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Chemistry and Physics of Solid Surfaces VI

Editors: R. Vanselow and R. Howe

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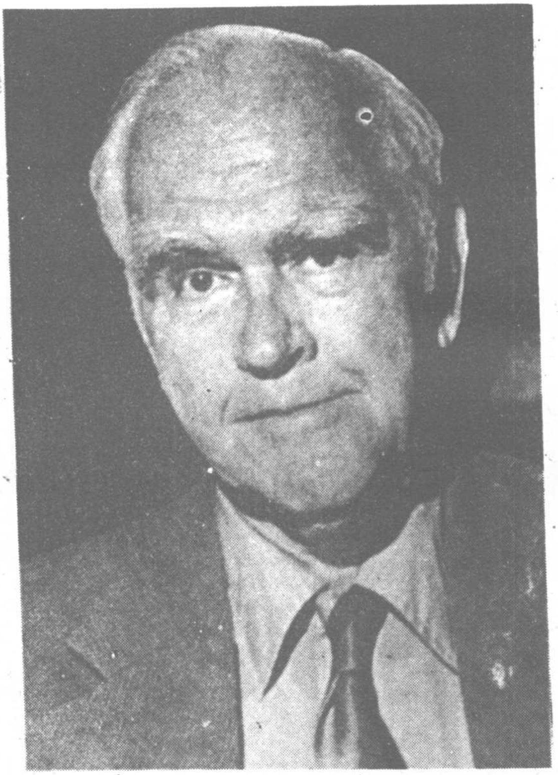
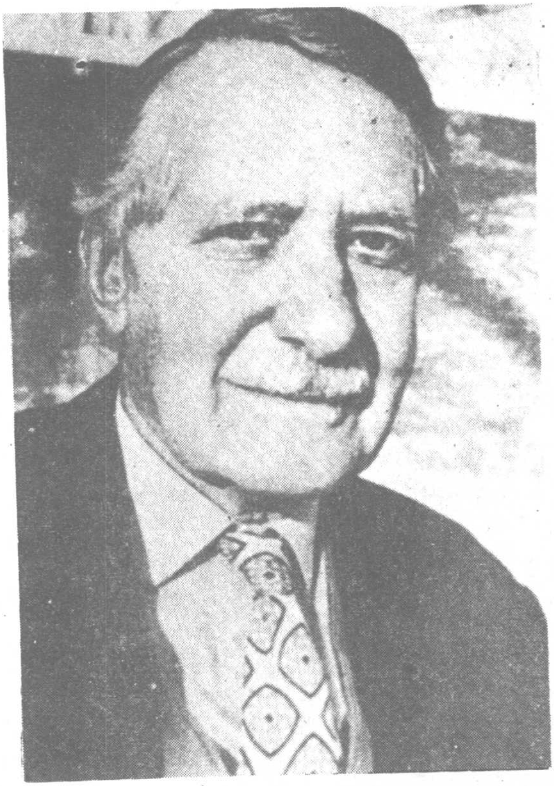
This volume is dedicated
to two former co-authors,
both pioneers in the field
of modern catalysis

Paul H. Emmett
(1900–1985)

Georg-Maria Schwab
(1899–1984)



Paul H. Emmett



Georg-Maria Schwab

Preface

This volume contains review articles which were written by the invited speakers of the seventh International Summer Institute in Surface Science (ISISS), held at the University of Wisconsin - Milwaukee in July 1985. The form of ISISS is a set of tutorial review lectures presented over a one-week period by internationally recognized experts on various aspects of surface science. Each speaker is asked, in addition, to write a review article on his lecture topic. No single volume in the series Chemistry and Physics of Solid Surfaces can possibly cover the entire field of modern surface science. However, the series as a whole is intended to provide experts and students alike with a comprehensive set of reviews and literature references, particularly emphasizing the gas-solid interface. The collected articles from previous Summer Institutes have been published under the following titles:

Surface Science: Recent Progress and Perspectives, Crit. Rev. Solid State Sci. 4, 125-559 (1974)

Chemistry and Physics of Solid Surfaces, Vols. I, II, and III (CRC Press, Boca Raton, FL 1976, 1979 and 1982), Vols. IV and V, Springer Ser. Chem. Phys., Vols. 20 and 35, (Springer, Berlin, Heidelberg 1982 and 1984).

The field of catalysis, which has provided the major impetus for the development of modern surface science, lost two of its pioneers during 1984 and 1985: Professors G.-M. Schwab (1899-1984) and P.H. Emmett (1900-1985). Both of these distinguished scientists have been associated with ISISS; Professor Emmett presented the opening lecture at the first Summer Institute in 1973 [P.H. Emmett: "Fifty Years of Progress in Surface Science", Crit. Rev. Solid State Sci. 4, 127, 1974] and Professor Schwab's opening lecture at the fourth Summer Institute appeared as a review article in Volume III of this series [G.-M. Schwab: "Development of Kinetic Aspects in Catalysis Research," Chemistry and Physics of Solid Surfaces III (CRC Press, Boca Raton, FL 1982) p.1], although Professor Schwab was at the last minute prevented by ill health from attending the meeting. Chemistry and Physics of Solid Surfaces VI is dedicated to the memory of Professors Schwab and Emmett, and tributes to them are presented in Chaps. 1 and 2 by their former students Professors *J.H. Block* and *W.K. Hall*.

The links between classical catalysis and modern surface science pioneered by Schwab and Emmett are developed further in this volume by *Sinfelt*, who reviews the subject of catalysis by metals with particular emphasis on supported bimetallic clusters. *Hall* uses the molybdena-alumina system to illustrate progress in the understanding of supported transition metal oxide catalysts, while recent advances in the structure determination of zeolite catalysts are reviewed by *Thomas*. The use of model single-crystal surfaces to investigate the effects of promoters and poisons on catalytic reactions is discussed by *Goodman*. Models of a different kind are described by *Gates*, who reviews the use of organometallic complexes to prepare metal cluster catalysts supported on high-surface-area metal oxides. *Madix* describes the use of syrchrotron radiation to characterize adsorbed species, and the thermodynamics and kinetics of weakly chemisorbed phases are discussed by *Grunze*. The kinetics of surface reactions is covered by *Yates*. *Campion* describes how recent advances in instrumentation now permit Raman spectra to be obtained from adsorbed molecules on single-crystal surfaces without surface enhancement.

Advances continue to be made in the various forms of microscopy for examining surface structures. *Smith* describes the use of high-resolution electron microscopy to observe surface features, and the new technique of scanning tunneling microscopy for measuring surface topography is reviewed by *Behm*. *Tsong* describes the study of gas-surface interactions with the time-of-flight atom-probe field ion microscope, and *Melmed* gives an account of the current status of field emission microscopy.

Electron scattering from surfaces is considered from a theoretical viewpoint by *Tong*, while *Bauer* describes the use of low-energy alkali ion scattering to determine surface structures. *Kirschner* outlines the use of spin-polarized electrons in various surface analytical techniques. The relatively novel technique of inverse photoemission spectroscopy is reviewed by *Dose*. *Himpsel* discusses surface electronic states, and the subject of wetting of solid surfaces by adsorbed layers is covered in the the final chapters by *Passell* and *Ebner*.

As in previous volumes, an extensive subject index is provided.

We would like to thank the sponsors of ISISS: the Air Force Office of Scientific Research and the Office of Naval Research (Grant No. N00014-85-G0140) as well as the College of Letters and Science, the Laboratory for Surface Studies and the Graduate School of the University of Wisconsin-Milwaukee for making both the conference and publication of this volume possible. The cooperation of the authors and the publisher in achieving rapid publication is also acknowledged.

Milwaukee, Auckland
October 1985

R. Vanselow
R.F. Howe

Contents

1. Georg-Maria Schwab: Early Endeavours in the Science of Catalysis

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Georg Maria Schwab, one of the few Grand Seigneurs in the field of catalysis, died on 23 December 1984, at the age of 85. The sad news of his sudden death came as a surprise since he had been mentally sharp and in excellent health up to the last days of his life. Indeed, he was studying the weather forecast a few days before he died, planning to spend part of Christmas vacation skiing in the Alps. Schwab was active in science till the end of his life. At the VIII International Congress on Catalysis, of which he was the Honorary President, in 1984 in Berlin, Georg-Maria Schwab impressed a large international audience with his excellent scientific lecture. And a few years ago, long after his retirement, Schwab contributed with the "Development of Kinetic Aspects in Catalysis Research" to the 4th International Summer Institute in Surface Science.

The early development of science in catalysis is closely connected with the name Georg-Maria Schwab. He was, like Paul Emmett, one of the great old masters of catalysis, who introduced a scientific foundation to a field which was till then only poorly empirical. As a former student and junior colleague of Schwab in the 50s, the honor falls upon me to present here a sketch of his life and to describe the great influence his thinking and work had upon science.

There was much in Schwab's life that was unusual. The direct personal confrontation with contradictions early on in life may partially explain Schwab's independence. Although born in Berlin, in 1899, he had Bavarian citizenship, which in the Prussia of that time was equivalent to being a foreigner. The reason for this peculárity was his parents' origin in Bavaria; his father had been displaced to Berlin where he was managing editor of an important newspaper. Schwab's role as an outsider lead to a certain restraint regarding the military orientation of Prussia and the obedient respect for authority, which was so much a part of a Prussian upbringing. Consequently, when he was called to serve in World War I as a 18-year-old, he pledged his allegiance not to the Prussian flag, but to the Bavarian.

In 1918 he returned safe and sound from the battlefield of Flanders and began to study chemistry in Berlin. After his examinations he joined the laboratory of Walter Nernst, where he received his doctor's degree in 1923 with a work on the properties of ozone, which was performed under the guidance of Professor Riesenfeld. Today it is hard to remember that back in the 20s the question was still open as to whether ozone, as a high-atomic-weight modification of oxygen, also included oxozone, O_4. Schwab's task was to determine the amount of active oxygen species (that is, oxygen species higher than O_2) in the form of O_3 and possibly O_4 from vapor density measurements and iodine titration. The presentation of this early problem was argumentatious; typical for Schwab. He set forth a certain doubt or contradiction as his premise and then used the result of his experiments to solve the problem: Both methods, titration and vapor density, only give the right amount of O_3 and O_4 in the composition when used in combination with fractional distillation. In Schwab's own words: "Applied alone or together, they only lead to the correct molecular weight when this weight is assumed from the beginning. This logical error is inherent in most of the work done on ozone in the last century". And so, with his dissertation, G.-M. Schwab had refuted the theory of oxozone.

A similar situation, by the way, arose a few years later with hydrogen. Triatomic hydrogen, H_3, also called ozone hydrogen, was haunting the literature. Sir J.J. Thomson had found H_3^+ ions during his first studies with the mass-spectrometer and surmised that it was formed by the ionization of neutral H_3. Since the differences in characteristics and stability between neutral molecules and ions were not yet very clear, there were quite a few people who were searching for neutral H_3. Among them were Wendt and Landauer from Chicago, and also Paneth and co-workers from Berlin, who published methods for producing and identifying H_3. At that time Schwab and Seuferling were occupying themselves with the chemical processes of silent discharges (coronas), including those of hydrogen, and so they also investigated this question. They were particularly suspicious of the reaction of H_3 with elemental sulfur, which was supposed to yield easily traceable H_2S, so they developed a detection procedure using arsenic. The formulation of their results was logically consistent, but cautious: "We consider it proven that in silent discharges at 50 mm pressure some kind of active hydrogen is formed. For the time being we cannot and do not want to say anything about its nature. It could quite well be identical to atomic hydrogen" [quote from Z. Elektrochem. **34** (1928)].

Today we know that the identification methods used then were not very specific, and that, for example, vibrationally excited molecular hydrogen reacts differently from molecular H_2 in its ground state. And in fact, as early as in 1927 Paneth discredited the theory of "ozone hydrogen", so Schwab's cautious conclusion was indeed justified.