1. THEORETICAL

The Theoretical Approach

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1. A QUESTION

There are a number of areas in chemical kinetics where generalizations have been helpful in interpreting and correlating a large body of experimental data in gas phase or solution reactions. I am reminded here of Bronsted's relation between rate constants and equilibrium constants,[1] Eyring's and Evans and Polanyi's work on transition state theory,[2] Rice, Ramsperger and Kassel's work on unimolecular reactions,[3] later augmented to RRKM,[4] treatments of the curve crossing problems,[5] Hammett's $\sigma\rho$ relation and acidity function, and the subsequent equations they stimulated,[6] theories of three-body recombination of atoms [7] and of electron transfers in solution [8] and at electrodes,[9] simple BEBO calculations on activation energies,[10] the Woodward-Hoffman rules and their implications for activation energies,[11] Breit–Wigner and later treatments of resonances,[12] models for ion–molecule reactions,[13] to name a few. In the case of inelastic non-reactive collisions one would include the SSH theory,[14] distorted wave theory for some systems,[15] the Anderson theory of spectral line broadening [16] and its later extensions.[17]

The interested observer, as well as the seasoned practitioner, might well ask which of these generalizations of analytical thought apply to current problems of molecular dynamics, what new ones have been developed, or what experimental generalizations are there, if any, which literally cry out for a theoretical answer. He might ask, too, whether the present field is sufficiently different from the previous ones that the approximate analytical theory will be literally swept under by a Spartan-like phalanx of exact classical trajectories and their semiclassical and quantum mechanical counterparts, with much analytical thought going into this army.

We shall not attempt to answer all of these questions here, but shall summarize instead some of the trends which appear to be developing in the field. Calculations in the area are diverse, and some classification would be useful. A possible scheme for dynamical calculations is proposed in this introductory paper.

2. INTERACTIONS AND SURFACES

Perhaps it would be well to begin our inquiry with this chemical topic. Herschbach and his colleagues in some of their recent studies have obtained or inferred information about shapes, linear *versus* nonlinear, of activated complexes (i.e., of the

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" reaction geometry ") and have correlated the results with Walsh's rules based on molecular orbital theory.[18] The work of Grice and coworkers in this Discussion also treats this problem for methyl radical reactions. In their paper, Herschbach *et al.* comment on implications of the Woodward–Hoffman rules for four-centre reaction activation energies involving electron rearrangement, and the relation to their study.

Studies of infra-red chemiluminescence, notably by Polanyi and coworkers,[19] including the paper presented at this symposium, have revealed much on the disposition of energy in exothermic reactions. In turn such information has been correlated with characterization of the relevant potential energy surfaces as early downhill, late downhill, and mixed energy release.[19]

The purely theoretical quantitative calculations include the many LEPS surfaces, as well as the modest surprising-in-its simplicity BEBO method.[10] The latter, with its use of non-kinetic data, has yielded reasonably good results for activation energies of a class of reactions (one bond broken, one formed), give or take a few kcal/mol. The need for a knowledge of potential energy surfaces having the right shape is well-known, of course, to dynamicists, and several *ab initio* surfaces for reactions or inelastic collisions have been calculated, such as $H+H_2$, $F+H_2$ and Li^++H_2.[20]

Bernstein and Rulis, in their Discussion paper, have drawn our attention to the many facts which must be satisfied by any reputable $K+CH_3I$ surface. The rise and the subsequent rapid drop of reaction cross-section with increasing initial translational energy, and its possible relation to curve crossing, was considered earlier.[21]

3. MOTION ON THE SURFACES

The theoretical treatments for motion on these potential energy surfaces are now many, as recent reviews amply confirm. These theories can be classified as (1) dynamical, (2) statistical, (3) statistical-dynamical, a term coined elsewhere,[22] and (4) numerical or " exact ". We shall explore some of the current trends in these areas, beginning with a brief recall of some relevant history of the pre-beam era.

(i) EARLIER THEORY

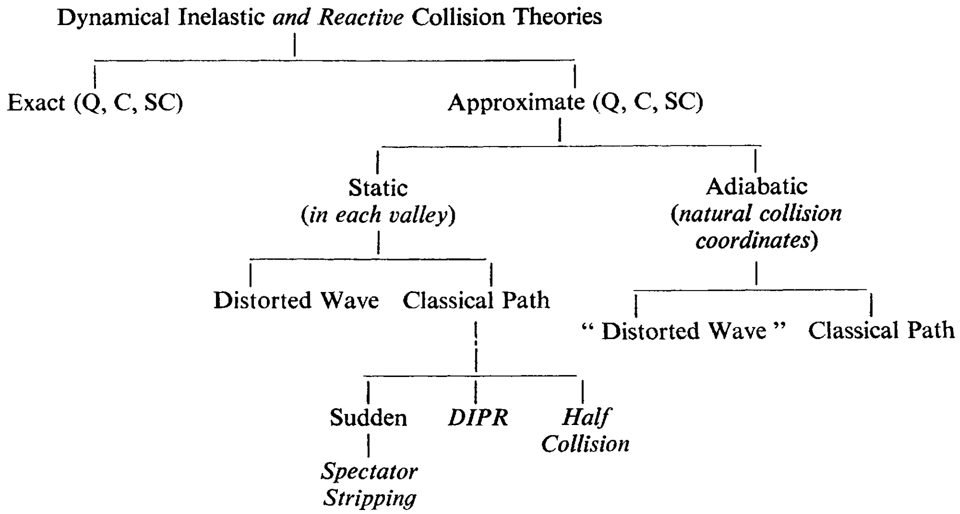
The earlier theory of reactive collisions had a flavour different from that of inelastic collisions, both because of the difference in data available and in complexity of theory: prior to the 1950's essentially all the data on reactive collisions were of a highly statistical, ensemble-averaged nature (rate constants of systems in averaged initial states) while much of the inelastic collision data offered dynamics fairly directly in the form of vibrational relaxation in sound dispersion experiments.[14] Thus, a statistical treatment of the former and a partly dynamical treatment of the latter was needed and responded to. Again, the complexity of the dynamics of reactive collisions, arising mainly from the fact that the coordinates of the reactants do not conveniently describe in a simple way the motion of the products, made a statistical treatment a matter of necessity in the 1920's to the 1950's. Even today, for most of the reaction rate data in chemistry in solution and the gas phase, statistical treatment is a matter of necessity.

While the chemical kinetics data lent themselves to statistical theory, it is refreshing to recall that many of the dynamical concepts in use today were considered in the earlier years, including the concept of adiabaticity for the internal motions, and the role of excess energy in stimulating vibrational excitation.[23] To be sure, in the 1960's and onwards these concepts have been further developed and made more quantitative. In the case of inelastic collisions, the dynamical grounds were laid in the early 1930's [15, 24] and fashioned into a practical tool, SSH, in the 1950's.[14]

(ii) CURRENT DYNAMICAL PICTURE

For purposes of examining current trends [25] in dynamical calculations, I would suggest a classification such as in table 1 :

TABLE 1.—A CLASSIFICATION OF DYNAMICAL CALCULATIONS



The non-italicized portion refers to inelastic collisions. All parts of the table, including the italicized ones, refer to reactive collisions. The abbreviations Q, C and SC denote quantum, classical and semiclassical, since the approximations can be formulated for each of them. *Quantum* is used in the sense that at least some of the internal coordinates of the system are treated quantum mechanically. *Classical* indicates that all degrees of freedom satisfy Hamilton's equations of motion. *Semiclassical* is used in the sense adopted in the papers by Miller, Connor and Marcus in this Discussion.

A principal distinction in table 1 is the " static " versus " adiabatic " approximation. The label " static " or " adiabatic " is one used for brevity in table 1 and is intended to signify the zero'th order calculation *plus* a higher order one needed for calculation of change of rotational-vibrational state. (Hence, for example, the " adiabatic " in table 1 includes the usual zero'th order adiabatic calculation plus a nonadiabatic correction.) We recall the difference in the zero'th order calculations for the static and adiabatic models as follows.

In calculations some reaction coordinate s is first selected, typically the radial coordinate in the case of inelastic collisions. The static model has, for the zero'th order s-motion, an effective potential obtained by averaging the interaction potential V over the *unperturbed* initial internal state.* In the adiabatic model, this effective potential is obtained instead by averaging V over the *locally adjusted* internal state at any s. That adjusted internal state is obtained beforehand by solving the equation for the internal motion at each s. In the case of a reactive collision, s is some curvilinear coordinate, leading smoothly from reactants to products in the adiabatic case.

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* The importance, at least in some instances, of using an averaged V instead of one which ignores the dependence of V on internal coordinates, has been noted.[26]

However, in the static case, s would be the radial coordinate of the reactants (products) when used for the unperturbed wave function of the reactants (products), with no possibility of having a smooth progress from one to the other.

I have extended the customary meaning of the terms " distorted wave " and " classical path " for use in table 1, in that " distorted wave " in table 1 indicates first or higher order perturbation theory, be it Q, C or SC; classical path in table 1 indicates a zero'th-order classical treatment of the s-motion and any order Q, C or SC treatment of the internal motions.* Conventionally, distorted wave was typically only used for a first or higher order perturbation of the quantum mechanical static case. The classical path approximation,[27] so-called by workers in the line broadening field [16, 17] and sometimes called semiclassical [28a] by other researchers, was usually reserved for the case where the relative motion is treated classically (and even approximated by straight-line trajectories in some instances), and where the internal motion is treated quantum mechanically. However, the basic idea underlying " distorted wave " and " classical path " can be applied to the C and SC cases also, and so an extended definition is useful. The " exponential approximation ",[25] not listed separately in table 1, is one method for achieving a high order, in certain respects, of perturbation.

The derivative nature of the remaining approximations in table 1 will be recognized: when the static " classical path " case is further approximated by neglecting energy differences of the internal states (and hence classically setting the frequencies of internal motion equal to zero) one obtains a " sudden " approximation.[29] Spectator stripping [13b, 30] could be regarded as a particular case of the latter approximation in which the initial internal energy is neglected. Use of a " classical path " model in the exit channel of a reaction, together with specified initial conditions for motion in that channel, leads instead to the DIPR approximation [31] (bimolecular) or to the half-collision approximation [32] (unimolecular dissociation). (One incidental application of table 1, by the nature of its emphasis, is the use of approximate C calculations, readily made and tested, to make predictions about the accuracy of Q and SC calculations for the same approximation.)

For the Q case, examples exist for many of the items in table 1. They include " exact " calculations for several three-dimensional inelastic collisions.[25] and for one-dimensional collinear reactive collisions.[25] There are no three-dimensional Q calculations of comparable accuracy for reactive systems with smooth potentials, though less accurate two- and three-dimensional reactive calculations exist.[33-35] There are static Q calculations, both with distorted wave and with classical path for inelastic collisions.[25] Adiabatic Q calculations have been made for collinear inelastic collisions using the distorted wave [36a] or classical path approximation,[36b] and for reactive collisions using distorted wave,[37, 38] or classical path.[36, 38, 39]

For the C case, the exact calculations are well-represented in this symposium and, of course, currently constitute the main link between molecular beam and infra-red chemiluminescence data and molecular properties. Examples of the C static classical path approximation are available for collisional rotational-translational [40] and vibrational-translational energy [41, 42] transfer. The adiabatic classical path approximation (including nonadiabatic calculations, as emphasized earlier) has been used for the C collinear inelastic [43] and reactive problems.[44] There are C examples of the spectator stripping,[13b, 30] DIPR [31] and half-collision models.[32]

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* Thus, for the C case the distorted wave and classical path approximations differ only in that the latter uses a zeroth order approximation for the s-motion, while the former may use higher order approximations.

For the SC case there are now many exact calculations (and some approximate ones). Several Discussion papers either refer to or make use of the calculations. We comment on SC theory later.

The adiabatic type calculations are much fewer than the static due to the greater complexity of the former. On the other hand the static calculations are sometimes quite inaccurate, because of considerable distortions of the internal motion during the collision. In the collinear vibration-translation problem, that static C calculation, for the case where a light atom is sandwiched between two heavy ones, yielded an error of as much as a factor of 4000 in the calculated energy transfer,[42] whereas an adiabatic C calculation involved only a 10 % error.[43] The static C calculation for rotation-translation energy transfer appeared to become poorer when the reduced moment of inertia ($I/\mu\sigma^2$, where σ is a Lennard-Jones distance parameter) became small.[40a]

The physical reason for the breakdown of the static calculation is probably the same in the two cases above: the motion of relatively light masses or molecules with a small moment of inertia is strongly perturbed in the usual collisions and is not well-represented by approximations which largely neglect these strong perturbations in zero'th order. For a different reason, namely the discontinuity involved in any " reactant channel " *versus* " product channel calculation ", the Q static distorted wave calculation was apparently poor for the one case tested ($H+H_2$).[45] Again, the first order static rotational-translational calculation can be inaccurate at low impact parameters $b(b/\sigma<1)$ [40b] and either higher order or a hard body [40b] (but exact) might be used there.

At high translational energies the adiabatic approximation itself cannot be as good as at lower energies, because the internal state of the system does not have time to adjust to this fast s-motion.

The adiabatic model (with nonadiabatic corrections included) for collinear reactive collisions has been treated with the aid of natural collision coordinates in the C classical path approximation,[44] in the Q classical path approximation [38] and in the distorted wave approximation.[38] Both the curvature of the reaction path and the vibration frequency along the path contributed to the change in quantum number (classical action variable).[38, 44] The results gave quite good agreement with exact trajectory results for the $H+H_2$ reaction.[44] However, the model should break down at large energy transfers: the usual classical path approximation is not a self-consistent one, since it doesn't allow for energy loss of the s-coordinate and so even allows an infinite build-up of energy in the oscillator (it is a " forced oscillator " [28b] problem).

TABLE 2.—SUMMARY OF THEORETICAL CONTRIBUTIONS*

	inelastic	reactive
Dynamical:		
Exact quantum	—	—
Exact classical	C13	A6, A7, D15
Exact semiclassical	A3, A4, A5	A3
Distorted wave	—	—
Classical path	—	—
Curve-crossing		A2
Statistical:	—	A6
Statistical–Dynamical	—	A6, A8, D20, D21

* The entries in this table refer to papers presented at this Discussion and are here identified by the surname of the first author: A2—Child; A3—Marcus; A4—Miller; A5—Connor; A6—Brumer; A7—Bunker; A8—Bernstein; C13—van den Bergh; D15—Ding; D20—Herschbach; D21—Lee.

Application of the model is made in the paper by Zare and coworkers to their results on vibrational energy distribution in this Discussion.

A number of calculations have been performed with hard-body type potentials (dumbells, spheres, etc.,) and might typically be labelled as " exact " though with these idealized potentials.[25] There is also, among the " exact " quantum mechanical calculations, a recent interesting development using averaged-over-*m*-states potentials to reduce the number of channels in an otherwise exact quantum calculation.[46]

All of the previous discussion concerned motion on one potential energy surface or curve, but the problem of curve crossing is an important one for chemistry.[18, 47, 48] The case of multiple curve crossings is considered by Child in his Discussion paper.

The theoretical contributions in the present symposium can be roughly categorized as in table 2.

Exact calculations are seen to predominate. A prescription for choosing between the exact and several of the approximate ones is suggested for inelastic collisions by Gordon in his Discussion paper. For reactive collisions, on the other hand, we have already noted the difficulty in finding good approximate dynamical theories.

There are a number of semiclassical contributions in table 2, and several pertinent aspects of exact semiclassical theory are considered in the next section.

(iii) SEMICLASSICAL THEORY

The ubiquitousness of exact classical calculations for reactive collisions and the current virtual absence of exact three dimensional quantum calculations suggest that " exact " semiclassical calculations [49-51] may be helpful for reactive (or indeed for inelastic) collisions.[52]

The main quantum effects expected for collisions are (1) quantum mechanical interferences,[48] (2) penetration of classically forbidden regions,[53] and (3) quasi-bound state effects.[54] The first of these is well-known in elastic collisions (rainbows, supernumeraries, superimposed oscillations on them) and also in curve crossing problems.[48] The interferences " wash out " when the phenomenon is state-dependent and the results are averaged over the states,[50, 55] but can be preserved in *sufficiently* state-selected experiments.

The second phenomenon, which can also be called *n*-dimensional tunnelling, does not " wash out ". It is of particular importance for any given state being formed either in a threshold region for formation of that state or in what we might term a " twilight region ", where the formation of this once important state has almost ceased (in a plot of probability of formation versus some parameter such as energy). Thus, the tunnelling is not limited to regions where the given state is just becoming energetically-allowed. In the threshold and twilight regions, one may expect semiclassically a significant contribution from complex-valued trajectories, and so the latter should not be neglected there.

The third phenomenon is treated semiclassically in the Discussion paper by the present author. Previous exact semiclassical calculations for nonseparable systems were concenrned only with direct collision trajectories,[49, 50] but in this latest paper the quasi-bound state trajectories were calculated and matched to direct collision trajectories to yield the S-matrix elements. The resulting quantum effects would be observed for quasi-bound complexes with sufficiently widely-spaced states. The elusive problem of semiclassical eigenvalues for bound state systems is also treated in this paper. An example of quasi-bound states for separable systems arises in the curve crossing problem for diatomic molecules.[48b]

A fourth quantum effect also exists: the probability distribution function of coordinates and momenta in the lowest quantum state(s) of an oscillator differs significantly from the classical value.

The exact semiclassical theory for direct collisions adopted in several papers of this Discussion was developed during the past three years using both Feynmann propagator [50] and wave function approaches.[49] Calculations on a number of systems have been performed, and many problems have been investigated. They include the following: (*a*) *inelastic collisions:* numerical calculations for vibration-translation energy transfer in one dimension,[49, 50] rotation-translation,[50, 51] rotation-vibration-translation,[50, 51] quasi-bound states [51]; (*b*) *reactive collisions*: one-,[50,51, 56,57] two- [58] and three-dimensions,[50,51] multidimensional potential energy surface-crossings [50]; (*c*) *other and related topics*: derivations,[49, 50] ranging from intuitive to the more rigorous; uniform approximations,[49-51, 59] complex-valued trajectories,[51, 60] selection rules,[49] Wigner 3-*j* coefficients,[50, 51] Wigner 6-*j* coefficients,[51] spectral line broadening,[51] canonical perturbation theory,[49] partial averaging,[50] and " exact " bound state eigenvalues.[51]

The paper by Connor in this Discussion considers the problem of a uniform approximation for multidimensional semiclassical integrals, a problem which arises in atom-diatomic collisions when attention is focused on formation of a given vibrational-rotational state, or in collisions involving polyatomic molecules when, as is typically the case with widely-spaced levels, a particular state of the several vibrations is needed.

The paper by Miller and Raczkewski describes the important method of partial averaging [50] of semiclassical results and its use in calculation of cross-sections for inelastic collisions.

4. STATISTICAL THEORIES

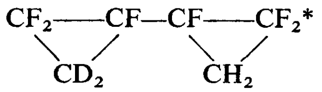
The most commonly used statistical theory for reaction rate constants is, of course, activated complex theory. Here, as is well-known, one assumes a quasi-equilibrium between reactants and systems crossing a particular hypersurface, " the activated complex ", calculates the probability of finding the system near the hypersurface, per unit length of reaction coordinate, multiplies the latter by the local velocity along that coordinate, integrates over all velocities, and sums over all states of the activated complexes.

Classical trajectories have been used, mainly by Karplus and co-workers, to test the activated complex theory of bimolecular reactions.[61-63] All tests apart from the first have compared the classical trajectory data with the classical form of activated complex theory (as they should), instead of with the quantum form. Comparison was made with the microcanonical form of activated complex theory,[62] which in turn is related by a Laplace transform to the usual theory. The agreement between exact and trajectory values of the reactive flux was good in the region of thermal interest. Breakdown in this comparison of bimolecular reaction rates occurred at the higher translation energies, because of reflection near the curved portion of the reaction path. The reflection led to a reduced rate both when the activated complex was in the initial channel (highly exothermic reaction) and so was recrossed to reform reactants, and when the activated complex was in the product channel (highly endothermic reactions) and so was never reached.

The quantum form of activated complex theory (ACT) has also been tested, though only for collinear systems, by comparing with the results of exact numerical solution of the Schrödinger equation for the $H+H_2$ reaction.[64] The exact results show more tunnelling in the threshold for reaction. It will be interesting to see how much of this difference occurs in three-dimensional calculations.

Unimolecular reaction rate theory in its RRKM form has been useful in interpreting rate constant versus pressure data, using the full number of degrees of freedom.[65] It has received support from trajectory calculations,[66] for molecules having lifetimes longer than an estimated intramolecular relaxation time $\sim 10^{-11}$ s. A comparison for another type of reaction, a four-centre reaction, appears in a paper by Brumer and Karplus in this Discussion, where it was found convenient to divide the trajectories into those for short- and long-lived complexes. The comparison with RRKM is made for the latter.

An example of breakdown has recently been found for molecules with lifetimes shorter than $\sim 10^{-12}$ s in the reaction involving the formation of the higher energy intermediate,



followed by elimination of a CF_2 from either ring.[67] It was estimated from pressure effect data on the vibrationally-hot intermediate that the time needed for randomization of energy among the two rings, i.e., for random emission of CF_2 from either ring, was $\lesssim 10^{-12}$ s.[67] In general, in other systems, one would expect an even greater intramolecular relaxation time at sufficiently low energies and correspondingly low anharmonicities.

Activated complex theory in its usual form is essentially devoid of dynamics. For example, it needs dynamics only in an infinitesimal interval $(s, s+\mathrm{d}s)$, and these dynamics are trivial. (When the curvilinear reaction coordinate is treated quantum mechanically, one uses dynamics over a somewhat larger s-interval, e.g., in the WKB approximation, to avoid conflict with the uncertainty principle.)

The lack of extensive dynamics suffices for calculation of canonical or microcanonical rate constants and the lack of need of dynamics is, in a sense, one of the strengths of activated complex theory. It is also its greatest weakness. For example, apart from the cited case of the loose activated complex, activated complex theory cannot be used to predict the dependence of reaction probability on initial state and on initial relative translational velocity; nor can it predict the relative formation rate of products in given final states and with given final velocities. One can adapt activated complex theory to make such calculations, by imposing added approximations. Measurements of final states or velocities, therefore, do not test activated complex theory, and hence do not test RRKM, but rather ACT (or RRKM) plus added assumptions. This point appears later in a discussion on the most interesting data of Y. T. Lee *et al.* in this Discussion.*

Sometimes this " strength " or " weakness " of activated complex theory has been misunderstood in a different way: while vibrational adiabaticity[23a, 37, 69] (or statistical vibrational adiabaticity[70]) have been used to understand activated complex theory under certain conditions, ACT is both more general and less powerful than VA. Any breakdown of VA or SVA does not automatically constitute a breakdown for ACT. Thus, the fact that an exothermic reaction yields products in highly excited vibrational states, even though the reactants were in low vibrational states, constitutes a breakdown of VA and SVA but not necessarily of ACT. In fact, such reactions frequently have an activated complex which is almost loose and their reaction

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* A new development in the field, involving the direct observation of the internal energy distributions of these products of molecular beam systems, by measuring their infra-red chemiluminescence, has been devised by McDonald and coworkers.[68] It promises to provide much needed information, nicely complementing the measurements of Y. T. Lee *et al.*

rate constants can be calculated by ACT using an essentially loose complex. The activated complex for the reaction rate does not necessarily, in fact usually does not, coincide with a " transition state " region where marked dynamical excitation or de-excitation occurs.

The phase space theory of reactions,[71] unlike activated complex theory, aims at predicting final states of reaction products without using properties of the potential energy surface for intermediate configurations. Because of the increased density of final rotational-orbital states with increasing energy, the common phenomenon of an inversion in the final vibrational state population requires an at least partly-dynamical, rather than a purely phase space, argument. The reaction cross-reaction, like the rate constant, depends on the dependence of the potential energy surface on internal coordinates. In the case of the loose activated complex, this dependence is simple and the cross-section can be calculated by phase space theory, as well as by ACT. For other complexes, a more detailed (statistical-dynamical) theory is needed. Never-the less, the idea of counting phase space states of products, like the idea of counting activated complex states, is a significant one for future modifications, and has had a very stimulating effect on the field. We return to the statistical-dynamical problem in the next section.

Recently, in a most interesting development [72-74] Levine, Bernstein and coworkers have found that the distribution of vibrational states of products of some A+BC reactions can be presented by $P_{ro}(E-E_v)P_v(E_v)$, where $P_{ro}(E-E_v)$ is the density of rotational-orbital states and for a rotational plus translational energy of $E-E_v$ and is proportional to $(E-E_v)^{\frac{3}{2}}$ for this system. $P_v(E_v)$ was found empirically to be $\exp(-\lambda_v E_v)$, where λ_v is a constant. (A vibrational population inversion corresponds to a negative λ_v). Such an exponential dependence can be derived on statistical grounds * if one allows the coordinate to take on unlimited (or almost unlimited) values of E_v, but such a situation presumably does not apply here and a different explanation must be sought. The phenomenology has been extended to a conditional rotational distribution.[74] The general development is discussed by Levine and Bernstein in their Discussion paper, both for product and angular distributions.

5. STATISTICAL-DYNAMICAL THEORY

A statistical-dynamical theory is one which would employ approximate dynamics for one or more of the degrees of freedom and use a statistical approximation for the remainder. For example, in a treatment of vibrational distribution of the products it might use analytic or trajectory calculations for collinear collisions to calculate an *ab initio* $P_v(E_v)$ in the preceding section (but caution is needed) and use the statistical $P_{ro}(E-E_v)$ for the remaining coordinates. One simple example, not appropriate to these highly exothermic or endothermic reactions but more appropriate to some thermoneutral reactions without marked reaction path curvature has been given.[22] It uses a vibrationally adiabatic approximation for the vibration. The remaining coordinates are treated statistically. An integral equation for the reaction cross-section was then solved. The results for the reaction cross-section were in reasonable agreement with trajectory data, without introducing any unknown parameters.[22] An analogous procedure could be employed for other models for calculating $P_v(E_v)$.

A classical path quantum calculation for collinear collisions has been used to relate $\langle E_v \rangle$ to reaction path curvature.[38] (Cf. also ref. (44), where the phase-averaged

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* e.g., in ref. (73) it was derived by maximizing an entropy $-k\sum_n P_v \ln P_v$ subject to a condition of a preassigned $\langle E_v \rangle$, i.e., $\sum_n E_v P_v$. The derivation placed no upper limit on E_v.

result is $\langle E_v \rangle$.) Thus, in a sense the $P_{ro}(E-E_v)P_v(E_v)$ in ref. (72) and (74) is a form of a statistical-dynamical theory, but only in some average way, since the form of $P_v(E_v)$ used [72, 74] differed from that estimated in approximate dynamical calculations.[38] We have already commented on the shortcomings of the usual classical path forced-oscillator problem for treating large excitations.

An example of a statistical-dynamical theory which relates RRKM theory for energy distributions in the activated complex to energy distributions of the products has been given by Herschbach and coworkers,[75] who treated the dynamics for the loose activated complex. Their result is the same, they note, as would be obtained from phase space theory. RRKM theory and phase space theory have been shown [76] to be equivalent for the case of a loose activated complex (and zero potential energy barrier). This result is not unexpected, since phase space theory [71] does not use any detailed properties of the surface on one hand, and since the dynamics from loose activated complex to products are simple, on the other.

As noted earlier, with other systems other models need to be considered and can be developed in order to attempt to deduce the properties of the activated complex from those of the products and vice versa.

6. SUMMARY

The extensiveness of references in recent reviews [25] reveals both the enthusiastic activity in this field and the sobering fact that much remains to be done, even in the field of inelastic collisions. Fully collinear inelastic collisions are reasonably well-understood analytically, and substantial progress has been made in the three-dimensional ones as well, at least when the interactions are not too strong. Suggestions range from the purely dynamical to a partial use of dynamics in one regime and a use of statistical in another.[25]

The situation for reactive collisions is qualitatively fairly well-understood for collinear collisions. There has been some progress quantitatively, both for the near-adiabatic and, to some extent, depending on one's willingness to accept the cited classical path estimate, in the more nonadiabatic regime as well. For the fully-three dimensional collisions there is again some qualitative understanding and, in the case of rather special models (e.g., spectator stripping; hard bodies), quantitative analytical insight. The progress is slowed, in comparison with the collinear case, by the absence of diagrams similar to the highly useful and much-studied skewed-axes plots of potential energy contours. (To paraphrase a quite different remark of Herschbach at an earlier Discussion, the trouble with three-dimensional systems is that they have two dimensions too many!)

For this reason, phenomenology such as that discussed by Levine and Bernstein for reactive collisions is a most welcome one, with its use of some statistical insight. The possibility, too, of extending activated comples theory with the addition of dynamical elements, i.e., of having statistical-dynamical theories is already with us. Two examples have been given in the previous section and more and better ones will undoubtedly be developed.

In the realm of exact calculations, exact classical theory remains the most potent method for treating experimental data on simple chemical reactions. Moreover, semiclassical theory may become a significant method for including the quantum effects absent in the purely classical calculations. While individual S-matrix elements are sometimes in error by a factor of two, the averaging that occurs when a reaction cross-section is calculated from S-matrix elements might reduce the error further, to the extent that some of the errors in the elements may be random.

The present symposium touches on many of these and related questions, and represents one more step toward answering some of the questions. At the very least, we all enjoy it.

[1] J. N. Bronsted and K. Pedersen, *Z. phys. Chem.*, 1924, **A108,** 185, cf. P. R. Wells, *Linear Free Energy Relationships* (Academic Press, New York, 1968), Chap. 5.

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