Rudy Marcus
Does Dynamite Work

by Douglas L. Smith

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Caltech's newest
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On Wednesday, October 14, 1992, Rudolph A. Marcus, the Arthur Amos Noyes Professor of Chemistry, became the 21st Caltech alumnus or faculty member to win the Nobel Prize. Marcus is the second faculty member to receive the prize for chemistry—the first being Linus Pauling in 1954—and the most recent winner since William A. Fowler, Institute Professor of Physics, Emeritus, got his for physics in 1983.

The Nobel citation read in part, "Marcus is being rewarded for his theoretical work on electron transfer—work which has greatly stimulated experimental developments in chemistry. The processes Marcus has studied... underlie a number of exceptionally important chemical phenomena, and the practical consequences of his theory extend over all areas of chemistry. The Marcus theory describes, and makes predictions concerning, such widely different phenomena as the fixation of light energy by green plants, photochemical production of fuel, chemiluminescence ("cold light"), the conductivity of electrically conducting polymers, corrosion, the methodology of electrochemical synthesis and analysis, and more.... In the mathematical connection the Marcus theory makes between theoretical and experimental quantities, experimental chemists gained a valuable tool."

When Marcus did the work that would win him the prize 30 years later, he was an associate professor just starting his academic career at Brooklyn Polytechnic Institute. (He came to Caltech as the Noyes Professor in 1978.) The problem Marcus originally tackled was to explain why, when you have a bunch of ions in solution,

electrons sometimes leap from ion to ion with dazzling speed, but other times don't seem all that interested in venturing forth. Iron, for example, has two common ionic forms: an electrically neutral iron atom (one with all its electrons) can give up two electrons to form the "ferrous" ion (Fe^{+2}), or it can lose a third electron and become the "ferric" ion (Fe^{+3}). If you have a mixture of Fe^{+2} and Fe^{+3} ions dissolved in water, it should be no great feat for that third electron on an Fe^{+2} ion to trade places by jumping to a nearby Fe^{+3}—which then becomes an Fe^{+2} ion—while the spurned Fe^{+2} ion becomes an Fe^{+3}. (The electron loss by the Fe^{+2} ion is called "oxidation," and the electron gain by the Fe^{+3} ion is called "reduction.") After all, no bonds are being broken or formed, and no atoms are being rearranged, so there should be no impediment to swapping electrons. And electrons are notoriously flighty, will-o'-the-wisp particles. Yet experiments to measure this so-called self-exchange rate have found that, at the acidity and ionic concentrations normally used, it takes several minutes for half of the ions to trade electrons. But if each iron ion is surrounded by a sextet of cyanide ions in what's called a complex ion, the same self-exchange reaction happens about 1,000 times faster.

(Chemists measure these reaction rates by "labeling" one of the participants isotopically. Isotopes are atoms of the same element that differ in the number of neutrons in the nucleus. An isotope with an extra neutron or two is marginally heavier than, but chemically identical to, its lighter brother. For example, the chemist could start with all of the original Fe^{+2} ions being of

ordinary iron, and a trace quantity of the Fe^{+3} ions being of iron-57—an isotope containing one extra neutron. At a fixed time later, the chemist separates the two isotopes and determines how many of the iron-57 atoms are now in the $+2$ state.)

So what determines how fast a reaction goes? In 1952, Willard F. Libby, then at the University of Chicago, realized that the solvent molecules immediately surrounding the ion held the key. Most solvent molecules, although uncharged as a whole, have a very specific internal charge distribution that causes the molecule to behave as a dipole. In a water molecule, for example, the oxygen atom attracts electrons more strongly than the hydrogen atoms do, so the oxygen end of the molecule winds up with a slight negative charge, and the hydrogen end with a corresponding positive charge. Though less than the charge of one electron, these partial charges are noticeable to the outside world. As a consequence, an ion in solution isn't merely awash in a sea of free-floating solvent molecules. It creates its own following in the half-dozen or so solvent molecules immediately surrounding it. Drawn by the ion's charge, this shell of molecules attempts to dance attendance on the ion like a group of sycophantic courtiers around a king. Each solvent molecule puts its best foot forward, presenting the portion of its anatomy that is most attractive—i.e., most oppositely charged—toward the ion. The molecules take up very specific posts around the ion. The exact position of each molecule relative to the ion, as well as the number of molecules allowed into the charmed circle, is determined by the specific ion being surrounded. Solvent molecules farther away feel the ion's presence also, but, as in any autocracy, their slavishness decreases as their distance from the center of power increases.

All this was well known, but Libby suggested that a principle formulated decades earlier to help interpret spectroscopic observations could describe how the self-exchange reaction works. The Franck-Condon principle (named for James Franck, who first postulated it, and E. U. Condon, who reformulated it in quantum-mechanical terms) points out that electrons have almost no mass relative to the atom that they're a part of, and so whatever an electron does (which, in the original postulation, meant leaping from one energy level to another within an atom or molecule) has no immediate effect on the much heavier atomic nucleus. If the nucleus somehow has to adjust itself to its new situation—altering its momentum, for example, to compensate for a momentum change in the electron—it takes a moment to catch up. If an electron weighed an

ounce, an iron atom would weigh 6,356 pounds. Picture a mouse trying to drag a full-sized pickup truck with the extended cab, dual rear wheels, and the high-rise four-wheel-drive package, laden with five good ol' boys and all their gear for a week-long hunting trip, and you get the idea.
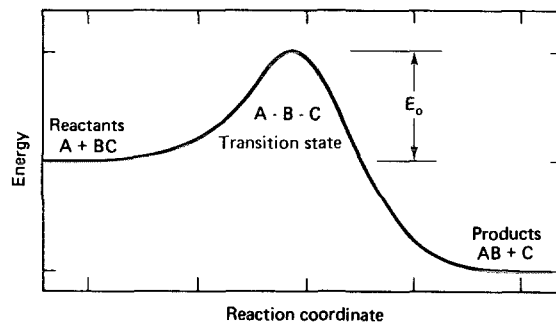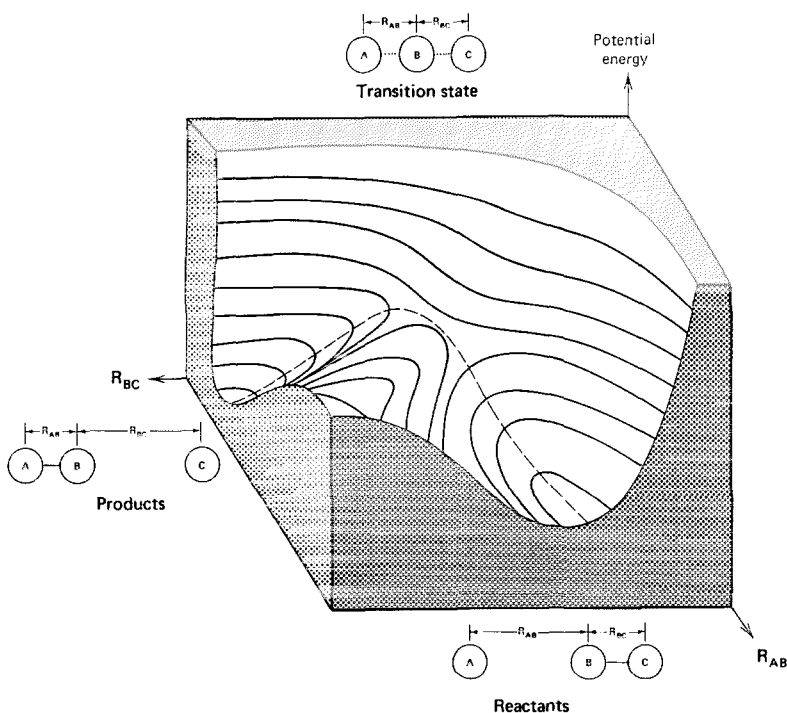
Libby extended this concept to surmise that the solvent molecules can't keep up with the electrons, either. (Although in the case of a water molecule, the poor mouse would only be towing a Ford Pinto.) Now an Fe^{+3} ion is only four-fifths the diameter of an Fe^{+2} ion. The more highly charged an ion, the smaller it is, as its remaining electrons are more strongly attracted to its nucleus. So at the very instant that a travel-minded electron takes wing from an Fe^{+2} ion, the remaining electrons feel the increased charge and plunge toward the nucleus, collapsing the ion to the Fe^{+3} size. Suddenly, the sycophantic solvent molecules find themselves too far away from the ion! Consternation ensues as they scramble to fit themselves into the new regime. Their movement, in turn, triggers a ripple of readjustments in the molecules behind *them*. And it is the amount of energy required to move everybody into their new positions that determines the rate at which the electron jumps. Similarly, at the electron's destination, a diminutive Fe^{+3} ion balloons without warning, throwing *its* courtiers into hasty retreat. This explains why transfers involving naked ions generally occur more slowly than when that same ion is at the center of a complex ion, as in the ferrocyanide case mentioned earlier. The distance between the iron and the cyanides changes by less than one percent, in contrast to the nearly ten-percent change in the distance between the naked iron ion and its six closest water molecules. The solvent molecules beyond the cyanides thus need make, at most, minute adjustments requiring very little energy, and the reaction proceeds quite swiftly.

(Incidentally, both Libby and Franck won the Nobel prize for other work. Franck shared the 1925 physics prize with Gustav Hertz, for discovering that atoms have characteristic ionization energies, confirming the quantum-mechanical postulate that atoms can only absorb energy in discrete amounts. And Libby took the chemistry prize in 1960 for discovering the carbon-14 dating technique now widely used to date archaeological specimens.)

Although Libby published his paper in 1952, Marcus didn't come across it until 1955. Recalls Marcus, "I saw the words *Franck-Condon principle*, and I thought, 'Gosh! I've worked on reaction rates, and I've never seen the Franck-Condon principle used! That's neat! That's *neat!*' And
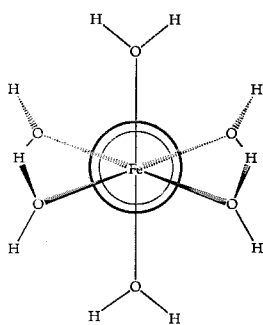
An iron ion surrounded by its six closest water molecules. The heavy outer circle represents the Fe^{+2} ion; the lighter inner circle is the Fe^{+3} ion. Solid arrows indicate bonds sticking out of the plane of the page; shaded arrows show bonds receding behind the plane of the page. (The water molecules can be considered to be tied to the iron ion by weak bonds between the oxygens and the iron.) Ionic radii and bond lengths are to scale.

Transition state

Potential energy

R_{BC}

Products

Reactants

R_{AB}

Reactants
A + BC

A - B - C
Transition state

E_o

Products
AB + C

Reaction coordinate

Above: The contour lines show a piece of the potential-energy surface for the reaction A+BC yields AB+C. The system's potential energy is plotted against the A-B distance and the B-C distance. The two valleys show the stable reactants and the stable products. (Note that the product valley, in the background, is deeper.) As A approaches BC, the system follows the dotted line, and the potential energy increases until the system reaches the transition state—the mountain pass—from which it can go downhill in either direction. Right: Slicing that graph along the dotted line and plotting potential energy against a "reaction coordinate" reflecting both the A-B and B-C distances gives this graph. E_o is the activation energy.

then I looked more closely at the article, and I felt instinctively that there was something wrong. And so I spent the next month trying to find the correct way of using the Franck-Condon principle." It turned out that Libby had run afoul of quantum mechanics. Libby had assumed, without explicitly saying so, that the electron had simply jumped from one ion to the other. This assumption was wrong. Marcus found that the only way that the electron could "simply jump" to its recipient and arrive there in a permitted quantum state was if a photon of light zapped the electron, punting it into an excited state from which it could legally slide into the other atom. But since electron transfers *do* happen readily in the dark, the law-abiding electrons obviously demanded a different mathematical treatment.

"Now how to treat that problem? In the textbooks of that time, most of the reactions that got detailed theoretical discussion were of the type A+BC yields AB+C. And you could almost *feel* that reaction. You could feel the bond B-C breaking as the bond A-B is forming. You could *sense* it." Theoreticians would draw a three-dimensional potential-energy contour map that plotted the total potential energy of the reacting chemicals versus a reaction coordinate. The potential energy reflected the energy needed to distort the electron clouds surrounding the atoms while they got close enough to each other to react. The reaction coordinate described in a single number the relative positions of A, B, and C. This potential-energy contour plot typically resembled two valleys separated by a mountain pass. The left-hand valley represented the poten-

tial energy of the reactants, A and BC, when they were too far apart to sense each other; the deeper the valley, the more stable the reactants. As A closed in on B while the B-C bond began to stretch, the system's potential energy increased—climbing the mountain toward the pass. The higher the pass, the greater the reaction's activation energy, and the slower it was likely to proceed. At the pass, or transition state, the A-B bond was more or less half-formed and the B-C bond about half-broken. From here, the reaction, like a boulder, could either slide down the slope into the right-hand valley to form the products, or tumble backward to the left and revert to the reactants. The deeper the right-hand valley, the more stable the products, and, typically, on comparing a series of similar reactions, the faster the reaction. "But with simple electron transfers, we were faced with quite a different situation. There are no bonds broken or formed, so we couldn't use that particular picture. Instead, we had to look at what coordinates *were* changing, going from reactants to products."

What was changing were the zillion coordinates that described the positions and orientations of all the solvent molecules. (The coordinates of the molecules closest to the ions undergo the largest changes, naturally, and beyond some distance one needn't worry about the others.) Marcus realized that, every now and then, random fluctuations in the orientations and positions of the solvent molecules would put them in arrangements equally appropriate to the products and to the reactants, at which point the electron transfer could occur without violating quantum mechanics or involving photons. The staggering number of calculations needed to figure out how all these molecules were behaving meant that simplifying assumptions were clearly needed. Marcus's first one was to replace all those partially polarized, dipolar solvent molecules with a dielectric continuum—a hypothetical, homogeneous medium that is everywhere polarized, with

These calculations required extensive knowledge of electrostatic theory. Fortunately, Marcus had acquired much of the requisite knowledge almost accidentally several years earlier.

the degree of polarization decreasing smoothly with increasing distance from the ion, an approximation commonly used when dealing with ion–solvent interactions. Into that polarization, he introduced local fluctuations to represent the nearby solvent molecules' fidgets around their equilibrium positions. The second assumption was that the medium's degree of polarization was directly proportional to the charge on the ions. The third was to cast the problem in terms of "free energy" instead of the potential energy that the theorists working on A, B, and C had used—a thermodynamic subtlety that collapses the zillion solvent coordinates into a single global reaction coordinate. "The 1956 paper used a phenomenological reaction coordinate. I replaced that with a detailed molecular reaction coordinate in the 1960 paper, where I had also replaced the dielectric continuum with a statistical-mechanical treatment for actual solvent molecules.

"The thing is, we couldn't use the standard electrostatics to describe these changes. In standard electrostatics, the dielectric polarization at any point in the medium is dictated by the given charge distribution on the reactants. There's a particular value at every point in the medium, and by solving electrostatic equations, you can find out what the equilibrium dielectric polarization at each point is. But we needed fluctuations. Cumulatively *large* fluctuations due to Brownian motion of the solvent molecules, not little piddly quantum-mechanical fluctuations. So we found a way of calculating the free energy associated with an arbitrary fluctuation, and then, having that fluctuation, we asked, 'What constraint results by imposing the Franck-Condon principle?' In other words, that electron transfer can occur only when the Franck-Condon principle will be satisfied." He was able to express that constraint—that the atoms remain fixed in position during the instant of electron transfer—as a function of three things: the polarization accompanying the charge distribution of, say, the reactants, the free energy of that charge distribution, and the free energy of that *reactants'* polarization but with the *products'* charge distribution.

These calculations required extensive knowledge of electrostatic theory. Fortunately, Marcus had acquired much of the requisite knowledge almost accidentally several years earlier, as a byproduct of a statistical mechanics course he taught. One Abe Kotliar, a grad student in that class, asked a question about polyelectrolytes—long, chainlike molecules with charges all down their backbones. In the course of trying to answer the question, Marcus immersed himself in electrostatics, going so far as to publish a couple

of papers himself. "I had looked through every textbook I could lay my hands on—I think there were 11 of them at the time—and read the relevant parts. The one that was actually the clearest to me for the purposes I needed later on [deriving the Marcus theory] was *The Electromagnetic Field*, by Max Mason and Warren Weaver. And that's a little ironic, because Mason was a professor at Caltech." (Mason was variously member of the board of trustees, chairman of the observatory council, and research associate in astronomy from 1936 to 1949.) The book covered not just equilibrium electrostatics, but dielectrics and polarization in homogeneous media, and expressed everything in very general equations that Marcus was able to apply to his random fluctuations. He found he could generate the fluctuations he needed in slow motion by creating a "reversible path." He'd slowly alter the charges on the reacting ions while letting the solvent atoms—and their electrons—move freely to readjust. Then, at some arbitrary moment, he'd hold the solvent atoms fixed while pushing the charges the rest of the way along to their distribution in the products. The electrons in the solvent molecules would continue to adjust to the shifting charges even though their atoms were frozen in position. This gave the overall system a known, albeit arbitrary, polarization at every point and thus a calculable free energy. Marcus would then do the same thing again, only working backward toward that same moment from the products. Using the calculus of variations and varying the moment when he "froze" the solvent allowed Marcus to find the path with the smallest free-energy change that satisfied the Franck-Condon principle, because the electron transfer happens at that moment when the solvent molecules are frozen.

"I worked very hard, and during the month, at various stages, I thought I had the answer, only to realize that no, I'd made some error or another. Or I got something that looked messy, and I had a feeling it should come out looking simple. I eventually got it in a form where it looked simple, and when I checked it by removing the Franck-Condon restraint, I got ordinary electrostatics coming out of it. And the expressions that I had made physical sense—the larger the ion, the smaller the electric field, and thus the smaller the solvent's reorganization, and so on. Everything just seemed to fit together, and it was at that point that I felt I really had it right. That feeling is hard for me to recapture now, but that was certainly the most exciting moment that I've had. It was really quite a high. I've had other highs—'Gee, I've finally got something,' after working and working and trying all sorts of
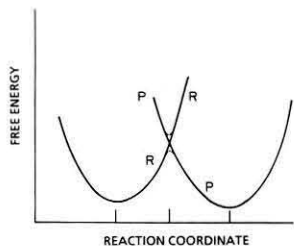
things, but that was the highest. It really was."

The equation that came out of that month's work is deceptively simple:

$$k=Ae^{-\Delta G^*/RT}$$

where k is the rate constant for the reaction (the actual reaction rate is the product of the rate constant and the reactant concentrations), A is a factor that depends on the specific type of reaction (for example, whether the reactants are freely swimming in solution, or are tethered to each other by virtue of both being parts of some large, rigid molecule), R is the universal gas constant (which crops up in the damnedest places), and T is the temperature. But ΔG^*, the reorganizational free energy of the reaction, conceals quite a bit, as shown in the sidebar at right.

What it all meant is that Marcus could define a single global reaction coordinate for the overall electron-transfer system, including the solvent molecules, in a very precise way—a feat that hasn't yet proven practical for the usual reactions where bonds are actually being formed or broken. This means that electron transfers could be subjected to far more detailed mathematical analysis than other reactions. Furthermore, the system's free energy, when plotted against the global reaction coordinate, becomes a parabola because multiplying out the right-hand side of the equation in the sidebar reveals that ΔG^* depends on ΔG^0 squared. Thus Marcus could draw one parabola for the reactants and the solvent, and another parabola—offset to the right—for products and solvent. The two parabolas intersect at the transition state, giving a picture that bears more than a passing resemblance to the two-valley picture of the A+BC goes to AB+C reaction. But if that potential-energy picture were drawn to include the solvent, it would have to be drawn in a zillion dimensions—one for each solvent coordinate. And the graph would have all sorts of little valleys, local minima where one solvent molecule's dipole or another was in its optimum orientation—an analytic geometer's nightmare. But the two-parabola, free-energy picture provided a simple, intuitive description of the system that allowed Marcus to make predictions that were neither simple nor intuitive. One result that fell out of his mathematics was that the reaction rate for *any* electron-transfer reaction, from rust to respiration, was predictable.

Marcus was originally interested in self-exchange reactions, but he derived his equations broadly enough to cover reactions between two different ions as well. Thus, for an electron jumping from vanadium to a ruthenium hexammine complex (a ruthenium ion surrounded by six ammonia molecules),
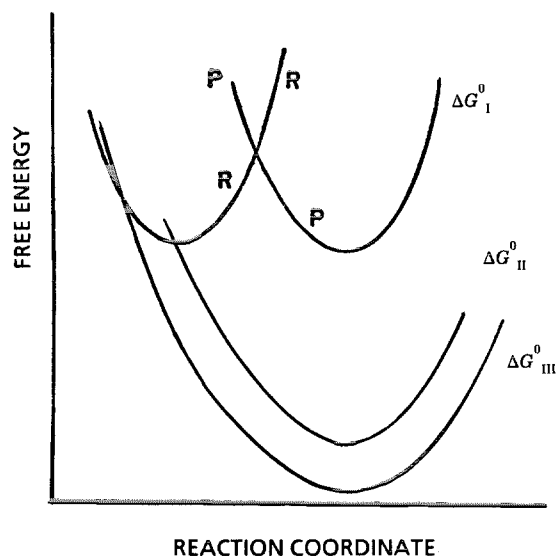
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FREE ENERGY

REACTION COORDINATE

Marcus's two-parabola picture. R is the reactant–solvent parabola; P is the product–solvent parabola.

What Lurks in ΔG^*

The reorganizational free energy, ΔG^*, describes what the solvent molecules are up to and the vibrations of the reactants themselves. It is the theory's crucial element:

$$\Delta G^* = \tfrac{\lambda}{4}\{1+{}^{(\Delta G^0)}/_{\lambda}\}^2$$

where ΔG^0 is the standard free energy of the reaction, a value readily measured experimentally, and λ, the reorganization parameter, is a can of worms in its own right: it represents what the energy barrier to the reaction would be if the products were as stable as the reactants. With the driving force removed, λ contains the factors intrinsic to the atoms involved. There's an "internal" parameter describing how the atoms of the reactants themselves and any molecules or complexes of which they are a part move, taking into account any changes in bond lengths that occur as a consequence of the reaction. An "external" parameter describes the motions of the solvent molecules, and it's here that those zillion coordinates get transmuted into something manageable. This parameter includes properties related to the solvent's dielectric polarization (which in turn depends on two intrinsic dielectric constants of the solvent that between them determine how sensitive the solvent is to electric fields in general), the radii of the reactants (which are assumed to be spherical), and the distance between them. The larger an ion, the farther the solvent molecules are from the bulk of its charge (which behaves as if it were concentrated at the ion's center), and the less strongly a solvent molecule is impelled to readjust; similarly, as the distance between the reactants decreases, they occupy a smaller portion of a solvent molecule's field of view—the molecule is less able to discern a difference in charge distribution and again feels less need to reorient itself.

REACTION COORDINATE

$$V^{+2} + Ru(NH_3)_6^{+3} \leftrightarrow V^{+3} + Ru(NH_3)_6^{+2}$$

proceeding at rate k_{VRu} and with an equilibrium constant K_{eq}, which tells what proportions of the reactants and products will remain when the reaction reaches equilibrium. Then

$$k_{VRu} \cong \sqrt{k_V k_{Ru} K_{eq} f_{VRu}}$$

where k_V and k_{Ru} are the self-exchange rate constants for vanadium and ruthenium hexammine, respectively, and f_{VRu} is a function of the particu-lar reaction whose value is usually close to one. And although reaction rates can be very difficult to measure, especially for fast reactions, equilibri-um constants had been measured in their thou-sands even then. Furthermore, self-exchange reactions had been extensively studied, and many of their rate constants had been published as well. This, therefore, was a concrete prediction that others could verify from existing data. Marcus published this prediction, with others, in another paper in 1960. "But if you just have an equation in a paper, it doesn't mean that people will pick it up. If you apply it to other people's real-life data, and show that it works, that acts as a primer. And I published tests of that and several other predictions from the 1960 paper in the 1963 paper. And ever since, this relation has been very widely tested." This equation is now known as the Marcus cross-relation, and has become a mainstay of chemistry.

Another prediction in the 1960 paper took 25 years to verify, and its confirmation apparently tipped the balance for the Royal Swedish Acade-my of Sciences. The prediction said that as the free-energy difference (ΔG^0) between the prod-

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ucts and reactants increases in magnitude—ΔG^0 actually becomes more negative as the parabola representing the products and the solvent sinks lower and lower relative to the other parabola— the reaction rate should get faster and faster. This was not exactly breaking news—it's exactly what you'd expect. But as the parabola continued to sink deeper, Marcus predicted, the reaction rate would max out and then begin to decline! In other words, once a certain point was passed, the more energetically favorable a reaction was, the slower it would go. The figure at left shows why. As the right-hand (product-solvent) parabola moves downward, the transition state slides down along the curve of the left-hand (reactant-solvent) parabola until the intersection lies at the left-hand parabola's lowest point. At this point, the activation energy—the height of the transition state above the most stable state of the reac-tants—is zero, and the reaction proceeds as fast as it possibly can. Then as the product-solvent parabola continues to descend, the intersection point begins to climb up the left-hand slope of the reactant-solvent parabola, creating a growing energy barrier once again and slowing the reac-tion. This prediction, called the inverted effect, flew in the face of common sense. For the next 25 years, chemists measured faster and faster reac-tions in a fruitless attempt to find a reaction fast enough to be slow. J. R. Miller, G. L. Closs, and L. T. Calcaterra of Argonne National Laboratory finally succeeded, using specially designed mole-cules that had an electron donor on one end and an electron acceptor on the other, held a fixed dis-tance apart by the rest of the molecule. When the molecule was zapped with a burst of elec-trons, the donor would catch an electron that, a few billionths of a second later, jumped to the acceptor as a spectrometer recorded its passage.

We have very good reason to be glad that this highly implausible process actually works, be-cause it probably underlies photosynthesis. In photosynthesis, a photon of light hits a pair of chlorophyll molecules, knocking one of their electrons into an excited state. Within three bil-lionths of a second, the electron departs for a nearby pheophytin molecule. About 200 bil-lionths of a second later the pheophytin passes the electron on to a quinone, and the metabolic machinery of the cell is off and running. The process is extremely efficient, ultimately convert-ing darn near 100 percent of the absorbed pho-tons into electric charge. But why doesn't the excited chlorophyll electron simply revert to its ground state? Why don't the electrons leak back from the pheophytin to the chlorophyll? Chloro-phyll's ground state is far less energetic than the

excited one, and therefore much more favorable. And the electron hangs around on the pheophytin for far longer than it sat on the excited chlorophyll, giving it ample opportunity to change its mind. It has been suggested that the reversion to ground state and the transfer back to chlorophyll both lie in the inverted region, making the less energetically favorable leaps to the pheophytin and eventually to the quinone the reactions that actually occur. It's not unlike a skier coming to the lip of a sheer cliff and, thinking the better of hotdogging over the lip and down it, opting to go down the less steep slope on the other side.

A 1965 paper invoked the inverted effect to explain certain forms of chemiluminescence—the cold light of fireflies and the glow sticks in your roadside emergency kit. Chemists had found that when an electrode in a solution was rapidly toggled between a large positive charge and a large negative charge, the process could create a pair of oppositely charged ions in very close proximity to each other, and the ion pair would emit light. One explanation given at the time was that a local hot spot—hot enough to glow—was created by some unknown mechanism between the ion pair. Marcus instead proposed that the electron transfer to neutralize the ion pair was *so* energetically favorable that it lay in the inverted zone. He speculated that upon electron transfer, one of the ions might go to an excited state instead of the ground state, thus avoiding the inverted zone. The excited state could then emit a photon of light during the return to a lower-energy state.

Reflecting on the Nobel experience, Marcus mused, "There's an interesting point here. In 1952 I wrote four papers related to RRKM theory, a unimolecular theory, and then I looked around and I didn't know what to work on. I didn't want to continue in that, because there were very few experimental data at the time on unimolecular reactions. I thought I would just be spinning wheels, because I wouldn't have anything to tie it to. I don't know if nowadays a young assistant professor can afford the luxury of not doing anything for a whole year! (I did direct some experimental work, however.) I remember only too well a friend of mine, a chap by the name of Frank Collins who was doing some very nice work on liquid-state theory, and every day he'd come downstairs with a new idea he wanted to bounce off me. It went on day after day after day for quite some time—and I didn't have any ideas!" Marcus laughed at the memory. "I wonder if today, with all the pressures of publication and tenure and so on, whether somebody would have the time to let the mind lie fallow like that. I could have continued the unimolecular work

and I could have generated more papers, but the fact that I didn't meant that the mind was free—open—for something else. I think that there's an advantage, if one can, in not getting too hooked into one particular thing so much that one stays with it beyond the point of diminishing returns.

"Another thing that helped me a great deal was going out to Brookhaven National Laboratory on Long Island, where there was a fair amount of work going on in isotopic-exchange reactions. I used to go out there about once a month, consulting. I certainly got as much out of it as they did, maybe more," he said with a chuckle. "I worked with Dick Dodson (BS '36 in chemistry), who was a pioneer there, and Norman Sutin. It's *so* important, I think, if one's doing the type of theory I was doing, to interact with the experimentalists. Otherwise you can do something which is far removed from the actual situation. And in turn, when I would discuss the theory with them, it certainly had an effect on the research. Especially on Norman's. He tested various aspects of the theory. The 1963 paper, in which I tested the predictions of the 1960 paper, was stimulated by discussions with him. His knowledge of the results from the reactions involved was truly impressive. Norman is an outstanding individual, and just a splendid scientist. He did things so that once they were done, they were *done*. You could rely on them. I benefited *enormously* from that interaction. Nobody at Brooklyn Poly was doing electron transfer."

"One of the great things here at Caltech is the *tremendous* amount of interaction between faculty, and between faculty and students. I interact a fair amount with Harry Gray. We're making calculations for his experiments [on proteins involved in cellular respiration]. Nate Lewis's work on semiconductors, and his and John Baldeschwieler's work on STM, is stimulating us to try to develop things along those lines. And then there's Fred Anson on his electrodes, Jackie Barton's electron transfer between fixed sites in polypeptides.... About half our work is in electron transfer, and the other half is in unimolecular reactions and intramolecular dynamics, where we have wonderful interactions with Ahmed Zewail next door, with Jack Beauchamp, with Aron Kuppermann in the basic understanding of quantum mechanics; I talk occasionally with Dennis Dougherty and Bob Grubbs about miscellaneous electron transfers, and this list could go on—it's just a wonderful place to be. From every point of view, but especially from that point of view. It makes things vital. And none of it is forced interaction—you want to know something, you find out." ▢

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