

tion rate limits of wire chambers. This multistage chamber uses parallel plates in place of wire planes. "It's such a good detector that, if I had invented it ten years earlier, wire chambers would be dead by now," Charpak asserts. Nonetheless the multistage avalanche chambers haven't as yet seen much use in experiments. "There's so much inertia in high-energy physics," explains Charpak. "If you've spent five years building a detector, and someone comes along with something better, you don't listen—because you can't."

Biomedical imaging

In recent years Charpak has given his attention almost entirely to devising detectors for use in biology and medicine. Much of this work is still done at CERN, but Charpak has also undertaken entrepreneurial ventures that supply detectors to hospitals and biological laboratories.

"The pioneering work on x rays with wire chambers was done by Victor Perez Mendez at Berkeley," Charpak told us. In the early 1970s Perez Mendez began using multiwire proportional chambers to do x-ray imaging with synchrotron radiation. "I started to get interested in biology in 1974," recalls Charpak, "when [Rudolf] Mössbauer told me there was a

real need for better x-ray detectors."

In a multiwire x-ray imaging chamber the avalanches at the anode wires are initiated by photoelectrons liberated by the x rays in a gas-filled drift region that precedes the wire plane. A very sophisticated "spherical drift chamber" built by Charpak's group in 1984 is still in constant use by protein crystallographers at the Orsay synchrotron light source.

Charpak has also developed imaging chambers for biological radiography with beta-emitting isotopes. The traditional method was simply to press the isotope-labeled sample up against a piece of photographic film. The result, Charpak contends, "was very ugly pictures that required high radioisotope levels and very long exposure times. I always thought you could replace film with detectors, just as we did in high-energy physics."

Charpak's beta-imaging detectors, one of which is in routine use at a Geneva hospital, do indeed exploit several ideas he developed first for high-energy physics in the 1980s. They are essentially parallel-plate multistage chambers whose avalanches generate light pulses imaged by CCD arrays. "In one afternoon you get a picture of a quality that would take three months with film," Charpak told us. "Last spring I made one

for the Institut Pasteur. After ten days they had a publishable paper."

Prisoners west and east

Charpak was born in Poland in 1924. The family emigrated to France when Georges was 7 years old. Having just turned 19 in the wartime summer of 1943, Charpak was jailed by the Vichy authorities in southern France as a "terrorist." After a year in prison he was deported by the Nazis to the concentration camp at Dachau, where he remained until the camp was liberated in April 1945. "Luckily I was only regarded as a Pole and a terrorist," Charpak told us. "They didn't know that I was a Jew."

Charpak became a French citizen in 1946. Two years later, with a civil engineering degree from the École des Mines in Paris, he went on to become Joliot's graduate student in nuclear physics at the Collège de France.

For many years Charpak has been a committed and visible champion of the cause of scientists imprisoned by despotic regimes. He was a founder and leader of the CERN chapter of the SOS committee for Soviet dissidents Andrei Sakharov, Yuri Orlov and Anatoly Sharansky. Charpak knows better than most what it means to be deprived of freedom.

—BERTRAM SCHWARZSCHILD

MARCUS WINS NOBEL PRIZE IN CHEMISTRY FOR ELECTRON TRANSFER THEORY

Rudolf Marcus of Caltech was at a meeting of the Electrochemical Society in Toronto when he learned that the Royal Swedish Academy of Sciences had awarded him the 1992 Nobel Prize in Chemistry "for his contributions to the theory of electron transfer reactions in chemical systems." The meeting participants were only too glad to raise their glasses to Marcus, for the fundamental theory he elucidated in the 1950s and 1960s underlies much of their work. Its applications include such diverse phenomena as photosynthesis, electrically conducting polymers, chemiluminescence and corrosion. As Marcus remarked to us, "the field continues to grow and grow."

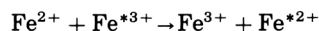
Out of a simple question...

Marcus told us that he was led to consider the problem of electron transfers between molecules when he was a young associate professor at the Polytechnic Institute of Brooklyn in 1955. At that time Marcus had already read 11 books and published

two papers on electrolytes, his interest in the subject having been stimulated by a question posed by a student in his class. Hence he was well prepared to critique some work by Willard Libby concerning the transfer of an electron between molecules in solution. Marcus was intrigued by Libby's approach but bothered by some aspects that didn't seem quite right. He tried his hand at the problem and added a key factor neglected by Libby: the role played by fluctuations in the dielectric polarization. Marcus published this work¹ in 1956, in the first of a series of papers that he wrote over a nine-year period developing what is now called the Marcus theory.

This theory focused on the transfer of electrons between two molecules that interact only loosely during the transfer, so that no bonds are formed or broken. One of the simplest such reactions is a "self-exchange" reaction in which an electron is transferred from one ion to another ion of the same element that is in a different

valence state. For example, in the following reaction, an electron is transferred from the ferrous ion, whose valence is +2, to the ferric ion (denoted by an asterisk), whose valence is +3:



Although this reaction is about the simplest one could imagine, its rate depends on a very large number of variables: the positions of the nuclei, their vibrational state, the type of solvent, the orientations of polarized solvent molecules, the temperature and so on. There are also thousands of spatial coordinates. The potential energy surfaces of the reactants and the products must be drawn in an N-dimensional space, where N is the number of coordinates.

Marcus collapsed all these coordinates to one composite "nuclear coordinate," which represents essentially the state of the entire system, so that the free energy could be plotted against just one variable rather than as a multi-dimensional surface. Mar-

cus then assumed that the solvent, or dielectric, would respond in a linear way to any changes in the charge distributions of the reacting molecules, and he found that the resulting free energies for the reactant-solvent system and for the product-solvent system were simple parabolas when plotted as functions of this composite coordinate. The left-hand panel of the figure on page 22 shows a sample free-energy curve for the reactants and three sample product curves. The curve labeled "I" describes the products of the self-exchange reaction, for which the minimal free energy of the reactants is the same as that of the products because the two are essentially identical systems. In systems where the products differ from the reactants, the minimum free energy of the products can be lower than that of the reactants, as shown by curves II and III.

In the Marcus picture electron transfer between the reacting molecules can occur only when the system is at the intersection of the reactant and product free energy curves. That fact follows from the Franck-Condon principle, which states that electron transfers occur so rapidly that the nuclei, which move far more slowly than electrons, have no time to rearrange as an electron jumps between ions. (This principle applies to electron transfer as described by the potential energy surfaces, rather than the free energy plotted against the composite variable.) Thus the nuclei must be in the same position immediately before and after the electron transfer. The reaction rate is governed in part by the Franck-Condon factors, which describe the degree of overlap between the initial and the final vibrational states.

But what provides the energy to lift the reactants to the energy of the intersection region, where the transfer can occur? The energy comes primarily from fluctuations both in the vibrational energy of the nuclei and in the orientation of the polarized solvent molecules. Thermal fluctuations can cause the reacting molecules and the surrounding solvent to become distorted enough to move the system to the intersection region. (Libby had suggested the relevance of the Franck-Condon principle, but his approach violated energy conservation because it included no source of either thermal or photonic energy.)

In developing this theory Marcus used standard molecular theory, representing the vibrational degrees of freedom as harmonic oscillators, and continuum theory to treat the dielectric solvent. Mark Ratner (North-

western University) told us that molecular theory and continuum theory were rather standard techniques, but that the combination was unique. In papers^{2,3} written in 1960 and 1965 Marcus went a step further and used statistical mechanics to analyze the dielectric continuum model of the solvent. The end results of Marcus's papers from the late 1950s and early 1960s were fairly simple but enormously useful equations that predicted how electron transfer rates vary with specified parameters. Not only could the equations predict rates for the various electron transfer reactions, but they also could relate the rates for self-exchange transfers to those for the corresponding cross-reactions. For example, if one knows the rate for the ferrous-to-ferric ion electron transfer as well as that for the chromous-to-chromic ion transfer, one can determine the rate for the cross reaction in which the reactants are ferric and chromous ions and the products are ferrous and chromic ions. Henry Taube (Stanford), who won the 1983 Nobel Prize in Chemistry for experiments on redox reactions in inorganic systems, told us that Marcus's cross relation is one of the most cited equations in the chemical literature.

Marcus is generally credited with reducing a complex system to a simple picture capable of generating experimental predictions. John Miller (Argonne National Laboratory) calls Marcus theory "one of those departures in science that had enormous impact because it gave a way of thinking about the subject where there once was only confusion."

Experimental tests

While Marcus was working on his theory of electron transfer at the Polytechnic Institute he frequently visited nearby Brookhaven National Laboratory, which had an active experimental program in electron transfer. Marcus discussed his predictions with Norman Sutin of Brookhaven, who proceeded to test them against the data. Sutin found that theory and experiment agreed impressively. He thinks that the excellent agreement of the predicted reaction rates with the experimental values provided encouragement for Marcus to continue, and he notes that these experiments, together with the theory, served to guide future experiments.

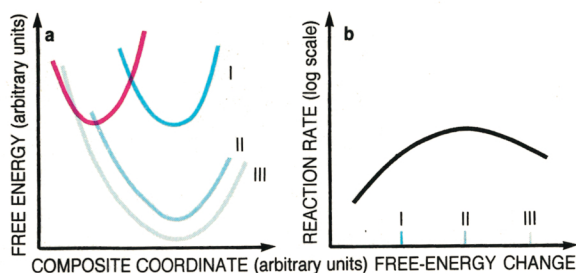
But one prediction, which seemed to contradict intuition, was not verified right away. That was the dependence of the reaction rate on the change in free energy of the reaction



Rudolf Marcus

(that is, the free energy difference between the minima of the reactants and the products), which is the "driving force" for the reaction. Marcus theory predicts that as this driving force increases, the reaction rate also increases but only to a point: For very large driving forces the rate begins to decrease, as shown in the right-hand panel of the figure on page 22. The section of the curve that turns down again is known as the inverted region. One way to understand this prediction is to examine the free energy surfaces labeled "II" and "III" in the left-hand side of the figure. These curves represent a successive lowering of the free energy curve for the product state. Curve II intersects the free energy curve of the reactants at its minimum. At that point the free energy barrier disappears and the reaction proceeds at its maximum rate. As the potential energy curve for the products drops still further (curve III), the intersection point starts to climb up the reactants' curve and the free energy barrier rises again. Another way to explain the inverted region is in terms of the Franck-Condon factors: As the products' free energy curve drops, the overlap between the initial and final states first increases and then decreases.

The inverted region was not demonstrated unambiguously until 1984, although several earlier experiments had hinted at its validity. One problem was that the decreased reaction rate that should signal the inverted region was masked by diffusion effects. In experiments where the reactants were free to diffuse, the electron transfer occurred so fast that its



Electron transfer reactions have rates whose inverted shape (right) is explained by the free energy curves (left). Electrons can be transferred only when the free energy curve of the reactants (red) intersects that of the products (blue). For curves I and III the intersection is above the minimum free energy for the reactants. But for curve II the free energy barrier disappears, and the reaction rate has its maximum.

reaction rate (even in the inverted region) was 1000 times faster than was needed to assure that the molecules would react every time they approached one another. The series of experiments that seemed to convince most doubters was conducted by Miller, Gerhard Closs and their colleagues at Argonne National Laboratory.⁴ Miller told us that the clearest demonstrations of the inverted region were experiments in which the donor and acceptor molecules were at opposite ends of a rigid spacer molecule, so that no diffusion was involved. With this technique they demonstrated for a number of reactant pairs that the electron transfer rates all slowed as expected for sufficiently high free energy changes.

Related work

Independent of Marcus and during the same time period, Noel Hush, working first at the University of Bristol in England and later at the University of Sydney in Australia, developed a similar approach to the problem of electron transfer.⁵ Like Marcus, Hush has continued to contribute to the theory of electron transfer, especially concentrating on the connection between thermal and photoinduced transfers.

In 1959 Benjamin Levich and Rezo Dogonadze undertook a quantum mechanical treatment of the electron transfer problem, which up to then had been treated semi-classically.⁶ These theorists treated the solvent as a collection of quantum mechanical harmonic oscillators. There have been a number of quantum mechanical treatments since then, including a notable contribution by Joshua Jortner and his colleagues at Tel Aviv University.⁷ One of the features these refinements have added is tunneling from one free-energy surface to another.

After developing his theory, Marcus extended it from electron transfers between molecules to the transfer of electrons at the surface of an electrode. Others have applied it to transfers of ions, atoms or groups of atoms; to the transfer of electrons

along bridging molecules; and to the movement of electrons within a single molecule. A particularly intriguing challenge is to explain the very rapid transfers of electrons over distances of 10–20 angstroms in biological molecules.

Modern extensions of electron-transfer theory are often based on the polaron model originally developed for electron transfer in solids by Theordore Holstein in 1969.

In the last decade several groups have undertaken studies of electron transfer using computer simulations of molecular dynamics. Such studies approach electron transfer from a microscopic point of view, considering hundreds of individual solvent (usually water) molecules. David Chandler and his coworkers at the University of California at Berkeley, who have done a number of these calculations, told us that they couldn't have done the work without the framework provided by Marcus theory. At the same time such simulations give a way to check some of the assumptions built into Marcus theory. For example, simulations by Arie Warshel and his colleagues at the University of Southern California⁸ and by Chandler and his coworkers⁹ have shown that the solvent does respond linearly, as assumed, to changes in the position of charges. The assumption of linearity in Marcus's theory is essential to getting parabolic free energy curves. The simulations have also uncovered new phenomena. Chandler's group found, for example, that the dominant fluctuations are ones that take the water into classically forbidden states.¹⁰ Warshel told us that his group has shown that such effects are present in photosynthetic proteins.

Marcus's career

Marcus was born in Montreal, Canada, and earned both his BSc and PhD in chemistry from McGill University there. After graduating from McGill in 1946 Marcus did postdoctoral research, first at the National Research Council of Canada and then at the University of North Carolina. In 1951 he became an assistant professor

at the Polytechnic Institute; by 1958 had risen to full professor. Marcus left Polytechnic in 1964 to join the faculty of the division of physical chemistry at the University of Illinois, Urbana-Champaign. In 1978 he moved to Caltech, where he is now the Arthur Amos Noyes Professor of Chemistry.

Marcus has remained active in electrochemistry, continuing to develop the theory of electron transfer, but he has also made contributions to several other areas. Among those he mentioned to us were unimolecular reactions and intramolecular dynamics, semiclassical theories of bound vibrational states and of collisions, and vibrational adiabaticity in reaction dynamics. Unimolecular reactions were the subject of his first theoretical postdoctoral work; his initials are one of four that label the RRKM theory regarding these reactions. As he now examines new aspects of that subject, Marcus said, he and his colleagues can calculate some of the things that were formidable before computational capability was so readily available.

—BARBARA GOSS LEVI

References

1. R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956).
2. R. A. Marcus, *Discuss. Faraday Soc.* **29**, 21 (1960).
3. R. A. Marcus, *J. Chem. Phys.* **43**, 679 (1965).
4. J. R. Miller, L. T. Calcaterra, G. L. Closs, *J. Am. Chem. Soc.* **106**, 3047 (1984).
5. N. S. Hush, *J. Chem. Phys.* **28**, 964 (1958); *Trans. Faraday Soc.* **57**, 557 (1961).
6. V. G. Levich, R. R. Dogonadze, *Dokl. Akad. Nauk SSSR* **124**, 123 (1959) [*Proc. Acad. Sci. Phys. Chem. Sect.* **124**, 9 (1959)].
7. N. R. Kestner, J. Logan, J. Jortner, *J. Phys. Chem.* **78**, 2148 (1974).
8. A. Warshel, *J. Phys. Chem.* **86**, 2218 (1982).
9. R. A. Kuharski, J. S. Bader, D. Chandler, M. Sprik, M. L. Klein, R. W. Impey, *J. Chem. Phys.* **89**, 3248 (1988).
10. J. S. Bader, R. A. Kuharski, D. Chandler, *J. Chem. Phys.* **93**, 230 (1990).