dulans.[77] This resonance is nonstructured, has a g factor of 2.0042, and is not readily saturated by microwave power. Formation and decay kinetics are complex for this species, and dichlorophenyldimethylurea has been demonstrated to inhibit the formation of this radical. Although Weaver has named this resonance signal III, we prefer not to apply this title until this species is demonstrated to occur in other algal species. A similar resonance has been detected by Norris, *et al.,*[78] in the thermophilic blue-green alga *Synechoccus lividus*. However, the *S. lividus* signal appears to be associated only with PS 1 and has been assigned to the flavoprotein flavodoxin.

Projections

Although a sizable number of radical entities have been observed by esr in photosynthetic organisms, future investigations must focus on those that are not presently detectable. Many of these "hidden" intermediates could provide the basis for cracking such difficult puzzles in electron transport as the oxygen evolution center, sites of photophosphorylation, and the nature of the intermediate electron-transport chain. Additionally, future research will increasingly be concerned with the formation of model systems and the reassembly of photosynthetic units from constituent parts.

(77) E. C. Weaver, *Nature (London)*, **226**, 183 (1970).
(78) J. R. Norris, H. L. Crespi, and J. J. Katz, *Biochem. Biophys. Res. Commun.*, **49**, 139 (1972).

Application of such powerful techniques as stop-flow, rapid-freeze, and flash photolysis will continue to dominate photosynthetic esr investigations. Extension of transient flash photolysis esr systems into the microsecond domain should make possible the search for short-lived radical components in the intermediate electron chain (*e.g.*, plastosemiquinone). Likewise, steady-state or light-modulation experiments can be expected to increase our knowledge of pool sizes and energy migration mechanisms. Although spin labeling has been generally neglected in photosynthetic studies, specially tailored cofactors could provide a means for esr to monitor changes of transition metal species at physiological temperatures or conformational changes of protein complexes involved in energy storage (photophosphorylation). Application of cross-relaxation phenomena may likewise allow the esr practitioner to view changes in the paramagnetic state of significant ion species (*e.g.*, Mn, Fe).

This overview of the contribution of esr to our current knowledge of photosynthesis has been necessarily brief. However, it is the authors' desire that the spirit of hope and anticipation for future success in esr investigations in the biological realm will be transmitted to the reader.

Simple Kinetic Models from Arrhenius to the Computer

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"I consider induction to be that form of demonstration which upholds the sense, and closes with nature, and comes to the very brink of operation ... for hitherto the proceeding has been to fly at once from the sense and particulars up to the most general proposition, as certain fixed poles for the argument to turn upon, and to derive the rest ... Now my plan is to proceed regularly and gradually from one axiom to another, so that the most general are not reached till the last; but then, when you do come to them, you find them to be not empty notions but well defined, and such as nature would really recognize as her first principles, and such as lie at the heart and marrow of things ...

Don L. Bunker was born in San Fernando, Calif. He obtained a B.S. in Chemistry in 1953 from Antioch College and earned the Ph.D. in Chemistry at California Institute of Technology in 1957, under the direction of Professor Norman Davidson. He was at first a staff member at the Los Alamos Scientific Laboratory, but moved to the University of California at Irvine when it was founded in 1965. He is now Professor of Chemistry there.

Those who aspire not to guess and divine, but to discover and know, who propose not to devise mimic and fabulous worlds of their own, but to examine and dissect the nature of this very world itself, must go to facts themselves for everything."

F. Bacon, 1620

"The principles of thermodynamics occupy a special place among the laws of nature ... their validity is subject only to limitations which, though not, perhaps, of themselves negligibly small, are at any rate minimal in comparison with many other laws of nature ... there is no natural process to which they may not be applied ... considerations of molecular theory are less suited to correct established thermodynamical laws than to be themselves accommodated thereto."

W. Nernst, 1917

"The underlying physical laws necessary for the mathematical theory of a large part

of physics and the whole of chemistry are thus completely known, and the difficulty is *only* that the exact application of these laws leads to equations much too complicated to be soluble."

P. A. M. Dirac, 1929
(italics added)

This is an article on chemistry, not the philosophy of science. But it is far from an impartial one. It will be consistent with the author's own predilection to begin with an observation: the vast majority of useful chemistry, pure or applied, is done and will continue to be done by Baconian inductive methods. The article is written to comfort and encourage other inductionists, some of whom may not have realized that they belong to a recognizable school with a definite scientific outlook. Deductionists—those who prefer the second or third of the above epigraphs— will not necessarily be pleased by what follows.

Induction in chemistry is the process of making ever more inclusive models of molecular (in this case kinetic) behavior. At first an inductionist's logical construct may explain only the results of a single experiment. The aim is to extend the description, adding or discarding elements, until the limits of its applicability to wider classes of phenomena become both intuitively clear and clearly describable. Chemists of this persuasion are pleased with themselves when they find they have guessed well which parts of physics are important for their purposes, and which are not; and when their reasoning leads them to unexpected insights and relationships they would not otherwise have seen. They like to have their chemical judgment vindicated, and they relish unexpectedness and the role of luck in their research.

Deductive thinking appeals to a quite different, usually more conservative kind of scientist. Deductionists would rather appeal to axiomatic authority than to crucial experiment. They value rigor—a word without any meaning whatever in inductive science. It is interesting to note that both thermodynamics and quantum mechanics began inductively, and were stylistically transformed later, after they became well enough established to attract formal theoreticians. Those who practice formal scattering theory in kinetics today are, on the whole, as different from Bohr and Planck as the Nernst quotation above is from anything that might have been said by Joule, or Helmholtz, or Boltzmann.

Chemistry can use a moderate number of deductionists, because their work is helpful to us in a variety of ways. In addition they impress us, and we respect them, for the skill and grace with which they execute their formal arguments. This should not distract us from the main flow of chemistry, though, or persuade us that deduction is more difficult than induction. Our principal focus should still be on the broadly challenging task of understanding and explaining what molecules really do, and the interplay of induction with formalism should not waver away from this for long. The story of the chemistry of elementary reaction rates illustrates this very well.

Arrhenius Had the Right Idea

A good inductive model should have several attributes.

(1) It should be intentionally incomplete. Those parts of basic principle that will only clutter up the description without contributing to understanding should be left out. It is true, as is often said, that (conversely to deduction) an inductionist wants to reason from the specific to the general—but certainly not the perfectly general. That is not the object of chemistry. We view the possible disproof of an inductive theory by counterexample not as a flaw of the method, but as an essential and welcome part of the process of understanding.

(2) At the same time, the model should be able to be refined. Experimental access to molecular dynamic detail continually improves, and it is poor inductive practice to foreclose the possibility of later insertion of unexpected new knowledge.

(3) Calibration to experiment is essential. An assessment of the uniqueness with which laboratory information determines model parameters is also very desirable. It is the process of calibration and subsequent use that makes the heaviest demands on one's chemical judgment. One has to decide what it is reasonable to use the theory for, and when it should not be applied. Every model has intentional limitations, and even with the most tempting opportunity for application or extension, one cannot ever afford to forget what these limitations are.

There is an old saying that "physical chemistry is the study of all those quantities whose negative logarithm is linear with $1/T$." This simply recognizes the large role that Boltzmann distributions play in the things that we observe. When Arrhenius wrote

$$k = Ae^{-E_a/RT} \tag{1}$$

he incorporated this idea into kinetics. The activation energy E_a clearly must be related to a kind of threshold of energization above which reaction may occur. We are invited to develop a systematics of E_a, by fitting this expression to observation, and to see whether the results make sense. The preexponential factor A is left undefined, for future refinement.

Associating it with a collision frequency, for bimolecular reactions, is a purely inductive forward step

$$A = P(8\pi kT/\mu)^{1/2}(r_1 + r_2)^2 \tag{2}$$

Letting collisions between reactants with reduced mass μ and equivalent rigid sphere radii r_1 and r_2 lead to reaction with probability P introduces the notion of collisional energization by structuring the previously undefined parameter A. (The additional temperature dependence is negligible compared to that arising from any appreciable E_a.) The steric factor P is now the quantity left open to further refinement of the model.

Transition-State Theory: The Deductionists' Revenge

It was natural for the thermodynamicists, when their position in physical chemistry was one of dominance, to anticipate that kinetics too would fall before the power of their methods. Despite Nernst's optimistic statement, subsequent history cannot be said to have fulfilled their expectations.

Transition-state theory (activated complex theory, absolute rate theory) has, in its most usual introductory presentation, a deceptively smooth and simple

appearance. Inductionists who try to look beyond the standard language often find it difficult to perceive what, if any, simplifying assumptions have been made. Perhaps there are none? A respected textbook[1] of chemical kinetics tells us that ". . . the equilibrium assumption (*see below*) is certainly valid when reactants and products are at equilibrium . . . the theory therefore correctly predicts rates at equilibrium. If the theory were significantly in error before the establishment of equilibrium, rate constants would be expected to change as equilibrium is approached. Such a phenomenon has not been observed.

"The problem of calculating the rate constant has been reduced by the Eyring treatment to evaluating the partition functions for the normal and activated states; for this to be done, the nature of the activated complex must be known or postulated. In principle, the structure of the activated complex can be determined by the methods of quantum mechanics . . ."

The literature abounds with similar statements encouraging the belief that, given accurate potential energy surfaces, we would always be able to calculate reaction rates in a simple and rigorous way.

Although the foundations of transition-state theory may seem at first obscure, the spirit and motivation of the theory are almost instantly evident. Transition state is the theory that preserves the maximum possible amount of both the authority and content of thermodynamics. As such, it is as anti-inductive as any treatment of kinetics can ever be. One simple indication of this is the occurrence of the description "absolute"—a word that an inductionist would be most unlikely to choose.

In the simplest description we are asked to contemplate an equilibrium between reactants (R_1, R_2, . . .) and activated complexes ($R^\ddagger$)

$$R_1 + R_2 + \ldots \rightleftarrows R^\ddagger$$

$$K^\ddagger = e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \qquad (3)$$
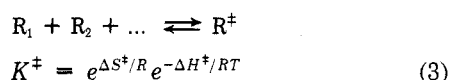
with subsequent decomposition frequency $\kappa kT/h$. The kT/h comes from conversion of the statistical mechanics of a vibrational mode of $R^\ddagger$ to a that of a translational coordinate of product separation. Separation in the direction of products occurs with probability κ, and

$$k = \kappa kT K^\ddagger/h \qquad (4)$$

Alternatively, we may express the thermodynamic quantities in eq 3 in statistical language.

If the equilibrium really exists, then the dynamics of the collisions between R_1 and R_2 that produce $R^\ddagger$ can never be important. Thus the theory avoids both the first ("absolute") and the second of the desirable attributes of inductive models. This leaves us at somewhat of a loss as to how to evaluate κ, though we may wish to keep it around to express definite auxiliary corrections such as the one associated with quantum-mechanical tunnelling.

A clearer view can be obtained if we go ahead and think about collision dynamics anyway. Two complicated molecules collide. Apart from the reaction coordinate, their internal degrees of freedom remain

at the initial equilibrium temperature T. How? In the gas phase, only if the reaction coordinate is completely separable from all the others; this is the easiest to visualize of the more precise attempts at justification. (More specifically, the nonreactive degrees of freedom remain in the same quantum state—"adiabaticity.") This assumption is certain to be inexact to some extent in any real reaction. It might of course turn out to be roughly correct, or perhaps true in an average way, in some large number of situations. This is the basis of the usefulness of the theory for correlating experimental data. But the point here is that we are still prohibited from using any knowledge that we might acquire about the actual behavior of the nonreactive degrees of freedom. A person who measures these things, asked to relate his findings to transition-state theory, has to grope for a sensible answer, because the question implies inductive properties that the theory does not have. Transferring the whole discussion to the liquid phase helps little. An infinite density of truly instantaneous binary collisions might fulfill the temperature relaxation requirement for the nonreactive vibrations, and give a diffusive definition to κ, while producing no other important effects. Even the most ideal solvent is surely far short of conforming to this description.

Is Unimolecular Kinetics Solved?

The theory is in a very satisfactory state; it has been summarized in fully elaborated form[2] and is available as a canned computer program.[3] But "solved" is a word one does not use lightly in inductive science. The development of theoretical unimolecular kinetics, from F. A. Lindemann through O. K. Rice and R. A. Marcus, was a masterpiece of induction. Its present chemical status, now that it is beginning to accumulate elements of deductive vocabulary, deserves thoughtful appraisal.

At the level proposed by O. K. Rice and others 35 years ago, the theory already selectively singled out the most important underlying physical phenomenon—the exchange of energy among the internal degrees of freedom of an energetic polyatomic molecule. "Oscillators" (definition left open to future refinement) randomly redistribute energy with frequency ν (experimentally calibrated, and about the same for similar reactions). The number of oscillators s also became, by usage, a part of the experimental calibration.

$$k = \int_{E_0}^{\infty} \frac{Z[M]P(E)k_a(E)}{Z[M] + k_a(E)} dE \qquad (5)$$

$$k_a(E) = \nu[(E - E_0)/E]^{s-1} \qquad (6)$$

The threshold is E_0, $P(E)$ is the probability of an energy E, and M represents the collection of all the colliders present. A plausible model must also be specified for the collision rate constant Z and $P(E)$, but this auxiliary problem is not very troublesome. The contribution of Marcus was positively to identify the oscillators as vibrational normal modes, whose properties need to be introduced explicitly; to provide for the inclusion of molecular rotation; and to let s rede-

(1) K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965.

(2) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley, New York, N. Y., 1972.

(3) QCPE-234, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind.
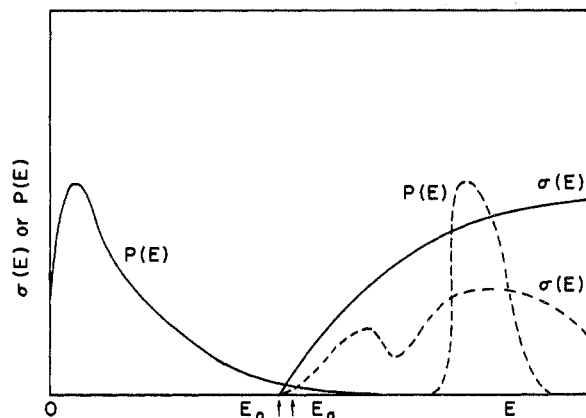
Figure 1. Cross sections $\sigma(E)$ and relative collisional energy distributions $P(E)$. Solid lines: Boltzmann thermal energy distribution and line-of-centers cross section; dashed lines: two of many other possibilities. E_0 is threshold energy; E_a is activation energy.

fine itself (with experimental assistance) as the actual number of modes. This leads to a specific statistical formulation of the formerly parametric quantity ν. The process of arriving at this was enlivened by the appearance of a competing model, now discarded, proposed by N. B. Slater. This model, although invented by a mathematician, deserves one of the highest accolades that chemical inductionists can award: it was of immense service by being wrong in an instructive way.

Examination of the details of the full theory, nowadays usually designated by the initials RRKM,[4] shows that it now has as few adjustable parameters as the transition-state theory does. It requires, for the evaluation of ν, that a critical configuration be defined, so that the quantum-state density of a molecule caught in the act of reaction may be evaluated. It is unnecessarily confusing that many people refer to this critical configuration as an "activated complex," even though it has neither a separable reaction coordinate over finite distances nor an implied equilibrium with unenergized reactant. (Transition-state theory is approached in a certain kind of limit, but not a practically attainable one.) The RRKM theory is now being used, perfectly legitimately if its simplifying assumptions are remembered, as a rationalizing treatment for wide assortments of chemical reaction rates. All this, perhaps together with a tendency for newcomers to assume that anything with partition functions must be transition-state theory, creates an impression of drift away from the original style in which the treatment was developed.

But the workers in this field will be able to stave off deductionism. The reason is that, inductively, compliance with the basic assumption, *random* redistribution of energy, is not obligatory but must be reconfirmed for every molecule. The possibility of its failure was first pointed out by Rice[5] (in 1930!). At the present time there is both lively discussion[6] and an actual experimental instance[7] of the possibility of "non-RRKM" unimolecular kinetics. This would never happen with an "absolute" theory. The anomalous molecule is

(4) Rice, Ramsperger, Kassel, and Marcus.

(5) O. K. Rice, *Z. Phys. Chem., Abt. B*, **7**, 226 (1930).

(6) The author's contribution to this may be found in *J. Chem. Phys.*, **59**, 4621 (1973).

(7) J. D. Rynbrandt and B. S. Rabinovitch, *J. Phys. Chem.*, **75**, 2164 (1971).

$$CF_2\text{---}CF\text{---}CF\text{---}CF_2$$
$$\diagdown\diagup\qquad\diagdown\diagup$$
$$CH_2\qquad\quad CD_2$$
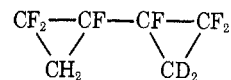
and there may be many others. Many unimolecular kineticists hope so. It is not as yet clear how the RRKM treatment is to be refined or modified to take account of this sort of thing, but there is refreshingly little absolutism being associated with the problem.

The Cross Sectionists Are Revolting

Bimolecular kinetics is much less solved than unimolecular, in any sense of the word. But important advances are being made.

The idea of a reaction's total cross section, as a description alternative to the rate constant, has been around for a long time. In eq 2, we let $P = 1$ and $\sigma = \pi(r_1 + r_2)^2$. Experimental calibration then tells us that it is as if the colliders had an effective cross section of σ. Of course, this does not necessarily imply anything about the actual sizes of the reactants, if some collisions lead to nonreactive scattering. It is merely a convention for summarizing reaction probability.

A very early model that uses this idea in a simple way is the Langevin construction of cross sections for ion–molecule collisions. A centrifugally corrected potential function for an ion–neutral interaction (reduced mass μ, polarizability α, impact parameter b, electronic charge e, relative translational energy E) is

$$U(r) = -(^1/_2)\alpha e^2/r^2 + Eb^2/r^2 \qquad (7)$$

Straightforwardly equating to a cross section the target area within the largest b that allows the maximum in this function to be traversed gives

$$\sigma = \pi(2\alpha e^2/E)^{1/2} \qquad (8)$$

This plays a role similar to that of all but P in eq 2. It allows experimental results to be systematized by comparison with what would be expected if every collision that surmounts the rotation barrier were effective.

Fractionating A into target area and relative energy parts for all reactions, not just ionic ones, reveals further underlying structure in eq 2. The relationship between $\sigma(E)$ and k is

$$k(T) = \int_0^\infty \sigma(E)P(E)dE \qquad (9)$$

in which at this stage[8] $P(E)$ is the thermal Boltzmann distribution

$$\pi\mu(2/\pi\mu kT)^{3/2}Ee^{-E/kT} \qquad (10)$$

Letting σ be constant above a threshold E_0 does not lead to eq 2; saying

$$\sigma(E) = \pi\sigma_0^2(1 - E_0/E) \qquad (11)$$

does. This corresponds to imposing a threshold on the radial ("line of centers") part of relative kinetic energy, disregarding the tangential part. Other choices are possible; the situation is diagrammed in Figure 1. The activation energy is located somewhere near the crossing of $\sigma(E)$ and $P(E)$ and is evidently a

(8) M. A. Eliason and J. O. Hirschfelder, *J. Chem. Phys.* **30**, 1426 (1959).

little higher than the threshold E_0. For the eq 11 model the difference is $\frac{1}{2}kT$. But it must be emphasized that E_0 and E_a are both purely experimental quantities. Close relationship to a potential barrier height, although very often conveniently present, is not inevitable.

This kind of formulation lays a temptation before us that is not present in transition-state theory. All we have to do to make a clean break with thermodynamic authority is to assert *either* that eq 10 is not the only feasible form of $P(E)$ or that E is not the only variable whose effect on σ will be of interest. Our armaments will be drawn from "the facts themselves": if even one such experiment can be found, the confining wall of transition-state vocabulary will have been breached. Thus, although all this could be discussed 50 years ago, it was only when the experimental cross-section avalanche began in the early 1960's that the non-Boltzmann movement gathered real momentum.

The great opportunity that this presents to inductive kineticists is for vastly accelerated and deepened model refinement. Such comparisions as can be made between transition-state theory and inductive models are at their most facile at the Arrhenius-simple collision level. Descending to the $\sigma(E)$ stratum largely leaves this behind; any $\sigma(E)$ contains enough information to evaluate k, but not *vice versa*. If more interesting models can be made in σ language, and their parameters can actually be calibrated experimentally, should we not explore the possibility of a still more fundamental level of description? The potential energy for the reaction, once specified, contains information equivalent (*via* mechanics) to a fully detailed $\sigma(E,$ reactant internal states, collision geometry, . . .), as well as any of its partly averaged forms like $\sigma(E)$, and eventually k. Perhaps we can make a simplified, refineable, experimentally calibrated potential energy model for a reaction, and then ask it directly to predict experimentally inaccessible molecular behavior that we would like to understand and describe.

Of course potential energy surfaces can also be calculated from the Schrödinger equation, and there are now several reactions for which we no longer have to add the qualifier "in principle." So we should expect to collide with a counterforce of quantum chemists. The place where we are most likely to meet them is at the computer.

Using a Computer Inductively

A computer is much more than a fast data processor. It is a research tool in itself, whose impact on chemistry is a long way from being fully felt. One of the best research modes of computing is that of simulation, in which sets of assumptions are made and their detailed consequences compared, by way of intervening logic or mathematics too complicated for unaided human execution.

This has been done in many fields, and in the kinetics discussed in this article it has been particularly useful in bridging the gap between potential energy surfaces and cross sections. Such a calculation is called a trajectory study. It ordinarily proceeds by representative random ("Monte Carlo" or other) sampling of initial conditions for reaction events, finding the outcome of each one by numerical step-

wise solution of Hamilton's equations of motion and classification of accumulated results in a form that can be compared with experiment. Samples of many thousands of reaction events can be handled, so that fairly good resolution of things like product energies and scattering patterns can be obtained.

All trajectory studies must look very much alike to the uninitiated. In reality they are strongly divided along the lines which form the main theme of this article. This is evident even before calculations begin. Should classical mechanics even be used? Will the coordinates and momenta initially have, or retain, meaning? Inductionists reason qualitatively about this for their particular reaction, and if favorably convinced, cheerfully accept a small risk that they might sometime be proved wrong. Then they go ahead and try to do something useful. Formalists are more likely to prefer a rigorous demonstration in advance. The quality of comparative quantum scattering *vs.* classical trajectory calculations has indeed slowly and steadily improved over the years, and it is now possible to have an *a priori* demonstration of the relationship of transition-state theory to reality.[9] But meanwhile much else has happened.

Once the potential energy for a system of atoms reaches the computer, there is little external clue to its origin. It might be a transcription of the results of quantum mechanics, or it might be an adjustable empirical function designed to do for three or more atoms what a Morse function does for two. Likewise there is little difference in the process of predicting the unobservable properties of the reaction. But the style of discussion surrounding the results will show there is a vast difference between attempting to make kinetics deducible and trying to find out what experiments collectively mean. There is also a prominent practical difference between using quantum mechanics and laboratory measurement as the ultimate source of truth: quantum mechanical deduction monopolizes, but is confined to, very simple chemical systems. There is no point any more in trying to make an empirical treatment of $H + H_2$ or $F + H_2$. Of course there will be borderline cases, in which more or less severe simplifying assumptions have to be made in the quantum calculation. Inductionists and quantum chemists will not necessarily agree on the quality of the results. A major example given below, $H + CH_4$, is a case of this sort.

Inductive computational simulation began with unimolecular reactions, helped establish RRKM theory, and still plays a significant role in this field. But the more typical and widely employed techniques have grown up around bimolecular reactions, which will be emphasized here. The first such reactions to be so studied were those famous for their early utility in molecular beam studies

$$M + CH_3I \longrightarrow MI + CH_3 \qquad (12)$$
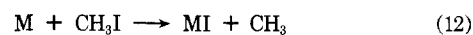
where M is an alkali metal. The display in Figure 2 shows old[10] and new[11] beam-derived data, of the sort that can be used for calibration or attempted predic-

(9) Both classical and quantum mechanical studies of naturally occuring adiabaticity and other transition state attributes of reactions have been made. Key papers are by S. F. Wu and R. A. Marcus, *J. Chem. Phys.*, **56**, 3519 (1972); K. Morokuma and M. Karplus, *ibid.*, **55**, 63 (1971); D. J. Diestler and M. Karplus, *ibid.*, **55**, 5832 (1971).

(10) D. R. Herschbach, *Discuss. Faraday Soc.*, **33**, 149 (1962).

(11) M. E. Gersh and R. B. Bernstein, *J. Chem. Phys.*, **56**, 6131 (1972).
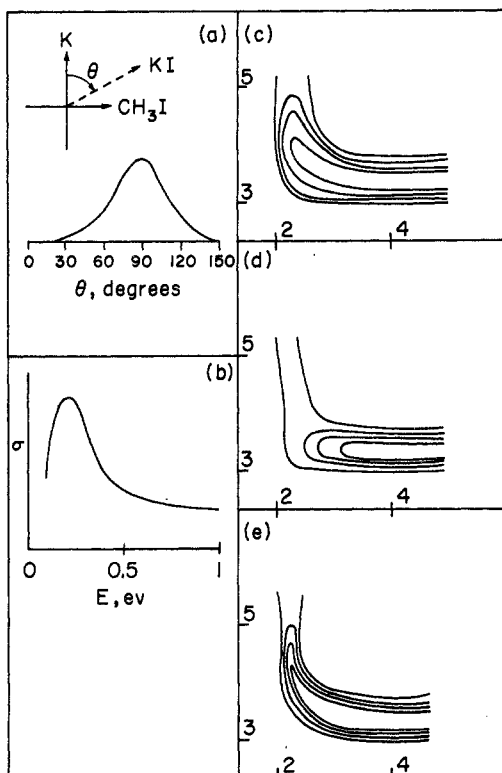
Figure 2. (a) Thermal molecular beam scattering data (1962), intensity *vs.* laboratory angle. (b) Cross section *vs. E*, 1972 K + CH₃I molecular beam experiments. In parts c–e the reaction path for a collinear encounter is from upper left to lower right; descending 5-kcal potential energy contour lines *vs. r* (alkali–I) and *r*(I–CH₃) in Å are shown. Map e is for Rb, the others for K. Figures a–e were drawn after ref 10–14.

tion, along with three[12-14] successive stages of refinement of the collinear part of the potential surface.

The history of this research is a tangled one, and the details should not be given here. In a general account, the following are the important points. The most difficult part of the work is that of developing computable representations for the potential energy. A recent review of the associated technology is available.[15] The standard, collinear potential maps of Figure 2 contain an ever smaller fraction of the important information as refinement proceeds. Only the latest of the three examples treats CH₃ as four particles rather than as a single lump. In this latest calculation the molecular beam experiments that use oriented CH₃I played a dominating part in the calibration, and the description of the noncollinear, angle-dependent forces is of as much importance as what is shown here. For M = Rb a provisional potential has been obtained, based on low-energy data; its predicted energy-dependent cross section is awaiting test by the experimentalists.[14] In general, one has to keep in mind an intended level of resolution up to which the calculation has been refined. The earliest trajectory study really distinguished only between the "early downhill" or "attractive" surface shown, and its converse; the later ones are more detailed. The overall level of resolution has to be estab-

lished by both mathematical and chemical reasoning and then clearly described. The results are sometimes challenged on the basis that no rigorous test of the uniqueness of an experimentally determined potential can ever be made. However, uniqueness tests of an inductive model can themselves be inductive without further disturbing anyone.

The computational techniques for three-body, (A + BC)-type reactions have become standardized and are being made universally available. Recent typical examples of their application to gas-phase non-Boltzmann problems include molecular beam interhalogenation[16] and alkali–diatomic halogen[17-19] reactions; chemiluminescence-related systems[20-22] like H + Cl₂, H + Br₂, Cl + HI; three-body diatomic dissociation and recombination;[23,24] ion–molecule reactions;[25] and a spate of work on the F + H₂ chemical laser system.[26-29] Most of these are empirical or partly empirical studies. Surveys of the systematics of these reactions, using fictitious species with arbitrarily variable atomic masses, etc., are also of interest.[30,31] Extensions of the same sort of technique to four-center hydrogen–halogen reactions have been made.[32,33] There is at least one trial extension to solution chemistry.[34]
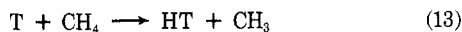
The CH₅ Problems

Reactions on the CH₅ potential surface have recently been subjected to an unusually successful series[35-37] of inductive studies. The latest calculation is in many ways the most ambitious attack of this sort that has ever been made. The CH₅ system is the most important one that is wholly independent of molecular beam data. Whether it can be treated deductively with present techniques is a controversial matter. Some unsuccessful or partly successful attempts to secure a nonempirical potential have been made; it is likely that sufficiently extensive and reliable *ab initio* results will become available sometime.[38] For all these reasons, CH₅ is a key problem, occupying the same kind of position that H₃ once did for A + BC problems.

(12) N. C. Blais and D. L. Bunker, *J. Chem. Phys.*, **37**, 2173 (1962).
(13) L. M. Raff and M. Karplus, *J. Chem. Phys.*, **44**, 1212 (1966).
(14) D. L. Bunker and E. A. Goring-Simpson, *Discuss. Faraday Soc.*, **55**, 93 (1973).
(15) D. L. Bunker, *Methods Computational Phys.*, **10**, 287 (1971). Minor errata available from the author.

(16) T. B. Borne and D. L. Bunker, *J. Chem. Phys.*, **55**, 4861 (1971).
(17) M. Godfrey and M. Karplus, *J. Chem. Phys.*, **49**, 3602 (1968).
(18) P. J. Kuntz, M. H. Mok, and J. C. Polanyi, *J. Chem. Phys.*, **50**, 4623 (1969).
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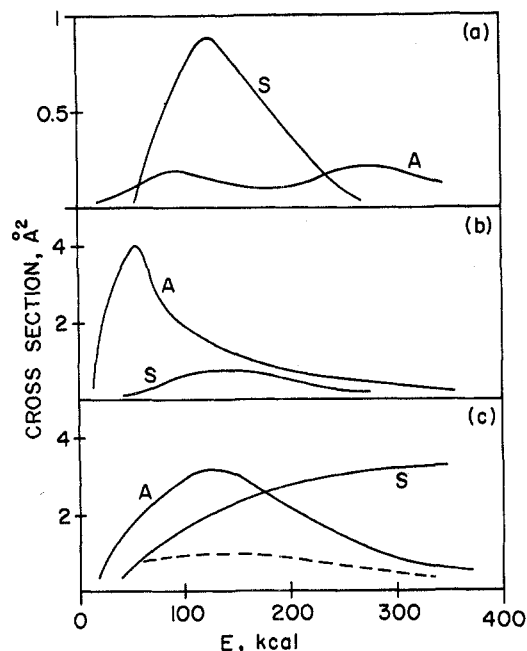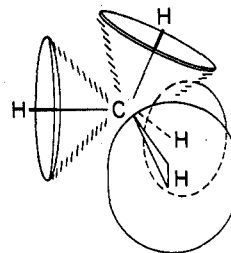
Figure 3. Cross sections for abstraction (A; eq 13) and substitution (S; eq 14) for the T + CH_4 reactions. Parts a–c were drawn after ref 35–37, respectively. In part c the dashed line represents the Walden-inverting component of substitution.

Figure 4. Approximate illustration of the deployment of the abstraction (inside cones) and substitution regions in the T + CH_4 reactions. Cones have been delineated, but in reality there are no sharp or impenetrable boundaries.

The information available for experimental calibration, not all of it equally satisfactory, includes relative cross sections for

$$T + CH_4 \longrightarrow HT + CH_3 \tag{13}$$

$$T + CH_4 \longrightarrow H + CH_3T \tag{14}$$

at a series of E below 65 kcal and yield measurements in recoil tritium systems, a variety of striking isotope effects, and the usual spectroscopic and thermochemical information for the various stable configurations of the atoms. Simulation experiments proceeded through three stages: (1) treating CH_3 as a single lump; (2) treating CH_3 as CH_3, but allowing only one H in CH_4 to be reactive at a time, with possible swapping of this reactive status between atoms during the calculation; (3) making a model that has no artificial limitations on the kinds of reactive channel that may be present. The best efforts of these three procedures to predict the unknown $\sigma(E)$ for eq 13 and 14 are compared in Figure 3. Only the final one corresponds to a potential that correctly reproduces both the cross-section ratio at low energies and all of the observed isotope effects.

The model that emerges from this is thought to be fairly unique, with respect to major features of the potential, at about the 0.5 Å, 5 kcal level of resolution. This means, for example, that it is only about 50% better than the top illustration in Figure 2 in its location of the most important feature—an abstraction barrier rather than a steep downward slope—along the collinear T–H–C reaction path. On the other hand, a system of this complexity has many more dimensions, many more topological features,

many more ways of projecting information into a planar map than A + BC has. To obtain this kind of resolution in a more or less comparable way for all of them is a useful achievement. Another way to express this is to point to the greatly increased number of alternative potentials that must somehow be rejected in the course of an inductive test of uniqueness, when the number of atoms becomes large.

Qualitatively, the final model may be described as follows. Using T as a probe of the forces resisting its insertion into CH_4, we would find these to be largest along the surfaces of four cones, surface-to-axis angle about 45°, as illustrated in Figure 4. The boundaries are shown fuzzy because there are no discontinuities, as in a hard-sphere treatment, and a sufficiently energetic T can pass through. Collinear approach, along a cone axis, leads to hydrogen abstraction over a potential barrier which increases from 10 kcal if the approach line deviates from collinearity in any direction. Outside the cones the higher energy T-for-H substitution is favored. The structure will be forced into a trigonal-bipyramidal configuration. Depending on whether the entering T and leaving H have equivalent positions—both axial or both equatorial—the reaction will or will not have Walden inversion. The inversion reaction predominates at relatively low energy and retention at higher energy. The principal variables of the model are the cone angles, the rapidity with which reactive potentials become unfavorable as ideal geometry is departed from, and the character of the collinear abstraction map. All of this is in practice expressed by a series of empirical equations which, once found and parameterized, have many other uses.

The success of this study opens the way for many others, and as a type of problem this is only one subset of those of modern kinetics. And not all kinetics occurs in gases, and not all of physical chemistry is kinetics. Inductive computing has grown slowly, as might be expected in view of its relative difficulty, demands on intuition and judgment, and other things already mentioned. But its practitioners think there are few research fields where so many simple, interesting, traditionally chemical problems are waiting for consideration.