

Nobel Centennial Essays

A Century of Chemical Dynamics Traced through the Nobel Prizes

W

1992: Rudolph A. Marcus

by J. Van Houten

Nobel Prize in Chemistry 1992
Rudolph A. Marcus (1923–)*for his contributions to the theory of electron transfer reactions in chemical systems*

This is the tenth in a series of essays, written in commemoration of the centennial of the Nobel Prize, examining the history of chemical dynamics in the 20th century (1).^W The four Nobel Prizes awarded during the 1990s culminate a century of chemical dynamics research. This essay describes the 1992 award, which recognized Rudy Marcus's development of a theoretical treatment of electron transfer reactions. It will focus on the history of Marcus theory (as it has long been known) and its relationship to ongoing work in a wide variety of areas.^{1,2}

Rudy Marcus's contributions have provided inspiration and guidance to an entire generation of chemists studying electron transfer in systems as diverse as transition metal complexes, polymer films, biomolecules (DNA, proteins, and photosynthetic reaction centers), conducting polymers, microelectrodes, and interfacial systems (2). Marcus theory's influence on Nobel Laureate Henry Taube (1983) was described in an earlier essay in this series (1*b*), in Taube's 1968 article in this *Journal* (3), and in his 1970 book (4) on electron transfer reactions.

Marcus began his scientific career in 1941 as an undergraduate at McGill University in his native Montreal. As was customary at that time, Marcus stayed on at McGill, working first on the war-related Canadian RDX project with Carl A. Winkler³ and receiving his Ph.D. in 1946 for work on the solution–phase kinetics of nitration reactions. He then joined the new postdoctoral program at the National Research Council of Canada in Ottawa, working on the photochemistry of gas–phase free radical reactions⁴ with E. W. R. Steacie. Marcus wrote in his Nobel autobiography, “the program at NRC later became famous, but at this time it was still in its infancy” (5). All three of the Canadian Nobel Laureates mentioned in this series, Henry Taube (1*b*), John Polanyi (1*i*) and Marcus, were once postdoctoral fellows at NRC, which was directed by Gerhard Herzberg, the first Canadian Nobel Laureate in chemistry (in 1971, see ref. 1*b*).

Although Marcus was trained as an experimentalist, he became interested in mathematical theory early on. He took more mathematics courses than other chemistry students at McGill, but when he was a student there were no theoretical chemists in Canada, so he “[did not] think [he] ever considered how or where theories were conceived”. At the conclusion of his experimental postdoctoral work at NRC in 1948, he decided to look for another fellowship—this time theo-

Rudolph A. Marcus



photo by Morton Z. Hoffman

retical. He said that he “had a tendency to break the glass vacuum apparatus, due to a still-present impetuous haste...[but] the realization that breaking a pencil point would have far less disastrous consequences played little or no role...in [his] decision to explore theory!” (5). Marcus “applied in 1948 to six well-known theoreticians in the U.S.” but doubted that any of them “might take on an untested applicant,...hardly qualified for theoretical research”. His only acceptance came from Oscar K. Rice at the University of North Carolina. In his Nobel autobiography Marcus reported that after joining Rice's group in 1949, “I never looked back. Being exposed to theory, stimulated by a basic love of concepts and mathematics was a marvelous experience. During the first three months I read everything I could get my hands on regarding reaction rate theory.”

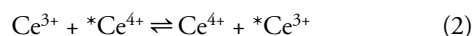
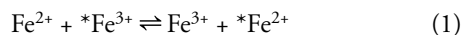
His first venture into theory led to his first major contribution: “Oscar gently nudged me into working on a particular problem. Fortunately for me Oscar's gamble paid off.” Marcus “blended the statistical ideas from [Rice-Ramsperger-Kassel] theory of the 1920s with those of transition state theory of the 1930s” (5) to formulate what has become known as RRKM theory (the M standing, of course, for Marcus), which he published in 1951 and 1952. The impact of RRKM theory on the field of chemical dynamics was mentioned in last month's essay (1*i*).

Despite his initial success as a theoretician, Marcus had difficulty obtaining his first faculty position. His “effort met with little success (35 letters did not yield 35 no's, since not everyone replied)” (5). He ultimately obtained a position in 1951 at Polytechnic Institute of Brooklyn, upon the recommendation of Seymore Yolles, who had been a graduate student in a course Marcus taught at the University of North Carolina when Oscar Rice was ill. Marcus's autobiography notes that at Brooklyn Poly his “life as a fully independent researcher began. I undertook an experimental research program on both gas–phase and solution–phase reaction

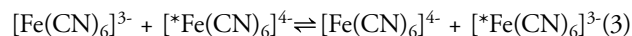
Nobel Centennial Essays

rates, wrote the RRKM papers, and wondered what to do next in theoretical research. I felt it was pointless to continue with RRKM since few experimental data were available. Some of our experiments were intended to produce more." In something reminiscent of Roald Hoffmann's observation on how teaching can enhance research (*1g*), Marcus said that a student in his statistical mechanics class who brought him a problem in polyelectrolytes drew his attention to electrostatics. This led him to "read everything I could on electrostatics" and he published two papers on the subject in 1954 and 1955.

In 1955 Marcus had his "first contact with electron transfer reactions" when he "chance[d] upon a 1952 symposium issue on the subject in the *Journal of Physical Chemistry*" (*6*). He was particularly struck by a paper in which Libby employed the spectroscopic Franck–Condon principle to explain the experimental finding that isotopic exchange reactions involving electron transfer between small metal cations in aqueous solution (e.g., reactions 1 and 2) were relatively slow,



whereas those involving larger anionic metal complexes (e.g., reactions 3 and 4) were relatively fast.



Libby explained the rate difference by noting that there was a large relative difference in size for the redox partners in reactions 1 and 2; whereas for reactions 3 and 4, where the redox partners were large complexes, the relative size difference was less. This led Libby to postulate that there was an energy barrier to electron transfer resulting from the different sizes of the oxidized and reduced forms of the ions and their solvation shells. Further confirmation of Libby's postulate came in the ensuing discussion when the extremely slow "self-exchange" reaction involving the cationic metal complexes, $[\text{Co}(\text{NH}_3)_6]^{2+}/[*\text{Co}(\text{NH}_3)_6]^{3+}$, was mentioned, and the very large difference in Co–N bond length in those redox partners was pointed out. (In considering the above reactions, it is worth noting that isotope exchange techniques were pioneered by the 1943 Nobel Laureate, George deHevesy [*1d*], and that the particular reactions above were central to the work of the 1983 Nobel Laureate, Henry Taube [*1h*].)

Marcus said in his Nobel lecture: "After studying Libby's paper and the symposium discussion, I realized that what troubled me...was that energy was not conserved: the ions would be formed in the wrong high-energy environment" which would require the absorption of light, but which could not happen thermally ("in the dark" as Marcus put it) (*6*). Recognizing that the Franck–Condon principle applied to spectroscopy, Marcus said "Libby had perceptively introduced the Franck–Condon principle to chemical reactions, but something was missing." Marcus asked himself "How does the reacting system behave in the dark so that

it satisfies both the Franck–Condon principle and energy conservation?" His attempt to answer that question led him to develop the now well-known Marcus theory of electron transfer. "I realized that fluctuations had to occur in the nuclear coordinates" of the redox partners and their solvent spheres in order to "satisfy both the Franck–Condon and energy conservation conditions [thereby to] permit the electron transfer to occur in the dark" (*6*).

Marcus formulated his picture of the electron-transfer process in a series of papers he published between 1956 and 1960 (*7*). He developed the idea of a "reorganization parameter" in the activation energy term of the classic rate equation (named for 1903 Nobel Laureate, Svante Arrhenius [*1b*]), showing that for

$$k = A \exp(-\Delta G^*/kT)$$

the free energy of activation, ΔG^* , could be written in terms of the standard free energy of the reaction, ΔG° , and a reorganization parameter, λ , that Marcus proposed.

$$\Delta G^* = (\lambda/4)(1 + \Delta G^\circ/\lambda)^2$$

For self-exchange reactions, such as reactions 1–4 above, $\Delta G^\circ = 0$, and the activation energy is simply $\lambda/4$. According to Marcus, "Obtaining the result for the mechanism and

Nobel Centennial Essays

rate of electron transfer was indeed one of the most thrilling moments of my scientific life" (6).

Marcus further developed his theory to make it applicable to "cross-reactions" where the redox partners are different chemical species, such as the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ by MnO_4^- . He reported the predictions of his theoretical work in a paper he presented at a Faraday Society meeting on redox reactions (7e), where he "hoped to stimulate discussions with experimentalists in the field." He went on to say (6): "At the time I certainly did not anticipate the subsequent involvement of the many experimentalists in testing them." An important and long-lasting collaboration with an experimentalist began in about 1962 when Marcus visited Norman Sutin at Brookhaven National Laboratory on Long Island. He said: "Norman had either measured...or knew rate constants that permitted the cross relation to be tested. I remember vividly the growing sense of excitement we both felt as, one by one, the observed rate constants more or less agreed with the predictions." (6).

In the four decades since 1962, literally thousands of experimental results have confirmed Marcus's predictions. Much of the ensuing work was stimulated by a quest for the so-called "Marcus inverted region" predicted in his 1960 paper (7e). The rate constants for a series of related reaction systems are expected to increase as the standard Gibbs energy change becomes more negative; but when $-\Delta G^\circ > \lambda$, the rate constant first levels off and then decreases. This behavior, which produces an inverted parabolic curve when the rate constant is plotted versus $-\Delta G^\circ$, was, in Marcus's words, "unexpected until the present theory was introduced" (6) in 1960. Although the inverted region is important for the basic research that it stimulated, it is even more significant in studies of the natural photosynthetic reaction center, artificial systems for solar energy conversion seeking to mimic natural photosynthesis, and a broad spectrum of other research problems too numerous to mention here. Marcus believes that "the best experimental evidence for the inverted region was provided in 1984...almost 25 years after it was predicted" (6). That evidence was provided by Miller, et al. (8) who measured the intramolecular reaction rate constants for a series of bifunctional steroids, A-Sp-B \cdot (B \cdot = 4-biphenyl, the electron donor; Sp = 5 α -androstane, a rigid saturated hydrocarbon spacer; and A = quinone or polycyclic aromatic hydrocarbon derivatives, the electron acceptors). The plot of k versus $-\Delta G^\circ$ for that system clearly shows the distinctive inverted parabolic shape expected from the theory.

In about 1960 Marcus realized "it was best...to bring the experimental part of my research to a close—there was too much to do on the theoretical aspects" (5). However at Brooklyn Poly he had found only one student interested in theoretical chemistry (2). He went on an extended sabbatical in 1960–1961 at the Courant Mathematical Institute in New York (5) "auditing many courses which were, in part, beyond me, but which were, nevertheless, highly instructive." He moved to the University of Illinois in 1964 where he "never undertook any further experiments", but where

he "never had any trouble attracting theoretical students" (2). At Illinois he expanded his theoretical research in a number of directions (2, 5).

In 1978 Marcus moved to the California Institute of Technology as the A. A. Noyes Professor of Chemistry. Although he found that his "semiclassical interlude of 1970–1980 was a very stimulating one" it lacked the interaction with experimental results of his earlier work. At Caltech he had access to the extensive experimental results of his new colleagues, leading him to observe: "Life would be easier if the experimentalists would only pause for a little while!...There was a time when I had wondered how much time had been lost doing experiments...at Brooklyn Poly,...NRC and McGill.... [But] in retrospect, I realized that this experimental background heavily flavored my attitude and interests in theoretical research. This interaction of experiment and theory, each stimulating the other, has been and continues to be one of the joys of my experience" (5).

The "interaction of experiment and theory" that Marcus spoke of works both ways, as his theories have inspired a generation of experimentalists, and are related to at least six Nobel Prizes in addition to his own. The connection to Henry Taube's experimental work has already been mentioned. The importance of RRKM theory to the work of Dudley Herschbach, Yuan Lee, and John Polanyi was discussed in last month's essay (1i). Marcus electron transfer theory contributed to the understanding of the photosynthetic reaction center by Dieneshofer, Michel, and Huber, who won the 1988 prize. Finally, some aspects of Marcus's work relate to the last three chemistry Nobel Prizes of the 20th century—the 1998 Prize to Kohn and Pople for computational methods, the 1999 Prize to Zewail for femtochemistry, and the 2000 Prize to Heeger, MacDiarmid, and Shirakawa for conducting polymers. Marcus concluded his Nobel lecture by saying that "It is naturally gratifying to see one's theories used" (6).

Because of his passion for research, Marcus has "never [been] tempted, even for a moment" to assume any administrative position that would interfere with his love for things that he considers "fun to study" (2). He has, nevertheless, shown a remarkable prescience in recognizing high quality research among others, as exemplified in his only paper published in this *Journal* (9)—a talk delivered at the Advisory Council on College Chemistry Conference on Chemical Dynamics in San Clemente, December 1966 (where Henry Taube also spoke [1h]). In that paper, Marcus referenced six future Nobel Laureates whose work has been discussed in this series: Manfred Eigen (1f), Ronald Norrish (1f), Henry Taube (1h), Dudley Herschbach (1i), John Polanyi (1i) and, naturally, himself.

Supplemental Material

A list of all recipients of the Nobel Prize in Chemistry, their affiliations, and the work for which the award was made, is available in this issue of *JCE Online*.

Notes

1. The details of Marcus theory and its applications are beyond the scope of this essay. The interested reader is referred to the following: *a.* Cannon, R. D.; *Electron Transfer Reactions*; Butterworths: Boston, 1980; *b.* Ebersson, L.; *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987; *c.* *J. Phys. Chem.* Vol. 90, No. 16, July 31, 1986. *Rudolph A. Marcus Commemorative Issue.* *d.* Bolton, J. R.; Mataga, N; McLendon, G., Eds.; *Electron Transfer in Inorganic, Organic and Biological Systems*; American Chemical Society, Washington, DC, and Canadian Society for Chemistry, Ottawa, 1991; *e.* *Chemical Reviews*, Vol. 92, No. 3, 1992; *f.* Isied, S. S., Ed.; *Electron Transfer Reactions: Inorganic, Organometallic and Biological Applications*; American Chemical Society, Washington, DC, 1997. Additional bibliographic materials are suggested by Bohning (*ref.* 2).

2. Marcus theory has been described a number of times in this *Journal* as well as in many textbooks at the advanced undergraduate and graduate level. The following articles offer background and applications: *a.* Newton, T. W. *J. Chem. Educ.* **1967**, *44*, 571; *b.* McLennan, D. J. *J. Chem. Educ.* **1976**, *53*, 348; *c.* Lewis, N. A. *J. Chem. Educ.* **1980**, *57*, 478; *d.* Neta, P. J. *J. Chem. Educ.* **1981**, *58*, 110; *e.* Scott, R. A.; Mauk, A. G.; Gray, H. B. *J. Chem. Educ.* **1985**, *62*, 932; *f.* Martins, L. J. A. and da Costa, J. B. *J. Chem. Educ.* **1988**, *65*, 176.

3. Winkler had been a Ph.D. student with the 1956 Nobel Laureate, Cyril Hinshelwood (*1e*), at Oxford.

4. Cyril Hinshelwood and Nicolay Semenov won the 1956 Nobel Prize for their work on free radical reactions, as discussed in an earlier essay (*1e*) in this series.

Literature Cited

- a.* Van Houten, J. *J. Chem. Educ.* **2001**, *78*, 1572–1573; *b.* **2002**, *79*, 21–22; *c.* **2002**, *79*, 146–148; *d.* **2002**, *79*, 301–304; *e.* **2002**, *79*, 414–416; *f.* **2002**, *79*, 548–550; *g.* **2002**, *79*, 667–669; *h.* **2002**, *79*, 788–790; *i.* **2002**, *79*, 926–933.
- Bohning, J. J. in James, L. K., Ed.; *Nobel Laureates in Chemistry 1901–1992*; American Chemical Society and Chemical Heritage Foundation: Washington, DC, 1993; pp 766–771.
- Taube, H. *J. Chem. Educ.* **1968**, *45*, 452–461.
- Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1970.
- Nobel e-Museum—Chemistry 1992 (with links to Prize Presentation and Biography pages). <http://www.nobel.se/chemistry/laureates/1992/index.html> (accessed July 2002).
- Marcus's Nobel Prize lecture, entitled "Electron Transfer Reactions in Chemistry: Theory and Experiment", is reprinted in *Angew. Chemie Int. Engl. Ed.* **1993**, *32*, 1111–1121.
- a.* Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966; *b.* **1957**, *26*, 867, 872; *c.* *Trans. 5. Y. Acad. Sci.* **1957**, *19*, 423; *d.* *Can. J. Chem.* **1959**, *37*, 155; *e.* *Discuss Faraday Soc.* **1960**, *29*, 21.
- Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Amer. Chem. Soc.* **1984**, *106*, 3047–3049.
- Marcus, R. A. *J. Chem. Educ.* **1968**, *45*, 356–358.

J. Van Houten is a member of the Department of Chemistry, Saint Michael's College, Colchester, VT 05439; jvanhouten@smcvt.edu.