$2p \rightarrow 3s$, $3d$, $4d$, $5d$ and $2s \rightarrow 3p$, where the d orbitals are designed to give good transition moments with the $2p$ Hartree–Fock function. A set of three doubly excited functions of the type $2p^2 \rightarrow 3p3d$ was also included in an eight-term function. For the five-term and eight-term functions α was .3508 and .4588 $\times 10^{-24}$ cm.^{3}, respectively, compared to an experimental value of .39 $\times 10^{-24}$ cm.^{3}. The calculated London force coefficients were 3.75 and 7.0 $\times 10^{-60}$ erg cm.^{6}, compared with a viscosity value of 9.5 $\times 10^{-60}$ erg cm.^{6} (the small value corresponding to the five-term, the larger value to the eight-term function).

Discussion on Chemical Reactivity

K. S. PITZER, *Chairman*

PITZER: It seems to me that it is high time that quantum chemical theorists started predicting chemical facts instead of just explaining what is already known from experiment! I refer primarily to the really basic energy values that determine the direction of chemical reactions, the stability of various possible molecules and the rates of reactions. I realize that a few predictions have been made; I have made a few myself; but predictions of this sort are very scarce in the quantum literature.

In past conferences on quantum chemistry, I am afraid I may have discouraged some of you by holding out 1 kcal/mole as the required standard of accuracy before predictions of energy would be useful in most cases. I believe this is correct for normal substances and room temperature reactions. But let me call attention to an area where calculations to 10 kcal/mole would be welcome. At very high temperatures, several thousand degrees Kelvin, the equilibrium constant is only about one tenth as sensitive to error in the energy as at room temperature. Furthermore, there is great difficulty identifying all of molecular species present under these conditions. Even if mass spectrometry identifies a substance by molecular weight, there is much more information needed. Astrophysical systems likewise invite attention to species unknown in the laboratory. Here is the opportunity for quantum chemists to predict the chemical species present and their properties in systems of real interest. To do so successfully, we must get away from a limitation to closed shells of electrons.

In addition to novel and high energy molecules, quantum chemists should also be dealing with activated complexes for reactions. Many of the same techniques will be applicable here. But now even the simplest case of H_3 is not well-treated.

One promising method comprises S.C.F. calculations including all electrons plus estimates of correlation energies by empirical methods. Such an approach looks encouraging and feasible for some molecules of interest. But it should be possible to omit inner shells in the heavier atoms with better results than have yet been obtained and this would open up many more cases to calculation with reasonable effort. In any event, methods for treatment of incomplete shells need more attention.

Approximations and empirical systems need to be checked against values for known substances, of course, but I urge calculations for the general sort of species for which predictions are to be made, i.e., radicals and other species with abnormal valence.

The explanations provided to chemistry by quantum theory have been very important, but they have come mostly from simple calculations. An apparent exception is the potential barrier to internal rotation about single bonds, which has not been explained in simple terms. But in general, complex calculations are valuable only if they are either extremely accurate or if they lead to predictions of previously unknown information. Since high accuracy of quantum mechanical calculation seems not yet possible for most chemical species, attention had best be concentrated upon substances where even very approximate data will contribute to knowledge.

Now I take the privilege of mentioning briefly a calculation on the $H_2 + H$ ($H_2 + D$, etc.) reaction rate problem which Dr. Mortensen carried out with me. A preliminary report on it will appear among the papers of the 1962 Sheffield Meeting of the Chemical Society.

We consider just the nuclear motion which requires quantum mechanics for light nuclei such

as the proton or deuteron. Any well defined H_3 potential surface can be used. The Born–Oppenheimer separation is made. We integrate numerically the Schrödinger equation for the two dimensional problem including R_{12} and R_{23} of a linear H_3 system. The angular coordinate for deviation from linearity is brought in by an apparently good approximation. By including R_{12} and R_{23} explicitly, one avoids the selection of a "reaction coordinate" which may be a poor approximation for this special case, since the de Broglie wavelength is of the order of other critical distances.

I shall not discuss results since we have only a few sample points and most of these will be in print soon. Also, we do not now have a really good H_3 electronic energy to serve as a potential surface. In principle, however, we can foresee an absolute, nonempirical calculation of rates for this particular simplest set of chemical reactions.

LÖWDIN: It is evident that the fundamental problem in the theory of chemical kinetics is the solution of the time-dependent Schrödinger equation

$$\mathcal{H}_{op}\Psi = -\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t}, \tag{1}$$

$$\mathcal{H}_{op} = \sum_k \frac{\mathbf{p}_k^2}{2m_k} + \sum_{k<l}\frac{e_k e_l}{r_{kl}}, \tag{2}$$

where m_k and e_k are the mass and charge of the particle k, and the sums go over all particles (nuclei and electrons) involved. This equation has a solution in the form

$$\Psi(t) = U(t,t_0)\Psi(t_0), \tag{3}$$

where U is the well-known evolution operator which is linear and unitary in character and is given by the explicit formula:

$$U(t,t_0) = \exp\left\{-\frac{2\pi i}{h}\mathcal{H}_{op}(t-t_0)\right\}. \tag{4}$$

The evolution operator has been studied in great detail in modern field theory, even in the case when $\mathcal{H}_{op}$ depends on time in a commutative or noncommutative way. In the former case, the exponent in (4) has to be replaced by an integral over time and, in the latter case, one has further to apply Dyson's chronological order-product operator.

The quantum mechanical concept of "transition probabilities" can be based exactly on the evolution operator through the relation

$$S_{k\to l}(t,t_0) = |\langle \varphi_l | U(t,t_0) | \varphi_k \rangle|^2, \tag{5}$$

where φ_k and φ_l are the wave functions for the initial and final states involved. This approach leads to a rather neat theory of time-dependent processes which has been treated at the winter institute, and it turns out that the main problem will actually be connected with the question of the "phase" of the wave function $\Psi(t_0)$ at the initial time $t = t_0$.

The purpose of this remark is to point out the importance of the evolution operator approach also in connection with chemical kinetics and the key role of the phase problem. One needs a theory of chemical reactions which is sufficiently general to be applicable also to the biochemical field, and I believe that the evolution operator may prove conceptually useful in this connection.

HIRSCHFELDER: The quantum mechanical problems of reaction kinetics on idealized potential energy surfaces are very interesting [J. O. Hirschfelder and E. Wigner, J. Chem. Phys. **7**, 616 (1939); H. M. Hulburt and J. O. Hirschfelder, J. Chem. Phys. **11**, 276 (1943)]. The problems can be divided into the three general categories: tunneling, change of vibrational quantum number, and effects of curvature in the potential-energy surface.

HOFACKER: In connection with Professor Hirschfelder's remarks, I would like to point out that for homogenous reactions in the gaseous state we may always write the rate R of a chemical reaction formally as

$$R \simeq e^{-\Delta F^*/kT}, \tag{1}$$

where ΔF^* is the free energy of a fictitious molecule M^*, but the structure of this molecule cannot be found by the idea of activated complex as created in the earlier and some later versions of transition state theory. The equilibrium assumption for the activated complex does not even hold in the case of chemical equilibrium between reactant molecules and products. However, there are equilibrium statistical weights for all chemical trajectories crossing the saddle between reactants and product-configurations on the potential energy surface, but, as the reaction path is not a normal coordinate of the supermolecule, the set of reaction trajectories in the saddle-region can only be understood as being produced by very particular interferences between free and bound motions of the system points. Thus, the representative points crossing the saddle cannot be interpreted as corresponding to any equilibrium canonical ensemble of molecules having the potential energy of the supermolecule in the saddle-region.

Writing down the number of representative points crossing the barrier per unit of time one can find an expression like (1). The fictitious molecule M^*, however, to which ΔF^* refers has very little to do with the activated complex as proposed by transition state theory and we must solve the whole complicated problem of the mechanics of the supermolecule in order to find the partition function of M^*.

Speaking in terms of quantum mechanics, the corresponding statements hold, and the arguments are very similar to those given above. For the calculation of chemical reaction rates, quantum mechanics is more suitable than classical mechanics even in the case of nearly classical systems, because it avoids the calculation of a representative number of classical characteristics. So one of the most important problems in chemical kinetics is to solve Schrödinger's equation for the motion of representative pointwaves on the hypersurface of potential energy of the supermolecule. This, however, is an impossible task in most cases, not the least because our knowledge of such hypersurfaces is very limited. What we can do is to try to develop the quantum mechanics of the wave packets with large statistical weights, i.e., those traveling along the reaction path. Approximations must be found suitable for different kinds of chemical problems. [L. Hofacker, Z. Naturforsch., 1963 (to be published)].

Moreover, we should define the rate of a chemical reaction more carefully. According to the principles of quantum-statistics a macroscopic quantity should be found by forming the trace of the product of the system-density matrix and some operator. The operator of chemical reaction rate turns out to be closely connected with the quantum mechanical streaming operator, giving the flux of system points along the reaction path. In the case of a bi-molecular reaction, the matrix elements of the reaction rate operator may simply be defined by

$$r_{\alpha\beta} = \frac{1}{2M_r i}\int_0 \left(\varphi_\alpha^* \frac{\partial}{\partial x}\varphi_\beta - \varphi_\beta^* \frac{\partial}{\partial x}\varphi_\alpha\right)\sigma dq'$$

where M_r is the reduced mass of the reacting molecules, q' indicates all coordinates except the reaction coordinate x, 0 is a surface $x = \text{const}$ (at large distances) from the saddle and $\sigma\, dq'$ the surface element.

Then in a gas with only two-molecule-interactions where there is a reaction

$$\mathrm{A} + \mathrm{B} \rightarrow -------$$

one has to define a reduced two-molecule density matrix $\rho(\mathrm{A}, \mathrm{B})$ so that the rate of the above reaction becomes

$$R = \mathrm{Tr}\,[\rho(A,B)\mathbf{r}]\,.$$

This expression defines the rate of the reaction in equilibrium as in nonequilibrium.

The definition of the reaction rate operator may in a suitable way be given for unimolecular reactions, dissociations as well as intramolecular conversions.

HIRSCHFELDER: Walter R. Thorson, J. Chem. Phys. **37**, 433 (1962) has the best formulation of the quantum mechanical theory of reaction kinetics.

DEWAR: It is perhaps worth pointing out that the Hückel rule is not as commonly stated, a simple consequence of MO theory. MO theory either in the Hückel form or in the various SCF

approximations, does *not* indicate a significant qualitative difference in stability between $4n$ and $(4n + 2)$ membered rings. The argument that $4n$-membered rings do not have closed shell structure applies only to monocyclic hydrocarbons, not to corresponding heterocycles. The same difficulty arises in the bicyclic nonalternant hydrocarbons when all the MO treatments predict similar stabilities for pentalene, azulene, and heptalene. Of these only azulene is aromatic. The only treatment that leads to the correct predictions, that $4n$-membered rings should be less stable than analogous open chain compounds, and that pentalene and heptalene should *not* be aromatic, is a simple perturbation treatment which I introduced ten years ago [J. Am. Chem. Soc. **74**, 3350 (1952)]. It is certainly surprising that this, a perturbation form of the Hückel treatment, should succeed when all the more elaborate approximations fail.

J. CHEN: I agree with Löwdin that one should begin to investigate the time-dependent formulation of chemical reactions, and I believe that such research has been in progress at several laboratories.

I would like to say a few words about dissociative reactions, in particular, the process of dissociative electron capture. Recently, I have been working on the reaction of the type,

$$AB + e \rightarrow A + B^- ,$$

and found for the transition probability $W_{0\rightarrow f}$ the relation

$$W_{0\rightarrow f} \approx |2A_{f0}\langle\chi_f|\nabla_R|\chi_0\rangle + B_{f0}\langle\chi_f|\chi_0\rangle|^2$$

where the χ's are the nuclear wave functions (note that χ_f is in the continuum) and A_{f0} and B_{f0} are the Born–Oppenheimer off-diagonal coupling matrix elements involving an electron in the continuum. [J. C. Y. Chen, Phys. Rev. **129**, 202 (1963)]. In the case A_{f0} is comparable with B_{f0}, one would find in addition to the contribution due to the Franck–Condon factor $\langle\chi_f|\chi_0\rangle$, there are contributions from the term $\langle\chi_f|\nabla_R|\chi_0\rangle$. These contributions sometime give rise to the fine structure in the excitation function. An experimental example was found by Schulz for the reaction

$$H_2 + e \rightarrow H + H^-$$

[G. J. Schulz, Phys. Rev. **113**, 816 (1959)].

BAUMAN: I would like to ask a question concerning what can now be calculated. Consider the hydrogen molecule, for which an energy and wave function, say E^0 and ψ^0, can be accurately calculated for the equilibrium internuclear distance. If the molecule is vibrationally excited, the total dynamic problem must obey the virial theorem in the form $\overline{T}_t = -\frac{1}{2}\overline{V}_t = -E_t$, since only Coulombic forces are important. However, the vibrational energy and vibrational kinetic energy of the nuclei are quite well defined, and obey a different virial theorem; $\overline{T}_v = \overline{V}_v = \frac{1}{2}E_v$. Combining these conditions, it follows that $\overline{T}_{el} = -(E_{el} + \frac{3}{2}E_{vib})$.

Displacement of the nuclei from the equilibrium distance r_0 to some other point, r_1, can occur by vibrational excitation. The calculation of the forces acting on the nuclei at the point r_1 by means of the wave function ψ_0 should give the wrong answer. Similarly, calculation of a new wave function ψ_1, and energy E_1, at the distance r_1 as if this represented a stationary state should give the wrong answer. Is there a way of calculating forces, and hence force constants, accurately for such a system?

HOFACKER: In the field of chemistry we should look for experiments providing us with systems for which we can assume:

a. well-defined nonequilibrium density-matrices for some initial time and measure the characteristic parameters for the approach of the system to equilibrium;

b. stationary state nonequilibrium density matrices.

This is the only way to get an idea of the magnitude of the parameters governing mass-momentum and energy transfer between subsystems of a larger system, as in most cases it is extremely difficult to find these parameters by calculations. Well-known examples of type (a) are a gas behind a shock wave or any chemical reaction with nonzero rate, whereas type (b) besides various stationary transport phenomena includes unimolecular decomposition reactions

and intramolecular conversions (in the latter case we have even to deal with an initially non-diagonal density matrix).

Experimental studies of such processes, however, still do not allow us to specify the mechanisms of the transport processes involved with sufficient accuracy and we have to look out for further possibilities. For the moment, the most valuable experiments of the desired kind to give us detailed information about transport parameters are done with molecular beams.