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The scientific impact of Kurt Schwabe: a historical account

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Introduction

29 May 2005 would have been the 100th birthday of the very important German electrochemist, Kurt Schwabe. From 1949 to 1970 he was director of the Institut für Elektrochemie and Physikalische Chemie at the Technische Universität Dresden and from 1949 to 1983 he was in charge of a private electrochemical research institute in Meinsberg, Saxony. This article aims at appraising Schwabe's scientific achievements from today's point of view. First, a short description is given of Schwabe's curriculum vitae.

Short curriculum vitae

Kurt Schwabe was born in Reichenbach, Vogtland/Saxony. From 1924 to 1927 he studied chemistry at the Technische Universität Dresden, where as early as 1927 his interest in electrochemistry was already apparent in his degree thesis [1]. In 1928 he was awarded his doctorate [2]. In 1933 he habilitated on the subject of anodic behaviour of metals in saline solutions. From 1933 he was a lecturer, and from 1939–1940 professor in Dresden. In 1933, for political reasons, he gave up his full time job at the Technische Universität Dresden and accepted a practical employment. After a temporary job with IG Farben in Bitterfeld, from 1928–1929, he became chemist-in-charge at the Kübler & Niethammer paper mill in Kriebstein, Saxony, where he was concerned with tasks of applied chemistry. This paper mill had been founded based on the invention of the ground pulp process by Friedrich Gottlob Keller (1816–1895) in the small Saxon town Hainichen in 1843. Keller had developed a successful process for producing paper and carton containing wood by mechanically grinding fir, pine and poplar wood to produce a fibrous material. In this

classic process, peeled, untreated wood is wetted with water and pressed under pressure against a roughened, rotating millstone to produce fibrous material.

Schwabe initially turned a great deal of his attention to chemical/technological tasks of interest to the cellulose industry. This is reflected by his publications [3, 4] and patents [5], only a few of which can be mentioned here. Evidently he also became aware of electrochemical problem at that time: A book [6] on the significance and execution of pH measurement in papermaking, annotated and with margin notes by Schwabe, probably was the starting point for his research into pH measurement, which he continued over many decades. However, there are also patents which document his early interest in fuel cells [7], corrosion processes [8] and questions of technical electrolysis [9] which he was to continue to pursue later on when he was appointed professor at the Technical University of Dresden.

In 1944 Schwabe founded the “Forschungsinstitut für Chemische Technologie” was at the centre of much of his scientific work for 50 years, right up to the end of his life. In 1949 he was appointed professor of Electrochemistry and Physical Chemistry at Technische Universität Dresden, as already mentioned. He took over as director of the Institut für Elektrochemie und Physikalische Chemie at the university without appreciably reducing his work in Meinsberg. Of the numerous positions and appointments which he held during his professional life, several others need to be mentioned: From 1959–1969 he was director of the Institut für Radiochemie at the Zentralinstitut für Kernforschung Rossendorf near Dresden, from 1961–1965 Prorektor of the University of Dresden, from 1965 to 1980 President of the Sächsische Akademie der Wissenschaften zu Leipzig (Saxon Academy of Sciences) in Leipzig, from 1965 to 1971 director of the Zentralinstitut für Korrosionsschutz in Dresden (which he founded) and vice president of the International Society of Electrochemistry. Supervision of 545 degree theses, 414 doctoral theses and 51 habilitation theses bears witness of his prolific influence. Schwabe's curriculum vitae and a list of almost all his publications can be found in Emons and Berg [10]. In total

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Schwabe produced about 530 publications and patents. These will be discussed in the following sections with the main focus on an assessment of Schwabe's lasting achievements.

Scientific work

pH measurement

Schwabe's earliest known publication on pH measurement [11] dates from 1935, which was acknowledged by the famous analytical chemist and author Kordatzky [12] in 1949 as being a fundamental work on pH measurement. In 1940 Schwabe applied for his first patent [13] relating to glass electrodes. pH measurement and the development of glass electrodes became a field of research which was to occupy Schwabe until the end of his life. He is rightly known as one of the pioneers of pH measurement, advancing the methodology of liquid analysis more than almost anyone else in Germany and adapting it for use in numerous branches of industry such as sewage control, sugar production, biotechnology and process engineering. Schwabe's best known publication, giving a comprehensive review of his research results, is his book "pH-Messtechnik" (pH measuring technique) which was published and then republished in revised editions in 1953, 1958, 1963 and 1976 [14].

In total, Schwabe published about 50 works on how glass electrodes work and on the development of new types of electrode glass. Only some of these can be given prominence here, namely those to which reference is still often made today: At an early stage Schwabe set out to develop glass with a high electrical conductivity for use as electrode glass [15]. Electrode glass, with both low resistance and favorable electrode characteristics for pH values up to pH=13, is discussed in his publication of 1957 [16]. It improved on the well-known and widely used MacInnes glass (72% by weight SiO₂, 22% Na₂O and 6% CaO) by adding uranium oxide and other heavy metal oxides. The works on the theory of glass electrodes and how they function [17, 18], published in the 1960's, have been widely influential, particularly on the introduction of radioactive indicators [19, 20]. Schwabe was also concerned with the investigation of the alkali error in glass electrodes [21]. Recently Cheng [22] has cited several works of Schwabe as evidence for modern theories on how glass electrodes function. Baucke et al. [23], too, cite Schwabe's works on pH measurement but in a more critical light, discussing a hypothesis on how electrodes work which differs from Schwabe's interpretation. Nonetheless, Schwabe's basic initial thesis—that hydronium ions are replaced by the alkali ions of the glass when electrode glass comes into contact with an aqueous phase of the solution—is still true today. Moreover, it has been explicitly corroborated in recent studies by Thomas et al. using nuclear magnetic resonance (NRM) analysis [24].

Despite its early date of publication, one of Schwabe's most important publications still today concerns pH

measurements under extreme conditions [25]. It discusses extremely acidic and extremely alkaline solutions. It goes into measurements at high and low temperatures and under increased pressure. Finally non-aqueous solutions and the use of metal electrodes are discussed. For certain technical applications, particularly with extremely alkaline solutions, glass electrodes are not suitable as the glass surface is too severely affected; this led to Schwabe's successful investigations [26, 27] into the use of bismuth electrodes for pH measurement.

Corrosion

A second important pillar of Kurt Schwabe's scientific work was his research into corrosion and the passivity of metals. His fundamental knowledge was based on studies by G. Kreysa and U. Ebersbach [28]. According to these authors, even the build up of a single layer of oxide on the "pure" surface already creates an important barrier to the passage of metal ions through the phase boundary. He summed up his views jointly with the authors in their joint Chemisorption Theory of Passivity. Schwabe took the results of studies regarding the behaviour of water in the course of the formation of passive layers as additional proof of this theory. As Ya. M. Kolotykin had done before him, Schwabe also provided evidence that water without passivity could not exist. These studies were carried out in non-aqueous sulphuric acid [29].

Due to the lack of a suitable test method there has been no direct evidence to support the Chemisorption Theory to the present day. The theory of the passivity of metals and the structure of the passive layer of iron—stating that these consist of an Fe₃O₄ layer on the metal side and an Fe₂O₃ layer on the solvent side, derived in particular from thermodynamics by K. Vetter—while known to Schwabe were not used by him to extend his own investigations because an immediate practical connection to the chemisorption theory could not be made, in particular where the development of new materials was the main objective. The chemisorption theory today has diminished in significance [30]. Nonetheless various reference to it have appeared in recent papers on corrosion (for example F. Mansfeld [31] on Schwabe's work [32, 33] concerning the influence of neutral salts on kinetics of corrosion).

Schwabe's pupil and the successor to his chair, Prof. Dr. Wolfgang Forker, has developed a concept of corrosion theory [34–36] strongly influenced by thermodynamic and following the approach of K. Vetter and K.-F. Bonhoeffer. In close cooperation between electrochemists and materials scientists, the active dissolution of the iron was investigated, augmented by crystallographic investigations (at atomic level) of the surface finish of iron and of the general metal surfaces. It was shown that both the binding state of the hydroxo-complexes or oxo-complexes as well as the charge of the cations have an effect on the forming passive layer. From this, a crystallographic model theory of passivity was derived which was compatible with the thermodynamics-based approach. For alloys—especially

Fe-Cr alloys—this provided an explanation for the much discussed limit condition of 13% Cr (by weight) for the resistance of steel to corrosion under atmospheric conditions. This led to the development of a new corrosion resistant steel, free of copper, with approx. 1 % by weight of silicon.

This presentation shows that the scientific achievements of Kurt Schwabe in the field of corrosion were of great significance at the time and had a wide influence and seminal effect on research, both in East Germany and beyond. In contrast to the field of pH measurement described earlier, the state of scientific research in this field has meanwhile advanced so far that the current relevance of his achievements now takes second place to the undiminished historical importance of his contribution to passivity and corrosion. Despite this, many of his experimental results still attract attention even today, for example his discovery that for the formation of a passive layer of iron and nickel in acetonitrile, dimethyl formamide and dimethyl sulphoxide a very small amount of water is absolutely necessary [37]. Contributions on instruments for corrosion measurement are also still of interest, such as the development of a multi-channel potentiostat [38] for checking up to six samples of the same material in a common solution under simultaneous polarization. And, finally, Schwabe also made fundamental contributions to the theory and practice of understanding the kinetics of corrosion processes [39]. He was also the first to use coulometric measurements in corrosion research [40].

In 1975, the International Symposium [41] on “Problems of the Passivity of Metals” was organized by the Sächsische Akademie der Wissenschaften zu Leipzig (Saxon Academy of Sciences) in Schwabe’s honour, as a tribute to his international reputation. The international elite in the field of corrosion research from Germany, Belgium, France, Poland, Hungary and Russia gathered in Dresden for Schwabe’s 70th birthday and paid tribute to him in scientific lectures by M. Pourbaix, I. Epelboin, M. Karšulin, M. Prazák, W. Forker, C. Weißmantel, M. Smiałowski, H.-J. Engell, V. Spitzin, I. Rosenfeld, N.D. Tomaschow, L. Kiss and others.

Books

The monographs on pH measurement referred to above are outstanding under Schwabe’s books, as well as the updated paperback edition of “pH-Messung” [42]. The three-volume “Physikalische Chemie” [43] published as a “late work” and subsequently republished in two volumes; the third edition, edited by H. Kelm, was published posthumously. Schwabe also wrote books on Polarography (1957) and an Introduction to Statistic Thermodynamics (1971), together with H. Kammer, as well as on the Thermodynamics of Irreversible Processes (1984, published posthumously). For more information see the bibliography [10].

History of science

Schwabe made a remarkable contribution to keeping alive the memory of famous electrochemists of the past, especially Wilhelm Ostwald. Around 1974 he played a major part in setting up the Wilhelm Ostwald Memorial in Großbothen [44], where the memory of the founder of physical chemistry and Nobel prize winner Wilhelm Ostwald is preserved in exemplary fashion to this day. Schwabe referred to Wilhelm Ostwald in many lectures and publications [45, 46] which cannot be mentioned individually here. Other scientific historical appraisals by Schwabe concern prominent electrochemists such as Fritz Foerster, Walter Nernst [47], Wilhelm Hittdorf [48], Max Volmer and Jaroslav Heyrovský. For further details, see also the list of publication by K. Schwabe [10].

Concentrated electrolytic solutions

A third dominant field in Schwabe’s work concerns his investigations into the behaviour of concentrated electrolytic solutions, on measure of acidity [49] and on the activity of single ions [50, 51]. Some of the applications and results in this area are to be found again in his corrosion research and research into pH measurement: for example, the investigations into corrosion in non-aqueous media [52] and in trifluoroacetic acid [53]. Schwabe’s main teaching leads to the conclusion that “in principle no single ion activities (beyond the Debye-Hückel range) can be determined” or calculated (see [22], pp. 181–182). In a number of more theoretical publications, Schwabe demonstrates that the solvation energy of ions is responsible for the formation of a short-range order structure of the solvent. One of the most important publications on this topic contains a review [54] of the basic experimental principles and theoretic derivations.

Measurements of the mean activity coefficient in galvanic cells of electrochemical chains in solution with differing or equal anions are investigated. The findings showed that the mean activity coefficient of anions and cations varies greatly, which can be explained by a modification of the specific inductive capacity, especially in the case of small ions. Besides potentiometric measurements, he also tried out other measurement methods such as the isopiestic method [55]. According to Schwabe’s measurements, quoted by G. Kortüm [56], the polarization of zinc is practically independent of the anion in pure aqueous zinc salt solutions and low H^+ ion activity, while it clearly depends on the anion for the existence of other inhibitors (ethyl alcohol and dibenzyl sulphoxide among others [57]). This shows that Schwabe constantly aimed at connecting different research fields, such as here galvanisation and the theory of electrolytic solutions.

The last publication which Schwabe [58] was able to hold in his own hands in 1983, shortly before he died, was dedicated to the electrochemist A. J. Parker, who died in Australia in 1982. (Several other works were published posthumously.) It demonstrated once again—by measuring

the free standard energy of the transition of ions in organic solvents—that single ion activities cannot be achieved without non-thermodynamic assumptions. In addition it strengthened the evidence that a pH shift, detected when water is replaced by organic solvents, can be explained by a diminution of the dielectric constant and an increase in coulomb attraction. As two references show, even today many of the above works are still cited [59, 60].

Further fields of work and summary

Kurt Schwabe worked for about five decades in the field of electrochemistry. He devoted his time both to a university institute and a private research institute cooperating with industry, and for a while also to a corrosion research institute. In the present overview only the main fields in which he produced results of lasting value could be discussed in any detail. In the following I want to touch briefly on some other areas of his activities. Schwabe worked for several years in the field of polarography [61], leading to about 10 individual publications and an anthology. After the Czech physical chemist, Jaroslav Heyrovský (1890–1967), received the Nobel prize for chemistry in 1959 for his invention of polarography, Schwabe cannot have expected any more future-oriented development opportunities at his institute for polarography.

With regard to new developments in instrumental analysis even outside electrochemistry Schwabe was always open minded. Thus in 1964 his pupil, Reiner Radeglia, was able to use a tool with a proton frequency of 25 MHz built at the Dresden Institute for his doctoral thesis entitled, “Study of the behaviour of strong inorganic acids in solvent mixtures using nuclear magnetic resonance”.

At an early stage Schwabe drew attention to environmental protection problems, both in general and in his own field of electrochemical analysis [62].

Concerning Schwabe’s works on fuel cells, on which he published about 10 papers, I would like to recall his then ground-breaking investigations into the activation of oxygen electrodes by radiation [63]. In particular, he researched the difficulties of establishing a three-phase gas/electrolyte/electrode boundary when gaseous reactants (H_2 , O_2) are used. He achieved this using carbon with optimum grain-size distribution and by making the carbon electrodes water-repellent. In doing this, he took up an idea of Wilhelm Ostwald, the founder of physical chemistry in Leipzig, who long ago had proposed burning carbon in a galvanic element.

Schwabe felt committed to yet another field of technical electrochemistry, chlor-alkali electrolysis, perhaps because of the brief period he spent at IG Farben in Bitterfeld from 1928–1929, and because a number of his pupils also had gone to work at Bitterfeld as industrial chemists. This led to several papers [64] on the development of amalgam and diaphragm resp. membrane electrolysis process.

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