glass bulb the principle of which the authors obviously borrowed from Cremer (cf. Fig. 2 and Fig. 1).

In the 1909 article, Haber is quite self-reliant and clearly condescending to Cremer. Though he introduces the work of Cremer by refering to its "physiological interest", he does not acknowledge Cremer's experimental work as the obvious precursor to his own. About the relevance of his results, he points out:

> One will find out that the ideas and experiments available in the present paper will clearify these observations in a manner that will not diminish their physiological interest.[35]

Haber clearly rejects the applicability of the theory of the semipermeable membranes to the glass electrode. He claims that his results deliver a solution to Cremer´s problems and gives an extensive discussion of the theory of the cause of the electric potential on the basis of Nernst´s equation.[36] In a simplified, general form applicable to the case here, the latter is: emf = $(RT/n) \ln(c_1/c_2)$.[37] The authors use several drawings of neutralisation curves to illustrate their main point, which is, in modern terms, the acidimetric potentiometric titration. These curves make it obvious that the relation between potential and concentration is logarithmic (which in fact is what is the core of the Nernst equation). Cremer, however, by no means denied the importance of Nernst´s law here. The main difference between the two interpretations is rather located in their differing description of the mechanism. Rudolf Beutner, another electrophysiologist and former co-worker of Haber, discusses the discrepancies between these two in more detail.[38] He calls Cremer´s approach "interphasic", and that of Haber "phase border potential theory" (*Phasengrenzkrafttheorie*). Cremer claims that positive and/or negative ions of the electrolyte wander more or less into the membrane due to their different velocities. In contrast, Haber categorically rejects the idea of intruding ions. He seems to be not interested in further theoretical speculations about what happens in the membrane. Cremer, on the other hand, tries to expand the interphasic approach to all types of membranes. The specifity of the glass electrode is not as central to him, as it is to the two researchers from Karlsruhe, because his main interest is membrane biochemistry. Hence, he was partly correct with

respect to his explanation of the glass electrode´s functionality, but yet without sound arguments. And at the same time he was partly wrong, because other membranes do not behave like thin glass.

The disagreement between Cremer and Haber mirrors a common conflict in chemistry, namely between kinetic and thermodynamic explanations of processes. There is some quotidian chemical saying that some processes are kinetically driven, and others by the free energy. From a thermodynamic point of view, the chemical potential (free energy) is the necessary condition for the realization of any chemical process; however, specific details of that process (e.g., reaction paths and rates) are not determined by the potential. On the other hand, it would also be wrong to consider the kinetics (or mechanics) necessary and the potential secondary. Cremer, to be clear, did not claim a kinetical priority for the mechanism of the glass electrode. Rather he expressed an interest in the pertinent mechanism and claims some intrusion of ions due to their mobility. As it turned out later, this idea was not as wrong as Haber thought. If we were to answer the question for the priority of the invention of the glass electrode, we would have to divide the credit: Cremer found the phenomenon, and Haber and Klemensiewicz outlined the application.[39]

4.2 The specifity of glass

The early investigations on the glass electrode and the formulation of the pH concept belong to the end of the long 19th century. In retrospect it becomes clear that after the initial activity we witness a period of a somewhat retarded development in that field. In the preface to the third edition of his important monograph on the determination of hydrogen ions, which contains an exhaustive bibliography, W. Mansfield Clark shows a graph with numbers of publications in the field from 1910 to 1927. In the early years before World War I, he counts fewer than 100. There was a resurgence of activity by 1920 with 300 publications in that year, and for 1927 almost 1,500.[40] However, the glass electrode did not become a main feature until the 1930s.

The American chemist Malcolm Dole (1903–1990), who himself was involved in the development of the glass electrode, says:

> Between 1920 and 1930 pH measurements by means of indicators and by means of the quinhydrone and hydrogen electrode reached a high state of perfection . . . . At the same time the true thermodynamic significance, or perhaps I should say the lack of thermodynamic significance, of the pH concept finally became understood. Yet the glass electrode was practically unknown . . . . [The 1930s] actually witnessed the most valuable development from a practical standpoint that

has ever been made in the field of pH, namely, the invention of glass electrode pH electrometers which have literally swept the country and are now so extensively used that they are manufactured by mass production methods.[41]

Dole is referring to the then-standard measurement methods, those which Michaelis was writing about when he emphasized the advantages of the pH from his point of view.

It is not easy to decipher, however, what Dole means by the "lack of thermodynamic significance". It would be outright contradictory, for example, to state that the pH measurement yields logarithmic data (as Michaelis does, too) on the one hand, that is to accept the accordance with Nernst´s theory, and to claim that the pH suffers from a lack of thermodynamic significance, on the other. It seems that Dole is addressing the fact that the pH concept does not involve a redox process, as would perhaps be suggested by the general formula for the reaction quotient Q (customarily, the concentration of oxidized substance divided by the concentration of reduced substance). Rather it is a concentration cell, but even that fact would have to be interpreted thermodynamically.

Hence, both pH and glass electrode exhibit certain theoretical weaknesses.[42] Intriguingly, the applicabilities of both were not diminished by that fact. Although almost all published experimental work since the 1920s is accompanied by some theoretical discussion, the practical success is of highest priority. In a survey of the actual developments from 1935, Kurt Schwabe (1905–1983) states the obvious:

"The most important property of the glass which determines the electrode function is its composition."[43]

Accordingly, research was conducted in order to find out the most appropriate material for the design of the electrodes.[44] Like most of the researchers before them – particularly Walter Hughes – Duncan MacInnes and Malcolm Dole from the Rockefeller Institute for Medical Research (the latter at Northwestern University later), both central figures in the further development of the glass electrode, recommended "soft glass" for the preparation of the electrodes according to their results.[45] Accordingly, Dole summarizes the international research work up to 1940 as follows:

the best glass for glass electrode work except in the range of high temperature and high pH is the Corning 015 glass, glass having the composition SiO_2 72 %, Na_2O 22 %, CaO 6 %.[46]

During the years to come further improvements were made, the most important of them being the partial replacement of the glass modificator sodium by lithium with its more mobile ions. This part of the story, however, is beyond the scope of the present study.

4.3 More biological relevance of pH-measurements

The first scientific paper on the applications of the glass electrode listed in the Chemical Abstracts of the American Chemical Society after World War I is about the determination of hydrogen ions in blood, from 1925. While working on her Ph.D. thesis at University College London, the British chemist (and later also physician) Phyllis Margaret Tookey Kerridge (1901–1940) designed a new apparatus to determine the pH of biological samples. Her apparatus, illustrated in Figure 3, consisted of a glass bulb filled with a solution of known acidity; the top part of this bulb was a very thin concave glass membrane, making a small inverse bulb as it were, a "spoon" into which the solution of unknown acidity would be placed. The spoon had a volume of only about 1 cm³, which was very convenient for analyzing small samples of physiological fluids. Compared to the previous arrangements such as those shown in Figures 1 and 2 above, the main advantages of Kerridge's design were clear:

> The membrane blown in this way seems to be under less strain than when blown at the end of a tube, and does not break so easily, and the quantity of liquid required for the spoon is very small.[47]

Kerridge also devised another form of the apparatus, in which the solution of unknown pH was made to flow through a glass tube that included a section blown into a thin-walled spoon shape. In either version, the two solutions are connected with calomel electrodes and the potential is measured with a quadrant electrometer of the Dolezalek type. One main advantage of the application of the modified apparatus is that it can easily be put in a thermostat. Kerridge gives more important methodical hints which throw some light on the possible complications and suggestions on how to handle them:

> Newly-blown glass electrodes require careful cleaning with chromic acid, steaming for about 2 hours and soaking in distilled water for 24 hours before they can be used. Even after this treatment there may be a potential at the glass surface of 40 millivolts or more, which decreases slowly with time until after about 2 days it reaches a constant level of 4 or 5 millivolts which it will retain for weeks.[48]
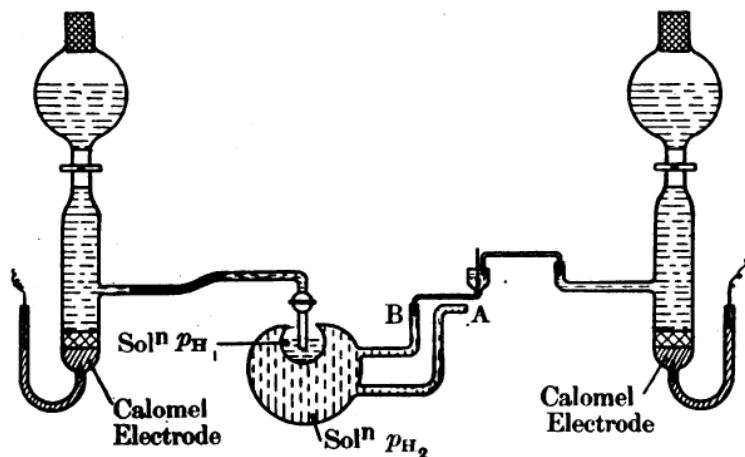
Fig. 3: Kerridge's modified apparatus for pH measurement (Fig. 2 from Kerridge, "Glass Electrode", p. 612)

Considering these empirical insights, it becomes obvious that there is a complex chemical reaction involved here.

The following are a few selected results from the 450 pH-measurements Kerridge made in her study (presumably at 18° C):[49] blood (human-oxalated) 7.42; blood (dog-defibrinated) 7.75; bean seedlings (aqueous extract) 5.87; Phosphate solution 7.37; Phosphate solution by hydrogen electrode 7.39; Sycamore leaves (aqueous extract) 4.88; Sycamore extract by hydrogen electrode 4.91.

Finding a satisfying consistency between glass electrode and hydrogen electrode measurements, Kerridge felt justified in avoiding theoretical discussions of the apparatus, at least for the time being:

> The chemical and physical theories as to the behaviour of the glass are not considered here, as
> the true explanation does not yet seem to have been found beyond dispute.[50]

4.4 History of science mingles with history of economy

That pH electrometers "literally swept the country" (the United States of America), as Dole put it, was due to the extraordinary industrial success of an invention by the analytical chemist Arnold Orville Beckman (1900–2004), which provides another important biological moment in our story.[51]

At the end of 1934 Beckman met an old classmate from their student days in Illinois, Glen Joseph, who worked for the California Fruit Exchange (later Sunkist). Beckman says:

> He had to measure the acidity of lemon juice that had been treated with sulfur dioxide. He was making by-products from lemon juice – pectin, citric acid, things like that. He couldn't use a hydrogen electrode or quinhydrone electrode, and he couldn't use colorimetric indicators, because the sulfur dioxide would react. So he had to use a glass electrode.[52]

At the beginning of that project, the main problem was the electrical measurement. To achieve suitable sensitivities the electrodes had to be large, but if they are built too big they tend to break. The galvanometers were another drawback with respect to sensitivity and ruggedness. Beckman, who had great familiarity with modern electronics from his work at the Bell Laboratories, applied the quite novel vacuum-tube voltmeter as the measuring device, and built himself[53] the first "acidometer" (later "pH meter") for the California Fruit Exchange. Together with his student Henry Fracker he applied for a patent in October 1934, which was approved in October 1936.[54]

Asked whether he in the beginning of his commercial activities relied a lot on the contacts he had from the years in the academic world, Beckman answered:

> No, not really. At that time [the middle of the 1930s], pH was a new term. A few physical chemists knew about hydrogen-ion concentration and were familiar enough with it to work with the negative logarithms encountered in pH. But pH was just coming on the scene. The symbol had been proposed by the Danish biochemist Sørensen years before, but it hadn't taken hold. But now about this time, chemists, and particularly biochemists, were beginning to realize that hydrogen-ion concentration was an essential factor in many chemical reactions. So the interest in hydrogen-ion determination rose rapidly. That, coupled with the fact that our instrument made it so easy that anybody could measure pH accurately, without having a lot of training.[55]

Beckman sold hundreds of pH meters during the first years, which was entirely unexpected by the colleagues and companies whom he had asked before about the prospects. The production of the pH meter was the start of a company operating world-wide (first called National Technical Laboratories, later Beckman Instruments, and finally Beckman Coulter). Beckman Instruments developed into a major firm, recording an overall annual revenue of $228,6 million by 1975.[56]

The practical applications of the glass-electrode pH meter were many and varied, among which "acid rain" is perhaps the most important. Natural rain is not

pH-neutral. Because all gaseous combustion products (from forest fires, volcanic emissions, and animals) soluble in water cause an increase of the hydrogen-ion concentration, the pH of natural rain is already lower than pH 7. In the last third of the 20th century environmental concerns became reasonably strong, and one key concern was the anthropogenic influence on the pH of rain.[57] It is hardly possible to give the correct number of all the pH meters ever used for the monitoring of acid rain, but it is certainly in the order of many thousands.

After Beckman's invention, it became unnecessary to have specific training for acidity measurement, and pH meters are now not to be found in laboratories only. The simplified handling is, however, not without risks:

> In many respects the glass electrode makes possible the ideal measurement, a measurement in which the glass bulb is inserted into the solution whose *p*H is to be determined, a switch pressed and the *p*H immediately read off the dial; as simple and as quick as the measurement of temperature with a mercury thermometer. However, the very ease and speed of the method may lead the unwary scientist into a deluded sense of experimental security; it is not always possible or usually advisable to rely uncritically upon the *p*H reading of these convenient measuring instruments.[58]

These risks, of course, can become even more serious than Dole is describing, because in practice it is only very rarely the "unwary scientist" who performs the measurement. Sometimes even laymen and amateurs do the job. It is unlikely, however, that significant errors occur in cases like acid-rain monitoring and most pertinent biomedical situations, because extreme degrees of acidity and alkalinity are very rare. The next short section describes systematic measurement errors of the pH electrode, which the researchers became aware of in the 1930s.

4.5 An extension of the biological applications – alkali error and acid error
Though a good part of the monograph by Malcolm Dole is devoted to biological and medicinal topics,[59] it contains two chapters of more general interest, which go beyond the merely practical question of applicabilty and tell us more about the "nature" of the glass electrode. These chapters (»Limitations of Glass Electrode in Alkaline pH Range« and »Limitations of the Glass Electrode in Acid and Nonaqueous Solutions«) are devoted to what is sometimes called the alkaline error and the acid error, respectively. These typical aspects of the behavior of the glass electrode were found by systematic research. In order to quantify some preliminary observations, Dole designed an "experimental method of measuring glass electrode error". His apparatus allowed for simultaneous measurements by, and thus a comparison of, glass electrodes and hydrogen electrodes. He found

out that the presence of alkali-metal ions in the analyzed solution led to a significant deviation of the glass electrode readings from the hydrogen electrode measurements. The emf, measured with the hydrogen electrode, does not go linearly with the electrode's pH value in elevated regions, particularly if sodium is in the solution. Interestingly, sodium-free solutions of a pH up to 13 (realized by solutions of tetramethylammonium hydroxide[60]), do not cause an electrode error. Dole concludes that we must consider the glass electrode as a "mixed electrode" in that at higher sodium concentrations the mechanism is no longer exclusively influenced by hydrogen ions only. To put the point simply: if the sodium ions are in the majority, they act like adding to the activities of the hydrogen ions such that the solution seems to be less alkaline than in reality. Dole describes the situation of this very specific chemical situation in a telling thought experiment:

"If a glass could be invented into or out of which sodium ions would not migrate in an electric field, electrodes of this glass would have no sodium errors."[61]

On the other side of the scale, at very low pH values, the measured values are also lower than expected theoretically (or determined by the hydrogen electrode). This is what is called the "acid error" by the specialists. Again, Dole had an ingenious idea to pin down the cause of this effect experimentally. Because he found no direct dependencies of this electrode error upon the concentration of anions and cations, among them hydrogen ions, he concluded:

> the negative errors must be caused by a decrease in the chemical potential or vapor pressure of the water in the solution in contact with the glass surface. This conclusion was tested by adding ethyl alcohol to the solution at constant pH, and measuring the error which was found to be negative in sign and entirely similar to the errors produced by adding concentrated acids to the solution.[62]

Hence, his central hypothesis is that water plays a crucial role in the mechanism of the glass electrode, which is definitely not the case for the hydrogen electrode. What matters according to Dole's interpretation is that hydrogen ions carry water molecules with them. And because these hydrated hydrogen ions (the famous H_3O^+ of modern textbooks or even bigger aggregates[63]) diminish the water concentration of the analyte, the quotient of inner and outer water concentration, which Dole calls the "water activity", becomes different from 1. In all those cases, whether realized by larger amounts of non-aqueous liquids (e.g. ethanol) or by higher acidity, the pH reading becomes smaller (more acidic) than what corresponds to the actual hydrogen ion concentration.[64] Hence, the cations, particularly those of sodium and of hydrogen, although only if present in high con-

centration, can have an unwanted lowering impact on the readings of the glass electrode.[65]

5 The voice of the pH-electrode

In the modern interpretation of the mechanism of the glass electrode the mobility of the alkali-metal cations is the central point.[66] Sodium ions – partly exchanged by the smaller and even more mobile lithium ions – move much more freely in the outer aqueous gel surface layer[67] than for example calcium ions do. In contrast, the silicate net with its negatively polarized oxygen atoms is almost entirely stationary, such that the two different local concentrations in the measurement situation lead to different electrical potentials at the measurement and the comparison electrodes, respectively. It is just the extreme mobility of hydrogen ions in wet glass that causes this result. There is no redox process involved at all.

As we have seen, the history of the glass electrode is full of pieces of scientific reasoning, yet cannot be described as a result of theoretical reasoning as in the classical verification/falsification mode. There are several unexpected (and unexpectable) aspects – among them discoveries like the outstanding selectivity of the glass electrode for hydrogen ions and the independency of the measured potentials from reduction or oxidation – which turned out to be crucial. This is a typical situation in chemistry. In fact, the glass electrode is a kind of "experimental abstraction" in that its extraordinary selectivity for hydrogen ions in aqueous solutions is "luckily" applicable to the characterization of acidity.

Although it may sound weird, the applied glass electrode is a kind of chemical reaction without stable products. The intermediate situation – a metastable state – allows for a reliable and reproducable electrical measurement that can be calibrated in many (though not all) interesting cases.[68]

In comparing chemical work in the classical period of "wet chemistry" to that of modern spectroscopic analysis, the British historian of science David Knight says:

> Chemists did not understand the basis of spectroscopy, while they were familiar with the diagnostic reactions underlying the analysis tables; spectroscopes had to be made foolproof before they would find their way generally into chemistry laboratories.[69]

The main point of this description can also be applied to the early history of the glass electrode. One main similarity is the missing understanding of the pertinent mechanisms in the early stages of development. But the glass electrode simply worked, and there was no need to make it foolproof, because it was already near-
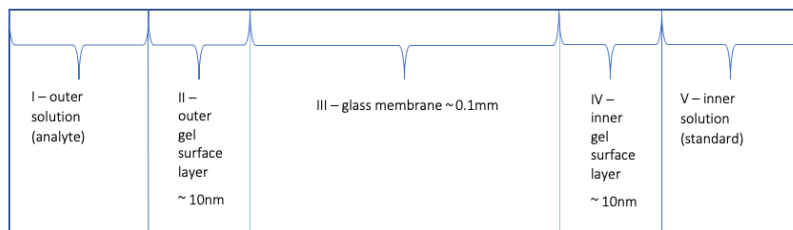
| I – outer solution (analyte) | II – outer gel surface layer ~ 10nm | III – glass membrane ~0.1mm | IV – inner gel surface layer ~ 10nm | V – inner solution (standard) |

Fig. 4: Schematic cross section of the glass electrode. Because the alkali glass modifiers (Na$^+$ or Li$^+$) migrate into the direction of the lowest H$^+$ concentration (the highest pH) particularly in the hydrated regions II and IV, a potential is caused between regions I and V. The net-building and the stabilizing constituents of the glass (Silicates and Calcium) are immobile. The chemical reactions in the glass phase are very quick but do not reach equilibrium under usual conditions. (Drawing by the authors.)

ly so from the start. In most chemical cases success comes before understanding. What makes the glass electrode even more unusual is the fact that it developed almost entirely independently from what is sometimes called the instrumental revolution, and independently from the core modes of research in the chemical sciences, namely synthesis and analysis, too.

Our main conclusion from the present study is the following: The pH concept and the glass electrode, which at first glance very much look as if they are typical results of physico-chemical activities, turn out to be biochemical achievements. In 1941, Malcolm Dole stated: "The importance of the glass electrode in the world of biology and biochemistry has become so great that any book on the glass electrode that did not treat fully this aspect of the subject would be incomplete."[70] In this paper we have attempted to provide an informative account of the biochemical dimension of the glass electrode. But going beyond Dole's statement about the applicability of the glass electrode, we have also tried to show that biochemical contexts were crucially important in the development of the pH concept itself as well as its measurement.

Summary

This paper examines the early histories of the pH concept and the glass electrode, the device that enabled a convenient measurement of pH. Contrary to the common impression that the pH concept arose as part of the establishment of physical chemistry in the work of Arrhenius, Nernst and others, we show that both the pH concept and the glass electrode have been motivated by biochemical ideas and demands. Among those working in the biochemical contexts were:

Sørensen, who invented the pH concept in 1909; Cremer, who made the first usable form of the glass electrode in 1906; Kerridge, who devised a particularly effective form of the electrode for physiology in the 1920s; and Beckman, who invented the widely commercialized form of the pH meter in the 1930s. Even though the value of pH is straightforwardly deducible from hydrogen-ion concentration, both the particular logarithmic scale that is our familiar pH measure and the glass electrode for its measurement were practical solutions particularly suited to the needs of biochemistry. The successful uses of the glass electrode for pH measurement preceded the theoretical understanding of its workings in physical chemistry by several decades, which is understandable given that the glass electrode functions through chemical reactions without stable products.

Notes

[1] For recent work on the crucial role of glass in modern chemistry, see Catherine M. Jackson, "The »Wonderful Properties of Glass«: Liebig's Kaliapparat and the Practice of Chemistry in Glass", *Isis*, 106 (2015), 43–69; Catherine M. Jackson, "Chemical Identity Crisis: Glass and Glassblowing in the Identification of Organic Compounds", *Annals of Science*, 72 (2015), 187–205. For earlier history see Marco Beretta, ed., *When Glass Matters: Studies in the History of Science and Art from Graeco-Roman Antiquity to Early Modern Era* (Firenze 2004).

[2] P. Linder, R. G. Torrington, D.R. Williams, *Analysis Using Glass Electrodes* (Milton Keynes 1984), p. 1.

[3] In a very informative collection of papers from a symposium on the history of chemistry of the American Chemical Society held in Chicago, the author of the introductory text, the American chemist John Taylor, shows a clear appreciation of the importance of improvements in pH measurement, but neither he nor any other contributor takes the initiative to elaborate on the peculiar history of the glass electrode, while detailed attention is given to spectrometry, chromatography, balances, and even blowpipe analysis. John T. Stock & Mary Virginia Orna, eds., T*he History and Preservation of Chemical Instrumentation* (Dordrecht 1986), p. 2–3.

[4] Rüdiger Simon, *Chemie – Dialektik – Theorienentwicklung* (Berlin 1980), p. 10. Translations from German-language sources are by the authors if not otherwise noted.

[5] Max Cremer, "Über die Ursache der elektromotorischen Eigenschaften der Gewebe, zugleich ein Beitrag zur Lehre von den polyphasischen Elektrolytketten", *Zeitschrift für Biologie*, 47 (1906), 562–608.

[6] In 1888–89, Walter Nernst found what now is called the Nernst equation. Wilhelm Ostwald gives a detailed historical account of this episode in Wilhelm Ostwald, *Elektrochemie – Ihre Geschichte und Lehre*, (Leipzig 1896), pp. 1134–1136.

[7] Wilhelm Ostwald, "Elektrische Eigenschaften halbdurchlässiger Scheidewände", *Zeitschrift für physikalische Chemie*, 6 (1890), 71–82.

[8] For biographical information, see Wilhelm Trendelenburg, "Nachruf auf Max Cremer", *Ergebnisse der Physiologie, biologischen Chemie und experimentellen Pharmakologie*, 37 (1935), 1–11. The fact

that the author does not refer to the "invention" of the glass electrode shows that Cremer´s scientific community was that of physiologists, biologists, and pharmacologists, rather than that of the inorganic, material-oriented scientists.

[9] See plate IX in John Frederic Daniell, "On Voltaic Combinations", *Philosophical Transactions of the Royal Society of London*, 126 (1836), 107–124. Ostwald reports Daniell´s construction with the "Ochsengurgel" as diaphragm in detail in his *Elektrochemie*, p. 603. Hence, we may assume that this experimental setup paved the way for what we call membrane science now.

[10] Ostwald, "Scheidewände", p. 81.

[11] Cremer, "Elektrolytketten", p. 573.

[12] The former has a fixed magnet and a moveable coil, and a pointer attached to the coil so that it can move over a suitably calibrated scale. The d'Arsonval galvanometer is the basis for most modern galvanometers. The Einthoven type makes use of the movements of a silver-coated glass capillary as carrier of the potential or current to be measured between the poles of two strong magnets. It became famous as instrument in electrocardiography, and its inventor, the Dutch physician Willem Einthoven (1860–1927), was honored with the Nobel Prize in 1924. To Cremer, being an electrophysiologist himself, it must have been natural to use such an instrument, see Max Cremer, "Das Saitengalvanometer von Einthoven und seine Leistungen", *Sitzungsberichte der Gesellschaft für Morphologie und Physiologie München*, 1 (1905), p. 5.

[13] In a recapitulation of the early phase of this episode, however, Cremer relativizes the direct influence by Helmholtz and Giese; see Max Cremer, "Ursache der elektrischen Erscheinungen", in Bethe, H., Bergmann, G.v., Embden, G, Ellinger, A. (Eds.), *Handbuch der normalen und pathologischen Physiologie*, Band 8, Zweiter Teil (Berlin 1928), pp. 999–1053.

[14] The specific materiality of glass opened up the path to the making of electrodes. No other material was capable of being formed easily and at the same time reasonably stable in the solidified form (which, as we know today, does not entirely lose its liquid properties). In chemistry education at the time, glassblowing was a fixed part of the technical instructions of chemists, cf. the manual Wilhelm Ostwald, *Hand- und Hilfsbuch zur Ausführung Physiko-chemischer Messungen* (Leipzig 1893).

[15] Cremer, "Elektrolytketten", p. 601.

[16] For an informative account of the prehistory of Cremer´s findings see Fritz Scholz, "From the Leiden Jar to the Discovery of the Glass Electrode by Max Cremer", *Journal of Solid State Electrochemistry*, 15 (2011), 5–14.

[17] In the first edition of his pioneering monograph on aqueous acidity, for example, Leonor Michaelis did not yet make any reference to the glass electrode: Leonor Michaelis, *Die Wasserstoffionenkonzentration* (Berlin 1914). A few years later, this situation has changed. In the following electrobiological monograph Cremer´s work is discussed, and his priority (before Haber & Klemensiewicz) emphasized: Rudolf Beutner, *Die Entstehung elektrischer Ströme in lebenden Geweben* (Stuttgart 1920). The second edition of Michaelis´ book from 1922 also contains references to the glass electrode.

[18] Cremer, "Ursache" (1928), p. 1014. The authors gratefully benefited from the translation of this statement by Fritz Scholz, "Cremer".

[19] Ernest Baldwin, *The Nature of Biochemistry* (Cambridge 1962), p. 31.

[20] Søren Sørensen, "Enzymstudien II – Über die Messung und die Bedeutung der Wasserstoffionenkonzentration bei enzymatischen Prozessen", *Biochemische Zeitschrift*, 21 (1909), 131–200.

[21] Sørensen, "Enzymstudien", p. 131.

[22] Sørensen, "Enzymstudien", pp. 159-160.

[23] Michaelis, *Wasserstoffionenkonzentration*, pp. 20, 22.

[24] Ludwig Kratz, *Die Glaselektrode und ihre Anwendungen* (Frankfurt 1950), p. 5. The manuscript of that book was finished in 1944.

[25] Malcolm Dole, *The Glass Electrode – Methods, Applications, and Theory* (New York 1941), p. 14.

[26] Cf. Einar Biilmann, "Oxidation and Reduction Potentials of Organic Compounds", *Transactions of the Faraday Society*, 19 (1924), 676–691.

[27] See the informative survey of Albert Baker, "A History of Indicators", *Chymia*, (1964), 147–167. Baker mentions Robert Boyle as the initiator of the application of indicators for qualitative analytical purposes (which seems to be consensus among the historians of chemistry).

[28] Hans Friedenthal, "Die Bestimmung der Reaktion einer Flüssigkeit mit Hilfe von Indikatoren", *Zeitschrift für Elektrochemie*, 10 (1904), 113–119, here p. 113. See also Eduard Salm, "Die Bestimmung des H-Gehaltes einer Lösung mit Hilfe von Indikatoren", *Zeitschrift für Elektrochemie*, 10 (1904), 341–346.

[29] Kurt Schwabe, *Fortschritte der pH-Messtechnik* (Berlin 1953), p. 36.

[30] Kratz 1950, *Glaselektrode*, p. VII. We translate the German „Kennzahl" as "reference number".

[31] Note, however, that the pH is (could) not yet (be) referred to in their paper from 1909, which is the publication of a presentation by Haber before the Karlsruhe Chemical Society from January 28, 1909: Fritz Haber & Zygmunt Klemensiewicz, "Über elektrische Phasengrenzkräfte", *Zeitschrift für Physikalische Chemie*, 67 (1909), 385–432.

[32] As to the role of Klemensiewicz and his professional career see Romuald Piosik, Renate Peper and Walter Jansen, "100 Jahre Glaselektrode", *Chemkon*, 17 (2010), 19–24. Merely celebrating the two authors are: Barbara Marczewska & Krzysztof Marczewski, "First Glass Electrode and its Creators F. Haber and Z. Klemensiewicz – On 100th Anniversary", *Zeitschrift für Physikalische Chemie*, 224 (2010), 795–799.

[33] By "Thuringian glass" a material made of sand, lime, and soda is meant, which technically is also called "soda-lime-glass" or just "normal-glass".

[34] Haber & Klemensiewicz, "Phasengrenzkräfte", p. 410.

[35] Haber & Klemensiewicz, "Phasengrenzkräfte", p. 388.

[36] He does not restrict his attention to acidimetry alone: "In the first place the forces considered here are suited to combine two facts which are taught separately in the physiology of the muscle so far. One of these facts is expressed in the proposition that an active muscle part is always negative against ground . The other one is that of an acidic reaction of an active muscle. The considerations brought forward here and the subsequent experiments suggest that an acidic reaction at a phase border causes a negative charge of the phase which behaves as an ordinary aqueous solution . . . . For the formation of the forces it is not necessary for the [muscle] fibrils to be semipermeable." (Haber & Klemensiewicz, "Phasengrenzkräfte", pp. 388–389.)

[37] Walther Nernst, *Theoretische Chemie*, 8.Aufl. (Stuttgart 1921). *R* is the gas constant, *T* the absolute temperature, c_1 and c_2 the effective concentrations in the two cells (in a glass electrode that would be the inner and outer cell), and *n* a constant refering to the number and charge of "exchanged" ions. On p. 845 of this book, Nernst mentions the voltage according to a difference of one order of magnitude between the two cells, which is 58 mV.

[38] Rudolf Beutner, *Die Entstehung elektrischer Ströme in lebenden Geweben* (Stuttgart 1920), pp. 72–86. Note that in this book Beutner only mentions Haber and Klemensiewicz, but not Cremer, when he discusses the glass electrode. Nevertheless, he cites a personal communication by Max Cremer, in which the latter says, that *both* kinds of driving forces (the "interphasic" and the "phase border" kinds) might explain certain changes of potential.

[39] We should add that Haber, even though having the means and many co-workers from all over the world, was not involved in the further development of the glass electrode.

[40] William Mansfield Clark, *The Determination of Hydrogen Ions*, 3rd edition (London 1928). Clark gives the glass electrode 4 pages, within which he emphasizes the biological applications.

[41] Dole, *Glass Electrode*, S. vii. Dole, like the majority of researchers mentioned in the present contribution, was active as a biochemist, which becomes obvious throughout the cited book.

[42] The pH concept is a subject of debates up to the present time, see the elaborate study of Robert de Levie, "A pH centenary", *Electrochimica Acta*, 135 (2014), 604–639.

[43] Kurt Schwabe, „Sammelreferat – Die Glaselektrode für pH-Messungen", *Zeitschrift für Elektrochemie*, 41 (1935), 681–694.

[44] One of the earliest articles and thus a kind of reference for the upcoming work came from the Laboratory of Physical Chemistry in Cambridge: Walter Scott Hughes, "On Haber´s Glass Cell", *Journal of the Chemical Society*, (1928), 491–506.

[45] Duncan A. MacInnes & Malcolm Dole, "Tests of a New Type of Glass Electrode", *Industrial and Engineering Chemistry*, 1 (1929), 57–59.

[46] Dole, *Glass Electrode*, p. 78.

[47] Phyllis Tookey Kerridge, "The Use of the Glass Electrode in Biochemistry", *Biochemical Journal*, 19 (1925), 611–617, here p.613.

[48] Kerridge, "Glass Electrode", p. 615.

[49] Kerridge, "Glass Electrode", p. 616.

[50] Kerridge, "Glass Electrode", p. 611. Note that Cremer is missing in Kerridge´s reference list.

[51] Here we mainly follow the descriptions given by Beckman himself in an interview he gave in 1978: Arnold O. Beckman, Interview by Mary Terrall. Pasadena, California, October 16 – December 4, 1978. Oral History Project, California Institute of Technology Archives. http://resolver.caltech.edu/CaltechOH:OH_Beckman_A.

[52] Beckman, Interview, p. 28.

[53] Beckman has regularly taught courses on glassblowing at Caltech.

[54] U.S. Patent 2,058,761 (1936).

[55] Beckman, Interview, pp.41–42.

[56] See Arnold Beckman, William S. Gallaway, Wilbur I. Kaye, William F. Ulrich, "History of Spectrophotometry at Beckman Instruments Inc.", *Analytical Chemistry*, 49 (1977) No. 3, 280A-300A. Understandably in this self-description the pH meter does not play any significant role anymore. It is only present in the background of one photo.

[57] Some not systematically selected references from different times and perspective are P. Brimblecombe & D.H. Stedman, "Historical Evidence for a Dramatic Increase in Nitrate Component of Acid Rain", *Nature*, 298 (1982), 460–462; Lars O. Hedin & Gene E. Likens, "Atmospheric Dust and Acid Rain", *Scientific American*, (Dec. 1996), 88–92. Denny Ellerman et al. (eds.) *Markets for Clean Air – The U.S. Acid Rain Program* (Cambridge 2000); Anita Singh & Madhoolika Agrawal, "Acid Rain and its Ecological Consequences", *Journal of Environmental Biology*, 29 (2008), 15–24.

[58] Dole, *Glass Electrode*, pp. vii–viii.

[59] See particularly chapter 11 (»Special Applications of the Glass Electrode in Biological Chemistry«) in Dole, *Glass Electrode*, pp. 179–202, but also the many references to natural materials and products all over the whole volume, for example under the index entry "pH". All specific properties described here refer to the "MacInnes-glass" and the similar Corning glass 015, both soda-lime-glasses of the approximate composition SiO_2 72%, Na_2O 22%, and CaO 6%.

[60] $N(CH_3)_4OH$. This salt contains no metal cation.

[61] Dole, *Glass Electrode*, p. 138.

[62] Dole, *Glass Electrode*, p. 276.

[63] Dole does not use this formula.

[64] The amount of this electrode error in the cases Dole describes ranges from about -1 to about -40 mV, see Tab. 8-1 in Dole, *Glass Electrode*.

[65] However, anions do not cause errors of this kind. Schwabe, *Fortschritte*, p. 96 states: "Generally, an influence of anions on the emf of the glass electrode, which occasionally was assumed even for the usual measuring range, does not exist, as was asserted by numerous careful measurements." He recommends to determine acidity in solutions of pH considerably lower than 1 by titration, in order to circumvent the problems discussed here (p. 97).

[66] For modern treatments of the working of the glass electrode, see Schwabe, *Fortschritte*, and Friedrich G.K. Baucke, "Fundamental and Applied Electrochemistry at an Industrial Glass Laboratory – An Overview", *Journal of Solid State Electrochemistry*, 15 (2011), 23–46.

[67] Note that the swelling of glass was known since the experiments of Faraday, and there was some knowledge of glass chemistry quite early, see for example: "Of the glass it is known that it has the property to take up water at the surface by a kind of swelling. In addition a very slow dissolution of alkali silicate takes place caused by water and acids, while a somewhat stronger attack on the silica appears during impact of alkali. As is generally known this chemical impact is so small that it only in exceptions has any impact on the application for chemical purposes." (Haber & Klemensiewicz, "Phasengrenzkräfte", p. 409.)

[68] At the same time, we gained chemical knowledge about the involved substances, among them hydrogen, oxygen, silicium, sodium, lithium, water, and glass.

[69] David Knight. "Then …and Now", in: *From Classical to Modern Chemistry – The Instrumental Revolution*, ed. by Peter J.T. Morris, (London 2002), p. 90.

[70] Dole, *Glass Electrode*, p. ix.

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