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A Short Account of RRKM Theory of Unimolecular Reactions and of Marcus Theory of Electron Transfer in a Historical Perspective

Francesco Di Giacomo*

Dipartimento di Ingegneria Chimica Materiali Ambiente, Sapienza Università di Roma, Via del Castro Laurenziano 7, I-00161 Roma, Italy

ABSTRACT: The RRKM Theory of Unimolecular Reactions and Marcus Theory of Electron Transfer are here briefly discussed in a historical perspective. In the final section, after a general discussion on the educational usefulness of teaching chemistry in a historical framework, hints are given on how some characteristics of Marcus' work could be introduced in courses of physical chemistry or chemical kinetics to show how experiments drive the formulation of theories and, on the other hand, how the predictions of theories may suggest experiments and even predate their results.

KEYWORDS: *Upper-Division Undergraduate, Graduate Education/Research, Physical Chemistry, History/Philosophy, Electrochemistry, Kinetics, Oxidation/Reduction, Theoretical Chemistry*

■ INTRODUCTION

Among the many different branches of Chemistry there of course exists that of chemical kinetics. As chemists well know, it is the branch that deals with the rates of chemical reactions, that is, of how quickly or how slowly a reacting system advances from reactants to products, this being one of the possible ways of looking at chemical reactivity and of studying it. The field began as an experimental science in 1850 when Ludwig Wilhelmy performed his famous experiments on the inversion of sucrose in acidic aqueous solutions.[1] At that time, physics and chemistry were two almost completely separate sciences, chemistry still being very much an empirical discipline. Suffice it to recall that only after the famous Cannizzaro's contribution to the Karlsruhe Chemical Conference of 1860 "was the distinction clarified between molecules and atoms"[2] and that Wilhelmy's work itself "received very little credit from his contemporaries...because of its strong physical−chemical orientation".[3] However, fifty-one years later things had changed, and the first Nobel Prize in chemistry was awarded to Jacobus Henricus van 't Hoff, who happened to be also the first physical chemist and, more importantly in general, the first theoretician ever to win it. In 1884, van 't Hoff had published his research on chemical kinetics, titled *Études de Dynamique chimique* ("*Studies in Chemical Dynamics*"), in which he described a new method for determining the order of a reaction, a fundamental concept in chemical kinetics. The Prize was awarded "...for his pioneering work in chemical dynamics and osmotic pressure in solution. As a result of his investigations in the fields of atomic and molecular theory van 't Hoff has made the most important discoveries in theoretical chemistry since Dalton's time."

Professor Rudolph A. Marcus, the recipient of the 1992 Nobel Prize in chemistry, has been following in the steps of van 't Hoff and other scholars in the fields of theoretical chemistry and chemical dynamics, like Nobel Laureate Cyril Hinshelwood, of whom Carl Winkler, Marcus' research advisor, was research associate, and Oscar Knefler Rice, of whom Marcus was a research associate.

Two important chemical theories happen to bear his name: the RRKM (Rice, Ramsperger, Kassel, Marcus) theory of unimolecular reactions and the Marcus theory of electron transfer. In the following, both of them will be looked at briefly. A final section of the paper is devoted to a discussion of the relation of the history of chemistry with the teaching and learning of it, and hints are also given on how some characteristics of Marcus' work may be used in courses of physical chemistry or chemical kinetics.

■ RRKM AND MARCUS' ELECTRON-TRANSFER THEORY: A VIGNETTE

An up-to-date bibliography on the theory of unimolecular reactions is in refs 4−13. Shorter introductions may be found in books on chemical kinetics or physical chemistry.

The two most common kinds of reactions are the bimolecular reactions, in which two molecules react with each other to give some product molecules, and the unimolecular reactions, in which a single molecule, *A*, decomposes for instance into the product molecules *B* and *C*, according to the global reaction $A \rightarrow B + C$, or rearranges its atoms and bonds and isomerizes into another one, as in the case, for instance, of the cyclopropane isomerization *cyclo*-$C_3H_6 \rightarrow CH_3CH{=}CH_2$. More in general: "Unimolecular reactions are those involving a change in only one molecular or ionic structure... According to the existing notions, unimolecular processes occur at a non-zero rate only if the reacting molecules possess an internal energy exceeding a certain threshold value known as the activation energy. Such molecules are called "active". Active molecules are produced in the course of a chemical reaction either by inelastic collisions with the heat bath molecules (thermal activation) or by photoactivation, by light irradiation, electron impact, etc. (non-thermal activation)."[14] Active molecules may also be produced by reactive collisions (see ref 15).

In the case of thermal activation, then, the molecular excitation is due to energy exchange with the activating

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particles. The reacting molecule obtains sufficient energy to react by collision with another molecule with a high relative kinetic energy.

The first successful explanation of unimolecular reactions was provided by Frederick Lindemann in 1922[16] and then elaborated by Cyril Hinshelwood. In the Lindemann–Hinshelwood mechanism, it is supposed that a reactant molecule A becomes energetically excited by collision with another molecule M:

$$\begin{aligned} &A + M \xrightarrow{k_a} A^* + M && \text{activation} \\ &A^* + M \xrightarrow{k_d} A + M && \text{deactivation} \\ &A^* \xrightarrow{k_E} B && \text{reaction of energized molecule} \end{aligned} \qquad (1)$$

Here, A is the reactant, A* is an "energized" reactant molecule, that is, one with enough energy to react, M is either another molecule of reactant or a molecule of some added inert gas, and B denotes products in general (several different species may be formed). The reaction rate is given by

$$\frac{d[B]}{dt} = k_E[A^*]$$

where [A*] and [B] are concentrations of A* and of B, and k_E is the rate constant.

"An improved model was proposed in 1926 by O. K. Rice and H. C. Ramsperger and almost simultaneously by L. S. Kassel, which is now known as the Rice–Ramsperger–Kassel model (RRK model)"[17] in which the molecule "is a system of s identical harmonic oscillators, each of frequency ν. These oscillators are said to be "loosely coupled": they interact enough so that energy can flow from one oscillator to another, but not strongly enough to perturb each other's energy levels. Thus, the reactant gas is in a double statistical assembly: at the intermolecular level, molecules interchange energy at every collision; whereas at the intramolecular level, energy is exchanged randomly among the oscillators, between the times of molecular collisions."[18]

"The essential feature of the model is that, although a molecule might have enough energy to react, that energy is distributed over all the modes of motion of the molecule, and reaction will occur only when enough of that energy has migrated into a particular location (such as a bond) in the molecule".[17] This situation is a reminder of a compound nucleus in nuclear physics in which the energy "may "by accident" again be concentrated on one particle so that this particle can escape".[19]

"Another approach has been used by Rice and Marcus who have combined essential features of activated complex theory and RRK theory to produce what is commonly called the RRKM formulation of unimolecular rate constants..." The reaction scheme of eq 1 is expanded slightly to include an additional step:

$$A + M \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_E} A^\ddagger$$

$$A^\ddagger \xrightarrow{k_r} B$$

In these equations, A* and A‡ are in a particular energy range. It is important to distinguish between A*, the energized molecule with energy greater than the critical energy for reaction, and the activated complex A‡, which also has $E \geq E_c$ but, "in addition, has some specific configuration...".[18] "The RRKM procedure uses statistical mechanics to calculate a probability density, namely the chance per unit of reaction coordinate for an energized molecule to have the A‡ configuration. One then multiplies this probability density of A‡ along the reaction coordinate, crossing the boundary in phase space between A and B, by the velocity along that coordinate, and obtains a flux. Finally, one integrates over all velocities and sums over all vibrational–rotational quantum states of the transition state to obtain the reaction rate at a given energy and total angular momentum of the energized molecule A."[20] "In this improved form of the RRK theory, account is taken of the way in which the various normal-mode vibrations and rotations contribute to reaction, and allowance is made for the zero-point energies."[21] It should then be noted, a brief history of the field written by Professor Marcus himself:

"The field of unimolecular reactions and bimolecular recombination processes[4−13] has undergone a number of changes during the past 90 or so years. In the middle 1920s, the theories of Hinshelwood, Rice/Ramsperger, and Kassel were developed at a time when little was known about potential-energy surfaces. So the theory was phrased in terms of the sharing of energy in a dissociating or isomerizing molecule among "squared terms", meaning the kinetic energies and potential energies of harmonic molecular vibrations. In fact, in those early days, before the development of gas-phase free-radical mechanisms, the latter were assumed to be non-free-radical dissociations. They were realized, in the 1930s, to be largely dissociations, followed by subsequent free-radical reactions. (Hinshelwood received the Nobel Prize for his free-radical work.) On the theoretical side, transition-state theory emerged in the mid 1930s, and in 1951–1952, I was involved in blending it and RRK together,[12,13] resulting in what later became known as RRKM theory."[22,23]

Examples of unimolecular reactions using different methods of preparation of the active energized species are the following: Rabinovitch et al. made unimolecular falloff measurements of the alkyl isocyanide isomerization:

$$CHNC + Ar \rightarrow CH_3NC^* + Ar \rightarrow CH_3CN$$

"One of the most significant achievements of RRKM theory is its ability to match measurements of k_{uni} with pressure. The unimolecular falloff measurements made by Rabinovitch and co-workers of alkyl isocyanide isomerization have provided some of the most thorough comparisons with the theory." (ref 15).

The chemical activation process

$$F + C_2H_4 \rightarrow C_2H_4F^* \rightarrow H + C_2H_3F$$

was studied by Y. T. Lee et al.; see ref 15 and references therein.

Klippenstein, Khundkar, Zewail, and Marcus[24] investigated the photoactivated reaction

$$NCNO \xrightarrow{h\nu} NCNO^* \rightarrow NCNO\ (\text{vib. hot}) \rightarrow NC + NO$$

The treatment of unimolecular reactions offers a good example of a theory presented in its historical development: one starts from the Lindemann theory and then, passing through the Lindemann–Hinshelwood and RRK intermediate steps, one finally reaches the RRKM theory.

For the Marcus theory of electron transfer (ET) reactions, a book is being currently prepared by the author with Professor Marcus' input. More or less extended introductions to the theory can be found in books of chemical kinetics and physical chemistry and, moreover, in the many review papers written by Marcus himself, as, for instance, in refs 25−27. About a dozen contributions about Marcus' work have been published on this Journal, the last one being a very interesting one by Silverstein.[28]

The electron-transfer reactions are the simplest oxidation−reduction reactions, and in general the most simple reactions of chemistry. They are those elementary oxidation−reduction reactions, in which no bonds are broken or formed, when the electron is transferred between reagents:

$$\mathrm{A\,(red) + B\,(ox) \rightarrow A\,(ox) + B\,(red)} \tag{2}$$

Two examples, in which observed and calculated rate constants in $M^{-1}\ s^{-1}$ are reported below the reactions, are

$$\mathrm{Fe(CN)_6{}^{4-} + IrCl_6{}^{2-} \rightarrow Fe(CN)_6{}^{3-} + IrCl_6{}^{3-}},$$
$$k_{12,\mathrm{obs}} = 3.8{\cdot}10^5,\ k_{1,2\mathrm{calcd}} = 1{\cdot}10^6$$

$$\mathrm{Ru(NH_3)_6{}^{2+} + Ru(NH_3)_5py^{3+} \rightarrow Ru(NH_3)_6{}^{3+} + Ru(NH_3)_5py^{2+}},$$
$$k_{12,\mathrm{obs}} = 1.4{\cdot}10^6,\ k_{1,2\mathrm{calcd}} = 4{\cdot}10^6$$

"Good agreement is generally found when the couples involved are substitutionally inert."[29] A thorough discussion of theoretical versus experimental results with tables and examples of ET in electrochemical and biological systems can be found in ref 29.

The simplest ET reactions are the "self-exchange" reactions such as

$$\mathrm{Fe(H_2O)_6{}^{2+} + Fe^*(H_2O)_6{}^{3+} \rightarrow Fe(H_2O)_6{}^{3+} + Fe^*(H_2O)_6{}^{2+}},$$
$$k_{\mathrm{obs}} = 4.2,\ k_{\mathrm{calcd}} = 3$$

in which from a thermodynamic point of view, nothing happens because the products are the same as the reactants, but the orientations of the water solvent dipoles around the ions are clearly dependent on the ionic charges. In this reaction, two isotopes of iron are used—one of them, Fe*, radioactive—to follow the ET between the ions because without the use of isotopes, the reagents and products systems look the same. It was "in this small corner of inorganic chemistry" (Marcus) of isotopic exchange reactions, where all the stories of ET in polar solvents began. In reactions such as these, in which reactants and products are the same, the standard free-energy difference between final and initial states is zero, and the thermodynamic control of the reaction is missing. They are very interesting because in such reactions, the "intrinsic factors" that control their chemical kinetics come to the fore: the structure of the transition state (TS) and the nature of the reaction coordinate.

In the early 1950s, it was possible to determine the rate of a number of electron-transfer reactions between inorganic ions. Some of the reactions were very slow, something surprising in view of the fact that after all, only one electron changes its location as result of the reaction. At that time, it was believed that such an insignificant change should not give rise to a large activation barrier. From 1956−1965, Marcus published in a series of papers his theory of electron transfer reactions and explained, among many other features of the ET reactions, the reasons for the greatly varying reactions rates.

Marcus made two assumptions about the reacting molecules. First, that there was a very weak electronic interaction between them. Second, the surrounding solvent molecules would play a role indispensable for the reaction to happen, they would be an essential part of the reactants system and of the products system. In the case of a thermal reaction in the dark, that is, in the absence of absorption of light, the electron would transfer only if the reactants system immediately before the transfer and the products system immediately after the transfer would have the same free energy. This could only happen by an appropriate fluctuation of the solvent molecules prior to the ET (vide infra in the words of Marcus himself). In this case, the ancient (but by no means universal) Latin adage of the alchemists "corpora non agunt nisi soluta" ("compounds do not react unless dissolved") had a new, unforeseen and unthought-of application, because here it is a particular statistical dynamics of the solvent molecules that is necessary condition for the reaction to happen.

Marcus found out how to calculate the activation energy of the reaction and so calculate the reaction rate. He later extended the theory to include the energy changes associated with changes in bond lengths between reactants and products.

"Marcus considered the case that the motions required to reach the transition state can be treated as classical thermal motion on harmonic (parabolic) free energy surfaces. This is an appropriate approximation when the nuclei involved are sufficiently heavy and the temperature is sufficiently high that the quantum mechanical delocalization of the nuclei can be safely ignored, and they can be treated as classical particles... In the classical harmonic limit, the activation free energy ΔG^* depends on both the reorganization energy, λ, and the "driving force" ΔG^0 of the reaction, in a fairly simple way:[30]

$$\Delta G^* = (\lambda/4)(1 + \Delta G^{\circ}/\lambda)^2 \tag{3}$$

The reaction rate constant is then

$$k_{\mathrm{rate}} = Ae^{-\Delta G^*/k_{\mathrm{B}}T} \tag{4}$$

"where ΔG^0 is the standard free energy of reaction 2, λ is a "reorganization energy" that was expressed in terms of properties of the solute (e.g., size, vibrational bond lengths changes), λ_i, and of dielectric properties of the solvent, λ_o. An equation analogous to eq 4 was derived for electron transfer at electrodes, with ΔG^0 replaced by the activation overpotential $e\eta_{\mathrm{act}}$ of the electrode reaction 5:

$$\mathrm{A\,(red) + M \rightarrow A\,(ox) + M\,(}e\mathrm{)} \tag{5}$$

Some "work terms" to bring the reactants to a suitable electron transfer distance and to separate the products are omitted for brevity in eq 3. The value of A in eq 4 depends on the strength of the electronic coupling between the two reactants.

He later showed that eq 3 is actually more general than the dielectric continuum model on which it was originally based. Using a statistical mechanical description, a special (global) reaction coordinate ΔU was introduced, and a linear response approximation for the solvent medium was then used (e.g., the dielectric polarization is proportional to the electric field). In this case, the free energy of a suitable fluctuation becomes the quadratic function of ΔU, which leads again to eq 3. "This ΔU is, for any configuration q of the nuclei of the entire system, the difference of the potential energies U^{p} (q) and U^{r} (q) for the entire system, for the products and reactants, respectively."[31]

The reorganization energy λ is, in general, the sum of an inner vibrational component λ_i and an outer solvent component λ_o

$$\lambda = \lambda_i + \lambda_o \qquad (6)$$

The expressions for λ_i and λ_o are, respectively,

$$\lambda_i = \frac{1}{2}\sum_j k_j(\Delta q_j)^2 \qquad (7)$$

and, in a dielectric continuum model,

$$\lambda_o = (ne)^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad (8)$$

where, in the vibrational contribution λ_i, when stretching motions of the bonds are principally involved, Δq_j is the difference of equilibrium lengths in the corresponding jth normal coordinate on both sides of reaction 1, k_j is a bond force constant, and the sum is over all normal coordinates. Equation 8 gives λ_o "in the case that the fluctuations in solvent polarization are treated by the dielectric continuum theory".[26] There, n is the number of electrons being exchanged, a_1 and a_2 are the reactants radii including coordination shells, R is their distance, D_{op} and D_s are the optical and the static dielectric constants, respectively. Eq 8, for the homogeneous case, changes into

$$\lambda_{o,e} = \frac{1}{2}(ne)^2\left(\frac{1}{a} - \frac{1}{R_e}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$$

for the electrode reactions case.

From eq 3, we see that if $\Delta G^0 = 0$, then $\Delta G^* = \lambda/4$; if $\Delta G^0 = -\lambda$, then $\Delta G^* = 0$; and if $\Delta G^0 = \lambda$, then $\Delta G^* = \lambda$.

One of the major initial predictions of the theory stemmed from a very useful additivity property of λ: the λ for a cross reaction like reaction 2, that is, an electron transfer between two different redox systems, A and B, is approximately the mean of that for the self-exchange reaction of A and that of B, $\lambda_{12} = (1/2)(\lambda_{11} + \lambda_{22})$. A consequence of this result, in conjunction with eqs 3 and 4, is the "cross-relation" between the rate constant k_{12} and the two self-exchange rate constants, k_{11} and k_{22}:

$$k_{12} \cong (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (9)$$

where K_{12} is the equilibrium constant of reaction 2 (recall the fundamental relation $\ln K = -\Delta G^0/RT$ between the equilibrium constant and the standard free energy of reaction), and f_{12} in the right-hand side of eq 9 is a known function of the three other quantities and is usually close to unity.

A second prediction from the equations concerns the effect of systematically varying ΔG^0 for a series in which one of the reactants is held constant, but the other is varied so that λ is approximately constant, frequently achieved by varying a substituent in some aromatic ligand. The prediction was that the dependence of $\ln k_{rate}$ on ΔG^0 is given by eqs 3 and 4. For example, the slope of a $\ln k_{rate}$ versus $\ln K$ plot, where K is the equilibrium constant, was predicted to be 0.5 when $|\Delta G^0|/\lambda$ is small. Curvature was predicted when $|\Delta G^0|/\lambda$ becomes larger. A dramatic prediction that was subsequently widely explored was the "inverted effect": when ΔG^0 is made increasingly negative, the k_{rate} at first increases, according to eqs 3 and 4, but then decreases when $-\Delta G^0$ is so large that $|\Delta G^0| > \lambda$."[31,32]

The theory predicts many other effects that have all been tested experimentally. Miller, Calcaterra, and Closs in 1984[33] demonstrated the existence of the "inverted effect" about 25 years after the prediction was first made in the literature. They considered solutions of a series of molecules, each made up by an electron donor D and an acceptor A separated by a rigid molecular framework, the same for the eight synthesized molecules. Intramolecular ET reactions between the fixed D and different A's have different $-\Delta G^0$ values. They found a falloff of k (s^{-1}) ET rates at higher $-\Delta G^0$ (eV) values, which shows the existence of an "inverted region" in their famous Figure 1.[34]

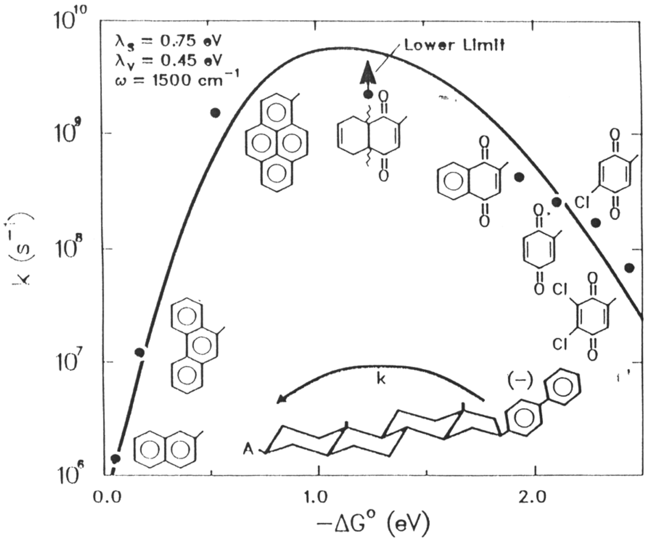

Figure 1. Structures of 4-biphenylyl donor and of eight acceptors. Reprinted with permission from ref 34. Copyright 1986, American Chemical Society.

In recent electrochemical measurements,[35] symmetrical and antisymmetrical functions of the force constants have been used that had been introduced by Marcus in Appendix IV of ref 32, back in 1965.

The Marcus Nobel lecture gives further information about the breadth of applications of the theory. It is noted that "One of the applications of the inverted effect, for example, is in solar energy conversion. The efficiency of the photosyntetic reaction system has been attributed, at least in part, to that effect."[30]

■ SOME FINAL REMARKS ON THE HISTORY, TEACHING, AND LEARNING OF CHEMISTRY AND MARCUS' WORK

Science, and chemistry in particular, is a fascinating field of study that, in the opinion of practitioners, should simply and evidently arouse the interest of everybody, in particular of every student. Sad everyday experience, however, tells teachers a completely different story: science is naturally loved and immediately appreciated only by a minority of people. Most people find it dry, dull, abstract, and boring if not outright repulsive.

Teaching chemistry in a historical perspective notoriously adds a human side to the narrative and so helps in presenting it as an interesting and lively subject. Another useful strategy in arousing the students' interest is of course that of showing its usefulness and practical importance in real life. This is the reason why, for instance, the classical general chemistry book of Linus Pauling,[36] a "blend of real-life descriptive chemistry",[37] interspersed with historical references, was so much liked by Dudley Herschbach when he was a student. Again, while chemistry can be intimidating, it also constitutes an immensely impressive intellectual construction that can be a source of fascination. A wonderful description of the awe and intimidation that the cathedrals of science can inspire in many people's minds is the one found in the introduction to the classical treatise on thermodynamics by Gilbert Newton Lewis and Merle Randall, revised by Kenneth S. Pitzer and Leo Brewer,[38] "the book that still heads my list of favorites" in the words of John B. Fenn.[39] There, Lewis and Randall remind us of the importance of not only seeing the finished cathedral, but also imagining entering it while it was being built "by the efforts of a few architects and many workers", that is, the importance of going through the history of the construction because just looking at the completed work of art may be daunting to the neophyte and leave him or her with the false impression of its having been built "by some superhuman agency". The history of the construction of these great structures allows one instead to appreciate them as "the result of giving to ordinary human effort a direction and a purpose". Another false impression the great structure may give is the one mentioned by Patrick Deville in his book on the life and work of Alexandre Yersin, discoverer in 1894 of the bacillus *Yersina pestis*: "The history of sciences is often retraced as an avenue that brings straight from ignorance to truth, but that's false. It is really a tangle of blind alleys where the mind goes astray...".[40]

Of course, the historical approach is not only useful with young students, it may also be appreciated by learned people; therefore, Martin Karplus, in his recent 2013 chemistry Nobel lecture on the "Development of Multiscale Models for Complex Chemical Systems", begins the lecture by recalling his studies on the hydrogen exchange reaction $H + H_2 \rightarrow H_2 + H$ and even quoting Ralph Waldo Emerson, Titus Lucretius Carus, and Canaletto. The historical approach can even go so far as to tell amusing personal anecdotes, as Peter W. Higgs did in the opening of his own 2013 physics Nobel lecture.

We end here with three last remarks.

First, teaching chemistry with interesting historical references and in a historical perspective is different from teaching the history of chemistry as such, and therefore, the order in which scientific facts, theories, and information are taught must not always be the historical one. We see then that Pauling, in the preface of the 1969 edition of his book, says that he will introduce statistical mechanics before thermodynamics "because I have found that an understanding of statistical mechanics...is more easily obtained by the beginning student than an understanding of chemical thermodynamics."[36] For another example, the first of many of Marcus' reviews of the electron-transfer theory that a student should read is, in my opinion, the one written in 1975[26] because it is the simplest and easiest to understand, rather than, for instance, the great review of 1964.[25]

Second, in teaching physical chemistry or chemical kinetics courses, Marcus' work may be used as a good example of the fact that experiments often, as in the electron transfer case, drive the formulation of a new theory. Therefore, new experiments drove Willard Libby's ideas, and the latter in turn drove Marcus' ideas. More generally, the development of the electron-transfer theory demonstrates the importance in science of the close interaction of theory and experiment. It is also a beautiful example of how the predictions of good theories can precede experimental results, even by many years.

Third, with this paper, I hope to have been able to demonstrate that a theory may be complex, but understanding the essence of it may be simple.

AUTHOR INFORMATION

Corresponding Author

*E-mail: francesco.digiacomo@uniroma1.it.

Present Address

Via Paolo Barison 110, 00142 Roma, Italy.

Notes

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