Theory, Experiment, and Reaction Rates. A Personal View†

R. A. Marcus

Noyes Laboratory of Chemical Physics,‡ California Institute of Technology, Pasadena, California 91125
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Occasionally as scientists we have the good fortune to stumble onto problems whose significance and solution turn out to be more far-reaching than may have been anticipated at the time. Such proved to be the case in my own experience with unimolecular and electron-transfer reactions and, to a lesser degree, with a few other problems as well. I am particularly indebted to the organizers of this issue for their recognition of 35 years of "RRKM" theory and 30 years of the electron-transfer theory. Also, I am especially indebted to my many colleagues who have contributed to the field and to this issue.

I have been asked to write about the period when I first worked on these problems, the state of these fields at the time, their subsequent, and possibly their future directions. With the benefit of hindsight and without any well-tested soothsayer's ball, I shall try to do so in this article.

The 1920s, it may be recalled, was indeed a glorious period for unimolecular reactions. The need to explain how unimolecular reactions acquired their energy, the resulting Lindemann's hypothesis, Hinshelwood's treatment, Rice–Ramsperger–Kassel (RRK) theory, and the many ensuing experiments on the rates of unimolecular decomposition of organic molecules, all contributed to this era. But then its own success led to its own demise: The detailed studies led to the recognition that the "simple" unimolecular reactions investigated, and with which the RRK theory was being compared, were really complicated free radical chain reactions. The lone exception appeared to be the classic N_2O_5 decomposition. Its puzzling features ultimately led to this last remnant of the 1920s being recognized in the 1950s as also involving free radicals and consisting of several reaction steps instead of just one.

I had spent some time studying several free radical reactions experimentally as a postdoctoral fellow in E. W. R. Steacie's laboratory in the late 1940s and decided to learn more about theories of chemical reactions. I was overjoyed, therefore, when Oscar Rice, to whom I had applied for a postdoctoral fellowship, told me that his proposed Office of Naval Research Grant was going to be funded. In January of 1949, I was on my way to learn about what life might be like in the world of theory. There were no theorists in chemistry in Canada at the time. Steacie himself had, I believe, some skepticism of theory, perhaps because of the adjustable parameters so frequently used in calculating activation energies of reactions in those days. In any event, the notion of trying to avoid them, or at least restrict their influence, left its indelible mark on me.

Life with Rice and in Chapel Hill was a delight. After 3 months of reading earlier theoretical papers on reaction dynamics (alas, mostly in German—I have hung on to my original translations!), together with weekly discussions with Rice on their assumptions (he would point out those I had missed), and auditing a course in quantum mechanics taught by Nathan Rosen, I started, at Rice's suggestion, to look more closely at unimolecular reactions. In addition to the RRK theory there was a heat-bath type of theory of Landau of the mid-thirties, some early ideas of Polanyi and Wigner in the late 1920s on phase coherence of the harmonic oscillators (a precursor of N. Slater's theory of the mid 1950s), and some ideas of Rice and Gershinowitz on entropic effects in the mid-thirties. There was also a large body of literature on Eyring's activated complex theory of chemical reactions or, as it was called on the other side of the Atlantic, the transition state theory of Evans and Polanyi. (The TST term prevailed.)

As a result of becoming thoroughly immersed in most of these articles, and in particular in RRK and in transition state theory, I put bits and pieces of them together, and after 3 months of hard work obtained a version of RRKM theory for the recombination of methyl radicals and iodine atoms.[3] Milton Burton later visited Chapel Hill and, on hearing about the work, suggested to Oscar that I present it at an Anomalies in Reaction Kinetics Symposium in 1950. This was my first symposium and third paper. A generalization followed shortly afterward,[6] with some extension later.[58] (Some decades later I also learned that one of the key equations was a chemical analogue of an equation obtained by Bohr and Wheeler for nuclear fission.)

There was essentially no experimental work of any consequence on pressure effects in unimolecular reactions at that time. As a young faculty member (1951), I consequently decided to look elsewhere, and began by doing experiments—returning thereby to the concrete world.

How different the field of unimolecular reactions is today, some 35 or so years later. The many experimental systems investigated, and the many new experimental techniques introduced in the interim, have enriched the area in complexity and scope. The unimolecular field is now, and indeed has been since the early 1960s, a booming one, some of whose developments I will comment on later.

It was easy, at the time, not to continue the theoretical work on unimolecular reactions, given the absence of data, and to pigeonhole any unfinished manuscript. Not as easy was the choice of what to do next. Prompted by a student's question in one of my lectures in a statistical mechanics course, I looked into polyelectrolytes and their electrostatic free energy. Two papers on this aspect of polyelectrolyte solutions resulted (1954, 1955).[10,13] I never followed them up, though others have since made use of the theory. But the knowledge I gained about electrostatics was

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‡ The reference numbers refer to a publication list given elsewhere in this volume. The fields described in this article have been broad, actively pursued, and enriched by many investigators. In sketching some of the developments it has, regrettably, not been practical to give detailed references or to cite each author by name. Nevertheless, to give some "body" to the discussion the various illustrative examples include a sampling of names of the contributors. Detailed references and citations for several of the topics appear in ref 48, 105, 168, 204, and 219.

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to prove useful when I happened to chance on a 1952 symposium issue on electron-transfer reactions.

The study of the rates of electron transfers was very active at that time and continues to be to this day (extended now to include organic and biological systems). It was stimulated by the accessibility of many radioactive isotopes due to nuclear developments in World War II. Such ready availability permitted the investigation of many isotopic exchange reactions involving electron transfer. These reactions, self-exchange reactions as they are now called, are the simplest of all electron transfers (products same as reactants, only their identity exchanged) and perhaps the simplest of all chemical reactions, at least when no bonds are broken. By the time of the 1952 symposium issue, a number of them had been studied. One result was the slowness of the self-exchange reactions of simple ions such as ferrous–ferric or cerous–ceric, compared with those of certain complex ions such as ferrocyanide–ferricyanide or manganate–permanganate. This result was attributed by Libby to the large difference of equilibrium solvation for the two redox states of the small simple ions. (This idea also provided an explanation of the slowness of the self-exchange of the hexaamminecobalt ions, which had a large difference in equilibrium Co–N bond lengths.) In this paper, Libby made the suggestion that the origin of small rate constants could be seen using the Franck–Condon principle. Libby had in mind a vertical transition, as in the typical application of the Franck–Condon principle to spectroscopy. The large change in initial and final equilibrium solvations of each of the two ions made for a large energy barrier to the transfer. He then gave a back-of-the envelope electrostatic calculation for the energy barrier (change of solvation energy).

I had been familiar mainly with more conventional reactions, where the Franck–Condon principle does not enter, and Libby's proposal was intriguing—it had a nice ring. His back-of-the envelope calculation, on the other hand, seemed to me to be in error, though at first I could not quite identify how. It was this calculation which provoked my own interest in the field. I immersed myself in some of the relevant literature, including Platzman's and Franck's calculation of the spectrum of the halide ions in solution—a valid application of the Franck–Condon principle.

Fortunately I was able to obtain a solution to the problem a month after reading Libby's article, and published the results in two 1956 papers.[16,17] It was, I believe, the most exciting moment I had ever experienced. It became clear that what was needed to satisfy the quantum mechanics for thermal electron transfers was not a vertical transition—absorption of light would instead be involved in that—but rather a suitable fluctuation of the solvent polarization (and indeed of the vibrational coordinates also, but this I did not treat until later that year). With an appropriate fluctuation and by satisfying the Franck–Condon principle, the electron could transfer without absorption of radiation. During that month I managed to find a reversible thermodynamic path for producing arbitrary fluctuations in dielectric polarization of the solvent and, from the reversible work, calculated their free energy of formation.[17] Minimizing the free energy subject to the constraint imposed by the Franck–Condon principle led to a characterization of the transition state for the reaction and to a calculation of the reaction rate constant itself.[16] The theory was presented at a symposium on Electron Exchange Reactions in 1956.

Unlike RRKM theory, which lay dormant for some 8 or 9 years, the electron-transfer theory aroused immediate attention. In the next few years I extended the theory to include intramolecular vibrational effects (1957, 1960),[21,30] numerically calculated rates of self-exchange[21] and "cross" reactions (1957),[20] and also to include electrochemical electron-transfer reactions (transfers with electrodes, 1957, 1959, 1965),[28,53,129] chemiluminescent electron transfers (1965),[57] relation between nonequilibrium and equilibrium solvation free energies for arbitrary geometries (1963),[43,45] and spectral charge-transfer processes (1965).[54] The 1959 paper gave a relation between homogeneous and electrochemical electron-transfer rates.[28] Electrochemistry was quite new to me, and I benefitted considerably from the precision of Parsons' clearly written article on the electrical double layer and from reading Randles' paper on his measurements of fast, simple electrochemical electron transfers. (I shied away from treating the popular electrochemical reaction of the day, the hydrogen overpotential reaction, because of the uncertainties in the potential energy surface, stemming from the various bond ruptures and formation.)

The 1960 work contained a derivation of a "cross-relation" that related the rates of electron transfer reactions between two different redox systems to those of the individual self-exchange reactions of each system and to the equilibrium constant. In this relation there occurred a cancellation of the various molecular properties whose values were in part unknown at the time. For that reason, perhaps, the relation became the most widely used aspect of the theory and the subject of numerous experimental tests and applications.

Frequent visits to the Chemistry Department of the Brookhaven National Laboratory during this period and discussions there of experiments with Dick Dodson and Norman Sutin served as a considerable stimulus. It was indeed in a conversation with Norman around 1962 that I mentioned the cross-relation to him. Norman had the various rate constants at his fingertips and, to our delight, the relation seemed to work. This result and tests of other predictions were published in 1963.[41] During the sixties and seventies Norman pioneered, among his many other studies, the experimental testing of the cross-relation, its applications to biological molecules (cytochrome *c*), and the related predictions on the effect of the standard free energy of reaction on the rate.

In a later paper (1965) I generalized the derivations of the 1956, 1957, and 1960 results, so that the approximations entering each, e.g., "symmetrization" of the potential energy surfaces, became more sharply defined.[53] Among the other predictions of the 1960 paper was that of an "inverted" effect. In the latter, the rate constant of a series of related reactions was predicted to initially increase as the driving force (negative of the standard free energy of reaction, $\Delta G°$) was increased. This was as expected and was the "normal region". Then, with further increase of $-\Delta G°$ the predicted rate passed through a maximum and subsequently decreased—the "inverted region". The latter prediction was at variance with the usual trend expected for typical chemical reactions. In retrospect, one can see that that trend was confirmed experimentally by Siebrand some years later for radiationless transitions, a behavior now known in that field as the energy-gap law. Numerous investigators tested electron transfers for the predicted inverted effect. (Difficulties, interferences, and quantum effects were discussed in ref 164.) The best evidence thus far came in 1985, some 25 years after it was proposed, in the study of a series of intramolecular electron transfers by Miller, Calcaterra, and Closs.

Meanwhile there had been several interesting theoretical developments in the electron-transfer field. Levich and Dogonadze published in 1959 a quantum treatment for the motion of the solvent molecules (the dielectric polarization) in electron-transfer reactions. As they noted, their work was related in part to my classical study and in part to the quantum treatment of Kubo and Toyozawa for radiationless transitions. The work of Levich and Dogonadze, but extended to the intramolecular vibrational motion rather than just the solvent polarization (Sutin, Dogonadze, and Kuznetsov, Jortner and others), has largely served as a basis for the many further quantum studies in the field which appeared in the 1970s. Some of the quantum studies were introduced to treat biological electron transfers at very low temperatures (Hopfield, Jortner) and some were introduced to treat the inverted effect (Van Duyne and Fischer, Efrima and Bixon, Ulstrup and Jortner).

Other significant theoretical developments included Taube's clarification of inner- vs. outer-sphere electron transfers, the treatment of vibrational effects of self-exchange reactions by Orgel and by George and Griffith, the work of Hush on charge-transfer spectra, complemented by the experiments of Taube, the treatment of electron transfers through bridged or conjugated systems by Halpern and Orgel and by Larsson, both Gerischer's and Dewald's

treatments of electron transfers at semiconductor electrodes, and the discussion by Hopfield of the role played by separation distance on the rate of reactions between reactants fixed in position in membranes in biological systems.

The study of electron transfers has been growing in several directions, and in 1985 Norman Sutin and I reviewed the field.[204] Experimentally, the role of the separation distance in electron-transfer rates is being investigated in proteins (particularly by Gray and by Hoffman, McLendon, and their co-workers), in organic molecules (Miller and Closs, Isied, Dervan, Michel-Beyerle, Paddon-Row and Hush, and co-workers, among others), and in organic monolayers (Kuhn et al.), giving information which will be very useful in biological applications.[204] The study of electron transfers in a variety of biological systems—reaction centers in photosynthesis, particularly with the recent crystal structure results, transfers in cytochrome oxidase and the coupled proton pumping, illustrated by my colleague Chan's work, and the many electron transfers in proteins—all provide exciting new areas for investigation. The challenge in this field, particularly as detailed structures become available, is considerable for those who are mechanistically inclined.

New electrochemical studies include those of modified electrodes by Murray, Savéant, Anson, Albery, and others, and of metal or semiconductor colloids by many investigators. Recently a number of studies have also appeared on other aspects of electron transfers, as in the role of slow solvent dynamics on their rates (and indeed on those of other reactions). Most of the latter has been theoretical thus far, but interesting experiments have appeared, together with an anomaly. Hitoshi Sumi and I considered them recently, and managed to obtain a simple approximate formula for certain conditions.[211,213,214] Another topic for which experimental data have only begun to appear is that of orientation effects on electron-transfer rates. A rough but simple model has been introduced to treat these effects,[201,209,210] and more accurate models will undoubtedly become available.

Unimolecular reactions were left, in this review, in their state in 1952. RRKM theory lay unused until about 1960. In part, the relevant experimental data were sparse, and, in part, an elegant treatment of unimolecular reactions due to Noel Slater appeared, largely in the fifties. This latter theory was particularly attractive because of its relatively sophisticated mathematics and its statistical and dynamical elements. It did contain, on the other hand, two restrictive assumptions: classical motion for all molecular vibrations, including the high-frequency ones, and a harmonic oscillator approximation. In the way the latter was used dynamically in Slater's work, a molecule of N coordinates had N constants of the motion (N actions) which led to its moving only on an N-dimensional subspace of the $2N$-dimensional phase space. Some carefully planned experiments, and increasing recognition of the limitations of these approximations, eventually led to a decline in its use. I believe the dynamical issues it raised, however, had and rightly continue to have an influence on thinking about these reactions.

A turning point in the unimolecular reaction field occurred around 1960 when Seymour Rabinovitch and his students undertook their classic series of experiments on chemical activation reactions and unimolecular reactions. They began to analyze their extensive data using RRKM theory. Their work led directly to the many later applications of the theory. It also included experiments which offered some indirect estimate (about 1 ps) for the time of redistribution of energy in these high-energy molecules formed by a chemical activation reaction.

During the fifties and later there were, complementary to the study of unimolecular reactions of neutral molecules, the investigations of mass spectral patterns of fragmenting molecular ions. The theoretical underpinning of this field involved the energy-dependent unimolecular dissociation of the parent ion, which proceeded by a number of competitive paths ("branching") to form the different observable fragments. A theory of this fragmentation, the "quasi-equilibrium theory" (QET) of mass spectra, had been developed in 1952 by Eyring and co-workers and had much in common with RRKM theory. An approximation, which was, however, specific to it, was a classical treatment of the molecular vibrations. By 1961–1962, difficulties in the application of QET to the mass spectral data began to appear. They were recognized by Rabinovitch and by Wolfsberg as due to the classical treatment for the high vibration frequencies. They used a quantum expression given by RRKM theory and removed the orders of magnitude discrepancies that had arisen.

During the subsequent period there were a number of influential developments in theory: In the mid-sixties, phase-space theory was formulated by Light and Pechukas for bimolecular (and unimolecular) reactions having "loose" transition states. It took full account of angular momentum conservation. One of its consequences was to make predictions of the yields of various quantum states of the reaction products and of reaction rates. In the seventies, Quack and Troe introduced their "statistical adiabatic channel" model, to treat reactions in which the transition state is not necessarily loose. They assumed a "vibrationally adiabatic" motion of this reacting system along the reaction coordinate and an approximate interpolation formula for correlating the energy of the initial state of the parent molecule with a final state of the fragments that it formed. Reaction rates and energy distribution of the reaction products were calculated.

Beginning in the late sixties and accelerating in the ensuing decades, new types of experiments were introduced. With the work of Rabinovitch on the relation between experiment and theory as a background, RRKM began to be extensively applied to the new studies as well. The latter included the measurement of the translational energy distribution of the products of transient complexes formed in molecular beams. Initially, triatomic complexes formed from the reaction of alkali halides and alkali atoms were so studied by Herschbach and co-workers in the late sixties and, in the seventies, Lee and co-workers similary examined chemical activation reactions in beams. Extensive comparisons of the results with RRKM theory and with phase-space theory were made, and numerous interesting results were obtained. The need for using systems having no complicating effects (no exit channel effects[112,127]) became clear. Most of the systems so studied appeared to behave statistically, in the absence of exit channel effects. A few did not, and for these there was some evidence that the lifetime of the transient complex was very short, perhaps too short for internal redistribution of energy in the complex.

This work was nicely complemented by McDonald and co-workers on the infrared chemiluminescence of the reaction products of these halogen atom–olefin chemical activation reactions. Their studies provided information on the vibrational energy distribution of the reaction products.

Another series of studies was also initiated in the seventies, the infrared multiphoton dissociation of molecules in molecular beams. Taking into account the various steps of absorbing radiation and reacting, using RRKM for the latter, Lee obtained a consistent interpretation of his results on the translational energy of the reaction products. Experiments by Setser at the time tested the theory by studying molecules having two reaction pathways and seeing whether the kinetic behavior was statistical or not. In still other multiphoton dissociation experiments by Stephenson, the vibrational energy distribution of the reaction products was determined and was also consistent with RRKM theory.

Particularly in the cases of unimolecular reactions as a function of the pressure and in infrared multiphoton dissociations, there is a distribution of the energies of the dissociating or isomerizing molecules, rather than a very narrow distribution. There is also some distribution, though to a lesser degree, in chemical activation reactions. An effort in recent years has been made to reduce the width of the initial distribution of energies using optical excitation. In some special cases, an electronically excited molecule undergoes an internal conversion to form a vibrationally hot molecule the width of whose energy distribution is more or less that of the parent unexcited molecule.

The most recent type of excitation used for testing the theory has been the excitation of the molecule either vibronically or by exciting a high, e.g., a fifth or sixth, CH or OH overtone vibration of the molecules, in bulk by Berry, Crim, Moore and Zare and their co-workers, and, more recently, in a supersonic molecular beam by Zewail and co-workers. RRKM theory has frequently

been used in comparisons with the data. The angular distribution of products of molecular beam reactions involving transient intermediates has been determined by Bernstein and co-workers, and RRKM theory has been used in its interpretation (Holmlid et al.). In the parallel field of dissociation of molecular ions, significant developments, including coincidence measurements, have provided information on the initial energy of the ion (Baer), theoretical contributions by Bowers, and an interesting combination by Brauman of RRKM and the group transfer theories.

Most of the experiments mentioned previously have involved measurements of reaction rate constants as a function of temperature, pressure, or, in some cases, excitation energy. A number of other experiments involved the measurement of the translational or vibrational energy distribution of the products in molecular beams. In bulk, the yields of final rotational and vibrational quantum states are now being determined for other reactions (Wittig, Crim) and, most recently, real-time rate constants for formation of these states are also being determined in supersonic jet–picosecond excitation and detection systems (Zewail).

Prompted at first by the more conventional experiments, Wardlaw and I recently extended the analysis of unimolecular dissociations based on RRKM theory, so as to include a treatment of the complicated and highly coupled bending vibrational–molecular rotational motion, which determines the transition state of the reaction.[195,205,220] Recently, introducing an adiabatic approximation,[221] I extended the method to yield the final distribution and the time evolution of the product states. Tests of the latter are being explored.

In summary, the entire field of unimolecular reactions has broadened immeasurably from its base in the late 1940's when I first became familiar with it. Its growth was slow at first, then notably enhanced in the sixties and seventies. It now includes many types of experiments, such as those mentioned above, and is still expanding.

Where can one expect experiment and theory in this field to be going? There is already evidence from Levy's work that in van der Waals complexes, in which one of the partners is highly vibrationally excited, a dynamical model is more applicable than the statistical one. (In this case the release of even one such quantum into the relative motion of the two fragments can cause dissociation before internal equilibration.) Mode-specific effects are also evident in some low vibrational energy quantum beat studies of Zewail. With the increasingly detailed and shorter-time experiments, deviations from statistical theory should become increasingly detectable in more general systems.

Again, the theoretical study of intramolecular nonlinear dynamics has been extensive during the past decade.[168] It includes the topic of "chaos" vs. quasi-periodic motion,[157,183] discussed also by many physicists and by chemists such as Brumer, Heller, Kay, Reinhardt, and Rice, among others. It is being applied to the treatment of restricted energy transfer between parts of the molecule[183] using semiclassical theory in some instances. (Applications have been made to heavy-atom systems and intramolecular energy transfer.[212,215]) Most of the published theoretical work has been initiated, however, without the benefit of a substantial body of experimental results. As "pump–probe" experiments begin to provide more direct information on intramolecular transfer, one can expect the theory of the latter for real molecules to take a decisive step forward. Along a related but different direction, information as to the nature of the rotational–vibrational quantum states of high-energy molecules is becoming known from the stimulated emission pumping experiments of Kinsey and Field and their co-workers.

A different aspect of calculations on unimolecular reactions will be the improvement of the potential energy surfaces themselves. As increasingly accurate data on reaction rates become available, more accurate potential energy surfaces for locating the transition state will be desirable for tests, or applications, of the theory. The use of existing unimolecular theory and of potential energy surfaces is currently providing insight into what parts of the surfaces contribute the most.

This article has been concerned mainly with the unimolecular and electron transfer areas. However, I would like to comment on a few of the other areas which we have enjoyed investigating and which, in many cases, have touched on these two main topics. (Miscellaneous areas which were fun to study theoretically but which are not considered further here include reactions of solvated electrons,[60] electron transfers with negative activation energy,[110] quantum effects in electron transfers,[163,164] a two-site behavior in photosynthesis,[145,204] a unified approach to the electrochemical hydrogen evolution reaction,[134,154] microcanonical transition state theory and its consequences,[62,63,85,112] vibrational nonadiabaticity[138] and curvilinearity[49,50,56] in transition state theory, conformal transformation and reaction coordinates (with Connor),[87] Lie mechanics,[84,165] microwave transients,[115,116] complex isotopic exchange reactions,[14] and a surprising equality of energies of "conformal pairs" of conjugated molecules.[59])

The areas considered below include free energy relations and the cross relation for other types of transfer reactions, reaction coordinates, tunneling in chemical reactions, semiclassical theory of collisions and reactions, and semiclassical treatment of bound states.

In the first of these, reactions with bond ruptures and formation were treated, using a very simple model.[69] A resulting cross relation for such reactions, or free energy aspects related to it, has been tested by various investigators for reactions such as methyl, proton, hydride, sulfuryl and phosphoryl transfers (led by Albery, Kreevoy, Lewis, Murdoch, Williams, and their co-workers, among others). Such physical organic chemistry has provided a particularly interesting extension of ideas begun in the electron-transfer studies. For some reactions "perpendicular effects" are now being added. Kochi and Eberson have each discussed a number of other organic reactions in terms of electron-transfer theory.

The topic of reaction coordinates is interesting in that it has served to bridge the gap between modern chemical dynamics and transition state theory. It has also led to a new set of developments. In atom- or group-transfer chemical reactions one can imagine two limiting dynamical situations. In the first of these, a pair of reactants moving from the reactants' valley in the potential energy surface over a pass into the products' valley does so smoothly—"adiabatically". An adiabatic approximation, specifically an approximation in which the system remains in the same vibrational–rotational quantum state for the motion transverse to the reaction coordinate, had been postulated by various authors. The present writer was led to the idea in explaining, on that basis, a surprising classical trajectory result of Wall and co-workers.[56]

The adiabatic approximation, which was used to derive a quantum version of transition state theory, first appeared in a paper by Hirschfelder and Wigner in 1939. Later I used it in a "statistical-dynamical" theory of chemical reaction crosssections,[63,66] the high-frequency vibration being treated adiabatically and the remaining coordinates statistically, and in a related treatment for exit channel effects in dissociations.[112,127]

After a lecture in a 1965 summer school, I recall being asked by a student as to just how the particular motion, which I had termed "vibrationally adiabatic",[56] actually took place. It occurred to me that to provide both a detailed and a physically appealing answer, it would be desirable to design a coordinate system which passed smoothly from one appropriate to the reactants, through one appropriate to the transition state, and then to the one appropriate to the products, as the system is moved along the reaction coordinate. Curvilinear coordinate systems had indeed been used in the past for calculating transmission coefficients in activated complex theory, hyperbolic coordinates, for example. But they did not have the desired limiting forms at large separation distances. Curvilinearity had also been used in a theory of reactions by Hofacker.

I noticed in a physics text a coordinate system used for treating betatron oscillations in a particle accelerator problem (the coordinates were the distance along an arbitrary curve and the shortest distance from that curve to the point in space) and was able to use it for collinear collisions,[64,65] and extend it to three-dimensional collisions.[75] These collisional coordinates, termed "natural collision coordinates",[75] have found use in some numerical and analytical calculations of reaction rates. More recently, the

Hamiltonian based on these coordinates[75] was extended by Miller to include the effect of bending motion and other motions on the local curvature of the reaction coordinate and is being extensively applied by him ("reaction path Hamiltonian") and by Truhlar and their co-workers.

For another limiting situation a quite different coordinate system appears to be appropriate: in the transfer of a hydrogen atom or proton between two heavy masses $X + HY \rightarrow XH + Y$, there is, for certain conditions, an impulsive aspect to the transfer: the heavy masses X and Y approach slowly and in some range of XY distances the H "jumps" from one site to the other, either by surmounting the energy barrier or by nuclear tunneling. Polar coordinates[134] provide a vehicle for treating the dynamics of these reactions, together with a Born–Oppenheimer approximation to separate the light and heavy atom motions.[162,186] (Ovchinnikova used a related but somewhat different route.) Kuppermann has nicely shown in his work on three-dimensional systems that a multidimensional extension of the polar coordinates (hyperspherical or Delves coordinates as they are known) is also especially useful in numerical treatments of the dynamics of these and indeed for more general systems as well.

Directly related to such questions is that of nuclear tunneling in chemical reactions. A classic case treated in chemical kinetics texts is the $H + H_2 \rightarrow H_2 + H$ reaction, an example of an approximately vibrationally adiabatic reaction. The conventional prescription for the tunneling calculation for the transferring H atom in the texts had been to plot the potential energy along a reaction path from reactants to products (along the valley floor of the former, through the saddle-point region of the potential energy surface, and along the valley floor of the products' region) and calculate the tunneling rate through that barrier as a function of the initial energy. However, accurate quantum mechanical calculations (Kuppermann and co-workers) for typical potential energy surfaces disagreed with those tunneling calculations of reaction probability by factors of 10 to 100, depending on the surface.[125]

With this fact in mind Coltrin and I realized that the usual tunneling path was not, in semiclassical terms, a path that described the best overlap of the reactants' and products' wave functions.[125] It was not the shortest tunneling path between their regions of coordinate space. By minimizing the total action of the tunneling integral (least action) for a particular class of paths, a more probable tunneling path was found for the $H + H_2 \rightarrow H_2 + H$ reaction and corresponded in our case to a path consisting of end-points of the vibrational motion.[125] With such a path, the discrepancy with the quantum mechanical results was immediately reduced to a factor of about two.[125] Closer agreement would require a more detailed semiclassical theory for the tunneling.

For the transfer of an H atom or proton between two heavy masses, a different tunneling path arises. In this system there is a severe case of "cutting the corner" in the usual skewed mass-weighted coordinate system—shades of Harold Johnston's earlier and disarmingly perceptive treatment of tunneling in reactions. Polar coordinates[162] or least action paths have proved useful for treating these reactions (Truhlar and others). The detailed dynamics of such systems involving the transfer of a light atom, and the role played by other coordinates, offer interesting challenges.[188] One can expect this particularly to be the case as data from various new sources become increasingly available, supplementing the data on transfers in solution: transfers in supersonic and, thereby, vibrationally and rotationally cold molecular beams, and transfers at low temperatures in condensed phases.

We referred earlier to semiclassical theory as a theory which has provided added insight into the treatment of reactive collisions and of intramolecular dynamics. It had its antecedents in the Wentzel–Kramers–Brillouin theory of the late twenties, and was further extended by Keller, by Maslov, by Berry and, in a lovely article on elastic scattering, by Ford and Wheeler. Further excellent contributions were made by Connor and by Child. The field was especially stimulated by Pechukas' use of Feynman propagators to treat atomic collisions and by Miller's impressive extension of the latter to molecular collisions.

In my own approach to that problem, I used a semiclassical wave function to describe the collisions.[89,90] Numerically calculated classical trajectories, action-angle variables,[76,79] and action integrals were employed. The area itself has had its share of novel features for me—seeing how interferences lead to rotational selection rules in inelastic collisions[90] and to a Feshbach-type resonance in a reaction,[109] how tunneling in phase space leads to classically forbidden inelastic transitions,[97] and how a particular canonical transformation leads to a more satisfying derivation of a semiclassical integral expression for the scattering matrix.[95,103] While there have been some applications of semiclassical treatments of inelastic and of reactive collisions to experiments, e.g.,[114,116,132] I believe that the more appealing aspect of semiclassical theory has been the insight it offers into the relationship between classical and quantum mechanics and into the limitations on the validity of using classical trajectory calculations to treat chemical dynamics. Trajectories were effectively used, it may be recalled, by Polanyi and Karplus and their co-workers, and by others, for treating experimental data on the dynamics of bimolecular reactions, and by Bunker, Hase, and others for discussing theoretical aspects of unimolecular reactions.

One semiclassical problem that we considered in the scattering studies, the treatment of certain Feshbach resonances,[100] proved, unexpectedly, to lead to a quite new field of study. The positions of resonances should occur near the eigenvalues of the quasi-bound states, and a question which we examined, therefore, was how to find the latter semiclassically for (nonseparable) dynamical systems. Einstein had pointed out in his work in old quantum theory in 1917 that the eigenvalues of bound states of nonseparable Hamiltonian systems could be calculated if topologically independent phase integrals $\oint \mathbf{p}\cdot d\mathbf{q}$, the actions, could be found. These canonical invariants could then, he noted, be quantized. In 1958 Keller showed in a seminal paper how to obtain them for the particle in a box problem, the box being of various curvilinear shapes. It was a delight, therefore, when Eastes[107] (1974) discovered a way of calculating them for systems of a more molecular type, i.e., for systems with smoothly varying potentials.[107] He did so by numerically computing a classical trajectory and then calculating the phase integrals for it by integrating the trajectory data along the "caustics".

In the following year Noid introduced a method[113] which proved to be more amenable to treating trajectories with more complicated shapes—shapes distorted by internal resonances.[124,144,219] Noid integrated the trajectory data along Poincaré surfaces of section. Since that time many methods have been devised, and Noid has also extended his method to more complicated systems. With Koszykowski, he also introduced the idea of determining infrared spectra from trajectories[123,175] and used the spectra as a diagnostic tool for detecting classical chaos.[123] There is now a wide choice of methods for calculating semiclassical eigenvalues, some more useful than others for application to realistic molecular systems, and new developments continue to appear each year.

In some cases, as for example in the photodissociation of methyl iodide to form methyl radicals and iodine atoms, the experimental results on the emission spectrum led to attention being focussed on only two coordinates of the many-coordinate system—the C–I stretching and CH_3 umbrella motions. A current theoretical treatment of that problem using the wave packet method of Heller utilized some semiclassical ideas. Other instances where the dynamics may be usefully reduced to a two- or three-coordinate case may arise, and several of the existing semiclassical methods may find application to those experiments.

While the calculation of individual scattering matrix elements or of individual eigenvalues has been a challenge, there has also been a trend more recently toward the direct calculation of somewhat coarse-grained observables, usually with some added approximation, when many coordinates are involved. A calculation of the numerous individual matrix elements or eigenvalues, compared with the usually few observables, tells us more than we may wish to know about the subject! One may expect that the experience gained in the earlier and more detailed calculations for simple models will prove useful in addressing these newer, challenging, physically more interesting and certainly experi-

mentally more accessible problems. It is encouraging to see how new methods, and revitalized older methods, based in part on ideas introduced many years ago by Feynman, are being adapted to these and to related topics. With a blend of dynamics and statistics, future understanding of the dynamical problems appears bright.

In reflecting on the developments over the decades, it is interesting how excitingly active the electron-transfer and unimolecular areas continue to be, experimentally and theoretically. In electron transfer, for example, questions arise, and can be or are being addressed experimentally, such as how far the electron can effectively transfer in a given time, the relative role of through space vs. through bond transfers, the dependence on the intervening medium and on the orbitals of the reactants, the effect of mutual orientation of the reactants on electron transfer rates, and the effect of solvent or other environmental dynamics, diffusive and inertial, on the rate.

Others questions concern the treatment of electron transfers involving the rupture of chemical bonds and the accompanying complicated change of solvation, and discussions of distinguishing whether some organic reactions proceed via successive inner- or outer-sphere one-electron steps, or by another mechanism. Searches for further examples of the inverted effect are in progress. It would be useful, also, to determine whether that effect is the principal reason for the efficient charge separation across a membrane, resulting from an electron transfer from the photoexcited chlorophyll or chlorophyll pair in a photosynthetic system. Does the inverted effect cause it to proceed efficiently to the quinone rather than revert in a reaction energetically downhill to the chlorophyll?[204]

Comparisons of theory and experiment for electron transfers in proteins are utilizing structural information in the form of separation distances between reacting sites. Again, answers to questions such as the problem of the coupling of electron and ion transport (the striking chemical problem of ion gating) will make use of structural data, presently only incomplete.

In the area of unimolecular reactions, some of the current questions include the extent of randomization prior to the dissociation, perhaps seen in a biexponential time behavior, the relative roles of anharmonic vibrational–vibrational (Fermi resonances) and vibrational–rotational couplings in intramolecular energy redistribution, the description of the states of highly vibrationally excited molecules, as reflected in their absorption or emission spectrum, and the conditions under which mode-specificity becomes significant. In that vein the question arises as to whether the rate of intramolecular energy transfer can be reduced sufficiently, perhaps by a heavy central atom or by some other means, to make a laser-selective chemistry of interesting unimolecular reactions an actuality.

Only a few years ago some of these problems were considered but could not be directly addressed. With the background of decades-long studies and the introduction of incisive new techniques, the more detailed questions are being raised, and answered in some cases, while new ones arise, and progress continues.

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