

# The Life and Work of Heinz Gerischer

by Adam Heller, Dieter Kolb, and Krishnan Rajeshwar



HEINZ GERISCHER

Heinz Gerischer was born on March 31, 1919 in Wittenberg, Germany. He studied chemistry at the University of Leipzig between 1937 and 1944 with a two-year interruption because of military service. In 1942, he was expelled from the German Army because his mother was born Jewish; he was thus found "undeserving to have a part in the great victories of the German Army." The war years were difficult for Gerischer and his mother committed suicide on the eve of her 65<sup>th</sup> birthday, in 1943. His only sister, Ruth (born in 1913), lived underground after escaping from a Gestapo prison and was subsequently killed in an air raid in 1944.

In Leipzig, Gerischer joined the group of Karl Friedrich Bonhoeffer, a member of a distinguished family, members of whom were persecuted and murdered because of opposition to Nazi ideology. Bonhoeffer descended from an illustrious chemical lineage of Wilhelm Ostwald (1853-1932) and Walther Hermann Nernst (1864-1941), and kindled Gerischer's interest in electrochemistry, supervising his doctoral work on periodic (oscillating) reactions on electrode surfaces, completed in 1946. He followed Bonhoeffer to Berlin where his PhD supervisor had accepted the directorship of the Institute of Physical Chemistry at the Humboldt University, and also became the department head at the Kaiser Wilhelm Institute for Physical Chemistry in Berlin-Dahlem (later the Fritz Haber Institute). Gerischer himself was appointed as an "Assistent." Many years later, Gerischer would return to this distinguished institution as its director. With the Berlin Blockade and the prevailing economic conditions the post-war research was carried out under extremely difficult conditions.

Gerischer met his future wife, Renate Gersdorf, at the University of Leipzig where she was doing her diploma-work with Prof. C. Weygand. They were married in Berlin in October, 1948. In 1949, Gerischer moved his young family to Göttingen to join Bonhoeffer as a research associate at the newly-established Max Planck Institute for Physical Chemistry. Renate started her doctoral thesis at the Georg August University also under Bonhoeffer, studying the catalytic decomposition of hydrogen peroxide on metallic platinum. Her thesis work was interrupted by the birth of Cornelia (1950) and Ulrike (1951). Heinz and Renate published a joint paper on the discovery of the binding of intermediate radicals on Pt during the catalytic decomposition of hydrogen peroxide [*Z. Physik. Chem.* **6**, 178 (1956)]. After completing her doctoral thesis in 1954 Renate dedicated herself to raising four daughters and did not work as a chemist.

In Berlin and Göttingen and especially during the period from 1949 to 1955, Gerischer was interested in electrode kinetics and developed instruments and techniques for their study, including the electronic potentiostat and the monitoring of fast electrochemical processes by double potential step and

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This article is based on two articles of DK J. *Electroanal. Chem.*, **228**, 1 (1987) and **384**, 1 (1995) and on a plenary lecture that AH gave at the Gerischer Symposium on Nanostructured Materials and Interfaces at the 203<sup>rd</sup> Meeting of The Electrochemical Society in Paris, France, April 27-May 2, 2003.

## Selected Papers of Heinz Gerischer

Heinz Gerischer had, in the view of the authors, the greatest impact through his following accomplishments:

- ▶ **Relating Concentration Polarizations and Electrode Potentials** (Kaiser Wilhelm Inst. Berlin, 1951) "Concentration Polarization Due to the Initial Chemical Reaction in Electrolytes and Its Contribution to the Stationary Polarization Resistance Corresponding to the Equilibrium Potential," H. Gerischer and K. J. Vetter, *Z. Physik. Chem.*, **197**, 92 (1951).
- ▶ **Theory of AC Electrochemistry** (Max Planck Inst. Phys. Chem. Göttingen, 1951) "Alternating-Current Polarization of Electrodes with a Potential-determining Step for Equilibrium Potential," H. Gerischer, *Z. Physik. Chem.*, **198**, 286 (1951).
- ▶ **Discovery of Radicals on Electrodes** (Max Planck Inst. Phys. Chem., Göttingen, 1956) "Catalytic Decomposition of Hydrogen Peroxide on Metallic Platinum," R. Gerischer and H. Gerischer, *Z. Physik. Chem.* **6**, 178 (1956).
- ▶ **Observation of the Different Electrochemical Etching Rates of p- and n-Type Semiconductors** (Max Planck Inst. Metallforsch., Stuttgart, 1957) "Solution of n- and p-Germanium in Aqueous Electrolyte Solution under the Action of Oxidizing Agents," H. Gerischer and F. Beck, *Z. Physik. Chem.*, **13**, 389 (1957).
- ▶ **Invention of the Potentiostat** (Max Planck Inst. Metallforsch., Stuttgart, 1957) "The Electronic Potentiostat and Its Application in the Investigation of Fast Electrode Reactions," H. Gerischer and K. E. Staubach, *Z. Electrochem.*, **61**, 789 (1957).
- ▶ **Explanation of Stress Corrosion** (Max-Planck-Inst. Metallforschung, Stuttgart, 1957) "Electrochemical Processes in Stress Corrosion," H. Gerischer, *Werkstoffe u. Korrosion*, **8**, 394 (1957).

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### Selected Papers of Heinz Gerischer

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- ▶ **Discovery of Adatoms, the Existence of Adsorbed Atoms on Electrodes** (Max-Planck-Inst. Metallforschung, Stuttgart, 1958) "Mechanism of Electrolytic Discharge of Hydrogen and Adsorption Energy of Atomic Hydrogen," H. Gerischer, *Bull. Soc. Chim. Belges*, **67**, 506 (1958).
- ▶ **Observation of Differently Reacting Valence and Conduction Band Carriers** (Max-Planck-Inst. Metallforschung, Stuttgart, 1959) "Oxidation-Reduction Processes in Germanium Electrodes," F. Beck and H. Gerischer, *Z. Elektrochem.*, **63**, 943 (1959).
- ▶ **Relating Band Positions to Electrode Kinetics** (Max-Planck-Inst. Metallforsch., Stuttgart, 1960) "Kinetics of Oxidation-Reduction Reactions on Metals and Semiconductors. I & II General Remarks on the Electron Transition Between a Solid Body and a Reduction-Oxidation Electrolyte," H. Gerischer, *Z. physik. Chem.*, **26**, 223 and 325 (1960); **27**, 48 (1961).
- ▶ **Use of Single Crystal Electrodes** (Techn. Hochsch. Munich, 1963) "Preparation of Spherical Single Crystal Electrodes for Use in Electrocrystallization Studies," D. K. Roe and H. Gerischer, *J. Electrochem. Soc.*, **110**, 350 (1963).
- ▶ **Role of Surface States in Electron Transfer at Semiconductor-Solution Interfaces** (Tech. Hochsch., Munich, 1967) "Surface Activity in Redox Reactions on Semiconductors," H. Gerischer and I. Wallem Mattes, *Z. Phys. Chem.*, **52**, 60 (1967).
- ▶ **Dye Photosensitization of Zinc Oxide** (Tech. Hochsch., Munich, 1969) "Electrochemical Studies on the Mechanism of Sensitization and Supersensitization of Zinc Oxide Single Crystals," H. Tributsch and H. Gerischer, *Ber. Bunsen-Gesellschaft*, **73**, 251 (1969). "Use of Semiconductor Electrodes in the Study of Photochemical Reactions," H. Tributsch and H. Gerischer, *Ber. Bunsen-Gesellschaft*, **73**, 850 (1969).
- ▶ **Electrochemistry of Electronically Excited States** (Fritz-Haber-Institut der MPG, 1973) "Elektrodenreaktionen mit angeregten elektronischen Zuständen," H. Gerischer, *Ber. Bunsenges. Phys. Chem.* **77**, 284 (1973).
- ▶ **Photodecomposition of Semiconductors** (Fritz-Haber-Institut der MPG, 1977) "On the Stability of Semiconductor Electrodes Against Photodecomposition," H. Gerischer, *J. Electroanal. Chem.*, **82**, 133 (1977).
- ▶ **Relating Fermi Levels to Redox Potentials** (Fritz-Haber-Inst., Max-Planck-Ges., Berlin, 1983) "Fermi Levels in Electrolytes and the Absolute Scale of Redox Potentials," H. Gerischer and W. Ekardt, *Appl. Phys. Lett.*, **43**, 393 (1983). ■



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AC modulation methods. This work laid the foundation for a mechanistic interpretation of electrode reactions and impacted vastly on our present understanding of electrode kinetics. This work was recognized by the newly-minted Bodenstein Prize of the Deutsche Bunsen-Gesellschaft, which Gerischer and Klaus Vetter jointly received in 1953. Despite his superior accomplishments Gerischer did not obtain a teaching qualification (Habilitation) from the local university, a fact that partly reflected the animosity that existed between universities and the Max Planck

Institutes. Nevertheless, he was appointed in 1954 to the position of Department Head and Senior Research Fellow at the Max Planck Institute for Metal Research in Stuttgart, and a year later, he received the Habilitation from the University of Stuttgart for his comprehensive study of the discharge of metal ions.

The years 1954-1961 in Stuttgart were prolific and it was here that Gerischer began his work with semiconductor electrochemistry. It began with a short note on the electrochemistry of n- and p-type germanium; a study that grew out of a seminar on solid state physics at the university, where the recent results of Brattain and Garrett on germanium were discussed. Gerischer recognized immediately the enormous implications of semiconductor electrochemistry, both for theoretical studies of charge transfer and for potential applications in photochemistry and photovoltaic devices. Thus important papers appeared on the differentiation between



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Faradaic reactions of electrons and holes (1959) and on the theory of electron tunneling at semiconductor-electrolyte interfaces, solution Fermi levels, and densities of states. He continued his studies of metal electrodes with papers on the electronic potentiostat (1957), stress corrosion (1957), hydrogen evolution and hydrogen adatom formation (1957), on the monitoring of fast electrode processes (1960), and on the reaction kinetics of water dissociation as probed by the microwave pulse method (1961).

This work was recognized by an appointment as Associate Professor ("Extraordinariat") in Electrochemistry at the Technical University in Munich in 1962-63. Rapid promotion to the rank of full professor followed in 1964 and he became the Director of the Institute of Physical Chemistry and Electrochemistry. The period, 1964-1968, witnessed a flurry of studies from his group on photoelectrochemistry and photosensitization on electrode materials such as ZnO, CdS, GaAs, silver halides, anthracene, and perylene. In 1967-68, he spent a sabbatical as visiting professor with Charles Tobias at the University of California, Berkeley. In 1969-1970 he was the Dean of Natural Sciences at the Technical University in Munich.

Gerischer returned to Berlin in 1970, to assume the directorship of the Fritz Haber Institute where he continued his seminal studies of electrode kinetics, semiconductor electrochemistry, and photoelectrochemistry. He was a Distinguished Visiting Professor at the University of Florida, Gainesville in 1973 and in 1977-1978 he was the Sherman Fairchild Distinguished Scholar at California Institute of Technology. From 1987 through 1994, he was a Scientific Member Emeritus of the Fritz Haber Institute and he returned to Berkeley in 1987-1988 as a visiting professor. He worked with one of us (AH) in 1990-1991 at the University of Texas at Austin, on the rate-controlling role of adsorbed oxygen with photogenerated electrons in titania-assisted photocatalytic reactions.

The numerous honors and awards of Prof. Gerischer (and space constraints only afford a small sampling to be listed here) include: the ECS Olin Palladium Medal (1977); Centenary Lectureship, the Chemical Society, London (1979); DECHEMA Medal, Frankfurt (1982); Electrochemistry Group Medal, the Royal Society of Chemistry, London (1987); Galvani Medal, the Italian Chemical Society (1988); and the Bruno Breyer Medal, the Royal Australian Chemistry Institute (1992). His immense contributions were further recognized by the founding, in 2001, of the Heinz Gerischer Award of the European Section of The Electrochemical Society.

Heinz Gerischer died on September 14, 1994 of heart failure in Berlin. His immense contributions continue to leave an indelible mark, not only in electrochemistry, but also in physical chemistry and materials chemistry. His legacy lives on through his students, many of whom have carved out illustrious careers of their own.

## Acknowledgments

We thank Gerhard Ertl, Bettina Gerischer, Ulrike Gerischer, Walther Jaenicke, Ingeborg Reinhardt, and the late Konrad G. Weil for sharing memories and facts on the life and career of Heinz Gerischer.

## About the Authors

**ADAM HELLER** built the first neodymium liquid laser in 1965 and co-authored, in 1973, the first publication (in JES) on the lithium-thionyl chloride battery still used world-wide. He designed the first > 10% efficient electrochemical solar cells and the first >10% efficient hydrogen-generating solar photocathode. With Heinz Gerischer he defined, in 1992, the

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## 5<sup>th</sup> Gerischer Symposium in Berlin— “Photoelectrochemistry: From Fundamentals to Solar Applications”

*by Dieter M. Kolb*



*The Harnack-Haus in Berlin-Dahlem, venue of the 5<sup>th</sup> Gerischer Symposium.*

From **June 22 to 24, 2011**, an international conference on **“Photoelectrochemistry: From Fundamentals to Solar Applications”** will be held at the **Harnack-Haus in Berlin** as the 5<sup>th</sup> Gerischer Symposium. The organizers will be H. J. Lewerenz from the Helmholtz Center, Berlin and this writer.

The Gerischer Symposia, which are held triennially on different topics of fundamental research in electrochemistry, are dedicated to the memory of Heinz Gerischer (1919-1994), the great electrochemist and co-founder of modern physical electrochemistry. While the first Gerischer Symposium in 1999, for most obvious reasons, was devoted to semiconductor electrochemistry, the second one in 2002 dealt with new developments in electrode kinetics, again an area that has been immensely stimulated by Heinz Gerischer. The third Gerischer Symposium was devoted to electrocatalysis, a topic that nowadays combines electrode kinetics with modern surface analytical techniques, nanostructuring and tailoring electronic properties of catalysts. Again it was Heinz Gerischer who made seminal contributions to a fundamental understanding of electrocatalysis. Prof. Gerischer was working on a book chapter on exactly that topic in 1994, but fate did not allow him to finish that project prior to his untimely demise.

The fourth Gerischer Symposium in 2008 addressed studies of electrochemical processes with spatial and temporal resolution, the focus being with oscillating reactions. Gerischer's very first publication, co-authored by his thesis supervisor, K. F. Bonhoeffer, dealt with oscillating reactions on copper electrodes. With the fifth symposium, we return to the topic of the first one to demonstrate the enormous progress that has

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### 5<sup>th</sup> Gerischer Symposium in Berlin— “Photoelectrochemistry: From Fundamentals to Solar Applications”

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been achieved within the last 12 years. Internationally renowned scientists have agreed to come to Berlin and give lectures; many of them had known Gerischer personally for a long time. This fact and the beautiful ambience of the Harnack-Haus, the newly renovated conference center of the Max-Planck-Gesellschaft, will ensure a family-like atmosphere.

Each symposium had its special highlights and flair of its own. I shall mention just two. One evening of the first Symposium turned into a homage to Heinz Gerischer. All invited speakers shared their personal memories of Gerischer with the audience, where Mrs. Renate Gerischer and her daughters, Ulrike and Bettina, were our guests of honor. Thus, a very lively, human, and humorous picture of a great scientist came back to us. I saw Mrs. Gerischer absolutely happy that evening. It was the first and unfortunately, the last symposium she could attend.

The highlight of the third symposium was certainly the Heinz Gerischer Award of the ECS European Section, presented to Michael Grätzel, Lausanne. The ceremony opened with two musical performances, which by themselves were an almost unique event: Gerhard Ertl (piano) and Ludwig Kibler (piano, clarinet) played Franz Schubert's “March Militaire in D,” followed by the second movement of Mozart's Clarinet Concerto K.V. 622. I am absolutely sure that Heinz Gerischer, a passionate concert goer, would have enjoyed this performance as much as we all did.

I hope to see many of you in Berlin at the 5<sup>th</sup> Gerischer Symposium to pay tribute to a great man and to discuss exciting science in an exciting city. ■

reduction of adsorbed O<sub>2</sub> as the rate controlling step in TiO<sub>2</sub> photo-catalyzed oxidations and later developed, with his son Ephraim Heller, binders for the widely used photo-oxidatively self-cleaning architectural coatings. In 1989-1998 he pioneered the electrical wiring of redox enzymes, their electrical connection to circuits through electron-conducting hydrogels; and in 1996 assisted Ephraim in the founding of TheraSense, now part of Abbott Diabetes Care. The company introduced in 2000 a thin-layer microcoulometer for blood sugar monitoring requiring only a 300 nL blood sample. Abbott introduced in 2008 the continuous and accurate glucose monitor, based on Heller's electrical wiring of glucose oxidase. Heller has been a Professor of Chemical Engineering at the University of Texas at Austin since 1988. Among numerous awards, Heller received the 2007 U.S. National Medal of Technology and Innovation in a White House ceremony. He may be reached at heller@che.utexas.edu.

**DIETER KOLB** studied physics at the Technical University in Munich and did his PhD under the supervision of Heinz Gerischer. From 1969 to 1971 he did post-doctoral work at Bell Labs in Murray Hill. He returned to Germany to join Heinz Gerischer, then at the Fritz-Haber Institut in Berlin, where he worked in the area of electrochemical surface science. In 1990 he was appointed Director of a newly created Institute of Electrochemistry at the University of Ulm. He was President of the ISE in 2003-2004. He has received several awards, among those the Pergamon Gold Medal of ISE and the Olin Palladium Award of ECS. He is a Fellow of ECS and ISE and may be reached at dieter.kolb@uni-ulm.de.

**KRISHNAN RAJESHWAR** is a Distinguished University Professor and Associate Dean of the College of Science at the University of Texas at Arlington. He is the Editor of *Interface*. His research interests include photoelectrochemistry; solar energy conversion; renewable energy; materials chemistry; semiconductor electrochemistry; and environmental chemistry. Rajeshwar is a Fellow of ECS and received the Energy Technology Division Research Award of ECS in 2009. He has edited books, special issues of journals, and conference proceedings and is the author of over 450 refereed publications. He may be reached at rajeshwar@uta.edu. ■



Presentation of the Gerischer Award during the 3<sup>rd</sup> Symposium. From left to right: **Mrs. Grätzel**, **Prof. Grätzel**, **Dr. Ulrike Gerischer** and her daughter, **D. Kolb**, and **Dr. Ludwig Kibler**.