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fondé par Ernest Solvay

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tenu à l'Université Libre de Bruxelles
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CHEMICAL KINETICS

by **A.R. UBBELOHDE** *

Studies of rates of chemical change comprise one of the main branches of chemistry. Progressive refinements and extensions have depended in the main on progressive improvements in methods for detecting and analysing chemical change. Observation of nature in terms of chemical change is in its origins as old as man himself. Cleopatra watched the rate of dissolution of her famous pearl in vinegar, and every schoolboy has observed the rate of melting of ice in the sun. But in order to reduce such general observations to precise quantitative terms, methods of chemical analysis of sufficient accuracy had first to be developed. A long history shows that analysis was one of the earliest branches of chemistry to be taught as a science. For example, the Fuggers supported a school for analysts in Augsburg as early as 1500, in connection with their mining operations.

To be of use for measuring rates of change, methods of analysing the chemical make-up of a system must be as far as possible instantaneous. In practice this means that they must involve a time interval much smaller than the total duration of the rate process to be measured. We are familiar with this condition in measuring other rates of change. In order to time the boiling of an egg at all accurately, for example, each separate grain of sand in the sand glass must fall in a time interval very short relative to the total duration of the operation.

About 100 years ago, chemists began to use methods of analysis sufficiently rapid to determine rates of change. At first, the chemical

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* Cet exposé a été fait à l'occasion de la réunion extraordinaire du Conseil de Chimie en présence de Sa Majesté le roi Baudouin, le vendredi 9 novembre 1962.

This lecture was held at the special session of the « Conseil de Chimie » in the presence of His Majesty King Baudouin, on Friday 9 November 1962.

reactions studied were simple and quite slow. A favourite example involved the combination of alcohols with acids to form esters, a process which is of such dominant importance in the maturing of fruit and wine. In the present century, with the advent of more accurate knowledge about the structure of molecules, the subject of chemical kinetics has diverged into two main branches, whose methods and disciplines have separated progressively. One great branch of kinetics deals with rates of chemical change in what are known as condensed states of matter, which include liquids and especially solids. In such materials the atoms and molecules are tightly packed together, and the movements which lead to chemical rearrangements are under strong " social " or co-operative influence from neighbours. We all know from watching crowds of people, or the more disciplined displacements of a company of soldiers, that in such condensed systems hindrances to movement from nearest neighbours are of decisive importance. So it is in the chemical kinetics of condensed systems. Transformations of major technical importance such as the setting of cement, the development of a photographic image in grains of silver salts, or the conversion of carbon into diamond, illustrate to what extent profound scientific researches on kinetics of chemical change in condensed states of matter are also of very considerable economic interest.

Compared with reaction-rate studies in solids, physicists and chemists have made considerably greater advances in the second main branch of chemical kinetics, in reactions in gases (dilute solutions behave similarly). One reason is that rates of chemical change in gases can be interpreted theoretically, in relatively simple terms. What happens in the encounter or collision between two molecules can be isolated from all the rest, because in a gas at ordinary pressures the average separation between molecules is many times as great as the size of the molecules themselves. Thus, they can collide and interact in pairs, without any crowding or disturbance from neighbours. Anyone who reflects on the difference between human relationships " à deux " and what is possible in a crowd, will realise that even for simple molecules isolated collisions in the gas phase involve more distinctive interactions, than under the molecular crowding in condensed states of matter.

Studies of chemical reactions in gases were at first directed towards extremely simple examples of chemical change. These included the pairing of two atoms into a molecule

$$A + B \rightarrow AB$$

and the redistribution of atomic partners in the encounter between a pair of molecules

$$A\text{-}A + B\text{-}B \rightarrow AB + AB$$

Rate measurements soon led to a kinetic molecular theory for reactions conforming to these simple patterns. Quite early in the study of gaseous chemical reactions it was observed that many of them increase in rate very steeply as the temperature of the environment is increased. Following Arrhenius, this striking observation is interpreted on the basis that molecules must collect energy considerably in excess of the average, in order that a gaseous collision may be chemically fruitful.

Much modern research has explored the nature of the so-called " activation energy " required for chemical reaction. Understanding of its significance has been closely linked with the application of Quantum Theory to molecules. Three general comments can serve to indicate some of the most striking lines of advance : —

The first comment is concerned with chain reactions, or chain activation. In the simplest case collisions between a pair of atoms or molecules in the gas lead to isolated chemical reaction. Provided sufficient activation energy is available, rearrangement of chemical linkages takes place during the collision; new chemical species separate and any excess (or deficit) of energy above the average is rapidly distributed over other gaseous molecules in subsequent collisions. For example, physical chemists have frequently examined the collision between molecules of hydrogen and of iodine. By rearrangement of atomic partners these give a new molecule, hydrogen iodide, if sufficient activation energy is available, and that is all. But in a chain reaction, one or more products of a chemically fruitful collision *remain active* and can immediately enter into a succession of similarly fruitful encounters. The most easily demonstrated examples of chain reactions involve a free atom as one of the collision partners. Thus an atom of hydrogen colliding with a molecule of chlorine gives rise to a stable molecule of hydrogen chloride, together with an atom of chlorine which can immediately attack another molecule of hydrogen without requiring fresh activation. The succession of such reactions does not cease until the atoms are trapped or removed in some way. Concepts of chain-linked chemical reactions have proved highly significant for the understanding of explosions, and have also influenced the development of nuclear reactions in atom bombs and nuclear power stations.

A second striking line of advance in kinetics refers to the chemical reactions associated with biological processes. At present study of these is relatively less developed; but there is reason to believe that the preparation needed by a molecule to ensure successful reaction in an encounter often requires its passage into a special configuration of low probability instead of just the collection of large amounts of activation energy. Chemists describe this special feature in the critical requirements for reaction, in terms of an entropy factor in addition to the better known energy factor. Related concepts are of great importance in general problems of the catalysis of chemical reactions.

The third line of advance in the study of chemical kinetics refers to processes of energy transfer in gaseous collisions. At this 12th Solvay Conference, chemists from all over the world are engaged in discussing new attacks on this extremely fundamental aspect of what happens when two molecules collide in a gas. Its importance has been realised ever since Arrhenius first coined the term " activation energy " But analytical methods for observing rates of energy uptake by individual chemical molecules have become sufficiently rapid to be meaningful, only quite recently. In our discussions at Brussels this week we are particularly concerned with the rate of transfer of internal energy of molecules, for which characteristic time intervals range from 10^{-5} to 10^{-9} seconds, or even shorter. These time intervals can now be dealt with quite confidently, using modern spectroscopic techniques together with the most recent inventions of electronics. I will end by giving only one illustration out of many. It has been established that any molecule of ethylene in gaseous collisions with similar molecules transfers its vibrational energy only once in about three thousand opportunities. This reluctance of ethylene molecules to change their vibrational state can be reduced by catalysts, till about one collision in twenty-five is successful. Theoretical interpretations of these and other striking discoveries about the conditions for energy transfer between molecules are rapidly being developed. Such advances provide an essential foundation to existing knowledge about rates of chemical change. When it is remembered that hundreds of thousands of tons of ethylene are used every year in the high polymer and petrochemical industry, it is easy to show how close are the links between the most abstract advances in science, and the economic welfare of a nation.

SOME PROBLEMS IN ENERGY EXCHANGE RELATED TO CHEMICAL KINETICS

by **O.K. RICE**

Chemical reactions are in practically all cases the results of energy exchange processes. Certain reactions are the direct result of intermolecular energy exchange in a single collision. These are the recombination of atoms in the presence of a third body, the dissociation of diatomic molecules, and the dissociation of more complicated molecules at a very low pressure. In unimolecular reactions at high pressures the rate-determining step is intramolecular transfer of energy to some particular bond in the molecule. Of course, the rate of activation, which determines the rate of reaction at low pressures, is in all cases connected with the transfer of energy between molecules. In polyatomic molecules this is a very complicated process, since all kinds of interchanges of vibrational, translational, and rotational energy may occur. The dissociation of diatomic molecules activated by rare-gas atoms involves only exchange of translational energy with vibrational or rotational energy, but the situation is complicated by the fact that the vibrations are highly anharmonic. The relaxation of the lower, more nearly harmonic vibration states, is also very important as a process which must occur on the way to reaction. There is a reasonably well-developed theory for the exchange of vibrational and translational energy, which is fundamental to the whole subject, and which is the first topic with which we shall deal. There are, of course, other types of reaction in which interesting energy-transfer problems arise. In view of limitations of space and time, we shall confine ourselves to the ones specifically mentioned above.

I. INTERCHANGE OF VIBRATIONAL AND TRANSLATIONAL ENERGY

A. Theoretical treatment of diatomic molecules.

Attemps to understand the exchange of vibrational and translational energy generally employ a procedure due to Zener (1). Consider first the collision of a diatomic molecule and an atom, it being assumed that the atom lies in the line of centers of the molecule, so that the problem is essentially one-dimensional. If we let the distance between the atoms of the diatomic molecule be X, their equilibrium distance be X_e, write $x = X - X_e$, and allow Φ_n to be the wave function for a vibrational state n of the molecule, we may write for the wave equation, assuming a simple harmonic oscillator :

$$(h^2/8\pi^2\mu)d^2\Phi_n/dx^2 + (E_n - 2\pi^2\nu_0^2\mu x^2)\,\Phi_n = 0 \qquad (1.1)$$

Here h is Planck's constant, μ is the reduced mass, E_n is the energy of the state, and ν_0 is the frequency. It is more convenient to refer all distances to the center of gravity of the molecule. If we write $\mu_1 = m_1^2/\mu$, where m_1 is the mass of the atom which is closer to the colliding particle, and if we let $x_1 = X_1 - X_{1_e}$, where X_1 and X_{1_e} are distances of this atom to the center of gravity, it may be readily shown that we can write Eq. (1.1) in the form :

$$(h^2/8\pi^2\mu_1)d^2\Phi_n/dx_1^2 + (E_n - 2\pi^2\nu_0^2\mu_1 x_1^2)\,\Phi_n = 0 \qquad (1.2)$$

We suppose now that the mutual potential energy V of the molecule and the approaching atom is a function of the distance, $r - x_1$, between the approaching atom and the nearer atom in the molecule, r being the distance between the approaching atom and the center of gravity. The average potential energy when r is fixed, will be given by :

$$u_{nn} = \int_{-\infty}^{\infty} \Phi_n V \Phi_n dx_1 \qquad (1.3)$$

with Φ_n normalized so that :

$$\int_{-\infty}^{\infty} \Phi_n^2 dx_1 = 1.$$

In zero approximation the wave function R_{nm} for the relative motion of the molecule and the atom, with the former in the state n, may be taken as the solution of the equation :

$$(h^2/8\pi^2 M)d^2R_{nm}/dr^2 + (T_{nm} - u_{nn})R_{nm} = 0 \tag{1.4}$$

where M is the reduced mass of the system molecule and atom, and $T_{nm} = W_{nm} - E_n$ with W_{nm} the total energy of the system. The wave function of the combined system in zero approximation is :

$$\Psi_{nm} = \Phi_n R_{nm} \tag{1.5}$$

A convenient way to normalize R_{nm} is to set an arbitrary upper limit, r_∞, to r. This changes the continuum to a close-spaced set of discrete states, the energy between two adjacent energy levels being (2) :

$$\delta\varepsilon_{nm} = (T_{nm}/2M)^{1/2}h/r_\infty = (1/2)\, v_{nm}h/r_\infty \tag{1.6}$$

where v_{nm} is the velocity. R_{nm} is then a real function of sinusoidal type (which makes Ψ_{nm} real also), and will be normalized so that :

$$\int_0^{r_\infty} |R_{nm}|^2\, dr = 1 \tag{1.7}$$

We make use of the Dirac (3) method of variation of constants, in order to find the probability of transition to the translational states, m', associated with a new vibrational state, n'. We start with the time-dependent wave equation for the whole system :

$$\frac{h^2}{8\pi^2\mu_1}\frac{\partial^2\Psi}{\partial x_1^2} + \frac{h^2}{8\pi^2 M}\frac{\partial^2\Psi}{\partial r^2} - (2\pi^2\nu_0^2\mu_1 x_1^2 + V)\Psi = \frac{h}{2\pi i}\frac{\partial\Psi}{\partial t} \tag{1.8}$$

When :

$$\Psi = \Psi_{nm}\, e^{-2\pi i W_{nm} t/h}$$

is substituted in Eq. (1.8) it is not exactly satisfied. Instead, we substitute (what is still not a complete expression but sufficient for our purposes) :

$$\Psi = \Psi_{nm}\, e^{-2\pi i W_{mn} t/h} + \sum_{m'} c_{n'm'}\Psi_{n'm'}\, e^{-2\pi i W_{n'm'} t/h} \tag{1.9}$$

To reduce the resulting equation we make use of Eqs. (1.2) and (1.4) and the similar equations for the primed quantities, then multiply by one of the :

$$\Psi^*_{n'm'}\, e^{2\pi i W_{n'm'}\, t/h}$$

and integrate over all the coordinates, taking due account of the normalization and the mutual orthogonality of all the Ψ_{nm} and $\Psi_{n'm'}$ (and, indeed, of the Φ_n as regards integration with respect to x_1), and assuming that the $c_{n'm'}$ are small. We find :

$$\dot{c}_{n'm'} = -(2\pi i/h) V_{n'm'nm}\, e^{2\pi i (W_{n'm'} - W_{nm}) t/h} \tag{1.10}$$

where the dot means time differentiation and :

$$V_{n'm'nm} = \int\int \Psi_{n'm'} V \Psi_{nm} dx_1 dr = \int R_{n'm'} u_{n'n} R_{nm} dr \tag{1.11}$$

with :

$$u_{n'n} = \int \Phi_{n'} V \Phi_n dx_1 \tag{1.12}$$

Integrating Eq. (1.10) and evaluating the constant of integration by setting $c_{n'm'} = 0$ at $t = 0$ we obtain :

$$c_{n'm'} = \frac{-V_{n'm'nm}\,(e^{2\pi i (W_{n'm'} - W_{nm}) t/h} - 1)}{W_{n'm'} - W_{nm}} \tag{1.13}$$

We now wish to evaluate :

$$\sum_{m'} c_{n'm'} \Psi_{n'm'} e^{-2\pi i W_{n'm'}\, t/h} \; (= P_{m'}),$$

which may be changed to an integral by multiplication by $dW_{n'm'}/\delta\varepsilon_{n'm'}$, and it will suffice to evaluate it for large values of r and t. For large r we may write, neglecting the phase factor, which is essentially independent of $p_{n'm'}$:

$$R_{n'm'} = (2/r_\infty)^{1/2} \sin(2\pi p_{n'm'} r/h) \tag{1.14}$$

where $p_{n'm'}$ is the momentum associated with the state $n'm'$. If t is large the range of energies over which large contributions to the integral occur is small. We write p_0' for the value of $p_{n'm'}$ when the total energy is equal to W_{nm} and T_0' for $T_{n'm'}$ at this point, and set :

$$p_{n'm'} \cong p_0' + (dp_{n'm'}/dT_{n'm'})\,(W_{n'm'} - W_{nm})$$
$$= p_0' + (M/2T_0')^{1/2}\,(W_{n'm'} - W_{nm}) \qquad (1.15)$$

so that :

$$R_{n'm'} = (2/r_\infty)^{1/2} \sin(2\pi p_0' r/h) \cos[2\pi(M/2T_0')^{1/2}(W_{n'm'} - W_{nm})r/h]$$
$$+ (2/r_\infty)^{1/2} \cos(2\pi p_0' r/h) \sin[2\pi(M/2T_0')^{1/2}(W_{n'm'} - W_{nm})r/h] \qquad (1.16)$$

The integral arising from $P_{m'}$ is then seen to involve integrals of the type of Nos. 484 and 485 of Peirce (4), and indeed we find, after some transformations and cancellations :

$$P_{m'} = -(2/r_\infty)^{1/2}\pi(V_{n'm'nm}/\delta\varepsilon_{n'm'})\Phi_{n'}e^{-2\pi i W_{nm} t/h}\,e^{2\pi i p_0' r/h} \qquad (1.17)$$

if

$$r < t\,(2T_0'/M)^{1/2}$$

and zero if

$$r > t\,(2T_0'/M)^{1/2}$$

Since $(2T_0'/M)^{1/2}$ is the relative velocity v_0' of the particle and the molecule, it is seen that the condition for a nonzero value is $r < v_0' t$. Inside that distance there is a probability density of outward streaming particles (or, more precisely, pairs), equal to :

$$\int_{-\infty}^{\infty} |P_{m'}|^2 dx_1 = 2\pi^2 V_{n'm'nm}^2/(\delta\varepsilon_{n'm'})^2 r_\infty \qquad (1.18)$$

since :

$$\int_{-\infty}^{\infty} \Phi_{n'}^2 dx_1 = 1.$$

This is to be compared to the probability density arising from the original wave function Ψ_{nm}, which is seen from Eq. (1.7) to be :

$$|\Psi_{nm}|^2 = r_\infty^{-1} \qquad (1.19)$$

The probability $\gamma_{nn'}$ for transition to the vibrational state n', per collision, will be found by multiplying the ratio of (1.18) to (1.19) by the ratio of the velocities v_0'/v_0 or $(T_0'/T_{nm})^{1/2}$, and by 2, since only half of the pairs represented by Ψ_{nm} are approaching each other. This gives :

$$\gamma_{nn'} = 4\pi^2 V_{n'm'nm}{}^2/\partial\varepsilon_{n'm'}\partial\varepsilon_{nm} \tag{1.20}$$

If the normalization is such that $|R_{nm}|^2$ has an average value of 1, so that :

$$\int_0^{r_\infty} |R_{nm}|^2 dr = r_\infty$$

instead of 1, then in place of Eq. (1.20) we have, from Eq. (1.6) :

$$\gamma_{nn'} = 16\pi^2 V_{n'm'nm}{}^2/v_0'v_0h^2 \tag{1.21}$$

where now $V_{n'm'nm}$ is reckoned with the new values of the R_{nm}.

This rather standard theory has been presented here to bring freshly to mind the significance of the various factors involved. The rest of the development consists largely in setting up suitable approximations for obtaining the integral $V_{n'm'nm}$. Before doing this it will be well to review the physical meaning of the result.(5, 6, 7c, 8c) As the atom approaches the molecule, the latter begins to feel the force due to their mutual potential. If the approach of the atom is very gradual the force changes slowly, and in the limit does not vary appreciably over a complete vibration of the molecule, first accelerating, then retarding the vibrational motion; then there would be no net exchange of energy. The greatest exchange of energy would arise from a sharp blow. Thus the greater the change of the mutual potential V with the distance, and the greater the relative velocity, the more effective may one expect the exchange of energy to be. These factors will be reflected in the matrix component $V_{n'm'nm}$. The factors Φ_n and $\Phi_{n'}$ [Eq. (1.12)] are mutually orthogonal; if V did not depend at all on x_1 the integral would vanish, and, at least in a general way, the more strongly V depends on x_1 the greater $u_{n'n}$ will be. The functions R_{nm} and $R_{n'm'}$, while possibly not orthogonal, nevertheless represent translational motions of different velocities and have therefore different wave lengths. Thus, unless V depends strongly on r there can be much cancellation of positive and negative portions. The wave length depends inversely on momentum, and the longer the wave length the less cancellation there will be. This means that for a given energy the smaller the mass the less cancellation and the higher the transition probability; thus a light atom may be expected to be effective in energy transfer. On the other hand, a high velocity also has an inverse effect, since less time is allowed for the forces to act, and the relative velocity of atom and molecule does appear explicitly in the denominators of Eq. (1.21).

Note also that the greater the *difference* in energy between initial and final states the less R_{nm} and $R_{n'm'}$ overlap. Thus small transfers of energy are much more probable than large transfers, and it is easiest to transfer energy to or from a molecule with a very low frequency of vibration.

The repulsive forces are most important in causing energy transfer and V is usually assumed to have the form :

$$V = V_0 \, e^{\alpha(x_1 - r)} \tag{1.22}$$

On this basis Jackson and Mott ⁽⁹⁾ worked out the form of the wave function R_{nm} satisfying Eq. (1.4), and the integrals involved in $V_{n'm'nn}$. In so soing they assumed $u_{n'n'} = u_{nn}$. The result of this work is :

$$\gamma_{nn'} = \frac{256\pi^6 M^2 (\Delta\varepsilon_k)^2}{\alpha^4 h^4} \frac{\sinh g \sinh g'}{(\cosh g - \cosh g')^2} \left(\frac{u_{n'n}}{V_0} e^{\alpha r} \right)^2 \tag{1.23}$$

where :

$$\Delta\varepsilon_k = (M/2)\,(v_0'^2 - v_0^2) \tag{1.24}$$

is the kinetic energy transformed into vibrational, or *vice versa*, so that :

$$|\Delta\varepsilon_k| = h\nu_0 \tag{1.25}$$

and where :

$$\begin{aligned} g &= 4\pi^2 M v_0 / h\alpha \\ g' &= 4\pi^2 M v_0' / h\alpha \end{aligned} \tag{1.26}$$

The expression for $(\Delta\varepsilon_k)^2$ obtained from Eq. (1.24) can be transformed as follows :

$$\begin{aligned} (\Delta\varepsilon_k)^2 &= (M^2/4)\,(v_0' + v_0)^2 (v_0' - v_0)^2 \\ &= 2M\bar{\varepsilon}_k (v_0' - v_0)^2 = \bar{\varepsilon}_k (g' - g)^2 h^2 \alpha^2 / 8\pi^4 M \end{aligned} \tag{1.27}$$

where :

$$\bar{\varepsilon}_k = (M/2)\,(v_0' + v_0)^2/4 \tag{1.28}$$

is a sort of average of the relative kinetic energies before and after the collision. $u_{n'n}e^{\alpha r}/V_0$ is a dimensionless integral :

$$u_{n'n}\,e^{\alpha r}/V_0 = \int_{-\infty}^{\infty} \Phi_{n'}\;e^{\alpha x_1}\,\Phi_n dx_1 \tag{1.29}$$

In evaluating this integral it is generally assumed that $e^{\alpha x_1}$ may be written as $1 + \alpha x_1$ over the effective range of the integration. This may not be such a good approximation, especially for higher vibrational states, since α^{-1} is generally of the order of 0.2 Å, but it will at least give the order of magnitude. Then, in the light of the orthogonality of Φ_n' and Φ_n :

$$u_{n'n}\,e^{\alpha r}/V_0 \simeq \alpha \int_{-\infty}^{\infty} \Phi_n' x_1 \Phi_n dx_1 \tag{1.30}$$

If the motion is strictly harmonic, the Φ_n's are the normalized Hermite functions (10), the integral vanishes unless $n' - n = \pm 1$, and if $n' - n = \pm 1$ it becomes (10) :

$$u_{n'n}e^{\alpha r}/V_0 = (\alpha/2\pi)\,(hn_l/2\bar{\mu}\nu_0)^{1/2} \tag{1.31}$$

where n_l is the larger of n' and n. Since the collision can take place at either of the two ends of the diatomic molecule, $1/\bar{\mu}$ is the average value for the two ends ($1/\bar{\mu} = 1/2\mu_1 + 1/2\mu_2$).

Using Eqs. (1.27) and (1.31) in Eq. (1.23) we obtain :

$$\gamma_{nn'} = \frac{4M\bar{\varepsilon}_k n_l}{h\bar{\mu}\nu_0}(g' - g)^2\,\frac{\sinh g\ \sinh g'}{(\cosh g - \cosh g')^2} = (4M\bar{\varepsilon}_k n_l/h\bar{\mu}\nu_0)\mathrm{F}(g', g) \tag{1.32}$$

where $F(g', g)$ is defined by the equation.

Eq. (1.32) can be improved by allowing roughly for indirect effects of attractive van der Waals forces between the molecule and the colliding atom. To do this a curve of the form $e^{-\alpha r}$ is fitted as well as may be (two methods are considered (11, 12, 13a)) to a Lennard-Jones potential in the region $r < r_0$, where r_0 is the position of the

Lennard-Jones minimum. This determines the value of α. It also effectively lowers the potential energy by an amount ε, where ε is the depth of the minimum of the Lennard-Jones curve, and, assuming equilibrium to be established at r_0 the number of colliding pairs is increased by a factor $e^{\varepsilon/kT}$. Herzfeld and Litovitz (13b) have given an alternative proof for the multiplication of Eq. (1.32) by this factor, and some evidence in its support has been given by Blythe, Cottrell, and Read.(14)

An attempt was also made to adapt Eq. (1.32) to the three-dimensional case. If we neglect transfer of angular momentum between the molecule and the relative motion of atom and molecule we may, for specific rotational quantum number j of the relative motion, simply add to the potential energy the centrifugal potential: $j(j+1)h^2/8\pi^2Mr^2$. This varies slowly with r, and Takayanagi (15), in the course of a detailed and pioneering investigation of inelastic collisions, suggested that it be replaced by $\varepsilon_j = j(j+1)h^2/8\pi^2Mr_c^2$ where r_c is the distance (less than r_0) at which the relative kinetic energy of molecule and atom vanishes, i.e., the turning point in their relative motion. Then, by reasoning similar to that of the preceding paragraph, the probability of energy exchange for a given j assuming head-on collision will be multiplied by a factor $e^{-\varepsilon_j/kT}$. Over all j the total number of colliding partners, as compared to the number which would be found at the position r_0 will be given by the ratio:

$$\sum (2j+1)\, e^{-\varepsilon_j/kT}/Q(r_0)$$

where $Q(r_0) = 8\pi^2Mr_0^2kT$ is the rotational partition function for colliding pairs at average distance r_0. From the structure of the sum it is seen that this ratio is:

$$Q(r_c)/Q(r_0) = r_c^2/r_0^2.$$

Because not all the collisions are head-on, a further rough correction is made by multiplying Eq. (1.32) by 1/3, although it is not completely clear that these corrections are completely independent.

This deduction essentially assumes that a molecule and an atom are in collision if their mutual distance is r_0, or that the collision diameter is r_0. Actually, because of the attractive forces, more collisions occur than would be found in this way — one must correct by a factor of the Sutherland type, (16) which we shall designate as Y. The effects of the attractive forces on the probability of transition having already been taken into account, as related in the preceding paragraph γ_{nn}' must be divided by Y. Thus Eq. (1.32) is replaced by:

$$\gamma_{nn}' = \frac{1}{3}(4M\bar{\varepsilon}_k n_l / h\bar{\mu}\nu_0)\mathrm{Y}^{-1}(r_c/r_0)^2 \, e^{\varepsilon/kT} \mathrm{F}(g', g) \qquad (1.33)$$

Of course, in interpreting the experimental results the number of collisions should be calculated using the same correction.

Finally, it will be noted that γ_{nn}' depends specifically on the initial relative energy of the molecule and atom. This must be averaged over the initial energy with respect to the number of collisions per unit energy calculated from ε (one-dimensional) Maxwell distribution law. In doing this, however, it is convenient to use the form obtained by use of Eq. (1.25) rather than Eq. (1.24) or (1.27). To carry out the averaging some approximations are necessary. First the energy ε_m at which the maximum contribution occurs is found, and some slowly varying quantities in the integral are set constant at their value for this energy. The final result is (17), for deactivation, and for the case where $g' - g$ is large (poor resonance):

$$\gamma_{nn}' = \left(\frac{2\pi}{3}\right)^{1/2} \frac{32\pi^4 M^2 \nu_0 n_l}{3h\alpha^2\bar{\mu}Y} \left(\frac{r_c}{r_0}\right)^2 e^{\varepsilon/kT} \left(\frac{\theta'}{T}\right)^{1/6} \exp\left[-\frac{3}{2}\left(\frac{\theta'}{T}\right)^{1/3} + \frac{h\nu_0}{2kT}\right] \qquad (1.34)$$

where :

$$\theta' = 16\pi^4 M \nu_0^2/\alpha^2 k \qquad (1.35)$$

and where k is the Boltzmann constant. The value of r_c which is used is that which corresponds to the energy ε_m.

In connection with the three-dimensional case, we may note a paper by Salkoff and Bauer (18) in which, in addition to some differences in the approximations to the potentials used, and the method of separating the potential energy as between the vibrational and translational parts and the perturbation, the rotational potential was in effect added to (19, 20) u_{nn} in Eq. (1.4). The equations were then solved for each value of j, the azimuthal quantum number for the relative translational motion of the molecule and atom. Thus the contribution of the different values of j could be ascertained, and the whole summed to get the total cross section for inelastic collisions. This was applied to vibrational excitation in H_2. Of chief importance is the demonstration of the important range of values of j (up to 100 in the case considered), and of the fact that the interactions are sensitive to the intermolecular potentials.

B. Experimental material — simple molecules.

Our principal interest in the theory just outlined arises from its possible application in chemical kinetics. However, there are a number of other ways in which the transfer of energy between vibration and translation may be studied. Of most importance are the measurement of dispersion and absorption of sound, and a study of the structure of shock waves, whereby the time required for establishment of thermal equilibrium may be found. There are also other methods which have been less used. To a first approximation one may assume that there may transiently exist two distinct temperatures, one for vibration and one for translation, in the same system, and the experiments mentioned above give information concerning the relaxation time for attainment of equilibrium between the two parts of the system. This relaxation time is, at least to good approximation, related to the rate of transition between the lowest and next lowest vibrational states in a molecule, i.e., we are able to calculate γ_{10} and may compare it with Eq. (1.34) with $n_l = 1$. These experimental methods have been discussed in detail by Cottrell and McCoubrey (7a, b) and by Herzfeld and Litovitz (8a, b).

Eq. (1.34) has been compared by Herzfeld and Litovitz (8c) to many cases of energy transfer in diatomic gases. In so doing, it is assumed that the molecule whose internal state does not change acts like an atom. It has also been applied to some cases of exchange between a diatomic and a monatomic gas, obtained by experiments on mixtures of gases. In general, the process is quite inefficient; it requires anywhere from several hundred to about 10^8 collisions to effect an energy exchange. The probability of exchange increases markedly with the temperature, reflecting the fact that a large value of v_0 tends to favor energy exchange; for example, the probability of exchange for N_2 varies about one in 10^8 at 550^0 to about one in 8000 at 4600^0 K. The theory is rather successful in reproducing these varied experimental results, generally agreeing within a factor of 10. The theory also gives comparable results with some linear triatomic molecules. Some refinements, such as attempting to make some allowance for simultaneous exchange of rotational energy and a special treatment for the bending vibrations of such molecules as CO_2 and N_2O do not cause any appreciable improvement. In general, the situation may be said to be satisfactory. There are one or two special cases which deserve some mention. It is known that in mixtures of CO_2 and H_2O exchange takes place very readily, and H_2O acts as a catalyst for the relaxation of the CO_2 vibrations. This has been explained by Widom and Bauer (21) as the result of a considerable attraction between CO_2 and H_2O. However Eucken and Nümann (22) found that the efficiency for this mixture first rises and then decreases with temperature, which has no theoretical explanation, but which suggests the implication of a CO_2 - H_2O complex which would be less stable at high temperatures. O_2 - CO mixtures and Cl_2- CO mixtures show much more efficient exchange than is to be expected. Franck and Eucken (23) imply, in the latter case, that the incipient formation of phosgene Cl_2CO, might be responsible for the effect. However, it seems likely that the activation energy for a process $Cl_2 + CO \rightarrow Cl_2CO$ would be so high that it could be expected to have no appreciable effect.

C. **Calculations — Some comparisons.**

Many years ago the present writer (24) applied Eq. (1.21) to the discussion of deactivation of complex activated molecules. To gain some general ideas of the magnitudes involved, the first model used was that of an atom approaching an oscillator along the line of centers, just as above. Since the results appear at first sight to be very different from those obtained more recently, some comparison and discussion would seem to be in order. My methods of approximation, in particular the scheme for representing the potential-energy curves so as to get integrals which could be handled, were somewhat different. Also, since I was interested in deactivation of large molecules colliding with light ones, I assumed that the oscillator involved had an equilibrium position that was fixed in space. These differences, however, are not particularly significant. More important is the fact that I considered colliding atoms of specific energy, rather than averaging over the thermal distribution.

Collisions were considered having relative kinetic energy of 800 and 2400 calories per mole, and colliding atoms having masses M of 1, 2, and 4 atomic weight units (the latter two corresponding to colliding H_2 and He, the first being somewhat related to exchange of rotational energy with H_2). Values used for the vibrational frequencies were 500, 1000, and 1500 cm^{-1}. α ranged from 4 to 7×10^8 cm^{-1} and force constants, $\varkappa$, for the oscillator [$4\pi^2\nu_0^2\mu_1$ — see Eq. (1.21)] were 0.6, 1.2, and 5.0×10^5 dynes per cm. These values were chosen to be characteristic for the vibrations of organic molecules, it being assumed that the vibrations which actually exchanged energy would usually be those of C-C, C-O, or C-N stretchings or bendings (possibly in some case C-H bendings), but that the force between the colliding atom and the molecule would be exerted through the hydrogens on the outside of the molecule, so that a value of α appropriate to this situation should be used. Since $\nu_0 = 1000$ cm^{-1} and $\mu_1 = 15$ atomic weight units (as in a methyl radical) gives $\varkappa = 9 \times 10^5$ dynes per cm the range of values chosen for $\varkappa$ may have been a little low.

The calculations showed the expected trends, the transition probability decreasing with increasing frequency of vibration (reflecting the necessity of transferring more translational energy) and with increasing mass of the colliding particle, and increasing with increasing α, which defines the sharpness of the collision. It usually decreased with increasing $\varkappa$. The actual transition probabilities range from more than 1 to, in a few extreme cases, 0.0001 or less. A transition probability greater than 1 indicates, of course, that the perturbation method is breaking down. It may, indeed, break down, even when the calculated probability is less than 1, if the perturbations are great enough to give $\gamma_{nn'} > 1$ in the case of good resonance (i.e., when the frequency is very low and the amount of energy to be transferred between vibration and translation is consequently small). Methods of handling this situation have been worked out (20, 25) and applied (24).

On the whole, the transition probabilities are considerably larger than those cited by Herzfeld and Litovitz (8). However, the latter generally dealt with larger colliding masses and higher vibrational frequencies. The case which comes closest to the conditions I employed is that of Cl_2 colliding with He, for which M is about 4 atomic weight units. The value of ν_0 is 565 cm^{-1}, and that of μ_1 of Eq. (1.2) is 70 atomic weight units; these give $\varkappa = 1.4 \times 10^6$ dynes/cm. α^{-1}, according to Herzfeld and Litovitz (Method B) is 0.176×10^{-8} cm, or $\alpha = 5.7 \times 10^8$. My calculation corresponding most closely to these conditions ($\nu_0 = 500$, $\varkappa = 5 \times 10^5$, $M = 4$, and $\alpha = 6 \times 10^8$) gives a transition probability to the lowest quantum state from the next lowest of 0.04 to 0.08 depending on the approximation made. For the actual values of ν_0, $\varkappa$ and α indicated, the transition probability would probably be 0.01 to 0.02. Herzfeld and Litovitz find a transition probability of about 0.0006. My calculations were for a fixed initial translational energy of 800 cal/mole, whereas Herzfeld and Litovitz averaged over the energies at 288° K. However, in this particular case the efficiency of a collision does not change rapidly with energy (this would not be true for greater values of M), and Herzfeld and Litovitz's value is only slightly greater than it would be had they used an energy of 800 cal/mole. I have not made the correction for attractive forces (factor $e^{\varepsilon/kT}$) which would be small in this case, nor the correction for three-dimensional collisions; in particular, the factor of 1/3 has not been included. Even if we allow for this my value is 5 to 10 times that of Herzfeld and Litovitz. This is an appreciable difference but perhaps not unexpected in view of the different approximations made, and is not much greater than the difference between Herzfeld and Litovitz's " Method A " and " Method B ". It is of interest in this connection that the true rate of relaxation lies between the calculated values.

D. **Application of theory to more complicated situations.**

We wish to apply these calculations to activation and deactivation in chemical reactions, and it is clear that usually the situation is much more complicated than that encountered in the collision of an atom with a diatomic molecule. There can be exchange of rotational energy, exchange of vibrational energy from one molecule to another, and complex collisions, in which two vibrations within a single molecule change their quantum numbers simultaneously, generally one up and one down, thus resulting in exchange of smaller amounts of translational energy.

Some efforts have been made to discuss the exchange of rotational and translational energy, and its effect on the exchange of vibrational and translational energy. It was assumed that the atoms within a molecule acted separately and additively on a colliding atom. This introduced angular variables into the mutual potential. General equations were worked out by Curtiss and Adler (26) and by Takayanagi (27). A calculation on the collision between oxygen and helium (28) indicated that the possibility of rotational transfer did not enhance the probability of vibrational transitions greatly. The simplest approximation (8c) gives transitions only between rotational states whose quantum numbers do not differ greatly. Aroeste (29) has made a calculation for F_2O colliding with Ne in which he assumed that the atoms in F_2O acted separately with Ne, and in which large changes of rotational quantum number were found. He considered only transitions from the lowest vibrational state of each of the normal modes, and found probabilities of excitation from the lowest vibration state in the range 10^{-8} - 10^{-7} per collision. According to Herzfeld and Litovitz (8c) this is only a few times greater than the result of neglecting rotation altogether. Rotational motion might have more influence on activated molecules, in which there is more anharmonity and the bonds are more greatly stretched, especially small ones where the activation energy would be divided up among only a few degrees of freedom. This is a very complicated problem, which has not been worked out.

Complex collisions and collisions involving intermolecular vibrational exchange may be important, as noted above, on account of the rather modest transfer of translational energy required, (so-called " good resonance "). This possibility was mentioned by the present writer (24) and calculations have been carried out by Herzfeld (17) and collaborators and by Tanczos (30). In attempting to see what they can do we need to consider the nature of the normal vibrations. This was done in my earlier work (24) and in a more elaborate manner by the later writers (17, 30). Here we shall use a somewhat simplified picture. Since any given normal vibration involves principally atoms of similar masses restrained by similar forces, we shall assume all the masses and forces to be equal. We can then take as the coordinate q_i of the normal vibration the displacement of any one of the atoms, and the force constant, referred to this displacement, can be taken as $4\pi^2 \nu_0^2 z_i m_i$, where m_i is the mass of one of the atoms and z_i is the number of them involved. The effective mass for the particular normal mode of vibration is, then, $z_i m_i$. The actual displacement of some particular atom in some particular direction will be given by:

$$x = \sum_i q_i \cos \beta_i \tag{1.36}$$

where the sum goes over all the normal vibrations which are involved in a major way and β_i is the angle between the direction chosen and the direction of the displacement q_i due to the i^{th} normal vibration. We can now consider the effects of a collision from the selected direction. In place of the wave function Φ_n of Eq. (1.1) or Eq. (1.2) we would have a product $\Pi_i \Phi_{n_i}(q_i)$ and the wave function for the final state, Φ_n', would be replaced by another product $\Pi_i \Phi_{n_i}'(q_i)$; however, all the Φ_{n_i}' except two would be the same as the Φ_{n_i}. Let these two be designated by $i = 1$ and $i = 2$. Then we would have to replace $u_{n'n}$ in Eq. (1.11) or Eq. (1.23) by :

$$u_{n'n} = V_0 e^{-\alpha r} \int \Phi_{n_1}' e^{\alpha q_1 \cos \beta_1} \Phi_{n_1} dq_1 \int \Phi_{n_2}' e^{\alpha q_2 \cos \beta_2} \Phi_{n_2} dq_2$$
$$\times \prod_{i \neq 1,2} \int \Phi_{n_i}' \cdot e^{\alpha q_i \cos \beta_i} \Phi_{n_i} dq_i \tag{1.37}$$

Again we replace $\exp^{\alpha q_i \cos \beta_i}$ by $1 + \alpha q_i \cos \beta_i$, and for all the terms in the integral for which $n_i' = n_i$ we neglect the second term. Then, remembering the normality and orthogonality of the Φ_{n_i} we have for a collision involving changes in two of the n_i :

$$(u_{n'n}/V_0)\, e^{\alpha r} = \cos \beta_1 \cos \beta_2 \int \Phi_{n_1}' \alpha q_1 \Phi_{n_1} dq_1 \int \Phi_{n_2}' \alpha q_2 \Phi_{n_2} dq_2$$
$$= (\alpha^2/4\pi^2)\,(h^2 n_1 n_2 / 4 z_1 z_2 m_1 m_2 \nu_1 \nu_2)^{1/2} \cos \beta_1 \cos \beta_2 \tag{1.38}$$

[compare Eq. (1.31)], where the subscripts 1 and 2 indicate quantities to be associated with Φ_{n_1} and Φ_{n_2} respectively.

This may now be inserted into Eq. (1.23), using Eq. (1.24) and (1.26), but not (1.25), as in obtaining Eq. (1.32). We will wish to take an average value for $\cos \beta_1$ and $\cos \beta_2$. Assuming the two vibrations to be at right angles to each other the average of $\cos^2 \beta_1 \cos^2 \beta_2$ taken over the sphere is 1/15, which takes the place of the factor 1/3 in Eq. (1.32). If the angles are in the same direction the factor is 1/5 :

$$\gamma_{nn}' = \frac{1}{15}\left(\text{or } \frac{1}{5}\right) \frac{\alpha^2 M\bar{\varepsilon}_k n_1 n_2}{2\pi^2 z_1 z_2 m_1 m_2 \nu_1 \nu_2} F(g', g) \tag{1.39}$$

To orient ourselves we may consider the numerical evaluation of the first factor in this expression and in Eq. (1.32) in a typical case, taking, say, $\alpha = 5 \times 10^8$ cm^{-1}, $M = 20$ atomic weight units $m_1 = m_2 = 15$ atomic weight units [$\bar{\mu} = 15z$ atomic weight units in Eq. (1.32)] (typical of CH_3 group), $\nu_2 = \nu_1$ (or ν_0) $= 1000$ cm^{-1}, and $\varepsilon_k = kT$ for 300° K. This gives, for Eq. (1.32), with an extra factor 1/3 included, as in Eq. (1.33) :

$$\gamma_{nn}' = 0.4(n_l/z)F(g', g) \tag{1.40}$$

and, for Eq. (1.39). with the factor taken as 1/15 :

$$\gamma_{nn}' = 0.002(n_1 n_2/z_1 z_2)F(g', g) \tag{1.41}$$

It is also of interest to note that in this case :

$$(\alpha/2\pi)^2(hn_l/2\bar{\mu}\nu_0) = 0.03\ (n_l/z) \tag{1.42}$$

Aside from the factor 1/15 (or 1/5) instead of 1/3, one obtains Eq.(1.39) by multiplying Eq. (1.33) by this factor.

The factor $F(g', g)$ depends largely upon how much energy needs to be transferred from translation to vibration; i.e., upon how good is the resonance between the initial and final states of the system. As Herzfeld and Litovitz have pointed out, g and g', even in the most unfavorable case of a hydrogen molecule of mean thermal energy at room temperature, are at least equal to about 7 in which case :

$$\begin{aligned} \sinh g = \cosh g &= (1/2)\, e^{g} \\ \cosh g - \cosh g' &= (1/2)\,(e^{g} - e^{g'}) \\ &= (1/2)\, e^{(g+g')/2}[e^{(g-g')/2} - e^{(g'-g)/2}] \end{aligned}$$

and hence :

$$F(g', g) = (g' - g)^2[e^{(g-g')/2} - e^{(g'-g)/2}]^{-2} \tag{1.43}$$

This has the value 1 when $g - g' = 0$, and a value close to 0.3 when

$|g-g'|=4$, after which it falls off rapidly. This value of $g-g'$ may, therefore, be taken, roughly, as the limit of good resonance.

$g'-g$ is related to $v_0'-v_0$, whereas we would rather reckon the difference in terms of energy, expressing it in terms of $\Delta\varepsilon_k$. By Eq. (1.27) we have :

$$\Delta\varepsilon_k = (2M\bar{\varepsilon}_k)^{1/2}\,(g-g')\,h\alpha/4\pi^2M$$

If for orientation we take $\varepsilon_k = kT$, and try $T = 300^0$ K, $\alpha = 5 \times 10^8$, $|g'-g| = 4$ and $M = 20$ atomic weight units :

$$\Delta\varepsilon_k\,(\text{res})/kT = (h\alpha/\pi^2)\,(2/MkT)^{1/2} \sim 0.4 \qquad (1.44)$$

We have compared $\Delta\varepsilon_k$ to kT and have set $g'-g=4$ because it is evident that we need transfers of energy between vibration and translation of at least the order of kT to be effective in activation or deactivation of a reacting molecule, and it is at the same time necessary that the amount transferred be not very far out of the range of good resonance if the collision process is to be efficient. We note that the range of good resonance is stretched out by decreasing M and by increasing the sharpness of the collision as measured by α.

Since we wish to apply these equations to activation and deactivation in chemical reactions, and since these processes are believed to occur generally with high efficiency, we have made no attempt to take into account the distribution of velocities of the colliding particles. If the process is highly efficient, one must fix one's attention on collisions of average energy. Nor have we attempted to make the other corrections which appear in Eq. (1.33), for they would appear to be relatively unimportant in view of the uncertainties necessarily involved.

All these refinements were taken into account by Tanczos (30), who also made a much more careful analysis of the normal vibrations, in attempting to explain the acoustical effects in CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. He got fair to reasonably good agreement with experiment, and even accounted for a double dispersion in CH_2Cl_2. In these molecules a complex transition involving a change of quantum number of 1 in one oscillator and a change of 2 in another was of some importance. The transition probability in this case would involve expanding $e^{-\alpha x}$ to the term in x^2, which has a nonzero matrix component only for jumps of two levels. It introduces into the expression for γ_{nn}' another factor :

$$(\alpha/2\pi)^2\,(h/2\bar{\mu}\nu_0)\,(n_l - 1)/4 \qquad (1.45)$$

similar to the left-hand side of Eq. (1.42) but with n_l replaced by $(n_l-1)/4$.

E. Experimental material — Some complex molecules.

In considering polyatomic molecules it is generally assumed that the acoustical relaxation time is controlled (through an equation involving heat capacity of the molecule and of the particular mode) by the most rapid transition involving transfer between translational energy and the vibrational energy of a single mode, in general, the one with the lowest frequency (31, 32). It is assumed that equilibrium within and between vibrational degrees of freedom is established more rapidly, by complex collisions. Sometimes, however, this is not the case, and, as noted above, two relaxation times can be observed. Two relaxation times have also been observed in SO_2, and this has been analysed in detail by McCoubrey, Milward, and Ubbelohde (33).

Hudson, McCoubrey, and Ubbelohde (34) have recently made some acoustical measurements on energy exchange in C_2H_4, C_2D_4, and also the exchange between C_2H_4 and isotopically substituted ethylenes and between C_2H_4 and H_2O and D_2O. The number of collisions to effect energy transfer at room temperature range from 100 to 800 for the ethylenes and ethylene mixtures, and around 30 to 40 with H_2O and D_2O present. The isotopes are of interest, because with these experiments only the masses and frequencies are varied, and so the interpretation of comparative results is made simpler. Even so, it is, at least in some cases, rather involved and speculative. Using Tanczos' equations, McCoubrey, Milward, and Ubbelohde (35) have had some success in correlating energy exchange probabilities for a series of diatomic and polyatomic gases. The temperature coefficients of some very consistent sets of data were used to obtain that value of α which would best fit the data. The values thus obtained were in general somewhat larger than the values used by Herzfeld and Litovitz (8c), being in the range 6 to 8 × 10^8cm^{-1}, rather than around 5 × 10^8 cm^{-1}. The pre-exponential factors then found necessary to fit the data were somewhat low, indicating, if this higher value of α is correct, that the steric factor is somewhat lower than the value 1/3 guessed by Herzfeld and Litovitz.

Lambert and Rowlinson (32) have made an extensive series of sound dispersion measurements on organic compounds, and it is of some interest for our purposes, that the relaxation times of most flexible hydrocarbons correspond to collision efficiencies greater than 0.01, and that they conclude that interchange of vibrational energy between modes within the molecule is very rapid.

Extensive reviews of the literature have been given by Cottrell and McCoubrey (7) and by Herzfeld and Litovitz (8), and by Vines (36).

II. RECOMBINATION OF ATOMS

A. General considerations.

The recombination of atoms in the presence of a third body is a chemically important and simple example of energy exchange producing chemical reaction. In its simplest form the recombination of A and B in the presence of a third body M will proceed in the following way.

$$\mathrm{A + B + M \rightarrow AB + M} \qquad \text{(a)}$$

However, there are also undoubtedly cases in which the preliminary establishment of an equilibrium involving a loosely bond complex (37), say B · M, occurs. In this case the reactions are :

$$\mathrm{B + M \rightleftarrows B \cdot M} \qquad \text{(b)}$$

$$\mathrm{B \cdot M + A \rightarrow AB + M} \qquad \text{(c)}$$

or, perhaps in some cases (38) :

$$\mathrm{B \cdot M + A \rightarrow AB \cdot M} \qquad \text{(c')}$$

The complex in (b) and (c) could of course be A · M rather than B · M.

It is often more convenient to consider dissociation of the molecule AB. If k_a is the rate constant for reaction (a) and k_d the rate constant for the reverse reaction, then :

$$k_a = k_d K \tag{2.1}$$

where K is the equilibrium constant, (AB)/(A)(B). [(AB), etc., are concentrations.] In making calculations, k_d has the advantage of involving only two-body collisions. Reaction (a) and its inverse constitute the " collision mechanism ".

The mechanism involving (b) and (c) we refer to as the " complex mechanism ". In this case [using a prime to distinguish k_a from k_a of Eq. (2.1)] :

$$k_a' = K_{BM} k_{aM} \tag{2.2}$$

where K_{BM} is the equilibrium constant for reaction (b) and k_{aM} the rate constant for reaction (c). In the reverse reaction, the reverse of reaction (c) is the rate-determining step, and the rate constant therefore may be designated as k_d'. Again Eq. (2.1) holds.

Dissociation in the complex mechanism may take place through a sequence involving the reverse of reaction (c′) :

$$AB + M \rightleftarrows AB \cdot M \tag{d}$$

$$AB \cdot M \rightarrow A + B \cdot M \tag{e}$$

if the complex AB · M can be stabilized by dissipation of the association energy in the internal motions of AB · M. However, regardless of whether this stabilization takes place or not, the transition state or activated complex will be essentially the same as in the direct reversal of (c). This being the case, if the rate can be obtained from the usual equilibrium theory of the activated complex, the calculation is conveniently made through the assumption that AB · M is present whether it is or not. This gives then, for the dissociation :

$$k_d' = K_{AB \cdot M} k_{dM} \tag{2.3}$$

where $K_{AB \cdot M}$ is the equilibrium constant for (d) and k_{dM} the rate constant for (e).

In the decomposition of a diatomic molecule, the population of the high energy levels will be considerably depressed below its equilibrium value. In the recombination of atoms, molecules will be formed in the higher energy levels, and these may then dissociate again, so that they do not in the end contribute to the association reaction. It has been pointed out by a number of writers (39–44) that these effects can be of considerable importance, and it seems simplest to formulate the rate constants at once in terms of a series of energy transfer processes (45–47), involving all the vibrational levels, or at least all those near the dissociation limit. The rate constants k_a and k_d will clearly be smaller than those obtained if it is assumed that equilibrium is established throughout all these energy levels.

First we remark that, though k_a and k_d may be altered by lack of equilibrium, Eq. (2.1) will still hold under conditions in which rate constants can be determined at all (48). This has been doubted by a number of writers (40, 41, 43–45, 49), so requires some attention. We will assume that the only states which will not be essentially in equilibrium are states which would in any case contain a relatively small number of systems — in the case of dissociation because they have a high energy, in the case of association because they are associated states and hence occupy a restricted region of phase space. It is further assumed that the time required to establish equilibrium in these levels, were further reaction not to occur (which, for the dissociation, is just the relaxation time studied in Section I), is small compared to the overall time of the reaction; if this were not the case, the reaction would have an induction period, and one could not determine rate constants in any unequivocal fashion. Relaxation times have been measured (50) for vibrations in Cl_2 over a very large range of temperatures, by shock-wave methods. These are presumably long (8c) compared to relaxation times in Br_2, but it has been pointed out (48) that they are always short compared to the dissociation times in Br_2. The dissociation time decreases more rapidly with temperature than does the relaxation time, but the number of collisions required for dissociation can never become less than $e^{\Delta E/RT}$ divided by something of the order of less than 100, where ΔE is the dissociation energy. For 0_2 at 6000^0 K, $e^{\Delta E/RT}$ is about $10^{4.2}$, while the number of collisions required for energy exchange is (8) 1800 at 2900^0 K. These examples illustrate the general validity of the assumption. Camac and Vaughan (51) state the relaxation time and dissociation time of 0_2 became comparable at around

8000° K. At these temperatures it is, on this account, impossible to make a reliable determination of the rate constant. It is sometimes necessary to consider whether the third body, if more complex than an atom, is relaxed, but this is a different problem.

Let us consider now individual processes of association of $A + B$ or of dissociation of AB in the presence of a large excess of M, essentially the condition for measurement of the rate of the reactions we have considered. The fate of any AB molecule will depend on collisions with M, and will be unaffected by the presence of A and B atoms; likewise, the fate of any $A + B$ after it has provisionally combined into an excited AB will be independent of AB's present. Since either of these two opposing reactions would therefore go at same rate if A, B, and AB were present in equilibrium numbers a if the opposing reactants were absent, Eq. (2.1) must hold. If M were either AB, A, or B, the experiment would still have to be performed under conditions such that M was in excess for either direction of reaction, and hence for the equilibrium. Since such conditions cannot always be met, the test to be applied (perhaps not always carried out in practice) is whether the rate to be attributed to any given third body is dependent of the presence of others. It is probably generally justified to use Eq. (2.1).

It is seen that the condition postulated for the relaxation time is such that the populations which are not in equilibrium do come to steady states. The steady state populations of the higher vibrational states are less than the equilibrium populations. The steady state populations, in these same levels, which are produced in the association are such as to just supplement the lack of population in the dissociation, if association and dissociation are proceeding together in equilibrium. The lowering of the rate of dissociation is also just balanced by the lowering of the rate of association due to the back reaction of those pairs in higher vibrational states.

Pritchard (52) has suggested that Eq. (2.1) would not hold if there should be a " bottleneck " among the vibrational levels, through which reaction could proceed only slowly. However, unless the bottleneck occurs at a very low energy level, the statements of the preceding paragraphs will still hold. Passage through the bottleneck might well be the rate determining step, but it has the same effect in the two directions. The higher energy levels between the bottleneck and dissociation will fill up to their steady state levels, requiring relatively few molecules, rapidly compared with the rate of reaction. The ultimate fate of a dissociating molecule or an associating pair will still be independent of anything except the concentration of M, so our argument will go through as before. In the actual calculation of the rate proposed below, the possibility of a bottleneck is not taken into account.

B. Collision and complex theories.

It has been suggested that the proper approach to the problem of determining the populations of the excited vibrational levels and ultimately the rate of decomposition of a diatomic molecule reacting according to the reverse of (a) is to consider stepwise transitions from one vibrational level to the next. Eventually, then, one would wish to apply the ideas of Section I. However, before dissociation occurs anharmonicity becomes great, and in many cases the energy levels come very close together. Changes of vibrational quantum number considerably greater than ± 1 become common; the situation will differ, at least in detail, greatly from that considered in Section I, and it will, indeed, be expeditious to consider some aspects of the problem from the point of view of classical mechanics. It therefore appears to me (47) that it will be more realistic to assume that constant changes of energy, closely related to the average energy of the colliding particle M, will occur, rather than constant changes of vibrational quantum number. Actually there will be a range of possible energy exchanges, but it is hoped that a qualitative picture can be obtained by the assumption that the exchange of energy from vibration to translation always occurs in increments η equal to the average of the true exchanges. These can be assumed to include rotational changes, since these also shift the level with respect to the rotational barrier. It is not proposed to develop a complete theory in this way, but to lay a foundation for discussion of the experimental results.

We can think of the vibrational energy levels of the diatomic molecule as divided into zones of width η designated by a suffix i. Dissociation will always take place from the highest of these zones, for which we set $i = 0$; $i + 1$ refers to a *lower* energy than i. We can designate a molecule in state i as AB_i. We have a series of reactions, which can proceed in either direction, with rate constants as indicated :

$$AB_i + M \underset{k_{-(i+1)}}{\overset{k_i}{\rightleftarrows}} AB_{i+1} + M \tag{f}$$

but for $i = 0$:

$$AB_0 + M \overset{k_{-0}}{\rightarrow} A + B + M \tag{g}$$

We get a series of steady-state equations, in the usual way, by setting $d(AB_i)/dt = 0$. From $d(AB_0)/dt$:

$$k_{-1}X_1 - (k_0 + k_{-0})X_0 = 0 \tag{2.4}$$

and, in general :

$$k_{-(i+1)}X_{i+1} + k_{i-1}X_{i-1} - (k_i + k_{-i})X_i = 0 \tag{2.5}$$

where X_i is the concentration of AB_i, etc. The rate constants are of course mean values for the different zones. Each zone is characterized by a mean energy ε_i and the number g_i of energy levels contained in the zone. We take the zero of energy at the dissociation limit, so that $\varepsilon_0 \cong - \eta/2$, and write :

$$\eta/kT = a \tag{2.6}$$

and :

$$\varepsilon_i/kT = x_i \tag{2.7}$$

If all the k_i were known we could find all the X_i in terms of X_0 from Eq. (2.4) and (2.5) by simple iteration. The k_i are not known but certain relations between them are. From the law of microscopic reversibility we can write :

$$k_i/k_{-(i+1)} = (g_{i+1}/g_i)e^a \tag{2.8}$$

since this gives the correct ratio X_i/X_{i+1} at equilibrium. For the steady-state concentration, it seems natural to set :

$$X_i = c_i g_i e^{-x_i} \tag{2.9}$$

since if X_i were the equilibrium concentration all the c_i would be equal. The ratio c_0/c_∞, where c_∞ refers to a low enough energy for its X_i to practically coincide with its equilibrium value, is a measure of the deviation of zone 0 from equilibrium. Substituting Eq. (2.9) in Eq. (2.4) and (2.5), making use of Eq. (2.8), and setting :

$$y_i = k_i/k_i + k_{-i}) \tag{2.10}$$

$$y_{-i} = k_{-i}/(k_i + k_{-i}) \tag{2.11}$$

we get :

$$y_i c_{i+1} + y_{-i} c_{i-1} - c_i = 0 \tag{2.12}$$

which includes the results from both (2.4) and (2.5) if we set $c_{-1} = 0$. We rewrite Eq. (2.12) by replacing $i + 1$ by i to get it in a convenient form for the iteration :

$$c_i = y_{i-1}{}^{-1} c_{i-1} - (y_{-(i-1)}/y_{i-1}) c_{i-2} = (1 + b_i) c_{i-1} - b_i c_{i-2} \tag{2.13}$$

where :

$$b_i = y_{-(i-1)}/y_{i-1} \tag{2.14}$$

is the ratio of a jump upward to a jump downward from the same state. In general we can solve the set of equations (2.13) by iteration if the b_i are known. If b_i is taken as constant ($= b$), less than 1, then it is readily shown (in exact analogy to the case of the truncated harmonic oscillator (46, 53)) that :

$$c_i = 1 + b + b^2 + \ldots . b^i = (1 - b^{i+1})/(1 - b) \tag{2.15}$$

within a constant factor, and, approximately:

$$c_0/c_\infty = 1 - b \tag{2.16}$$

b will be closely related to the energy difference η, and we write :

$$b = f e^{-a} \tag{2.17}$$

where f is presumably not far from unity, which says that the relative probability of up or down transition is nearly equal to the Boltzmann factor.

We can now write down an expression for the dissociation rate constant ⁽⁴⁷⁾ :

$$k_d = \left[4\pi\sigma^2\left(\frac{kT}{2\pi M}\right)^{1/2}\right]\left[\frac{ng_0 e^{-\varepsilon_D/kT} e^{a/2}}{Q_{AB}}\right][1 - fe^{-a}]\left[\frac{fe^{-a}}{1+fe^{-a}}\right]\left(\frac{r_m}{r_0}\right)^2 \tag{2.18}$$

This may be understood by analysis of the factors involved. The first bracket is the collision frequency for collisions between AB and M with an effective collision diameter σ; M is the reduced mass of AB + M. In the numerator of the second bracket n is the number of attractive electronic energy levels, having the same asymptote as the ground state, from which dissociation can occur, g_0 is the average number of states in the zone $i = 0$ in these levels, ε_D is the dissociation energy so that $\varepsilon_D - \eta/2 = \varepsilon_D - akT/2$ is close to the average energy in zone $i = 0$. Thus it is seen that the numerator may be said to represent the partition function for the zone $i = 0$, and Q_{AB} is the partition function for the molecule AB (which, classically, equals $kT/h\nu_{AB}$); the ratio is equal to the relative number of molecules which are in a position to dissociate at equilibrium. The next factor, which comes directly from Equation (2.16), takes into account the deviation from equilibrium, and the fourth gives the relative probability of dissociation (rather than deactivation) at collision. This would complete the expression for a nonrotating molecule. Averaging over rotational levels, taking into account the effect of the centrifugal potential on the dissociation energy, introduces ⁽⁵⁴⁾ the factor r_m^2/r_0^2, where r_m is an average value of the internuclear distance in AB at the maximum arising from the centrifugal potential in the potential energy curve, and r_0 is the equilibrium distance for AB.

The difference, $\delta\varepsilon_v$ between energy levels near the dissociation is given roughly by a linear relation in the quantum number v.

$$\delta\varepsilon_v = \alpha(v_D - v) \tag{2.19}$$

where v_D is the quantum number at the dissociation limit, ε_D. If $\delta\varepsilon_{v_0}$ is the value of $\delta\varepsilon_v$ at $\varepsilon_D - kT$ it may be shown that :

$$g_0 = 2a^{1/2}kT/\delta\varepsilon_{v_0} \tag{2.20}$$

An earlier derived expression ⁽⁵⁵⁾ for k_d, neglecting any departure from equilibrium, which differed essentially from Eq. (2.18) in omitting the third and fourth brackets, was equivalent to :

$$k_d = \left[4\pi\sigma^2\left(\frac{kT}{2\pi M}\right)^{1/2}\right]\left[\frac{n(kT/\delta\varepsilon_{v_0})e^{-\varepsilon_D/kT}}{Q_{AB}}\right]\left(\frac{r_m}{r_0}\right)^2 \tag{2.21}$$

Steiner (56) had much earlier derived an expression for the association, which, used with Eq. (2.1), was essentially the same as Eq. (2.21), with the duration of a collision of the atoms A and B, designated as τ, substituted for $h/\delta\varepsilon_{v_0}$. The near equivalence of τ and $h/\delta\varepsilon_{v_0}$ can be demonstrated (55).

Eqs. (2.20) and (2.21) may be compared with what is obtained for the complex mechanism by evaluation of Eq. (2.3). We may set :

$$K_{AB\cdot M} = 4\pi a^2\delta a e^{\varepsilon_M/kT} \tag{2.22}$$

where a is the average distance of AB and M in the complex, δa is their average freedom of motion toward and away from each other, so that $4\pi a^2\delta a$ is the free volume (we assume the partners can rotate freely in the complex), and ε_M is the dissociation energy (bottom of potential-energy curve to the asymptote) of the complex. The reaction (e) we can consider as a unimolecular decomposition, and write :

$$\begin{aligned} k_{dM} &= n(kT/hQ_{AB})e^{-\varepsilon_D'/kT}(r_m/r_0)^2 \\ &\cong n\nu_{AB}\, e^{-\varepsilon_D'/kT}(r_m/r_0)^2 \end{aligned} \tag{2.23}$$

where ε_D' is the energy of dissociation for the reaction (e) involving the complexes. ε_D' will, of course, be close to ε_D. Combining Eqs. (2.22) and (2.23) with (2.3) we have :

$$k_d' = 4\pi a^2\delta a n(kT/hQ_{AB})\, e^{-(\varepsilon_D'-\varepsilon_M)/kT}(r_m/r_0)^2 \tag{2.24}$$

It is to be noted that unless ε_M is appreciably greater than kT, Eq. (2.24) will break down (at least with a usual definition of δa) because the bound states of $AB\cdot M$ will become filled (55), and $K_{AB\cdot M}$ will decrease more rapidly with temperature than anticipated, and Bunker and Davidson (57) have attempted a detailed calculation of this effect. Eq. (2.24) makes no allowance for lack of equilibrium in the higher vibrational states. This is probably all right if M is itself a polyatomic molecule and the complex AB · M actually exists. Otherwise a correction $1 - fe^{-a}$ should be included in the expression. It is instructive to divide k_d' by k_d as given by Eq. (2.21). Setting $\tau = \delta\varepsilon_{v_0}/h$ and $\delta\sigma = (kT/2\pi M)^{1/2}\tau$ (roughly distance traveled by M relative to AB during the time of a collision of A and B) in Eq. (2.21) we have :

$$k_d'/k_d = (a/\sigma)^2 (\delta a/\delta\sigma) e^{(\varepsilon_D - \varepsilon_D' + \varepsilon_M)/kT} \qquad (2.25)$$

Estimates have been made (55) of δa and $\delta\sigma$ and the ratio is likely to be near unity. Though a/σ may be somewhat more than unity, the possibility of k_d' being of greater importance than k_d will largely depend on the exponential factor, in particular, on $e^{\varepsilon_M/kT}$, and on the validity of (2.23) and (2.24). Both mechanisms can contribute comparably simultaneously.

The evaluation of Eq. (2.18) will depend upon the determination of a. As we have remarked, a collision between M and AB when the latter is in an excited state can probably be well handled classically. As during a considerable part of their vibration A and B will have a considerable separation, they will exert only small forces on each other, and will be moving slowly relatively to each other. Thus we might expect the transfer of energy from M to occur largely through collision with *one* of the atoms A and B, say B. We would expect to learn something about it by considering a collision between M and B in which B is stationary. The maximum amount of kinetic energy which can be transferred from M to B in this way is : $4m_M m_B/(m_M + m_B)^2$ times the original kinetic energy of M. We shall make the assumption that :

$$a = 4m_M\bar{m}/(m_M + \bar{m})^2 \qquad (2.26)$$

where $\bar{m}$ is the average of m_A and m_B. This is equivalent to supposing that if the masses were the same, the average energy transferred would be equal to kT, and we may hope that it will take care of the effect of the masses so that we can use the combination of Eq. (2.18) and (2.26) as a working tool to help in the analysis of experimental data. Eq. (2.26) should be applied, however, only when AB is heavier than M, so that AB may be considered, as a first approximation, not to be moving; then it can serve as a reasonable guide. Even in this case Eq. (2.26) undoubtedly exaggerates the effect of a difference in mass, since it can only be a rough approximation to suppose that the third body M, even if it is only an atom, collides with *one* of the atoms AB.

C. Phase space trajectories — The variational theory.

Before discussing the experimental material we will give a summary of the so-called variational theory of reaction rates of Keck (58). This is a development of an idea, apparently due originally to Marcellin (59), and applied by Wigner (60) to the problem under consideration. Again using classical mechanics, one considers the phase space for the system consisting of three atoms, A, B, and M. If the coordinates and momenta of the center of gravity are excluded, only motion relative to the center of gravity being considered, this is a 12-dimensional space. One now seeks a surface S (11-dimensional) which divides the phase-space into two parts, one corresponding to separated atoms A and B, the other to the molecule AB. Such a surface may be so chosen that, when the relative coordinates and momenta, M-AB, have any fixed value, and the polar angles made by AB, and the corresponding momenta, are fixed, the projection of the surface in the two-dimensional space, r_{AB}, p_{AB} (interatomic distance and relative momentum of A and B) lies at a constant energy just touching the maximum in the potential energy plus rotational potential curve for AB (see Fig. 1 — in the figure the relative energy ε_{AB} of AB replaces the momentum p_{AB} as a coordinate). This surface was modified by Keck, but for the cases of most interest it was essentially as described.

If the density of phase points at any point on S surface is ρ and if their vector velocity is $\mathbf{v}$, then the rate at which they will cross the surface per unit area at that point will be $\rho\,|\mathbf{v}\cdot\mathbf{n}|$ where $\mathbf{n}$ is a unit vector normal to S. They may be crossing in either direction, depending upon the particular point in the phase space. If we count only those which are crossing in the "positive" direction and integrate over that part, say S_+ of the surface corresponding to that particular direction, we obtain the rate of reaction in that direction, namely :

$$R = \int_{S_+} \rho\,|\mathbf{v}\,.\,\mathbf{n}|\,d\sigma \tag{2.27}$$

where $d\sigma$ is the element of surface, provided none of the points which thus cross S_+ recross at some other position later, which of course reverses the reaction. This last proviso means that this method of attack can give only an upper bound to the reaction rate. It will still be an upper bound if we substitute ρ_e for ρ, where ρ_e is the density of phase points at the surface in equilibrium with the distribution a great distance from the surface, since ρ could not exceed ρ_e. In general, over any particular area of the surface, if this area is small enough, the value of ρ should be equal either to ρ_e or to 0; it is 0 if the phase points at this part of the surface originated on the wrong side, having already crossed one in the wrong direction.

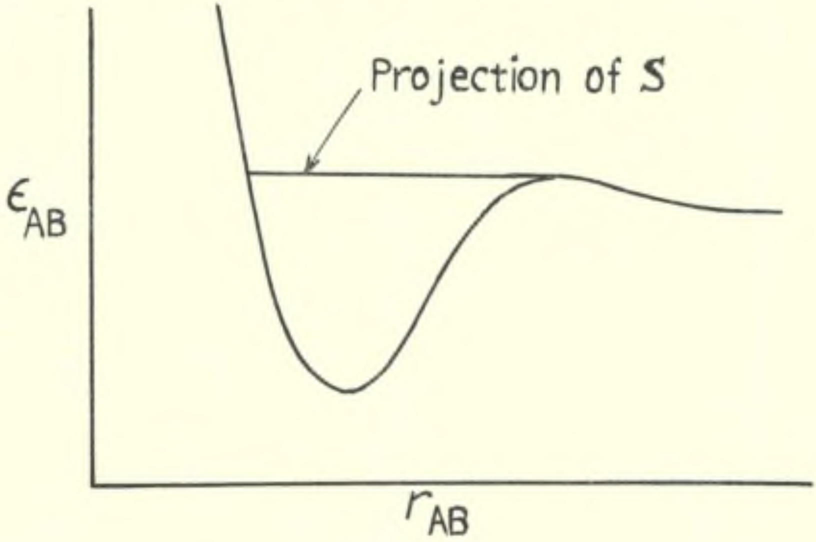

Fig. 1

For the dissociation reaction we may write, if the concentrations of AB and M are unity :

$$\rho_e = e^{-\varepsilon/kT}/h^6 Q_{AB} Q_r \tag{2.28}$$

where Q_{AB} is the partition function for the molecule AB and Q_r is that for the relative motion of AB and M, since $1/h^6$ is the number of energy levels per unit volume of phase space. Therefore :

$$k_d \leq (h^6 Q_{AB} Q_r)^{-1} \int_{S_+} |\mathbf{v} \cdot \mathbf{n}| \, e^{-\varepsilon/kT} d\sigma \tag{2.29}$$

Now let us define a function Φ of the six coordinates q_i and six momenta p_i such that at S we have $\Phi = 0$ and such that a unit change of Φ (at least at S) represents a displacement of unit length normal to S in the phase space. We may then write :

$$\int_{S_+} |\mathbf{v} \cdot \mathbf{n}| e^{-\varepsilon/kT} d\sigma = \int_0^1 \int_{S_+} |\mathbf{v} \cdot \mathbf{n}| e^{-\varepsilon/kT} d\sigma d\Phi$$

$$= \int_{\Phi=0}^{\Phi=1} (\mathbf{v} \cdot \mathbf{n})\, e^{-\varepsilon/kT}\, \Pi_i dq_i dp_i \tag{2.30}$$

assuming $\mathbf{v} \cdot \mathbf{n} e^{-\varepsilon/kT}$ to be constant between $\Phi = 0$ and $\Phi = 1$. Here $(\mathbf{v} \cdot \mathbf{n}) = |\mathbf{v} \cdot \mathbf{n}|$ if the flow is toward dissociation but zero otherwise. The components of $\mathbf{v}$ are the time derivatives $\dot{q}_i$, $\dot{p}_i$ and those of $\mathbf{n}$ are $\partial\Phi/\partial q_i$, $\partial\Phi/\partial p_i$.

Thus :

$$\mathbf{v} \cdot \mathbf{n} = \sum_i [\dot{p}_i(\partial\Phi/\partial p_i) + \dot{q}_i(\partial\Phi/\partial q_i)]$$

$$= \sum_i \left(- \frac{\partial H}{\partial q_i} \frac{\partial \Phi}{\partial p_i} + \frac{\partial H}{\partial q_i} \frac{\partial \Phi}{\partial q_i} \right)$$

where H is the Hamiltonian and we have applied the Hamilton-Jacobi equations. Since the last quantity in parentheses is the Jacobian J_i of the transformation of $dp_i dq_i$ to $dH d\Phi$, or in other notation, to $d\varepsilon d\Phi$, it is seen that the integral, confined, of course, to regions where the flow is toward dissociation, is transformed to :

$$\sum_i \int_{\Phi=0}^{\Phi=1} s_i e^{-\varepsilon/kT} \, d\varepsilon d\Phi \prod_{k \neq i} dq_k dp_k$$

$$= \sum_i \int_{S_+} s_i e^{-\varepsilon/kT} \, d\varepsilon \prod_{k \neq i} dq_k dp_k \tag{2.31}$$

where $s_i = J_i / |J_i|$ (i.e., $= \pm 1$, depending on the sign of J_i, since each transformed volume element is taken positive), or 0, if $J_i = 0$. We can now find k_d if we can find the limits of the various variables defined by S_+. This is a well-defined though still a complicated problem, which has been solved by Keck through further changes of variables. The mutual potentials of the atoms come in through the variable ε. Keck has represented the potential energy of AB by a Morse function, and he has made an estimate of the mutual potential energies A-M and B-M. The two-body potentials were assumed to be additive. The potential A-M and B-M include estimates for the van der Waals attraction (e.g., if A or B was an iodine atom, it was assumed for this purpose to be much like xenon), and the assumption was made that there was an equilibrium population bound by the van der Waals potential, so presumably both collision and complex mechanism were included.

Since this procedure gives only an upper bound, Keck (61) made some calculations on actual trajectories, so that he could make an estimate as to how great the overestimate might be. He randomly selected points in the phase space, all of which lay on the surface S_+ (he investigated association, but the information thus obtained is the same as for dissociation) in such a way that the surface density was proportional to the integrand of Eq. (2.29). The trajectories to which these points belonged were followed by use of a computer, both forward and backward, until M was reasonably far from A and B in both directions. One could then decide whether a given trajectory which crossed S_+ would result in reaction, how many would recross the surface once more and so not react, how many would cross again, etc. Also he could tell how many of those crossing the surface were actually in their second crossing, having originated on the other side of the surface. He investigated 2H + Ar, 2O + Ar, and 2I + Ar. In each case he considered temperatures such that $kT/\varepsilon_D = 0.01$ and $kT/\varepsilon_D = 0.1$. For 2H + Ar at $kT/\varepsilon_D = 0.01$ the ratio of reaction to crossings (counting double those cases where two crossings in the same directions occurred) was about 0.26, for 2O + Ar it was about 0.40, and for 2I + Ar about 0.64, it being a little less at the higher temperature for the first two and a little more for 2I + Ar. It was also possible to find the distribution of energies for the molecule formed when reaction occurred. In all cases close to half of the combined molecules were within $kT/4$ of the maximum of the potential energy plus rotational potential. Since a pair of colliding atoms will have an average relative kinetic energy of kT, this seems fairly reasonable if there is an average transfer of kT or a little less. There is no real test of Eq. (2.26), since only one case was treated in which the mass of AB was greater than that of M.

Another calculation, based essentially on a general analytic treatment of the paths in phase space, has recently been made by Light (62). Since he used a truncated harmonic oscillator model, it would be expected that these calculations could not be applicable to the actual reactions. As we will see, the increase in rate brought about by the density of levels near the dissociation limit seems to be a very essential feature. Yet, strangely enough, Light finds rates which are too high. It is not clear how this situation arises.

A quantum mechanical calculation has been made by Bauer and Salkoff (63) for the probability of transition on collision from excited vibrational levels to the continuum. The method used was quite similar to the method used by them to calculate the probability of transitions from one vibrational state to another (18) [see paragraph following Eq. (1.35)]. The apparent motivation for this work was to explain the high collision efficiencies for such a process, but in the following discussion we will see that these are well taken care of in Eq. (2.18) and in the older work. However, the results are of some interest in themselves. Application was made to the recombination of oxygen atoms to form O_2 in the $A^3\Sigma_u^+$ excited state, since for this state there are just ten vibrational states, all of which are known. It was found that, even up to 5000°, the contribution to decomposition was greater from the highest vibrational level than from the second highest, though the latter was only 340 cm^{-1} or 970 cal/mole below dissociation. The second highest was catching up, but it is surprising, in the light of Keck's calculations, that it never contributed as much as the highest level. It is possible that quantum effects were sufficiently important to upset this expectation in this case; but it should also be noted that Bauer and Salkoff made a rather arbitrary correction for perturbations which were so large as to cause apparent transition probabilities greater than 1, whereas actually this is a matter of considerable complication (20). Bauer and Salkoff made no allowance for the effect of lack of equilibrium, which would be rather extreme in this case. The fact that their results for the recombination of oxygen atoms to the $A^3\Sigma_u^+$ state alone tend to exceed the total observed rate for the recombination is, therefore, probably not significant.

D. **Experimental material.**

Early experimental work on the recombination of iodine and of bromine atoms at room temperature was done by Rabinowitch and co-workers (64–66) using a method which involved a photochemical steady state. More recently use has been made of flash photolysis for measurements up to 250° C, and of shock waves, combined with spectroscopic observations or density measurements back of the shock front using optical methods, for the dissociation of diatomic gases above 1000° C. Since association and dissociation are connected by Eq. (2.1) they can be converted one into the other.

Most work has been done on the recombination of iodine atoms. The recombination rate constants range from around 0.3×10^{-32} cc^2 $molecules^{-2}$ sec^{-1} for He as a third body to $25\text{-}50 \times 10^{-32}$ with benzene as a third body, and even higher for some large organic molecules, and 500×10^{-32} or more with I_2 as third body. Even with He the rate (expressed as a dissociation rate for I_2) is rather large compared with the expected number of collisions having the requisite energy. This is in large part because of the relatively large density of energy levels near the dissociation [the factor g_0 in Eq. (2.18); n and $(r_m/r_0)^2$ also contribute]; in other cases, the very large rates reflect the considerable stability of the complex $I \cdot M$.

In the association of I atoms in benzene a very direct comparison is possible. Atack and Rice (67) have made equation-of-state measurements of mixtures of I_2 and benzene. Judging from the magnitude of the deviations from the ideal mixing law, the forces between I_2 and benzene molecules are of the van der Waals type. The results of Atack and Rice were used to find the equilibrium constant for the formation of a van der Waals complex $I_2 \cdot C_6H_6$. This was then used directly (55) in Eq. (2.3), together with Eq. (2.23) to calculate k_d'. In Eq. (2.23) n was taken * as 5, $\nu_{AB}(=\nu_{I_2})$ was taken from the tabulation of Herzberg (69), $(r_m/r_0)^2$ was estimated as 5, and it was assumed that $\varepsilon_D' = \varepsilon_D$. In this way, and by use of Eq. (2.1), we found $k_a = 33 \times 10^{-32}$ cc $molecule^{-2}$ sec^{-1} which is to be compared with experimental values (66, 70, 71) of about 20 to 50×10^{-32}, the more reliable ones probably being in the lower part of the range. It is seen that the agreement is very good.

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* This value is used because there are three attractive states, connecting with unexcited atoms, for I_2, ${}^1\Sigma_g{}^+$, ${}^3\Pi_{1u}$, and ${}^3\Pi_{2u}$, the last two of which have twofold degeneracy. The ${}^3\Pi_{2u}$ has not been observed, but there are theoretical reasons for believing in its existence and its dissociation energy has been estimated (68). On account of the fact that iodine (and, indeed, also bromine) approaches *j-j* coupling it is likely that changes in multiplicity at collision are probable. If such transitions become comparable with energy exchange at an energy below the dissociation limit equal to several times the average energy transferred, the levels of all the electronic states must be considered together. The ${}^3\Pi_{1u}$ state is, however, so shallow that it is somewhat doubtful if this condition is fulfilled, and it may be that association to this state will be reversed before it can be stabilized by transfer to ${}^1\Sigma_g{}^+$ or ${}^3\Pi_{2u}$ and subsequent loss of energy. If this is true, n should be reduced to 3.

The assumption that $\varepsilon_D' = \varepsilon_D$ means that the stability of $C_6H_6 \cdot I$ is the same as that of $C_6H_6 \cdot I_2$. We actually have very little to go on in estimating van der Waals constants for I; it may be, however, a little surprising that I, with only half as many electrons as I_2, should have the same van der Waals attraction for benzene. Porter and Smith (71) have suggested that I forms a charge transfer complex with benzene. In this connection, however, it should be noted that Atack and Rice found that their van der Waals complex in the gas phase was at least six times as stable as the well-known I_2-benzene charge transfer complex, which was studied in solution by Benesi and Hildebrand (72). It is not certain that iodine atoms would be comparable in this respect.

The temperature coefficient of k_d' and of k_a' may be inferred by scrutiny of Eqs. (2.22) and (2.23), and use of Eq. (2.1). Unless the effective number of contributing electronic states changes with temperature, k_{dM} depends on temperature to any appreciable extent only through $e^{-\varepsilon_D'/kT}$ and r_m^2. If $\varepsilon_D' = \varepsilon_D$ the factor $e^{-\varepsilon_D'/kT}$ cancels the term $e^{\varepsilon_D/kT}$, which occurs in Eq. (2.1), when one obtains k_a'. r_m depends only slightly on temperature. Assuming that the attractive forces in I_2 at the distance r_m are chiefly van der Waals forces, having the form $-c/r^6$, where c is a constant, one finds (73) that r_m is proportional to $T^{-1/6}$. Eq. (2.22) depends on temperature chiefly through δa and $e^{\varepsilon_M/kT}$. δa can be shown to vary as $T^{1/2}$, and a similar free length will occur in K. It is seen, then, that we may expect :

$$k_a' \propto T^{2/3} e^{\varepsilon_M/kT}$$

which gives an energy of activation equal to $-\varepsilon_M + (2/3)\, kT$. Atack and Rice found an enthalpy ΔH of reaction for :

$$I_2 \cdot C_6H_6 \rightarrow I_2 + C_6H_6$$

equal to 2.44 kcal per mole, which, at the temperature used corresponds to a ΔE of reaction of about 1.55 kcal. Now $\Delta E = -RT^2$ $dlnK_{AB \cdot M}\, dT = (R/k)\varepsilon_M - 1/2\, RT$. So ε_M is equivalent to 2.0 kcal per mole, and the expected activation energy for association of iodine atoms around 400° K will be -1.5 kcal. Probably the most reliable determination is the recent one of Porter and Smith (71), who get

—1.7 kcal. All things taken together, we seem to have a reasonably good picture of the effect of benzene on the recombination of iodine atoms.

Porter and Smith have measured the recombination rate and its temperature coefficient for iodine atoms in a number of inert gases. In a general way, large rates go with large negative activation energies, as might be expected if a complex I · M is formed. Russell and Simons (70) had previously found high rates with third bodies which might be expected to have large van der Waals forces; however, as noted, Porter and Smith suggest that electron-transfer forces are involved.

Although in many cases the iodine recombination almost certainly proceeds through a complex I · M, it undoubtedly proceeds according to the collision mechanism with He, Ne, or H_2 as the third body. If I atoms exert forces comparable to I_2, then with argon the binding energy for I · Ar should render the contributions of the two mechanisms comparable (55). It will be be of interest to apply Eq. (2.18) to the reaction with the rare gases as third bodies. In doing this we take the experimental value of k_a as given and from it calculate σ, the effective collision diameter; we then decide whether the value of σ is reasonable. We again use $n = 5$ and $(r_m/r_0)^2 = 5$, and g_0 is taken from Eq. (2.20) using values of $\delta\varepsilon_{v_0}$ estimated from spectroscopic data and tabulated previously (55). a is evaluated from Eq. (2.26) and f is set equal to 1. The results of this calculation are given in Table I, and the values of σ found from Eq. (2.21) are also

TABLE I.

Recombination of I atoms in various gases.

Gas	He	Ne	Ar	Kr	Xe
$k_a \times 10^{32}$ (74) . . . . . . (cc^2 molec.$^{-2}$ sec.$^{-1}$)	0.335	0.46	0.92	1.125	1.495
σ (A°), Eq. (2.21)	1.1	1.9	3.1	3.9	4.9
a.	0.119	0.472	0.729	0.957	0.999
$1 - e^{-a}$	0.112	0.376	0.518	0.616	0.632
σ (A°), Eq. (2.18)	5.5	3.7	4.8	5.4	6.6

shown. The effect of the mass of the colliding atom seems to be fairly well taken into account by the factors involving a in Eq. (2.18), but the large value of σ found for He indicates that the effect, as should be expected, is somewhat exaggerated by Eq. (2.26). This conclusion is reinforced by the fact that the values of σ for the heavier gases would be reduced if allowance were made for the part of the reaction going through the complex mechanism.

If we assume that σ and a are temperature independent, take $Q_{\mathrm{AB}} \simeq kT/\nu_{\mathrm{AB}}$, allow for the temperature dependence, $r_m \propto T^{-1/6}$, use Eq. (2.20) for g_0, noting that $\delta\varepsilon_{v_0} \propto T^{1/2}$ and noting in addition that g_0 will probably decrease slightly with j, the average of which increases with T, we see that the temperature dependence of k_d is very closely $T^{-1/2} \exp^{-\varepsilon_{\mathrm{D}}/kT}$, and (assuming consistently with $Q_{\mathrm{AB}} = kT/h\nu_{\mathrm{AB}}$, that K has its classical value) there will then be practically no temperature dependence of k_a. However, even with He as third body there is an apparent activation energy (75) of —0.6 to 0.7 kcal*. If one compares the rate at room temperature and the rate determined in a shock tube (76) at 1300° K the apparent activation energy is about —1.3, but these are consistent with a rate roughly proportional to $1/T$. It has been suggested (42–46) that the temperature coefficient arises from the lack of equilibrium in the upper vibrational levels. This certainly would happen if η rather than a were constant. The calculations of Keck (61) on the trajectories in $2\mathrm{I} + \mathrm{Ar}$ seem to indicate that a is nearly constant, but an indefinite increase of η with T, might be hindered by a quantum effect, arising from increasingly poorer overlap of the vibrational wave functions as the energy levels get farther apart, especially for those collisions in which the two iodine atoms happen to be close together and hence cannot be considered separately in the collision. It is also true that the effective value of n might decrease, since at higher temperatures dissociation could take place more readily from the higher electronic states with relatively shallow minima. Glancing collisions would on the whole last a shorter time and thus be less effective at high temperatures. Finally, with Ar or heavier gases, the contribution of the complex mechanism would cause the negative

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* There appears to be an error in the activation energy quoted for He by Porter and Smith (71), since in this case their E_1 and E_2 do not seem to be mutually consistent.

activation energy to be higher. These suggestions, however, do not offer a quantitative solution of the problem.

The variational theory of Keck (58), based on Eqs. (2.29) and (2.31) offers a different approach to the cases where the third body is a rare gas atom. Calculations were carried out, using potential energies based on the assumption that, as far as concerns van der Waals forces I is close to Xe, as described following Eq. (2.31). In these calculations, in effect, only the ground state, ${}^1\Sigma_g^+$, was considered. These calculations resulted in good agreement with the experimental rate constants for the recombination of iodine atoms in the presence of rare gas atoms at room temperature, reproducing the observed trend very well. This good agreement actually seems strange, for not only does Keck's calculation give an upper bound, but, since it is an equilibrium theory, it should not be compared directly with the measured rate. It should be comparable with Eq. (2.18), if the correct value of σ is inserted, and the factor $1-e^{-a}$ omitted. This may well be closer to 1 than shown in Table I, as we already noted; however, it must be an appreciable factor. Thus Keck's calculated rate would appear actually to be too low. This may be due in part to neglect of the excited attractive electronic states, and in part to an underestimate of the attractive forces between iodine and the rare gases. On this basis Keck's calculation, after correction as suggested, would agree fairly well for He, but would give too high a rate for Xe, since for Xe the correction due to $1-e^{-a}$ would be negligible. It must thus be more of an overestimate the heavier the molecule.

It is of interest that Keck has stated that for a given potential energy surface, the rate constant is independent of the mass of the third body. This occurs because the density of points in phase space is independent of this mass, and the rate of crossing of S_+ depends only on the masses of the combining atoms. However, the rate of collision decreases with the mass of the third body. On the other hand, the time of a collision increases. This may allow more time for multiple transversal of S_+, thus increasing the upper bound relative to the true rate. The calculations on trajectories which were made by Keck give so far little indication as how this would vary with the mass of the colliding atom. Nor will they give information concerning the average absolute efficiency of collisions, since a very special type of collisions, namely those in which a phase point actually crossed the surface S_+, was selected.

Keck's calculations of the rate by his variation method in general give some decrease with temperature, but too small a one. This might be due in part to their giving a higher upper bound at the higher temperatures, but his calculations on trajectories indicate little reason for expecting this. He does not, of course, take non-equilibrium effects into account, and they may be the principal cause of this discrepancy in the cases involving such third bodies as He, as, indeed, our calculations based on the collision mechanism would suggest.

No other recombination reaction has been investigated as thoroughly as that of iodine atoms. A few experiments have been done on bromine atoms (42, 64). The general features are much the same as with iodine, but the rate constants for bromine recombination are roughly 2/3 of those for iodine recombination in the same gas, possibly with very slightly higher negative activation energies.

A number of experimental results in the region between 1000° and 2000° K have been obtained in shock tubes, both for bromine and iodine (76–80). On the whole, these do not correlate too well with the low temperature results. The shock-tube results tend to be a little higher than expected by extrapolation and to have a somewhat more pronounced temperature coefficient than those obtained by flash photolysis. For example, activation energies in shock tube have been reported (76) as —4.6 kcal for I in Ar and —8.0 for I in He. In some cases it is possible to draw a smooth curve through all the points, but it has considerable curvature on the usual log k_a *vs* T^{-1} plot (77). Often the data are fit reasonably well by a function proportional to T^{-n}, where n is in the neighborhood of 3/2 or greater. This has given rise to the suggestion, which keeps recurring in the literature, that the reaction involves a complex of three atoms (or more if the third body is not monatomic) and that the energy can be distributed in any way among the internal degrees of freedom. This, however, cannot be a relevant or instructive way of viewing the situation, for, before the reaction can take place, the energy must be redistributed in the right way, which can occur in only a small fraction of the cases and which will have a temperature dependence essentially cancelling that which arises from the calculation of the equilibrium fraction of the three-atom complex.

Bunker and Davidson (57) have made a calculation based on the equivalent of Eq.(2.24), but allowing for the fact that the vibrational levels of M against AB in the complex AB · M will become filled, as described following Eq. (2.24). This gives a rate constant with about the correct overall temperature dependence, but still does not correlate the high and low temperature results. This is clearly a problem which needs further consideration.

The recombination of chlorine atoms in argon has recently been calculated from shock wave results by Hiraoka and Hardwick (81). They find a rate at 1600° K perhaps 8 to 10 times those for bromine and iodine in argon, which have nearly the same rates at this temperature. (Hiraoka and Hardwick misquote the value for iodine at 1300° K.) This result is somewhat unexpected.

The recombination of oxygen atoms in argon has been discussed by Keck (58), who has compared his calculations with data obtained from shock tube experiments around 1500° K by Camac and Vaughan (51), and from discharge experiments with the atom concentration determined from the photon yield of $O + NO \rightarrow NO_2 + h\nu$ at low temperatures. The latter values are somewhat above Keck's upper bound (using in this case all the electronic states), but he does not consider the difference significant; actually Reeves, Mannella, and Harteck (82) have found a lower value. A summary of other experiments with references, has been given by Rink, Knight, and Duff (83). These experiments agree in order of magnitude but not in detail. The temperature coefficient is not very large. O_2 appears to be several fold more effective than best rare gas, Xe, and O is perhaps 10-fold more effective than O_2. Rather surprising is a reported increase (84) of 6-fold from Ar to Xe.

The recombination of N atoms near room temperature has been investigated (85–87) using a flow system, and titrating N atoms with NO, or investigating them by spectroscopic means. The rates are of the same order as for bromine and iodine, and show similar trends with the inert gases. They were expressed in terms of an effective interaction distance by Herron, Franklin, Bradt, and Dibeler (86), using an activated complex theory for the rate. However, they omitted in their expression any partition function involving the distance $N_2 — M$, so these numbers cannot have much significance. They reported zero temperature coefficient, and the results listed by Wray and Teare (88) around 4000° seem to show a small temperature coefficient, but when recalculated to k_a they are 10-fold smaller than the room temperature results.

Wray and Teare (88) have investigated the decomposition of NO, which shows no unusual features, as far as may be seen. It is to be noted that in all these cases an atom like N or O is a very efficient third body (except O for N_2).

The recombination of H atoms has been investigated in flow systems and in a static system, the atoms being generated by an eletcric discharge, and in shock waves. The static system would seem the most direct method, and Smallwood (89), using this method, found $k_a = 2 \cdot 4 \times 10^{-32}$ cc^2 molecule^{-2} sec^{-1} at room temperature, for :

$$H + H + H \rightarrow H_2 + H$$

This case is of some theoretical interest, because the effects of quantization may be important even near the dissociation limit. There is not more than about one vibrational state from which dissociation would be expected to occur. I have made a calculation, using Eq.(2.21) with Eq.(2.1), and taking $kT/\delta\varepsilon_{v_0} = 0.4$, $r_m = 2.5$ Å, and $n = 1$; then a value of σ of about 7 Å is required. This is a large distance for a small atom like hydrogen, even though the forces between hydrogen atoms are considerable. According to Smallwood the efficiency of H_2 is only about 1/50 that of H, so in this case no difficulty arises. However, others have given values for the efficiency of H_2 nearly as great as that which Smallwood found for H. Quite recently some shock tube experiments have been performed on hydrogen. The rates given at 3500° K for H as a third body range from 0.8 to 2.4×10^{-32} cc^2 molecules^{-2} sec^{-1}, with H_2 stated to be 1/3 to 1/10 as effective and the rare gases around one-half as effective as H_2, or less. (See Rink (90) for a summary; see also Patch (91) and Sutton (92)). There has also been some work on deuterium (92, 93) which indicates the possibility of some interesting isotope effects, though it seems advisable to wait for better experimental consistency before speculating on these. Sutton has presented figures which show the temperature dependence; for hydrogen and deuterium in the molecules themselves or Ar as third bodies, the rate is inversely proportional to T; for H or D atoms as third bodies the temperature dependence is greater, but for H as its own third body the rate seems to approach constancy at about Smallwood's value when the temperature drops to about 3000° K. Hydrogen in H_2 seems already to have gone above Smallwood's result for this reaction.

III. UNIMOLECULAR REACTIONS

A. Intramolecular energy exchange.

Unimolecular reactions involve both intermolecular and intramolecular energy exchange. Intermolecular exchange is of course required for the activation process; intramolecular energy exchange is involved in the transfer of the energy in the activated molecule to the bond which breaks or to the reaction coordinate, in order for the reaction to occur. Unfortunately, it is difficult to disentangle the effects of these two types of energy transfer, either experimentally or theoretically.

There are two different theories for the transfer of energy within the molecule which we may designate as the Rice-Ramsperger-Kassel-Marcus (RRKM) theory (94–98) and the Slater theory (99). The RRKM theory has a close connection (97, 98) with the transition-state theory (59, 100–105) of chemical reactions. One considers a quasi-equilibrium between all activated molecules having energy between ε and $\varepsilon + d\varepsilon$, and those molecules in the same range in which energy greater than the amount ε_m just necessary for reaction is localized in the reaction coordinate. For definiteness and convenience the zero of energy is taken as that hypothetical state in which all atoms of the molecule are resting in their equilibrium positions. If the energy not localized in the reaction coordinate is distributed in some one particular manner among the remaining vibrational and rotational degrees of freedom, the rate at which reaction occurs is proportional to the density, under this condition, of energy levels at ε associated with the reaction coordinate, and to the corresponding relative velocity of the parts of the molecule over the reaction coordinate. This problem can be treated as a one-dimensional problem and, since the rate of reaction probably does not depend specifically on the products, it may as well be supposed that the molecule is dissociated into separate fragments, which, however, are contrained from separating farther than some large distance r_∞. Then the number of energy levels in the " continuum " is equal to $(2r_\infty/hv)d\varepsilon$ [where v is the relative velocity of the fragments — see Eq. (1.6)]. The rate of crossing of the transition state in one direction by systems in any quantum state will be $v/2r_\infty$. The rate of reaction, $k_{\varepsilon,0}$, will be obtained by multiplying these two expressions together, and dividing by $N_\varepsilon d\varepsilon$, the number of discrete energy levels of the activated molecules (not activated complexes) in the range; thus :

$$k_{\varepsilon,0} = d\varepsilon/hN_\varepsilon d\varepsilon = 1/hN_\varepsilon \tag{3.1}$$

The division by $N_\varepsilon d\varepsilon$ must be carried out since we are considering a quasi-equilibrium process; the fraction of molecules in a transition state will be inversely proportional to the number of quantum states which are not transition states. Note that $1/N_\varepsilon$ is equal to the difference in energy, $\delta\varepsilon$, between levels of the molecule, whereas $k_{\varepsilon,0} = 1/\tau_{\varepsilon,0}$, where $\tau_{\varepsilon,0}$ is the lifetime of the state. Eq. (3.1) is, therefore, a form of the uncertainty principle, as it can be written in the form (106) :

$$\tau_{\varepsilon,0}\delta\varepsilon = h.$$

This implies that the energy levels are in this case broadened just sufficiently so as to overlap; and there is no difficulty in recombination of the fragments due to the necessity of matching energy levels.

If there are P_ε different ways in which a transition state can be set up, that is, P_ε different vibrational or rotational states of the molecules with energy between ε and $d\varepsilon$ and with sufficient energy already localized in the reaction coordinate, then the expression for the rate constant for the fixed energy range becomes :

$$k_\varepsilon = P_\varepsilon/hN_\varepsilon \tag{3.2}$$

We shall call P_ε the number of available continua. If the rate of activation is sufficiently high to maintain an equilibrium quota in all states of the reactant molecules, then the overall rate constant is obtained by multiplying k_ε by the proper weighing factor, which will be :

$$w_\varepsilon d\varepsilon = \mathrm{N}_\varepsilon e^{-\varepsilon/kT}\, d\varepsilon \Big/ \int N_\varepsilon e^{-\varepsilon/kT} d\varepsilon = N_\varepsilon e^{-\varepsilon/kT}\, d\varepsilon/Q \tag{3.3}$$

where Q is the partition function for the reactant, the integral being taken over all energies. Thus the unimolecular rate constant :

$$k_1 = \int_{\varepsilon_m}^{\infty} k_\varepsilon w_\varepsilon d\varepsilon = (Qh)^{-1} \int_{\varepsilon_m}^{\infty} P_\varepsilon e^{-\varepsilon/kT}\, d\varepsilon \tag{3.4}$$

Now we note that P_ε has different values in different ranges of ε, but is itself dimensionless. It is the total number of ways the energy $\varepsilon - \varepsilon_m$ may be divided among the various degrees of freedom and the reaction coordinate; hence we may write :

$$P_\varepsilon = \int_0^{\varepsilon-\varepsilon_m} P_{\varepsilon'}{}' \, d\varepsilon' \tag{3.5}$$

where $P_{\varepsilon'}{}' \, d\varepsilon'$ is the number of energy levels of the degrees of freedom other than the reaction coordinate lying between ε' and $\varepsilon' + d\varepsilon'$. Inserting this into the integral in Eq. (3.4) we may write :

$$\int_{\varepsilon_m}^{\infty} P_\varepsilon e^{-\varepsilon/kT} \, d\varepsilon = \int_{\varepsilon_m}^{\infty} \left(\int_0^{\varepsilon-\varepsilon_m} P_{\varepsilon'}{}' \, d\varepsilon' \right) e^{-\varepsilon/kT} \, d\varepsilon \tag{3.6}$$

and, integrating by parts setting $P_{\varepsilon'}{}' = P_{\varepsilon-\varepsilon_m}$ when $\varepsilon' = \varepsilon - \varepsilon_m$:

$$\begin{aligned} \int_{\varepsilon_m}^{\infty} P_\varepsilon e^{-\varepsilon/kT} \, d\varepsilon = &-kT \int_0^{\varepsilon-\varepsilon_m} P_\varepsilon{}' \, d\varepsilon' e^{-\varepsilon/kT} \Big|_{\varepsilon_m}^{\infty} \\ &+ kT \int_{\varepsilon_m}^{\infty} P_{\varepsilon-\varepsilon_m} e^{-\varepsilon/kT} \, d\varepsilon \end{aligned} \tag{3.7}$$

The integrated term drops out since the integral vanishes at the lower limit and $\exp^{-\varepsilon/kT}$ vanishes strongly at $\varepsilon = \infty$. Thus :

$$\int_{\varepsilon_m}^{\infty} P_\varepsilon e^{-\varepsilon/kT} d\varepsilon = kTQ^* e^{-\varepsilon_m/kT} \tag{3.8}$$

where Q^* is the partition function for the degrees of freedom other than the reaction coordinate, i.e., it is the partition function for the activated complex, reckoned from the energy ε_m. Thus :

$$k_1 = (kT/h)(Q^*/Q)e^{-\varepsilon_m/kT} \tag{3.9}$$

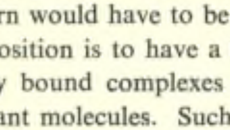
the ordinary expression for the transition-state theory.

In actually calculating P_ε for use in the RRKM theory, it is customary to leave out the three (or two) degrees of freedom of rotation of the molecule as a whole; i.e., it is neglected in Q^* and Q or supposed to cancel in them. This rotational energy presumably cannot be exchanged with the vibrational degrees of freedom because of the conservation of angular momentum, and the corresponding degrees of freedom have been called " adiabatic " by Marcus. It is true, if the moment of inertia in the activated complex, I_m, is different from that, I_0, in the equilibrium configuration, the centrifugal potential will be somewhat less in the activated complex than in the normal situation, and the extra energy will be available for redistribution, but in complex molecules this will be a negligible amount.

One may well question to what extent equilibrium can be established between all the degrees of freedom, other than the reaction coordinate, in the process of reaction. If complete equilibrium is not attained, Q^* may be interpreted as an effective partition function which includes only the states which, on the average, are available. Experimentally Q^* may be either larger or smaller than or approximately the same size as the partition function corresponding to the same degrees of freedom in the unexcited reactant. In the first case we refer to a " loose " activated complex and in the latter case to a " rigid " activated complex. If Q^* is smaller than in the case of a " rigid " activated complex, we will call it " constrained "; the implication is that some very special configuration is necessary for reaction, such as ring closure (which might be temporary). This would usually mean that some internal rotation, or torsional oscillations would be constrained to the equivalent of stiff vibrations, with consequent loss of entropy and decrease in the effective partition function.

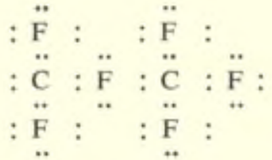
The rigid activated complex is often considered to represent the normal situation. In this case the partition function Q^* very nearly cancels the corresponding part of Q, leaving over a single vibrational partition function, and, as is well known, the pre-exponential factor generally has a value of about $10^{13}\ \mathrm{sec}^{-1}$. In many cases the pre-exponential factor has a considerably larger value than this. In these cases, a loose activated complex has been postulated, in which some of the vibrational degrees of freedom have been replaced by rotations which make a larger contribution to the partition function. For example, it is known that two methyl radicals recombine at about every collision. This means that they can be randomly oriented; correspondingly the rotations of the individual methyls must be excited in the decomposition of an ethane molecule, or there must be an equivalent multiplicity of states of the activated complex. Many other radicals recombine almost as efficiently. These reactions occur with little or no activation energy; then the potential energy curves do not have a maximum. If, however, the centers of gravity of the radicals have nonzero angular momentum with respect to each other, the effective potential energy, which includes the rotational potential, will have a small maximum. Unless this maximum is crossed, recombination will not occur. The number crossing the maximum can be readily calculated for any rotational quantum number *j*, and this result must then be averaged over *j*. Such a calculation has been carried out by Ree, Ree, Eyring and Fueno (107), assuming that the original potential-energy curve is the result of ordinary van der Waals interactions, estimated from the ionization potentials and polarizabilities. This yielded excellent agreement with the experimental data. However, the real problem of *why* the radicals combine at nearly every collision is not answered, and van der Waals forces are, indeed, not a sufficient cause. It has been pointed out (106) that it is not sufficient merely that the radicals should become " loose " in the course of a vibration of the C-C bond in such a case as the dissociation of ethane. If this happened in the course of a vibration which already had enough energy to decompose the bond, the determining factor would be the number of molecules having this much *vibrational* energy, before the loosening had occurred. There must exist a reservoir of molecules, not yet having sufficient energy to dissociate, and capable of coming into equilibrium with the activated complex, in which the radicals are already significantly loosened. In other words, it is not sufficient to have a loose activated complex; for such a complex to actually be rate-determining, there must be an already loosened state of the still stable molecule. Furthermore, there must be enough of these, and they must have a sufficiently long life, so that they can be maintained in a state of equilibrium, even though the reaction is proceeding.

We may make an estimate of the van der Waals forces between two methyl radicals by assuming that they resemble two methane molecules in this respect, which is closely equivalent to what was done by Ree, Ree, Eyring and Fueno. The heat of sublimation of methane is about 2500 calories per mole; the structure is a face-centered cubic array of methane molecules. We may estimate the van der Waals energy to be around 400 calories per pair-mole. This is less than RT even at room temperature, and relatively few molecules will be caught in such a shallow potential minimum. Indeed, there will be fewer molecules in it, than exist in a similar range of distances, but having higher energies. We can scarcely conceive that any large fraction of pairs of molecules which collide would be caught in this minimum. But even this would not be sufficient to assume a " loose " activated complex. For such a rapid intake into the potential minimum would be matched at equilibrium by an equally rapid output into the stream of separating pairs. And this in turn would have to be more than matched, if the unimolecular decomposition is to have a loose complex, by the rate at which these loosely bound complexes establish equilibrium with the substrate of reactant molecules. Such a process becomes believable only if there is a reservoir of loosely bound complexes in the potential minimum which is somewhat more than comparable with the equilibrium number of actually dissociating pairs within a comparable distance. Furthermore, a potential minimum as small as that which we have estimated for two methyl radicals is easily obliterated completely by the rotational potential if there is only a small amount of angular momentum. Thus a deeper potential energy minimum, which still allows free rotation of the separate radicals, or its equivalent, is needed. It has been suggested (106) that such an attractive potential might be provided by a three center bond of the type :



$$\begin{array}{cccccccc} & H & & & & H & & \\ & \cdot\cdot & & & & \cdot\cdot & & \\ : & C & \cdot & H & \cdot & C & : & H \\ & \cdot\cdot & & & & \cdot\cdot & & \\ & H & & & & H & & \end{array}$$

Such a bond would be very loose, would undoubtedly allow considerable freedom of motion of the parts of the molecule, and yet might be sufficiently stable to provide an intermediate condition with a sufficient lifetime against dissociation to allow equilibrium to be established with the normal stable form. In the case of the recombination of fluoromethyl radicals the intermediate would have the form :



$$\begin{array}{ccccccccc} & \cdot\cdot & & & & \cdot\cdot & & & \\ : & F & : & & : & F & : & & \\ & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & \\ : & C & : & F & : & C & : & F & : \\ & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & \\ : & F & : & & : & F & : & & \\ & \cdot\cdot & & & & \cdot\cdot & & & \end{array}$$

It must be supposed, however, that the bonds are sufficiently loose to allow considerable freedom of motion about the fluorine in the center.

Wieder and Marcus (108, 109) have suggested that the valence bonds lose most of their stiffness against bending when the bond is sufficiently stretched, and when the recombination reaction has zero activation energy. This is, of course, a possibility, but it must then already be true when the molecule does not have sufficient energy to break apart, and it must be possible to establish the equilibrium involving the rotational oscillations of the separate parts of the molecule. Thus a still stable molecule with a stretched C C bond must have a sufficient lifetime in this condition at least to match the average period of such a rotational oscillation. On the other hand, if the recombination requires an activation energy, Wieder and Marcus believe that near the saddle-point, the potential energy will have sufficient curvature in all directions to preclude anything resembling free rotation in an activated complex. There appears to be some evidence that reactions involving the splitting off of free radicals are especially likely to exhibit loose activated complexes, and these are, indeed, reactions in which the recombination is expected to exhibit little or no activation energy. However, in the case of azomethane, which has a loose activated complex (pre-exponential factor in the Arrhenius expression about (110) $10^{17.3}$) and gives free radicals on dissociation, evidence has been presented (111) to indicate the reverse radical recombination has an appreciable activation energy.

Recently data have accumulated on a considerable number of reactions in which the pre-exponential factor lies between 10^{15} and 10^{16}, larger than expected for a rigid complex but smaller than observed for some loose complexes. In these cases it may be that some of the vibrational frequencies have simply become lower in the activated complex (108, 109).

B. **Effect of pressure on a unimolecular reaction — RRKM theory.**

The effect of pressure on the rate of a unimolecular reaction is determined by the competition between intramolecular and intermolecular energy exchanges. This effect is calculated by assuming that a steady state is set up, the rate of activation of the molecules in any energy range being equal to the sum of the rates of deactivation and of reaction. It is generally assumed that the rate of activation is the same as it would be (that is equal to the rate of deactivation) if complete equilibrium were established. This supposes that sufficient energy is gained or lost on the average on collision so that the activation process in any energy range which contributes appreciably to the reaction is dependent upon collisions of molecules having an energy so much lower that they are present practically in their equilibrium quota. It is generally conceded (as would be anticipated from Section II) that even if this is not true (112), or if departure from equilibrium occurs similar to that described in Section II, (113, 114) the effect is not particularly important if the average transferred at collision is not much less than kT.

With the assumption of equilibrium, the fraction of molecules $w_\varepsilon d\varepsilon$ in an energy range ε to $\varepsilon + d\varepsilon$ is given by Eq. (3.3). The actual fraction in the range we may designate as $c_\varepsilon w_\varepsilon d\varepsilon$. Then the steady-state hypothesis gives :

$$Z\rho c_\varepsilon w_\varepsilon + (P_\varepsilon/hN_\varepsilon)c_\varepsilon w_\varepsilon = Z\rho w_\varepsilon \tag{3.10}$$

(deactivation + reaction = activation)

where Z is the effective collision number per unit volume per unit time at unit concentration (assumed independent of ε), and ρ is the total number of molecules per unit volume. This yields :

$$c_\varepsilon = 1/(1 + P_\varepsilon/Z\rho hN_\varepsilon) \tag{3.11}$$

This factor should multiply the rate constant k_ε in Eq. (3.4) in order to find the apparent unimolecular rate constant at the pressure corresponding to ρ. Thus we obtain instead of Eq. (3.4) the well-known equation :

$$k_1 = (hQ)^{-1} \int_{\varepsilon_m}^{\infty} \frac{P_\varepsilon e^{-\varepsilon/kT} d\varepsilon}{1 + P_\varepsilon/Z\rho hN_\varepsilon} \tag{3.12}$$

It will be noted that this equation contains the ratio of $k_\varepsilon = P_\varepsilon/hN_\varepsilon$ and the collision number Z; they cannot be obtained independently, although something may be learned about the dependence of k_ε on ε from the shape of the rate-pressure curve. If the pressure is very low the last term in the denominator predominates and the expression becomes in the limit :

$$k_2 = (Z/Q) \int_{\varepsilon_m}^{\infty} N_\varepsilon e^{-\varepsilon/kT} d\varepsilon \tag{3.13}$$

where $k_2 = k_1/\rho$ is the second-order rate constant for the activation process, which is now rate determining. Note that :

$$Q^{-1} \int_{\varepsilon_m}^{\infty} N_\varepsilon e^{-\varepsilon/kT} d\varepsilon$$

is the equilibrium fraction of activated molecules.

In order to evaluate Eqs. (3.12) and (3.13) a number of approximations have been made. Rice and Ramsperger (94) assumed that N_ε/Q was to be obtained from the classical formula for the number of molecules having a given number of harmonic oscillators in the given energy range and that $P_\varepsilon/N_\varepsilon$ was the fraction of these which would have the energy localized in one oscillator (actually, they assumed, in one squared term in the energy expression, which was less logical but caused no practical difference). They believed that the effects of quantization could be allowed for by using a somewhat smaller number of oscillators than were actually to be found in the molecules. Indeed, the hydrogen stretching vibrations in organic molecules are sufficiently high so that they are scarcely excited even in activated molecules. Kassel (95, 96) attempted to allow for quantization, and at the same time keep the expression in tractable form, by assuming a certain number of quantized oscillators (somewhat greater in number than in the classical case), all having the same frequency, which was chosen in the range of molecular frequencies.

Marcus and Rice (97, 98) attempted to find N_ε and P_ε by actual count of the energy levels. N_ε can sometimes be evaluated by a quasiclassical approximation. It can be seen that for a set of s frequencies :

$$N_\varepsilon \cong N_{\varepsilon,\nu_c} \prod_{i=1}^{s} (\nu_c/\nu_i)$$

where N_{ε,ν_c} is the value N_ε would have if all the frequencies had some value ν_c low enough so that the partition function Q_c could be written $(kT/h\nu_c)^s$ and so that $N_{\varepsilon,\nu_c}/Q_c$ could be obtained classically. Then :

$$\begin{aligned} N_\varepsilon/Q &= (N_{\varepsilon,\nu_c}/Q_c)(Q_c/Q) \prod_{i=1}^{s} (\nu_c/\nu_i) \\ &= (N_{\varepsilon,\nu_c}/Q_c) \left[\prod_{i=1}^{s} (kT/h\nu_i)/Q \right] \end{aligned} \qquad (3.14)$$

Thus if Eq. (3.13) is set up classically, it can be corrected by multiplication by the bracket in Eq. (3.14). This may not be adequate to handle the high C-H stretching vibrations, but these may be omitted in the calculation. It would seem that a rough criterion for omitting a frequency would be that Eq. (3.13) and (3.14) would give a higher rate if it were omitted. The classical expression for (3.13) is given below as Eq. (3.23). From these equations the criterion for omission of a frequency is roughly $h\nu_i > \varepsilon_m/s$. Intermediate frequencies can, if necessary, be handled separately.

Since P_ε is the total number of ways the energy $\varepsilon - \varepsilon_m$ can be divided among the reaction coordinate and the other degrees of freedom, it can be evaluated by direct counting if the latter are all vibrations. If the latter include some internal rotations, the number of rotational levels in a given range between ε_r and $\varepsilon_r + d\varepsilon_r$ must be found; this can be easily done if the moments of inertia are known. Then the number of ways the remaining energy $\varepsilon - \varepsilon_m - \varepsilon_r$ can be divided among the vibrations and the reaction coordinate must be found. The product of these two must be integrated between $\varepsilon_r = 0$ and $\varepsilon_r = \varepsilon - \varepsilon_m$. Recently an extensive set of calculations of this sort has been made by Wieder and Marcus (108, 109). Before discussion of their results, however, it will be well to review Slater's theory of unimolecular reactions, since their findings will throw some light on the relation between the two theories.

C. Slater's theory.

Slater's theory (99) states that a molecule reacts when the displacement q_1 of some particular bond distance exceeds a certain value q. The vibrations are assumed to be harmonic, though certain efforts have been made to correct for minor deviations from harmonicity. Also the vibrations have been assumed to be classical. Again some discussions have been made of the effects of quantization, with the general conclusion that, as far as the rate of reaction of an already activated molecule was concerned, the effects would not be great. These discussions appear to me not to be in a very satisfactory state : in any case, the actual calculations are based on the classical, harmonic model. A truly harmonic model would, of course, not show any dissociation whatever; what Slater has done is equivalent to the use of the so-called " truncated " harmonic model, in which the potential-energy curve has a kink at $q_1 = q$, remaining constant for $q_1 > q$.

The displacement q_1 is affected by all the normal modes of vibration in the molecule and — this is the important point — in varying degrees. Assuming harmonic vibrations, we may write q_1 in the form :

$$q_1 = \sum_i \alpha_{1i} \varepsilon_i^{1/2} \cos (2\pi\nu_i t + \gamma_{ji}) \tag{3.15}$$

where ε_i is the energy in the i^{th} normal mode, ν_i its frequency, γ_{ji} a phase constant, and α_{1i} is a constant coefficient. Slater's condition for dissociation becomes :

$$\sum_i |\alpha_{1i}| \varepsilon_i^{1/2} \geqslant q \tag{3.16}$$

One important difference between this formulation and that of the RRKM theory lies in the fact that not all molecules with energy above a certain minimum are capable of reacting; the manner in which the energy is distributed among the normal modes is also important. For example, if some particular α_{1i} were zero, no amount of energy in that mode could cause the molecule to decompose. The rate L, at which a given assembly of molecules decomposes, is a function of all the ε_i. The fraction of molecules with energies between ε_i and $\varepsilon_i + d\varepsilon_i$ is given by :

$$df = (kT)^{-s} e^{-\varepsilon/kT} \prod_i d\varepsilon_i \tag{3.17}$$

in the classical case, where

$$\varepsilon = \sum_i \varepsilon_i \, .$$

L then replaces k_ε and df replaces $(N_\varepsilon/Q)e^{-\varepsilon/kT}d\varepsilon$ so that Eq. (3.12) is replaced by :

$$k_1 = (kT)^{-s} \int_{\varepsilon_m}^{\infty} \frac{L e^{-\varepsilon/kT} \prod_i d\varepsilon_i}{1 + L/Z\rho} \tag{3.18}$$

L is calculated as one-half the long-time frequency with which $q_1 - q$ becomes zero. The one-half is introduced because only zeros should be counted in which q_1 is increasing. Actually it would appear that it should not be as low as one-half, for any time at which q_1 is greater than q is not a time during which the system represents an undissociated molecule. Further, it would appear that the average time before q_1 became equal to q, the active molecules being created in random phases by collision, would be less than the time between adjacent zeros of $q_1 - q$. Thus the value of L used by Slater may be somewhat too small, which, however, is of little importance in the general picture.

The actual evaluation of L is a complex mathematical problem, which has been handled by Slater with great skill. He has shown that the expression (3.18) can be reduced, for a molecule containing s modes of vibration, approximately to (115a) :

$$k_1 = \frac{\nu e^{-\varepsilon_m/kT}}{\Gamma(m+1)} \int_0^\infty \frac{x^m e^{-x} dx}{1 + x^m/\theta} \tag{3.19}$$

where Γ denotes the gamma function and where :

$$\theta = (4\pi)^m \Gamma(m+1)\, (\varepsilon_m/kT)^m (Z\rho/\nu) \prod_i \mu_i \tag{3.20}$$

In these formulas :

$$m = \frac{1}{2}(s-1), \quad \mu_i = |\alpha_{1i}|/\alpha \text{ (with } \alpha^2 = \sum_i \alpha_{1i}^2),$$

and ν is a kind of average frequency :

$$\nu^2 = \sum_i \mu_i^2 \nu_i^2 \,.$$

This may be compared with the form taken by Eq. (3.12) when the molecule is assumed to consist of s classical harmonic oscillators with a rigid activated complex (there is no provision for a loose complex in the Slater theory) :

$$k_1 = \frac{A e^{-\varepsilon_m/kT}}{\Gamma(s)} \int_0^\infty \frac{x^{s-1} e^{-x} dx}{1 + (A/Z\rho) x^{s-1}/(x + \varepsilon_m/kT)^{s-1}} \tag{3.21}$$

With a rigid activated complex the pre-exponential factor A is equal, at high temperatures, to a molecular frequency, which will not differ greatly from ν of Eq. (3.19). Further, since ε_m/kT is relatively large, it is seen that Eq. (3.19) differs from Eq. (3.21) chiefly in that m is substituted for $s - 1$ and that θ contains the factor :

$$(4\pi)^m\Gamma(m + 1)\prod_i \mu_i.$$

It is useful to compare Eqs. (3.19) and (3.21) at the low pressure end of the range. The bimolecular constants derived from the limiting forms are, respectively :

$$k_2 = (4\pi)^m(\varepsilon_m/kT)^m(\prod_i \mu_i)Ze^{-\varepsilon_m/kT} \tag{3.22}$$

and :

$$k_2 = [\Gamma(s)]^{-1}Ze^{-\varepsilon_m/kT}\int_0^\infty (x + \varepsilon_m/kT)^{s-1}e^{-x}dx$$

$$\simeq [\Gamma(s)]^{-1}(\varepsilon_m/kT)^{s-1}Ze^{-\varepsilon_m/kT} \tag{3.23}$$

One pecularity of Eq. (3.22) should be noted. It involves a product of the μ_i and any μ_i is a measure of the effectiveness of a particular normal mode in causing dissociation, as may be seen from the definition and Eq. (3.15). It is conceivable that the symmetry of the molecule may be such that one or more of the μ_i would be zero. This would make k_2 zero, which is obviously ridiculous. The difficulty arises from the approximations inherent in Eq. (3.19), and any mode of vibration should be discarded altogether and m correspondingly lowered if so doing will increase the value of k_2 obtained, that is, if $(4\pi\varepsilon_m/kT)^{1/2}\mu_i$ is less than 1. It may also be noted that in the case of degenerate frequencies only one of them (or a proper linear combination) can contribute effectively to the rate.

In actual practice values of ε_m/kT are around 40 and $(4\pi\varepsilon_m/kT)^{1/2}$ will therefore be near 20. Values of μ_i commonly lie between 0.1 and 0.5. We may then compare the $s - 1$ factors $(4\pi\varepsilon_m/kT)^{1/2}\mu_i$ of around 2 to 10, occurring in Eq. (3.22) and one factor involving only a μ_i and therefore smaller, with factors ranging from ε_m/kT to $\varepsilon_m/(s - 1)kT$ occurring in Eq. (23). The latter factors are, on the whole, larger, especially when s is relatively small, which is the only case in which the low pressure limit can be reached. Thus k_2 calculated from Eq. (3.23) is larger than that calculated from Eq.(3.22).

This is a manifestation of the fact that not all molecules with energy greater than ε_m can react in Slater's theory; this means that there are fewer effectively activated molecules, hence fewer activating collisions, hence slower reaction at low pressures. Altogether [note $m = (s-1)/2$] a Slater molecule acts something like an RRKM classical molecule with fewer active degrees of freedom. It was long ago suggested (116) that there might be, in some cases, a hindrance in the transfer of energy from one degree of freedom to another inside a complex molecule. One would, of course, expect to reach the limiting low-pressure (second-order) region at a higher pressure than would be found if the energy moved freely through the molecule. At a still lower pressure the internal transfer to the active degrees of freedom might become greater than the collision rate, providing a new means of activation, and the rate would tend to become first order again, or at least the unimolecular rate constant would fall off more slowly. Such an effect has presumably not been detected experimentally.

In any case, the Slater theory provides a specific mechanism for a hindrance of intramolecular energy exchange. This mechanism could break down in an actual molecule, where deviations from harmonicity are great. They reach what might be called the ultimate limit when a bond ruptures, but many times before the final decomposition a molecule with sufficient energy to decompose will have reached various configurations in which the anharmonicity, though not quite so extreme, is nevertheless considerable. This would lead one to expect free exchange of energy between quasi-normal modes. In any event, this is a question upon which some information may be obtained.

In order to bring out what is involved, we may briefly review a " new formulation " of rate theory, recently developed by Slater (115b) and somewhat modified by Bunker (117). In this formulation the activated molecules which are produced by collision are divided into classes, according to the amount of energy ε they contain and the length of time τ which it will require for them to decompose after being formed. Let $f_{\tau,\varepsilon}d\tau$ be the fraction of all molecules in energy range ε to $\varepsilon + d\varepsilon$ which would, if undisturbed, decompose between times τ and $\tau + d\tau$. These will, of course, not decompose if they are deactivated by collision. The probability that such a molecule will not have a collision in time τ and hence will decompose is $e^{-Z\rho\tau}$ where Z is the average collision number, and ρ the total molecular density, so that $Z\rho$ is the rate of collision suffered by a single molecule. The rate of deactivation of such molecules, at equilibrium, and hence, by the usual assumption, the rate of activation, will be $Z\rho^2 f_{\tau,\varepsilon} d\tau w_\varepsilon d\varepsilon$, where $w_\varepsilon d\varepsilon$ is the equilibrium fraction of the molecules in the range ε to $\varepsilon + d\varepsilon$. Hence the total number of reactions of such molecules per unit volume per unit time will be $Z\rho^2 f_{\tau,\varepsilon} w_\varepsilon e^{-Z\rho\tau} d\varepsilon d\tau$, the corresponding contribution from the range ε to $\varepsilon + d\varepsilon$ will be found by integrating with respect to τ, after dividing by ρ :

$$c_\varepsilon w_\varepsilon k_\varepsilon d\varepsilon = \int_0^\infty Z\rho f_{\tau,\varepsilon} w_\varepsilon e^{-Z\rho\tau} \, d\tau d\varepsilon \tag{3.24}$$

where $w_\varepsilon k_\varepsilon d\varepsilon$ is the contribution which would occur at high pressures and c_ε is the same factor introduced in Eq. (3.10). The assumption made in the RRKM theory is that the probability of decomposition of any molecule at any time depends only on its energy. Thus of a certain number of molecules activated to a certain energy range the fraction remaining after a time τ assuming no collisions, would be :

$$\int_\tau^\infty f_{\tau,\varepsilon} d\tau = e^{-k_\varepsilon \tau} \tag{3.25}$$

where k_ε is independent of τ. This is what Slater calls the " random gap " assumption. It can be shown (115*b*) that, with Eq. (3.24) it leads to Eq. (3.11).

D. **Calculations on intramolecular energy exchange.**

According to the Slater theory, Eq. (3.25) is not expected to hold, for, within any energy range, there will be different groups of molecules having different intrinsic reaction probabilities, depending upon how this energy is distributed; indeed there will be some which will never decompose. Bunker (117) has examined the behavior of classical molecules by setting up a program for a machine calculation which selected molecules within a specific energy range, but otherwise randomly distributed in phase space, and followed them through to dissociation. He did this for a linear model, like N_2O, and a triangular model, like O_3. In some cases the potentials were assumed to be harmonic (using Slater's criterion for dissociation); in others anharmonicity was introduced. Bunker was able to follow the process for only a relatively short time, corresponding to collision times which were only long enough to cause a slight decrease of the rate constant from its high pressure value. However, this was long enough to indicate an apparent residual of molecules which were not going to decompose in the harmonic case, and, as far as could be seen, the introduction of anharmonicity caused Eq. (3.25) to be fulfilled. The dependence of k_ε on ε agreed fairly well with what might be expected, assuming that all the vibrations were exchanging energy, including the bending one in N_2O (only motion in a plane was considered); the power of the dependence on $\varepsilon - \varepsilon_m$ seemed to decrease slightly going from the harmonic to the anharmonic case, probably because, in the harmonic case, there would be fewer molecules which never decompose the higher the energy. The general conclusions seem to accord fairly well with the RRKM theory. The effects of quantization, of course, cannot be tested in this way.

It would also be interesting to see the effects of a non-random selection of initial phase points, since the activation by collision cannot be counted upon not to favor some configurations over others The speed of approach to randomness would be an interesting aspect of the situation to investigate.

E. **Comparisons with experiment.**

A number of unimolecular reactions in the second-order region were analyzed by Wieder and Marcus (108, 109) in terms of Eq. (3.13), actually approximating by using Eq. (3.23) corrected by the use of Eq. (3.14). It will be observed that since the bracket in Eq. (3.14) depends upon the temperature, the value of ε_m which is obtained from the temperature coefficient of the experimental data will depend upon whether the quantum correction is made or not. The calculated pre-exponential factor A_2 for the relation :

$$k_2 = \mathrm{A}_2 e^{-E_2/RT} \tag{3.26}$$

where E_2 is the experimental activation energy, is then also affected. In their calculations Wieder and Marcus used the frequencies of the molecules as far as known and drew on the available reaction data; references may be found in their paper. In Table II we summarize their results.

TABLE II.

Unimolecular reactions in limiting low-pressure stage.

Molecule	σ	A_2 (expt)	$A_2(q)/A_2$ (expt)	$\varepsilon_m(q) - \varepsilon^0$	$\varepsilon_m(c)$
O_3	3.35	4.6×10^{15}	1.1	23.1	25
F_2O	4.5	2.5×10^{17}	0.12	38.4	40.5
N_2O	3.3	5.2×10^{15}	16.0	59.2	63.5
NO_2Cl	6.7	6.3×10^{16}	11.0	27.6	32
H_2O_2	3.5	4.6×10^{18}	0.07	48.0	54
N_2O_4	5.3	2.0×10^{17}	2.2	11.8	17
C_2H_6	3.5	5.5×10^{23}	2.9	85.0	100
N_2O_5	6.0	3.1×10^{19}	0.19	19.5	26

σ is collision diameter in Å.
A_2 (expt) is experimental value of A_2 using Eq. (3.26). Units: cc mole^{-1}sec^{-1}
(*c*) means calculated from Eq. (3.23); (*q*) means quantum correction used.
ε^0 is zero-point energy. Energies in kcal/mole.

In three cases, F_2O, H_2O, and C_2H_6 (dissociating into $2CH_3$ — calculated from the recombination) the calculated rate of activating collisions is appreciably less than the observed reaction rate. [The ratio of these two quantities is equal to $A_2(q)/A_2(\text{expt})$]. The difficulty in the case of F_2O had already been noted by Koblitz and Schumacher (118), and subsequently analyzed (55) by me. Two previously neglected factors needed to be considered. The effect of rotation mentioned after Eq. (3.9) will not, in as small a molecule as this, be entirely negligible; it can be taken care of approximately, as in the case of a diatomic molecule, by simply multiplying by the ratio of moments of inertia I_m/I_0. This ratio I estimated to be of the order of 3. It was also pointed out that anharmonicity would increase the density of energy levels of an excited molecule. If in such a small molecule any of the "normal" modes could lead to dissociation at about the same energy, then in an activated molecule any one of three vibrations would be about one-third excited to dissociation, and the spacing between levels of any one would be about 2/3 that at the ground level. Thus the density of levels and the number of excited molecules would be increased by another factor of $(3/2)^3 \sim 3$. We see that the agreement between observed and calculated rates is rather gratifying if we can indeed assume that deactivation takes place at every collision. Similar considerations will hold for H_2O_2. The effect of anharmonicity will be less, but I_m/I_0 may well be greater, since the hydrogens are light and the molecule will act much like a diatomic molecule as regards rotation.

The assumption of deactivation at every collision, though commonly made, needs to be scrutinized. Also it will be interesting to see if any clues can be found in this way as to differences in Table II. We will attempt to apply Eq. (1.39) [or (1.32)] and (1.44) to the smaller molecules in Table II. In Table III we have listed some or all of the vibration frequencies, and in Table IV we have applied the equations for the reactants and activators listed. We have in each case chosen as an activator an atom or a molecule which probably

TABLE III.

Vibration frequencies in cm^{-1}

Molecule	Frequencies	Ref.
O_3	705, 1043, 1110	(119)
F_2O	461, 826, 929	(120)
N_2O	596, 596, 1300, 2277	(121)
NO_2Cl	1293 (*a*), 794 (*a*), 1685 (*a*), 651 (*b*), 367 (*b*), 411 (*b*)	(122)
H_2O_2	3610, 1315, 877 (*c*), 230 (*d*)(?), 3614, 1266	(123)
C_2H_6(*e*)	821, 1379, 1486, 275 (*d*), 993 (*f*), 1155, 1375, 1460	(121)

(*a*) Vibrations involving principally the NO_2 group.
(*b*) Vibrations involving Cl.
(*c*) O-O stretching.
(*d*) Torsion.
(*e*) C-H stretching frequencies not listed.
(*f*) C-C stretching.

TABLE IV.

Application of Eqs. (1.39) and (1.44).

	Rel. eff. (*a*)	T(°K)	ν_1	ν_2	n_1 (*b*)	n_2 (*b*)	m_1 (*c*)	m_2 (*c*)	z_1	z_2	$\frac{\gamma_{n\,n'}}{F(g',g)}$	$\Delta\varepsilon_k$ (*d*)	$\Delta\varepsilon_k$ (res) (*d*)
O_3-O_2 (*e*)	0.34	370	1043	1110	2.7	2.5	16	16	2	2	0.009	191	267
F_2O-Ar (*e*)	0.55	530	826	929	5.5	4.9	19	19	2	2	0.069	294	291
N_2O-Ar (*f*)	0.20	900	596	—	8.8	—	14	—	3	—	6.2 (*i*)	1700	394
NO_2Cl-Ar (*g*)	0.30	475	367	411	4.5	4.1	40 (*h*)	40 (*h*)	2	2	0.018	125	254
H_2O_2-He (*f*)	0.11	720	230	—	12.2	—	1	—	2	—	64. (*i*)	655	850
H_2O_2-He (*g*)	—	—	1266	1315	2.2	2.1	1	1	2	2	0.14	137	—

(*a*) Relative activating efficiency of inert gas as compared to the reacting molecule. See Ref. (125), Chapter 7 of Ref. (7), and Ref. (8c).

(*b*) Obtained by dividing $\varepsilon_m - \varepsilon^0 + kT$ uniformly among all the vibrations, then dividing the result by the frequency expressed in energy units.

(*c*) Atomic weight units.

(*d*) Calories per mole. (For $\Delta\varepsilon_k$ multiply $\nu_2 - \nu_1$ by 2.85).

(*e*) Used factor 1/5 in Eq. (1.39).

(*f*) Used Eq. (1.32), with extra factor 1/3 as in Eq. (1.33).

(*g*) Used factor 1/15 in Eq. (1.39).

(*h*) Mean of NO_2, as a group, and Cl.

(*i*) Perturbation method breaks down. For method of handling see Ref. (20), (25).

Calculations made for case of best resonance. In general, use of one vibration only will give high $\gamma_{n\,n'}/F(g',g)$ but poor resonance.

α is taken as $5 \times 10^8\ \mathrm{cm}^{-1}$ throughout.

acts like a simple atom, to avoid complications due to vibrational transfer from one molecule to another. It may be noted that Mahan (124), in a study of complex collisions in chemical kinetics, suggested that this complication is actually not important, and that there is a correlation in the case of NO_2Cl, between the hardness of collision and the activational efficiency of an activator. However, the α's according to Herzfeld and Litovitz (8c) have a relatively small range of values; and the correlation obtained led Mahan to the conclusion that the average effective transfer of energy in activation or deactivation was improbably small.

Returning to Table IV, with F_2O-Ar it is seen that our calculated rate of activation is about 1/8 of the observed rate of reaction, assuming F_2O reacts at every collision with F_2O. We are within the limits of good resonance, but towards the edge; furthermore, in analogy to Section II, we might expect a factor :

$$\sim 1 - e^{-\Delta \varepsilon_k / kT}$$

due to departure from equilibrium. On the other hand, our estimate of $\gamma_{nn}'/F(g', g)$ may be somewhat low. n_1 and n_2 should perhaps be slightly larger and ν_1 and ν_2 slightly smaller because of anharmonicity. We must also consider other effects of anharmonicity, and possible contributions from transitions involving rotational changes. Furthermore, there are other possibilities, involving various combinations of frequencies, including a two-quantum jump in one of them. If the probability of such a jump is calculated by expanding $e^{\alpha x}$ to the second power in x, it is found an additional small factor, which has been written down in (1.45), is introduced. However, this may not be an accurate way of making the calculation, in view of obvious large interactions within the activated molecule, which has been shown (118) to have an average lifetime of less than 10^{-12} seconds, only an order of magnitude lower than the vibration frequencies, and the activated complex is loose (55). While these speculations cannot be said to explain the high collisional efficiency of argon, they make it seem not entirely unreasonable.

The calculations for H_2O_2 certainly indicate a reasonably high efficiency. The calculation has not been carried out for C_2H_6, but since there are several near resonances, since most of the vibrations involve hydrogen atoms, and since Ar is only 0.03 times as effective an activator as C_2H_6 itself, the C_2H_6-Ar reaction would seem to present no problem, even though the n's would be low in this case. CH_3CHO is, however, three times as effective as C_2H_6 itself (126); this seems a little difficult to account for.

Table IV suggests that the difference in the rates of F_2O and O_3 may lie in the collision efficiencies. The table, however, throws little light on the quite low efficiency of the NO_2Cl reaction. The low rate of activation of NO_2Cl may be used as an argument in favor of the suggestion that not all the energy in the molecule is available for transmission to the reaction coordinate, though the calculations of Bunker would make this solution seem unlikely. A direct comparison could made with Slater's equation, but in my opinion there would be no significance attached to this, since there is no allowance for quantization.

In the case of N_2O the low efficiency could be ascribed to the lack of good resonance, as in a calculation of its reaction rate made by Nikitin (127). However, some acoustical data are available from which indirect inferences concerning efficiency of transfer of energy may be made. From sound absorption measurements by Eucken and Jaacks (128), at lower temperatures, Patat and Bartholomé (129) estimated that at the temperature of reaction the collision efficiency for energy transfer between N_2O and H_2O would be not less than about 0.2. This, of course, refers to low energy transitions; probably the efficiency of transfer from an activated molecule would be at least this great. The efficiency of N_2O itself in acoustical experiments is much less; however, as an activator it is nearly as efficient as H_2O and argon is about 1/8 as efficient as H_2O. Apparently then, and surprisingly, the collisional efficiency is high, and this would mean that energy does not pass freely between all four vibrational degrees of freedom as was assumed by Wieder and Marcus. But just in the case of a linear molecule one might expect there to be some difficulty in transferring the energy of *both* the degenerate bending vibrations. If they were excited in phase, the molecule would vibrate in one plane, and nothing would be different from the situation if there were just one such vibration. If they were excited out of phase, there would be some angular momentum. Equivalently one could say that the vibrations make the molecule nonlinear, so that one of the bending degrees of freedom may be replaced by a rotation. All components of the angular momentum must be conserved between collisions, and if the angular momentum vector along the line of centers is conserved, transfer of vibrational energy from the bending vibrations will leave a small moment of inertia which for a given angular momentum will require a high energy. It is possible that some of this rotational energy could be eventually taken up in other modes of rotation, but that there would be some resulting hindrance of transfer of energy from the bending vibrations seems very probable.

In the calculation for N_2O_5 Wieder and Marcus made the assumption that one of the rotational degrees of freedom could exchange energy with the vibrations. There appears to me to be little justification for this assumption, but actually with a molecule as large as N_2O_5 this would make little difference, and might perhaps be about equivalent to taking the effect of adiabatic rotations and anharmonicity into account, so the result for N_2O_5 appears reasonable.

Very recently some experiments have been done on the decomposition of small polyatomic molecules in shock waves. The decomposition of cyanogen was studied by Tsang, Bauer, and Cowperthwaite (130), who found that the data would be reasonably interpreted in terms of the classical equation, Eq. (3.23) using $s = 6.5$. The decomposition of BrCN, studied by Patterson and Greene (131), presents a very different picture. If the rate constant for dissociation in the presence of Ar be expressed as a function $AT^{1/2} e^{-\varepsilon_D/kT}$, it is found that A is only about 0.1 the value found for the dissociation of Br_2 in the presence of Ar. This is very difficult to understand.

Hiraoka and Hardwick (132) have recently studied the decomposition of NO_2Cl in shock waves, with results which correlate well with the earlier work at lower temperatures. They find a slightly higher activation energy for Ar or O_2 as an activator, than for NO_2Cl itself, Ar and O_2 being less efficient than NO_2Cl. This change in activation energy goes in the same direction with increasing efficiency of third body as in the dissociation of I_2, but can hardly have the same interpretation.

Wieder and Marcus (108) also made an extensive series of calculations on the pressure dependence of a number of quasi-unimolecular reactions, based on the equivalent of Eq. (3.12),counting the energy levels, at least approximately, where necessary. In these calculations, since they were principally interested in fitting the pressure dependence of the unimolecular rate constant, they assumed a model for the activated complex which would give agreement with the rate at a high pressure. This involved in some cases the assumption of a loose activated complex, or one in which some of the vibrational frequencies had become lowered. The various reactions considered were the following : (a) isomerization of cyclopropane to propylene; (b) decomposition of cyclobutane to ethylene; (c) isomerization of methyl cyclopropane; (d) decomposition $N_2O \rightarrow N_2 + O$; (e) isomerization of cis-butene-2 to trans-butene-2; (f) $N_2O_5 \rightarrow NO_2 + NO_3$; (g) decomposition of ethyl chloride (which shows some evidence of complications). The pressure at which the falling-off of rate constant occurs would fit the theory if the following collisional activation efficiencies are assumed : (a) 0.28; (b) 0.17; (c) 0.22; (d) 0.028; (e) 0.042. The shape of the rate-pressure curve for N_2O_5 deviates sufficiently from the theoretical so that a consistent value is hard to give, but it is of the order of 1. The experimental curve for N_2O is somewhat flatter than expected, indicating that the rate of reaction depends more strongly on the energy of the activated complex than predicted theoretically for the number of vibrations available. This could be due to some partial inhibition of intramolecular energy transfer or to the effects of anharmonicity, which makes the higher levels come closer together. There are minor deviations in the shape of the curve in other cases. On the whole, the results give little evidence of any hindrance to the free transfer of energy among all the vibrations.

Free motion of energy within the molecule is also supported by a number of recent experiments, in which a " hot " molecule or radical is formed by chemical reaction (133–138), only to decompose before collision to give different products. Rabinovitch and coworkers (133–135) have, as a matter of fact, used the detailed theory of Marcus and Rice with success to calculate the relative rates of dissociation of the molecule formed knowing the excess of energy it contains from thermochemical considerations. An example of this is the decomposition of hot *sec*-butyl radicals, $CH_3CH_2CHCH_3$ to give $CH_3 + CH_3CH = CH_2$, the *sec*-butyl radicals having been formed by the addition of H to *cis*-butene-2. Butler and Kistiakowsky (137) formed methylcyclopropane by addition of CH_2 radicals with varying amounts of energy either to cyclopropane or to propylene. The methylcyclopropane rearranged to form a mixture of butenes, whose composition was essentially independent of mode of formation or of energy, again showing free intramolecular energy transfer. The decomposition of activated sec-butyl radicals from different sources also supports this view (136).

The theory has also been applied to the behavior of ions in the mass spectrograph (139).

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Note added after the meeting.

In the calculation of Table IV it is possible that z_1 *and/or* z_2 *should be 3 rather than 2 for the bent triatomic molecules involved. The vibrational motion will not be uniformly divided between the three atoms, but they will all partake to some extent in the motion. Thus the expected collision efficiency for the* F_2O *reaction will be somewhat decreased, increasing the difficulty of explaining the experimental result accordingly.*

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Discussion du rapport de M. Rice

M. Karplus. — You have discussed the phase-space (Keck) approach to reaction kinetics. In considering the significance of the point in phase-space crossing the boundary between the region where molecules and where dissociated atoms exist, respectively, one must define the initial and final condition associated with a trajectory. This determines whether crossing of the surface once (or an odd number of times) results in reaction, and subsequent recrossing must be substracted out.

M. Rice. — The final and initial conditions have been found by Keck by carrying his detailed calculations on individual trajectories forward and backward in time, and I think that he has properly counted and interpreted the crossings.

M. Wigner. — May I answer this question because I may be more familiar with the point that disturbs Dr. Karplus. The picture refers to a single three-body collision. If the sum E_s of potential and relative kinetic energies of the two atoms which may form the molecule crosses the $E_s = 0$ surface an odd number of times, a molecule will result from the collision; if it crosses it an even number of times, no molecule will result. Now what is easy to calculate, by an extension of the transition state method, is the total number of crossings, in unit time, of all $E_s = 0$ surfaces in all the three-body collision in a gas. If the number of crossings of the $E_s = 0$ surface is 1 or 0 at every three-body collision, the easily calculated total number of crossings gives the rate of association. Hence, Dr. Keck gives an upper limit to the rate of association reaction.

M. Slater. — To comment on Prof. Rice's comparison of the RRKM and Slater theories, I would say that the latter is closer in spirit to transition state theory than was the original RRK theory. For the essential point of transition state theory is that decomposition occurs when the molecular *configuration* passes geometrically through a critical configuration, whereas the original RRK criterion which most peaople still have in mind, is the accumulation of *energy* in an oscillator or degree of freedom, which is not the same as passage through a configuration. The " classical " Slater theory (classical now in the sense of Graeco-Roman antiquity, although less antique than the original RRK theory) was based on the model of exactly harmonic vibrations because this was mathematically tractable; and also this might not seem too bad an approximation for *large* molecules, where the amount of energy per normal mode might be small enough, even in dissociating molecules, to allow anharmonicity to be neglected.

Prog. Wigner justly remarks that anharmonicity is unlikely to affect appreciably the first-order (high-pressure) rate of my harmonic model. But, as Laidler and I have pointed out and Prof. Rice has reiterated, anharmonicity would considerably affect lower pressure rates (and would especially increase the limiting bimolecular form) : this would happen even if we merely regard anharmonicity as a mechanism for transferring energy between quasi-harmonic modes. Some heavy but very interesting calculations by Dr. Bunker and by D.J. Wilson and co-workers have shown large effects of anharmonicity for triatomic (mainly linear) molecules; it is difficult to guess what would happen in larger molecules. One difficulty here is to think up realistic anharmonic potential energy expressions. Profs. Wigner and Rice have usefully remarked that the anharmonic potential terms for all molecular bonds might be taken as for diatomics; but this leaves open the question of what anharmonic cross-terms should be inserted in the potential to connect pairs of bonds which might soon be stretched together.

M. Rice. — The original theory of Rice and Ramsperger, and of Kassel, was not directly related to the transition state theory, and, indeed, preceded it. However, the subsequent work of Marcus and Rice brought the unimolecular-rate theory into relation with the transition state theory, and, indeed, considered a transition state for each individual level of the decomposing, or otherwise reacting, molecule. Although the original theory antedated the transition state theory, it is of interest to note that the method of calculation of the rate of decomposition of an activated molecule, was, for the model considered, essentially what would be suggested by the transition state theory.

M. Wigner. — I would like to agree with Prof. Slater in one point, and differ with him in two. It seems to me also that it is *his* theory which is in consonance with the ideas of the transition state method. On the other hand I wish to differ with him when he considers his theory to be antiquated. It seems to me, in particular, that even though the anharmonicity may affect the history of any particular high energy molecule, its effect will average out if the dissociation of all high energy molecules is considered. Dr. Slater has to average anyway over the various amplitudes of normal vibrations. In reality, this averaging occurs partially within the life-time of a single molecule, not only over the fates of the different molecules as would appear from Dr. Slater's calculation. However, I feel sure that the effect on the final result will be quite small.

On the other hand, it does not seem to me that the effect of the anharmonicity, which I believe to be small in general, is necessarily even lower in large molecules than in small ones. Before a bond is stretched to the breaking point, it will be, as a rule, stretched *almost* to the breaking point several times. At these occasions, the harmonic approximation is very poor indeed. The point is that the anharmonicity is most pronounced if a bond is stretched too much, not if the energy in one of the normal vibrations is large. Furthermore, a larger molecule has a longer life time so that the anharmonic terms have more opportunity to influence the motion also at times when no bond is particularly stretched. It would seem, therefore, that the effect of anharmonicities is not restricted to small molecules.

M. Slater. — The harmonic and anharmonic models may give quite different results in the low-pressure (second-order) region, where there is time between collisions for the energy redistribution which the anharmonic model allows and the harmonic model forbids. The difference should largely disappear in the high-pressure (first-order) region, where the short lifetime between collisions implies that only a relatively small portion of the internal phase-space trajectory (leading over the critical barrier) is relevant to dissociation, and there is little scope for anharmonic energy redistributions or perturbations. At high pressures the anharmonic effect is confined largely to modification of the energy profile near dissociation, and this effect is probably of a smaller order than the low-pressure effect mentioned above.

M. Rice. — I agree in the main with the statements of Wigner concerning anharmonicity, but believe that the effects of anharmonicity will be of importance in the sense that they will cause exchange of energy between "normal modes of motion" (an approximate way of viewing the situation, of course), whenever anharmonicity is present. My views are, indeed, already stated in my paper (second paragraph from the end of Section III, C).

M. Karplus. — It seems to me that the complicated potential energy surface of a big molecule will have more important anharmonic effects than the simpler surface of a small molecule.

M. Duchesne. — It is true that anharmonic forces characterize the structure of a chemical bond so that I also believe that there is no reason why they should appear weaker in big than in small molecules.

On the other side, experiments performed in microwave spectroscopy have shown that the electronic structure of the chemical bonds is rather dependent upon the degree of vibrational excitation involved. This appears indeed from changes observed in dipole moments, quadrupole constants, and so on, with vibration.

Then the question which I would like to ask Prof. Slater should be this : has this factor concerned with electronic changes induced by vibrations ever been considered in handling the problem of energy exchange, as it ought to play a part, not necessarily small, in this process ?

M. Slater. — I have not considered this hitherto, but clearly this effect should be treated as well as the anharmonic effects mentioned earlier in this discussion.

M. Herzfeld. — My first remark is almost trivial : anharmonicities shift the energy levels, but do not produce transitions between these shifted levels, and therefore do not directly help in transferring energy.

On the other hand, the broadening considered by Rice is very important, since it does away with sharp levels. Broadening of these levels will also occur due to collisions (in nearly all collisions, even if no energy is exchanged, but only the orientations are modified). Therefore, there might be a pressure range at high pressures, where the total rate of collisions is larger than Rice's k_e, and therefore the number of states of importance might be changed, leading to an anomalous pressure dependence of the rate. (O.K. Rice points out below that the decay rate and therefore the level broadening by it may be appreciably larger than given by this expression, midway between 3.1 and 3.2.)

M. Rice. — At sufficiently high pressures, pressure broadening of the energy levels of a decomposing molecule may become greater than the broadening caused by the decomposition itself, however, decomposition, according to the RRKM theory, causes broadening just sufficient for the energy levels to overlap when the energy is so low that the molecule can decompose into only one continuum; i.e., there is only one possible way for the remaining energy to be distributed among the vibrational levels of the fragments. If there is more than one such distribution possible, which is the situation in the most important range of energies, the broadening will be greater. This would presumably lesser resistance to redistribution of energy within the molecule due to necessity for matching energy levels.

M. Goldfinger. — I would like to ask Prof. Rice, if there are more than 2 or 3 examples of monomolecular reactions which permit one to check the accurate shape of the „ fall-off " of monomolecular rate constants with pressure and especially the small difference expected in the RRKM and Slater theories respectively. J.P. Chesick [*J. Am. Chem. Soc.*, **82**, 3277 (1961)] for instance quotes three examples : the isomerisation of cyclopropane and methyl cyclopropane, and the decomposition of cyclobutane. The decomposition of N_2O_5 or of azo-compounds is probably too complex for obtaining data sufficiently accurate for such a comparison. As for the case of simple molecules which for most practical purposes are in the second order range of monomolecular reactions, E.K. Gill and K.J. Laidler [*Proc. Roy. Soc.*, **A250**, 121 (1959)] have discussed them recently and did not arrive at clear-cut conclusions.

M. Hornig. — The question has been raised as to whether all of the unimolecular reactions discussed are indeed unimolecular.

In this connection, I should like to mention that one of my students, Mr. Modica, has been studying the dissociation reaction,

$$N_2F_4 + M \rightarrow 2NF_2 + M$$

in a shock tube. Although it is closely related to the NO_2Cl decomposition, the rate of this reaction is linear in both the total pressure and the partial pressure of N_2F_4 (and hence second order) over the pressure range up to one atmosphere and at temperatures from 350 °K to 550 °K.

M. Slater. — Some of us take such a wide view of " unimolecular " theory that we are prepared to treat almost any second order dissociation reaction as a unimolecular reaction for which the nature of the molecule happens to put the first order region (and the region of approach to first order) at an inaccessibly high pressure.

M. Rice. — Wieder and Marcus [*J. Chem. Phys.*, **37**, 1835 (1962)], in their comprehensive comparison of experimental data on unimolecular reactions with the theory of Marcus and Rice, have considered seven reactions in which the fall-off of the unimolecular constant can be observed. These include the three mentioned by Prof. Goldfinger, but they also include two decompositions, N_2O_5 and C_2H_5Cl, which may involve some complicating factors. The decomposition of N_2O, which is among the reactions discussed by them, may not be entirely unequivocal. The seventh reaction, which I think should be a fair example, is the isomerization of cis-butene-2. Recently Schneider and Rabinovitch (personal communication) have very thoroughly investigated what appears to be an excellent example, the isomerization of methyl isocyanide. In my laboratory, Forst has investigated further the decomposition of azomethane; we believe that, using chain inhibitors, we have sufficiently disentangled the complexities so that the first step in the decomposition can be used as an example of a unimolecular reaction whose rate falls off at low pressures, though the detailed theory has not yet been applied. In general, investigators test for heterogeneity. In some cases chain reactions are involved, and this, of course, has led us to discard many reactions once believed to be unimolecular. However, it is possible to test for chain reactions with inhibitors; though I am not certain that this has been done with all the isomerizations, it seems unlikely that they would be influenced by chains. (The isomerization of methyl isocyanide is unaffected by the scavenger O_2, but is accelerated by introduced methyl radicals.)

As noted in my paper, the fall-off of most of these reactions agrees fairly well with the Marcus-Rice theory, and the isomerization of methyl isocyanide agrees very well. The rate of activation of one or two of the molecules which are at the extreme low-pressure end, notably NO_2Cl, are abnormally slow, as also noted in my paper, and the reaction mentioned by Dr. Hornig, the decomposition of N_2F_4, seems to be another of this kind. This may point to an inhibition of transfer of energy within the molecule, perhaps of the kind suggested by Slater.

M. Wigner. — The simplest formula which describes the transition from bimolecular to monomolecular kinetics is that of Stern and Volmer, according to which the rate has the concentration dependance $ac/(b + c)$. This has two constants : the slope a/b in the bimolecular region, and the asymptotic value a in the monomolecular region. My question then concerns the magnitude of the deviations of the experimental rate dependance on the concentration c, from the simple Stern-Volmer curve *if one adjusts the initial slope and the asymptotic value*. Such deviations must be expected if the dissociation probabilities of the various activated states of the molecule show a wide spread. If this is the case, the actual rate, in the region intermediate between bimolecular and monomolecular, will lie below the Stern-Volmer rate if the constants of this are adjusted in the way indicated.

I realize that it is not customary to adjust the constants in the way indicated. Nevertheless, the question seems to me to be relevant if one wants to arrive at an estimate of the importance of the anharmonic terms which we discussed. The calculation of Rice and Ramsperger assumes that the energy of all the proper vibrations is equally available, even of those which have a very small amplitude at the bond to be broken. This is one extreme which probably overemphasizes the rate at which the energy between the various proper vibrations is exchanged. The theory of Slater, in its original form, assumes, on the other hand, that the energy of the proper vibrations is available only to the extent indicated by their amplitudes at the bond to be broken; it assumes no energy exchange between the proper vibrations. Experimentally, the two theories differ giving different deviations from the Stern-Volmer curve. Hence, it would be important to know to what extent these deviations can be measured.

M. Rice. — Apparently most cases which have been worked out in detail (refer to paper of Wieder and Marcus mentioned in my report) agree with the Marcus-Rice formulation of the RRKM theory, as far as the pressure at which fall-off occurs is concerned. However, the difference in the *shape* of the rate-pressure curve predicted by the Marcus-Rice theory and that predicted by the Slater theory is not very great, and I doubt if one can expect significant experimental tests of this point. In any case, since quantum effects have at best been taken into the Slater theory in only a rough way, differences may not be significant from a theoretical point of view.

M. de Boer. — In the discussion which we witnessed between Dr. Rice, Dr. Wigner and Dr. Slater it is, apparently, taken for granted that the experimental data are correct, especially also with small atoms as a third body and at very low pressures. The question may be asked whether this assumption is right. Dr. Rice, himself, during his lecture, referring to Table I discussed the great variation in collision diameter obtained for He as a third body, when using different equations (Eq. 2.21 and Eq. 2.18), resulting in too low a value in the one and too high a value in the second case. This too low and too high relate to the experimentally obtained result. In this very case I must say that the experiments by Norrish and his school give the best guarantee that the results are not troubled by " wall "-effects; in other experiments recombination on the wall may very well trouble the results. A small " background " effect caused by the recombination on the wall is, of course, far more troublesome when small atoms are studied as a third body and also at low pressure. The wall, however, is not the only source for a heterogeneous recombination reaction. Many years ago, on the request of the Netherlands astronomers Oort and v.d. Hulst, I calculated the ratio between the homogeneous recombination of hydrogen atoms of interstellar gas clouds and the heterogeneous recombination by the tiny particles of solid ice, ammonia and methane of the interstellar ,, dust '' clouds : The result was that the heterogeneous rate was about 10^{12} times faster than the homogeneous one. It is, therefore, also necessary to be absolutely sure that no dust particles are there or are formed during the experiments. Only if one is completely sure that no wall effects and no effects caused by small dust particles disturb results, experimental data may be used to compare theoretical results.

M. Porter. — Whilst I agree with what Dr. de Boer says about the importance of heterogeneous reactions in many observations made at low pressures, I do not believe that the atom recombination results in Table I of Rice's paper which de Boer mentioned as a possible example, can suffer from this difficulty. These measurements are made at a pressure of the order of 1 atmosphere in a time of a few milliseconds and the time for diffusion from the wall to the center of the reaction vessel under these conditions is about a second. One of the advantages of fast reaction studies, compensating for some of the experimental difficulties, is that one can be quite certain that heterogeneous reactions are excluded.

M. Rice. — Most experimenters test the effects of walls by increasing the surface-volume by filling the reaction flask with tubing of similar glass. Some reactions may involve chains, but it is possible to test for these with inhibitors, and in some cases one can measure the inhibited reactions.

M. Widom. — One knows that the deviation of a rate constant from the value it would have with a Boltzmann distribution of reactant molecules, is proportional to the relaxation time. For example if product molecules are instantaneously removed from the system then

$$k = k_{eq} - \tau\,(<q^2> - <q>^2)$$

where τ is a mean relaxation time and q is the reaction probability per unit time from a given reactant state. Have you then been consistent in treating the relaxation time as negligible, while at the same time considering the deviation of k from k_{eq} ?

An interesting possibility connected with the question of whether or not the ratio of forward and backward rate constants is the equilibrium constant is the following : In a dissociation reaction the inverse reaction is of higher molecularity, and may therefore be one in which the idealization of instantaneous product removal is valid, whereas this idealization may be invalid for an isomerization; so there may be a deviation of k_f/k_b from K in the former case and not in the latter.

M. Ross. — In connection with the different problem of bimolecular reactions of structureless particles of the type $A + B = C + D$, I would like to remark that Mr. C. Pyun and I have derived the composition dependence of the first order deviation of the rate coefficient from its " equilibrium " value. Thus if the momentum distribution function of species A is $f_A = f_A^{\circ}(1 + \varphi_A)$, then φ_A, the deviation from the Maxwellian distribution f_A°, is given to lowest order in a Sonine polynominal expansion by

$$\varphi_A = (1 - e^{-\beta A})\, G/F\, (15/8 - 5\beta p_A^2/4m_A + \beta p_A^4/8m_A^2)$$

where A is the affinity, β is $(kT)^{-1}$, p_A and m_A are the momentum and mass of A. F is a composition-dependent determinant with elements given by certain averages of the elastic scattering cross sections of the various species; G is a composition-dependent determinant containing elements from F but is linear in certain averages of the chemical reaction scattering cross section. The ratio of the rate coefficient in the forward direction to that in the reverse direction equals the equilibrium constant apparently only in very special cases.

M. Rice. — The rate of the reaction $A + B \rightarrow C + D$ or of its reverse may well depend upon the amounts of products and reactants present, and so the quotient of the rate constant for the direct reaction when no C and D are present divided by the rate constant for the reverse reaction with no A and B present may not be equal to the equilibrium constant. I have attempted to avoid this difficulty in the reactions

$$A + B + M \rightleftharpoons AB + M$$

by having M in sufficient excess so that all energy transfer is due to it (M might still be A, B, or AB). Under these circumstances the fate of any pair A-B, whether starting as two atoms or as a diatomic molecule, is independent of A, B, and AB present. The rate constants for the direct and reverse reactions are then independent of whether the other reaction is occuring or not, provided the process by which an excited AB is deactivated is fast compared to the rate of reaction. Under these conditions k_a and k_d are definitely defined, and $k_a/k_d = K$. The activated molecules AB* which are lacking from the equilibrium quota in the dissociation reaction are just matched by the AB* which will redissociate or rather be deactivated (and hence not be counted as reacting) after being formed by association of A and B. It would be interesting to see if a similar conclusion could be drawn for the reaction $A + B \rightleftharpoons C + D$ under circumstances such that the environment could be considered constant.

The relaxation time may be short compared to the overall reaction time (which is relatively long because of small number of activated molecules or activated complex), but not small compared to the rates of transition between individual energy levels which give rise directly to reaction. Thus there is no inconsistency in treating the relaxation time as negligible compared to reaction time and still having a rate constant different from the equilibrium value.

M. Herzfeld. — Experimentally reaction rates are usually measured far from equilibrium. Ultrasonic measurements, on the other hand, measure rates very close to equilibrium.

M. Van Tiggelen. — When the rate constant of any elementary reaction and in particular of atom recombination is measured directly, a fundamental problem rises concerning its usefulness in deriving from the equilibrium constant the rate constant of the reverse reaction or in comparing with theoretically calculated rate constants. This is the unavoidable difficulty which results from the fact that the measurements are necessarily made neither in strictly isothermal nor in strictly adiabatic conditions.

Furthermore, even if we suppose a perfect isothermal system, the experimental rate constant will be the result of two simultaneous phenomena : the recombination process itself and the heat transfer to the walls and out of the system (into the system if a decomposition rate is to be determined).

On the other side, in adiabatic conditions, the measurements are not made at a constant temperature since at least a minimum of conversion is needed to render the experimental method sufficiently sensitive. At the same time even the randomisation of energy (residual vibration energy of the newly formed molecules) might possibly be delayed.

Of course such difficulties should have less importance either if the system is highly diluted with an inert gas, either if only a very small conversion is accepted, or if the measurements are made in a system which is already very near to the equilibrium; however the obtained data would than have less accuracy.

THE STUDY OF ENERGY TRANSFER IN ATOMS AND MOLECULES BY PHOTOCHEMICAL METHODS

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INDEX

I. **Introduction.**

The partition of energy between the translational rotational and vibrational degrees of freedom of molecules is conditioned by the principles of quantum mechanics, but the mechanism by which transfer takes place between the various modes is not well understood and can only be examined experimentally by observing systems not in equilibrium.

This is possible in principle because classical studies of photochemical reactions have indicated that the products of both primary and secondary processes, especially where atoms and free radicals are involved, may be associated with large amounts of energy completely out of thermodynamic equilibrium with the environment. It makes itself apparent by such phenomena as chemiluminescence and the propagation of chain reactions. Likewise the study of atomic and molecular spectra indicates the production of excited electronic species which may be reduced to lower electronic levels by fluorescent emission of radiation or by radiationless transfer of energy by inelastic collisions (collisions of the second kind). Such processes in molecules are associated with rotational and vibrational changes involving levels of very short duration, whose decay cannot be followed by the experimental techniques of classical kinetics.

Until recently kinetic measurement was only possible in the case of the transfer of translational energy to low vibrational levels and in some cases rotational levels by the study of the dispersion of a wide range of ultrasonic vibrations of very high frequency. Here the equilibrium of energy partition is suddenly disturbed by the rapid change of pressure in the wave front, and the " relaxation time " for its re-establishment may be derived from a measurement of the velocity of ultrasonic propagation; this in turn leads to an evaluation of the probability of energy transfer on collision.(1)

Methods of this kind have been amplified and extended. By the use of shock waves, a sample of gas can be heated homogeneously to very high temperatures : from the viewpoint of an observer travelling with the shock front, the kinetic energy of the movement of the gas into the front is converted to translational energy of the molecules behind it : this process occurs in times corresponding to the thickness of the front, or a few mean free paths in the undisturbed gas. The adiabatic relaxation process then corresponds to an increase in rotational and vibrational energy at the expense of translation and the (translational) temperature and pressure of the gas fall and the density rises until equilibrium is attained.

The time scales of rotational and vibrational relaxation are so different that for most gases they may be considered as independent processes. Rotational relaxation takes place in a time comparable to the number of collisions taking place in the shock front; it is therefore observed experimentally as an increase in the thickness of the front. These have been measured at pressures above 1 atmosphere using the reflectivity method developed by Hornig and co-workers;(2) and at low pressures by direct measurements of the shock front profile.

Behind the front, rotational relaxation is already nearly complete (except for hydrogen) and vibrational relaxation can be followed independently. Using interferometric methods (3) the change of density behind the shock wave can be measured as a function of time, or alternatively the temperature profile through the shock wave may be determined by sodium line reversal methods;(4) in favourable cases information may also be obtained by observing vibrational transitions directly by the use of infra-red detectors of rapid response.(5) These and other methods of observation make possible the determination of vibration- and rotation-translation relaxation, and are applicable in general to only the first few quantised levels. The higher quantised levels are excluded because the temperatures required for their generation lie to a large extent beyond the resources of the observational techniques available.

It is the purpose of this paper to show how the newer methods of photochemistry make possible the study of vibrational relaxation at high levels of quantisation under isothermal conditions, as well as the relaxation of metastable electronic states. It is hoped to show that the beginning which has been made holds forth considerable possibilities for future study, the results of which cannot fail to elucidate the manifold problems of chemical kinetics.

II. **Flash photolysis and kinetic spectroscopy.**

The techniques of flash photolysis and kinetic spectroscopy devised and developed in the Department of Physical Chemistry at Cambridge (6) make possible the observation of rapid physical and chemical changes in time intervals as short as a few microseconds or greater. By means of a powerful light flash, generated in a quartz tube usually half a metre in length and containing an inert gas, high concentrations of excited atoms, molecules, or free radicals can be generated in suitably reactive systems and their absorption spectra photographed by means of a second flash lamp as spectroscopic source, triggered electronically after the first at successive short intervals of time.

The arrangement of the apparatus is shown in Figure 1. The reaction vessel which consists of a quartz tube about 2 cm diameter with plane end plates is placed close and parallel to the flash tube. The two are surrounded by a cylindrical reflector coated on the inside with magnesium oxide. The second flash lamp also containing inert gas is arranged to pass a beam of light through the length of the reaction vessel on to the slit of the spectroscope (Hilger, Littrow mounting). The first lamp (the photoflash) is fired by dis-

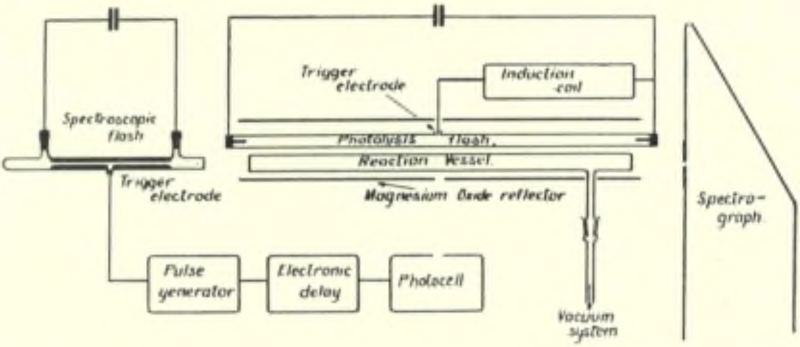


Fig. 1. — Diagram of apparatus for flash photolysis.

charging a capacity C of about 40 μF at 10 kV between robust tungsten electrodes. The energy of the flash, $1/2\ CV^2$ is thus of the order of 2000 Joules and its half-life 20-30 μ/sec, measured by means of an oscilloscope. Ideally the shortest flash for a given energy is obtained by making the capacity C as small as possible and the voltage V as high as possible, the self induction of the circuit being kept as low as practicable. The second lamp (the specflash) is fired electronically by the light from the photoflash, by discharging a capacity of 2 μF at 12 kV, giving a flash of about 150 Joules and 2-4 μ/sec duration. It is fortunate that neither lamp is discharged spontaneously; their firing is achieved by the passing of trigger currents from centred electrodes which break down the dielectric.

The photoflash may be triggered from the secondary of an induction coil by discharging a small capacity through the primary. The light from the photoflash falls on a photoelectric cell, and the photocurrent after passing through a variable electronic delay is amplified by a thyratron and applied to the trigger circuit of the specflash. Thus the whole system can be charged and fired by one switch operating the trigger circuit of the photoflash. In this way, by adjusting the electronic delay the specflash may be discharged at precise intervals measured in microseconds after the photoflash, and its intensity is sufficient to take absorption photographs of any spectrally responsive transient species generated in the reaction vessel. By carrying out successive experiments at increasing delays under controlled conditions, the growth and decay of any observable transient can be observed and measured by methods of plate photometry.

Of the energy emitted by the photoflash, some 10% can be shown, by using uranyl oxalate as an actinometer, to be useful photochemical light, lying between 2000 and 6500 Å. By employing double walled reaction vessels the annular space can be filled with suitable gases or solutions at adjusted concentrations to act as colour filters, and so limit the spectral range of the photoflash — a matter of importance, especially where two photochemically responsive species are involved. Even with colour filters the "instantaneous" light flux is so great as to generate high concentrations of transients in suitably reactive systems.

It soon became apparent however that the sudden dissipation of so much light energy within an absorptive system gives rise to enormous temperature rises, and that temperatures of many thousands of degrees are momentarily achieved in the gaseous reactant unless suitable precautions are taken. For example, a tube of pure chlorine at 1 atmosphere pressure is instantaneously exploded by a flash of 2000 Joules.

Adiabatic processes.

The appreciation of this effect made possible the application of the method of flash photolysis to the study of explosive reactions involving hydrocarbon and other fuels with oxygen, etc., using where necessary a photosensitiser such as nitrogen dioxide, if the reactants themselves have no absorption bands in the spectral region of the photoflash.(7) In this way induction periods, the growth and decay of intermediates in the explosive reactions and the effects of additives may be readily and usefully studied. Such cases, in which an " adiabatic shock " is administered to the system by the photoflash and no attempt is made to control temperature, may be called the adiabatic method. We are not further concerned with them here.

Isothermal processes.

For the study of relaxation and of reactions under isothermal conditions precautions must be taken to prevent a significant rise of temperature. In the case of gases, this is done by limiting the reactant to a few millimeters pressure, and adding one to seven hundred-fold pressure of inert gas to increase the heat capacity of the system. By this means the temperature rise may be limited to a few degrees, and kept below ten degrees. With liquid systems, involving solutions, there is of course no problem since the inert solvents act as suitable diluents and the heat capacity is such that no temperature rise can be detected. This technique of kinetic spectroscopy may be described as the " isothermal method ". It is the method used in all the examples which are cited below.

Relaxation times for the attainment of rotational equilibrium have been shown by methods of sound dispersion to be very short, and of the order of 10^{-8}-10^{-9} sec. Such processes are far too short for observation by the method of kinetic spectroscopy, where we are at present limited to a time scale measured in microseconds.

However, vibrational relaxation which lies in the range 10^{-3} to 10^{-7} sec may in many cases be studied to advantage. This may be illustrated by a comparison of the photochemical systems NO and NOCl or NOBr.

III. Vibrational excitation by primary photochemical processes.

Relaxation in nitric oxide.

The fluorescence and vibrational activation of nitric oxide was studied by Basco, Callear and Norrish.(8) The relevant absorption in this case is the 0-0 band of the γ system in the region of 2270 Å. There is no appreciable absorption at longer wavelengths, except a slight absorption at 2365 corresponding to the 0.1 band, and absorption at shorter wavelengths is effectively limited by the cut-off at 2000 Å by quartz. Thus the excitation was approximately by monochromatic light. The spectroscopic transition with which

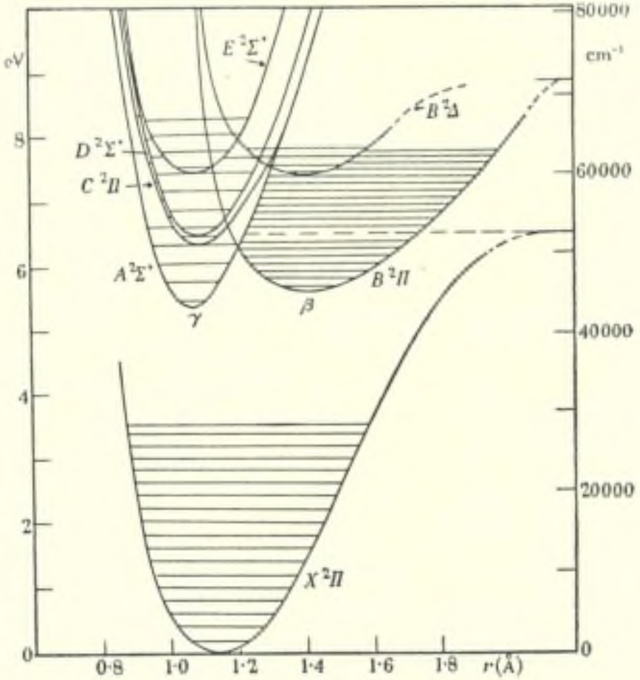
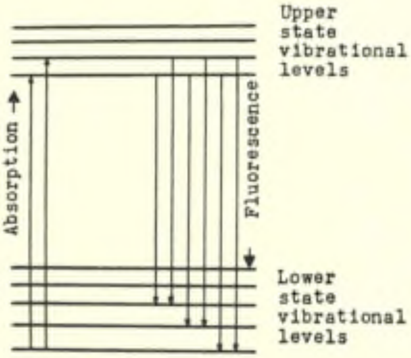


Fig. 2. — Potential curves of the NO molecule.
(After Dr. H.P. Broida.)

we are concerned and which gives rise to the γ bands is represented by $A^2\Sigma^+ — \mathbf{X}^2\Pi$. The two potential curves lie vertically above each other, and give rise to the fluorescence spectrum measured by Pearse and Gaydon (9) (Fig. 2).

On flashing a charge of 5 mm nitric oxide diluted with 600 mm N_2 as coolant, the result shown in Figure 3 (see p. 107) was obtained in which there is in evidence a high transient intensity of the 0.1 band and to a lesser degree of the 1.1 band of the γ spectrum. The origin of this vibrational excitation in the ground state is by fluorescent or collisional transition from the upper state as shown in Figure 4 and the momentary overpopulation of the $v = 1$ level



Diagrammatic excitation of lower levels by fluorescence

Fig. 4.

can be measured, and its decay followed quantitatively by plate photometry. This is possible because the 0.1 band is visible spectroscopically in absorption with nitric oxide at 1 atmosphere pressure; and since its concentration at equilibrium [NO*] is given by

$$[NO^*] = [NO]e^{-h\nu/kT}$$

the photometric curves can be calibrated to give absolute concentrations by choosing one particular line in the band for measurement.

Fig. . Decay of NO $^2\Pi(v = 1)$ with time.

Pressure of NO = 5 mm. Hg; pressure of N_2 = 600 mm. Hg. Flash energy = 1600 Joules.

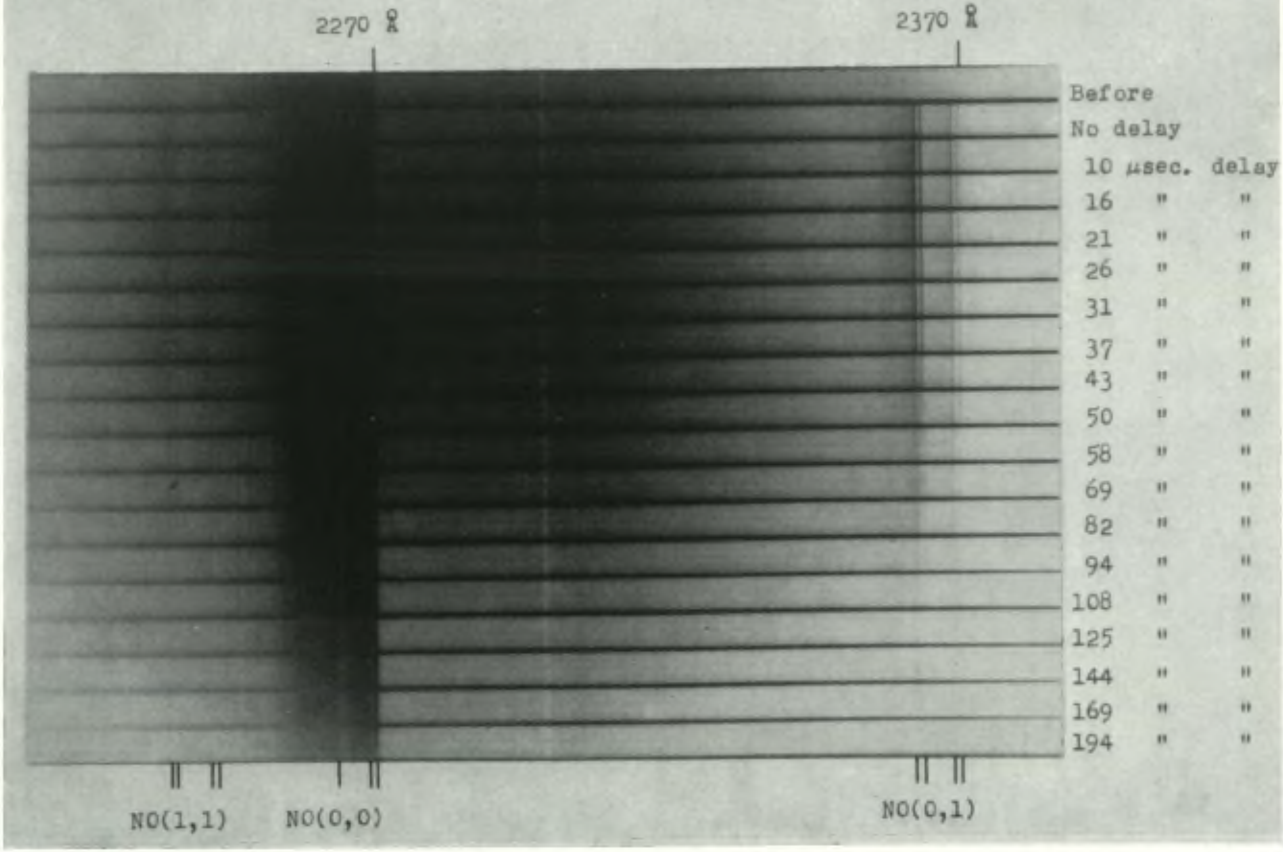


Fig. 3 — Decay of NO $^2\pi(v = 1)$ with time.

In this way the curves shown in Figure 5 were obtained : when

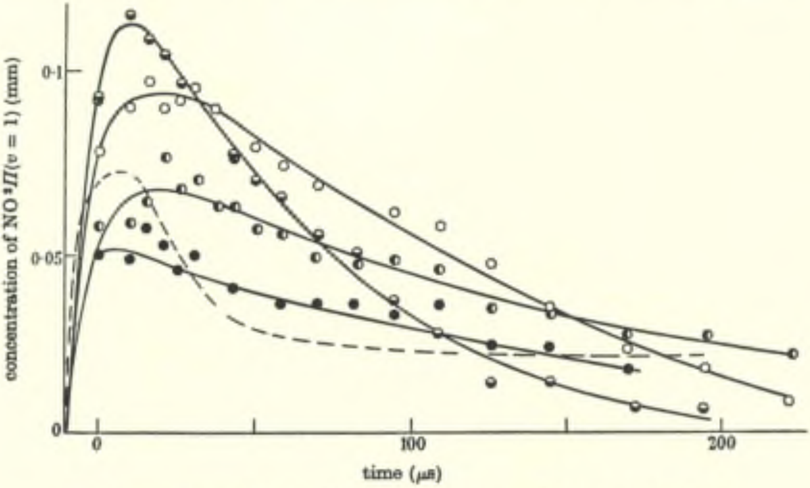


Fig. 5. — Rise and decay of NO $^2\Pi(v = 1)$ measured by plate photometry.

○ 2 mm NO + 600 mm N_2, 1600 J
● 2 mm NO + 220 mm N_2, 1600 J
◐ 1 mm NO + 600 mm N_2, 1600 J
◒ 5 mm NO + 600 mm N_2, 1600 J
--- 50 mm NO + 457 mm N_2, 900 J

plotted logarithmically they give good straight lines showing unimolecular decay, from which the unimolecular constant k_3 for the reaction

$$NO_{v=1} \rightarrow NO_{v=0}$$

can be obtained.

$1/k_3$ is the mean lifetime, τ. If the excited species suffers Z collisions per second then P_{1-0} the probability of energy transfer at one collision is given by

$$P_{1-0} = \frac{1}{\tau Z} = \frac{k_3}{Z}.$$

k_3 can be split into two terms depending on relaxation by NO and N_2 respectively. Thus

$$k_3 = k_4(NO) + k_5(N_2),$$

and k_4 and k_5 may be calculated from the various values of k_3 derived from the curves of Figure 5. Thus it is found that the value of P_{1-0} for NO is $3.6 \pm 0.4 \times 10^{-4}$ at 300 °K, in excellent agreement with the sound absorption results of Bauer *et al.*(10) and the extrapolated shock wave results of Robben as follow : (11)

Sound absorption	10^{-3} - 10^{-4}
Shock wave	3.8×10^{-4}

The value of P_{1-0} for nitrogen is calculated as 4×10^{-7} within an order of magnitude.

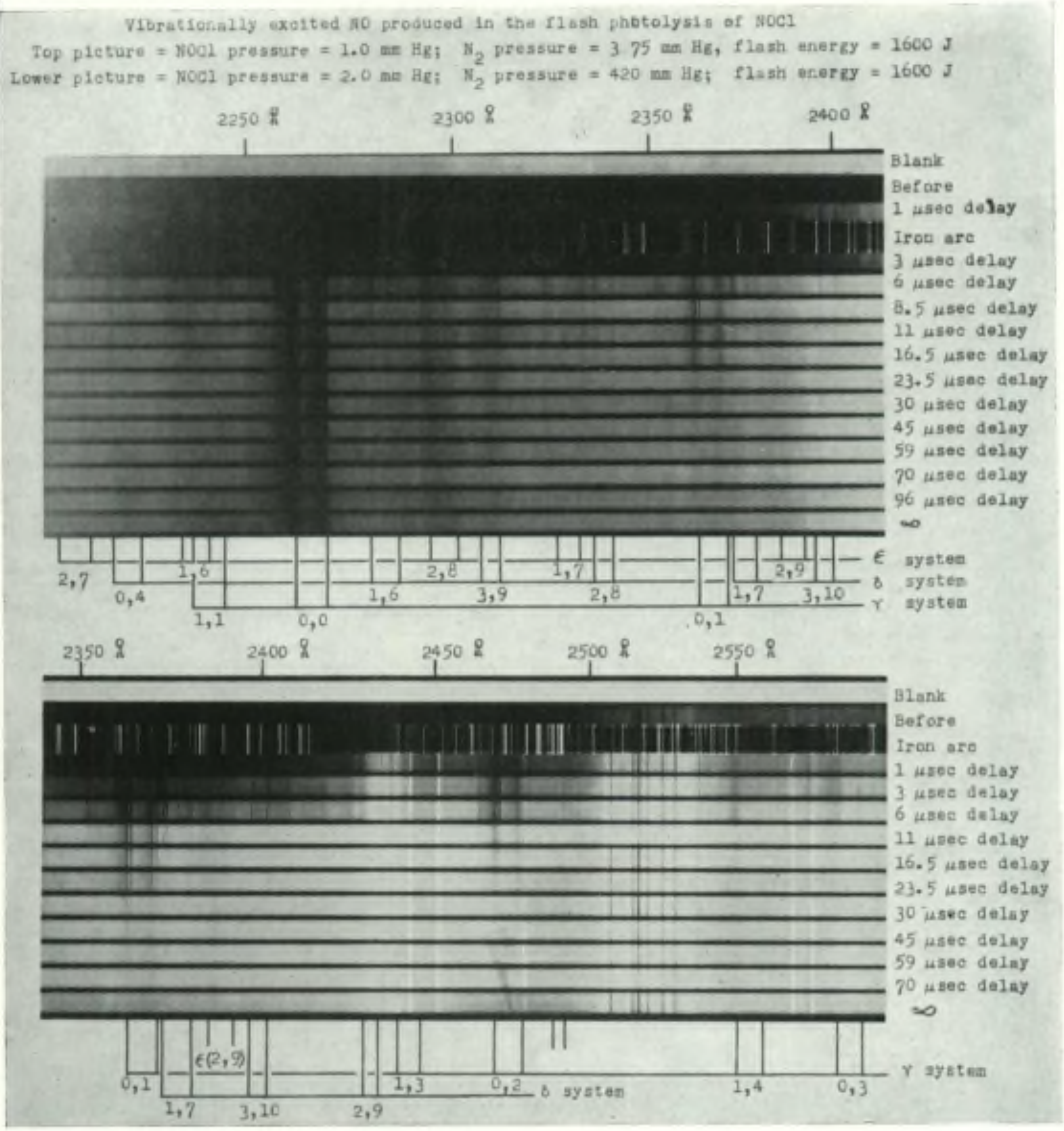
In a similar way it was found that small quantities of water and also added carbon monoxide or carbon dioxide in the presence of nitrogen decreased the concentration of $NO^2\Pi(v = 1)$ and increased its rate of decay. From the results obtained k_3 could be determined and the contribution of the additive determined, the following table gives the derived data.

TABLE I

Molecule	$k_5(s^{-1})$ for 1 mm	P_{1-0}	Pressure for half quenching (mm)
NO	3.2×10^3	3.55×10^{-4}	1 - 2
CO	2.0×10^2	0.25×10^{-4}	40
H_2O	10^5	7×10^{-3}	0.5
CO_2	2×10^3	1.7×10^{-4}	5
N_2	3.8	4×10^{-7}	>1000
Kr	—	—	>1000

The quenching data for CO_2 and H_2O are accurate to about an order of magnitude and it was concluded that the true value of P_{1-0} for CO_2 may prove to be somewhat lower. The relative high efficiency of NO for self quenching is to be noted, and it is suggested that the high efficiency of water may be due to chemical reaction with the electronically excited $NO \cdot A\Sigma^+$ since traces of water are very efficient in quenching the fluorescence.

By flashing with the photoflash alone it is readily possible to photograph the fluorescent emission, $v' = 0$ and $v' = 1$ progressions being observed up to $v'' = 5$ in the latter case. However, if the fluorescence is completely quenched by sufficient additive the $v = 1$ level is still observed to be overpopulated in the ground state,



Vibrationally excited NO produced in the flash photolysis of NOCl

Top picture = NOCl pressure = 1.0 mm Hg; N_2 pressure = 3.75 mm Hg, flash energy = 1600 J

Lower picture = NOCl pressure = 2.0 mm Hg; N_2 pressure = 420 mm Hg; flash energy = 1600 J

Fig. 6. — Vibrationaly excited NO from NOCl.

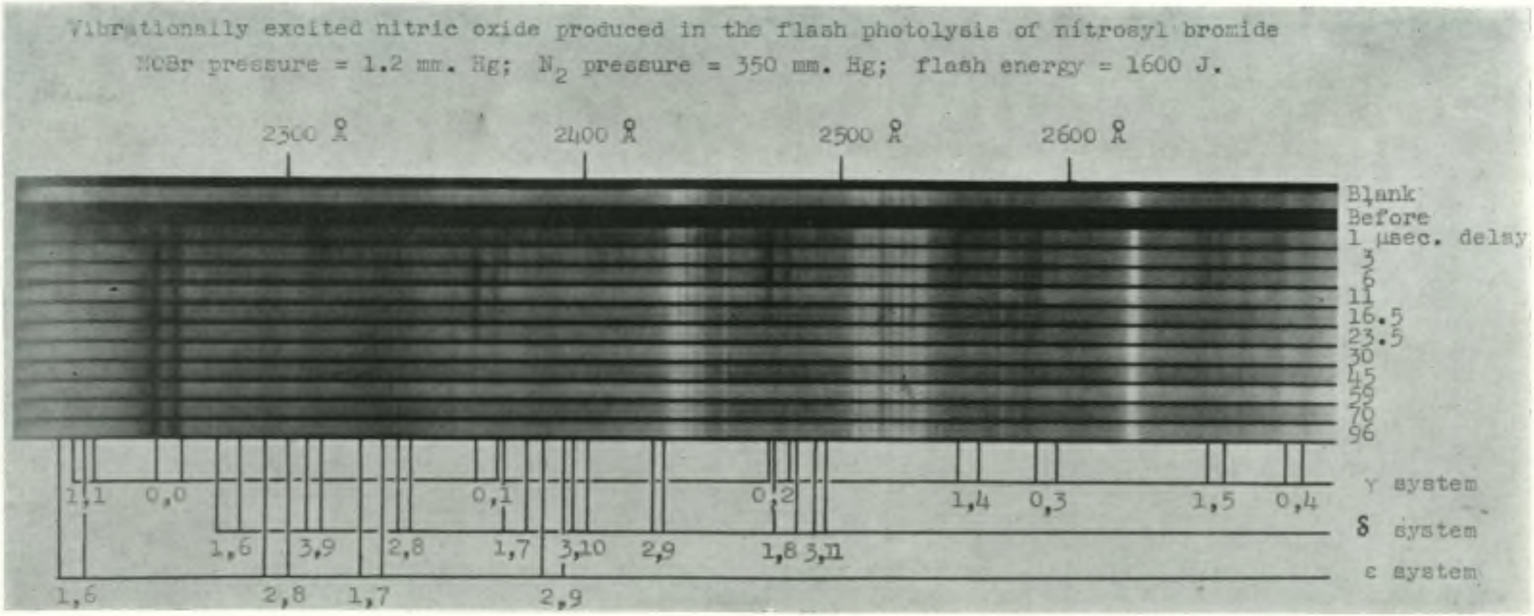


Fig. 7. — Vibrationally excited NO from NOBr.

which leads to the conclusion that the vibrational levels of the ground state may be populated not only by fluorescent emission, but also by collision deactivation

$$NO^2\Sigma^+(v = 0, 1, 2) + M = NO^2\Pi(v = 0, 1, 2...) + M.$$

It is however significant that by whichever process the vibrational levels of the ground level $^2\Pi$ state are populated, only the level $v = 1$ (and at times $v = 2$ *very* faintly) can be seen by kinetic spectroscopy. Thus since the vertical disposition of the two potential curves for the $^2\Sigma^+$ and $^2\Pi$ states, and the fluorescence spectrum indicate that the higher v levels of the ground state are initially populated, it must be concluded that the relaxation of the higher vibrational levels probably by self quenching is extremely rapid, and much too fast to be seen by kinetic spectroscopy. We shall return to this point when we have considered the results relating to the photolysis of NOCl and NOBr.

The photolysis of nitrosyl chloride and nitrosyl bromide.

The flash photolyses of NOCl and NOBr have been examined by Basco and Norrish.(12) They have shown, using suitable light filters surrounding the reaction vessel that strong photolysis takes place in the region of 2500 Å with the production of highly vibrating NO molecules in the ground state. All levels from $v = 11$ to $v = 0$ were observed in absorption in the β, γ, δ and ε systems (see Figs 6 and 7, pp. 111 and 112) and all the vibrational states, with the exception of ($v = 1$), were short lived and did not survive the period of the flash. By using nitric oxide as a light filter it was shown that these excited species did not have their origin in the secondary excitation of nitric oxide molecules and, in fact, after careful consideration of all other possibilities it was concluded that they are the product of the primary reaction of the halide, NOX :

$$NOX + h\nu = NO^* + X.$$

After careful comparison of a large number of plates a number of very significant facts emerged; I quote from the original paper :

" The relative population of the higher vibrational levels of nitric oxide observed increased as the halide pressure was reduced. This effect was most pronounced at relatively long delay times, but was appreciable over the range 2-0.05 mm even at 3 μ/sec delay. At the higher pressure the γ (0.1) band for example was stronger than the δ (1.7) while at the lower pressure the former was barely detectable and the latter still quite strong. Likewise the proportion of the molecules observed to be excited, as estimated from the increase in intensity of the γ (0.0) band with time increased as the pressure of nitrosyl halide was lowered.

" The decay of the excited levels was always rapid, the higher levels having increasingly short life times, so that only the first level is detectable after the photoflash. The rate of decay was determined by the halide pressure and was increased as this was raised. The effect of inert gas on the rate of decay was not detectable even at the lowest pressure of halide used. "

The rapidity of decay of NO* suggests that near resonance transfer processes are operating. Thus, for the range of levels $v = 11$ to $v = 0$ the vibration frequencies of NO lie in the range 1900-1600 cm^{-1}. For both NOCl and NOBr the frequency associated with the NO bond by Burns and Bernstein is 1800 cm^{-1}. For oxygen which materially accelerates the decay the frequency of 1560 cm^{-1} may be effective for the higher levels, and so also naturally NO itself. These effects and the almost complete absence of effect of nitrogen or noble gases give us a qualitative picture; but an anomaly at once appears when the behaviour of NO* produced from NO is compared with that derived from the nitrosyl halides. In the former case as we have seen the higher vibrational levels except $v = 1$ (and possibly $v = 2$) disappear more quickly than they can be observed by flash photolysis; if their disappearance is by resonant transfer, why is it so much quicker than that of NO* produced in the latter case ?

Resonant transfer.

It was stated in the passage quoted above that the tendency is for the higher vibrational levels of NO* produced from nitrosyl halides to predominate at lower pressures. It is also observed that the population of lower levels, e.g. $v = 2$ and $v = 1$ increases with time as the higher levels fade out, until only $v = 1$ and $v = 0$ are left. In view of these observations the following hypotheses may be made :

(1) The most favourable resonant collisions are between closely associated levels of the vibrating species, e.g.

$$NO_{v-n} + NO_{v-(n-2)} = 2NO_{v-(n-1)}$$

and owing to change in frequency of levels due to anharmonicity, the most favourable result will be obtained when the frequency levels differ by 2 as above.

(2) At the instant of production from the nitrosyl halide the NO* is formed in very highly vibrating states — say, $v = 12$, $v = 11$, $v = 10$. The vibrational energy of $v = 11$ is 55 kcal and since the bond strength of NO — Cl is 38 kcal there is plenty of energy available from the light quantum (say 98 kcal for 2800 Å) for this to occur. In consequence, there is a gap between $v = 10$ (say) and $v = 0$ and in the absence of any other deactivating species (inert gases inefficient) the higher vibrational levels cannot be relaxed. This of course is an ideal conception; lower levels will be built up by collisional deactivation by species such as the nitrosyl halides, but this will be comparatively a slower process. As the lower levels are populated in this way so will resonant self quenching increase, but there will always be an irregular distribution of levels and this in itself will cause a slowing down of resonant deactivation, and since high levels are continually fed in during the flash, this irregular distribution will be preserved and all levels will be observed during its operation.

These two hypotheses are in agreement with the observed results for the nitrosyl halides. Contrast now the case of NO* produced from nitric oxide by fluorescence or by collisional deactivation of the excited electronic state $^2\Sigma^+$ to the $^2\Pi$ ground state. The intensities of the $v' = 0$ progression in emission were found by Pearse and Gaydon (9) to be :

TABLE II

0.0	0.1	0.2	0.3	0.4	0.5
8	10	10	9	8	7

and it is considered that the 0.0 intensity may well be weakened because of reversal. Thus all ground states are populated " smoothly " by fluorescence, and we shall assume that collisional deactivation of the excited states gives rise initially to a similar smooth distribution of vibrational levels. Thus if there is no " gap " and each vibrational level is populated slightly less than the one below it rapid resonant deactivation is possible by the mechanism

$$\mathrm{NO}_{v=n} + \mathrm{NO}_{v=(n-2)} = 2\mathrm{NO}_{v=(n-1)}$$

progressively repeated as shown in Figure 8. The consequence of this is that all levels are rapidly deactivated to $v = 1$ when the

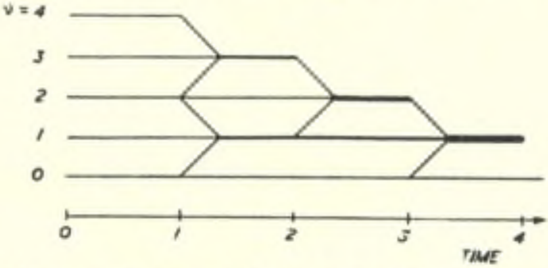
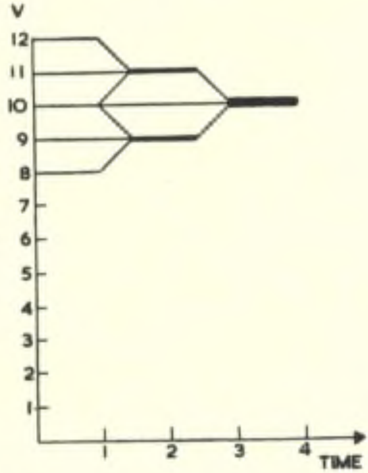


Fig. 8. — Diagrammatic scheme of vibrational relaxation by self resonant collisions.

resonant process must of necessity stop. Hence only the $v = 1$ level is seen to be over populated with the $v = 2$ level appearing very faintly and representing the last stage of the collapse of the vibrational pattern. Thus with smooth distribution we get very rapid vibrational relaxation, too rapid to be observed by kinetic spectroscopy, while if we have a gap in the vibrational distribution or a series of irregularities in the sequence of population of the pattern of vibrational levels, as with NO* derived from the photolysis of nitrosyl halides, resonant deactivation must be considerably slowed down, — sufficiently for over population of all levels to be observed by kinetic spectroscopy. (See fig. 8*b*).



Fib. 8b. — Diagrammatic scheme of the incomplete vibrational relaxation due to over population of the higher levels.

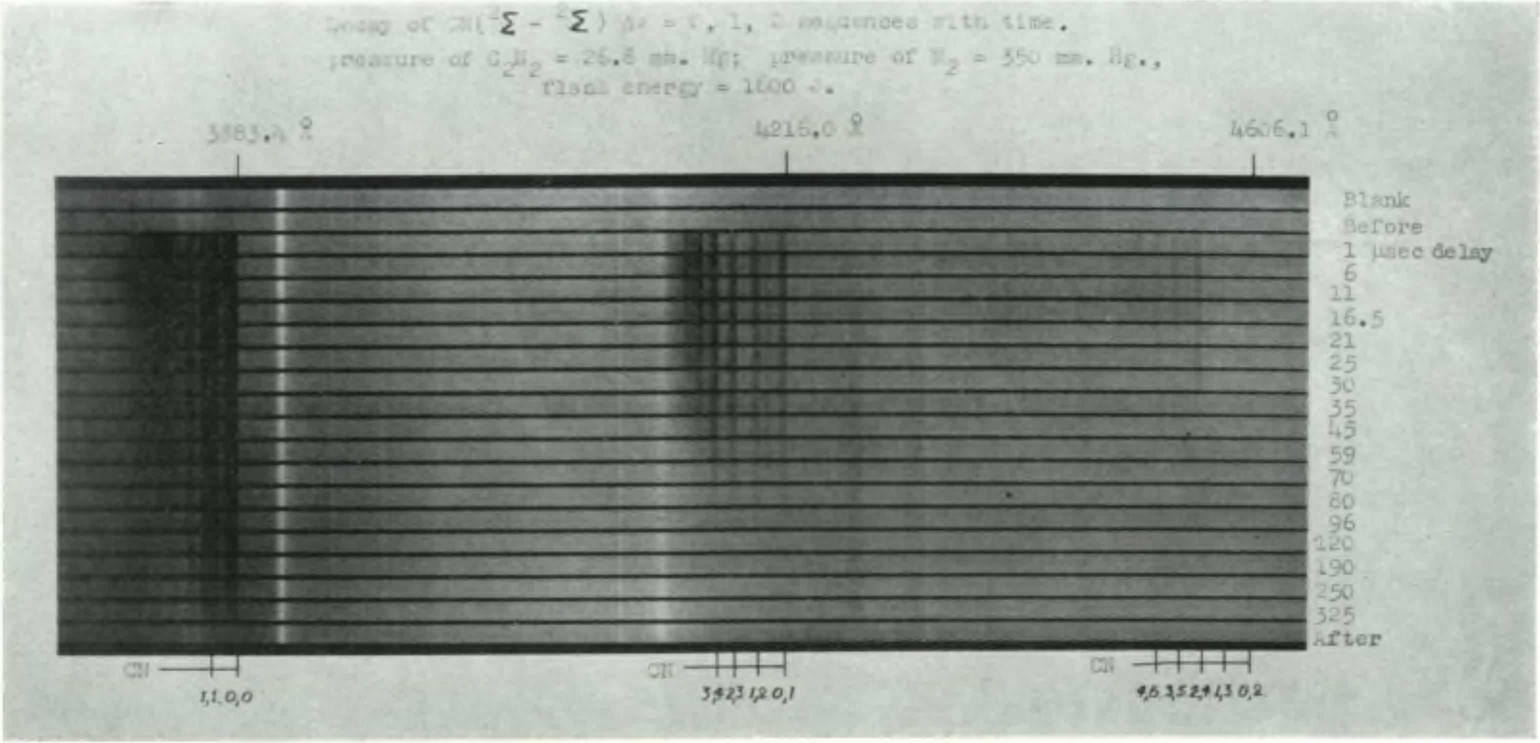


Fig. 9. — Vibrational excitation of CN from CN_2.

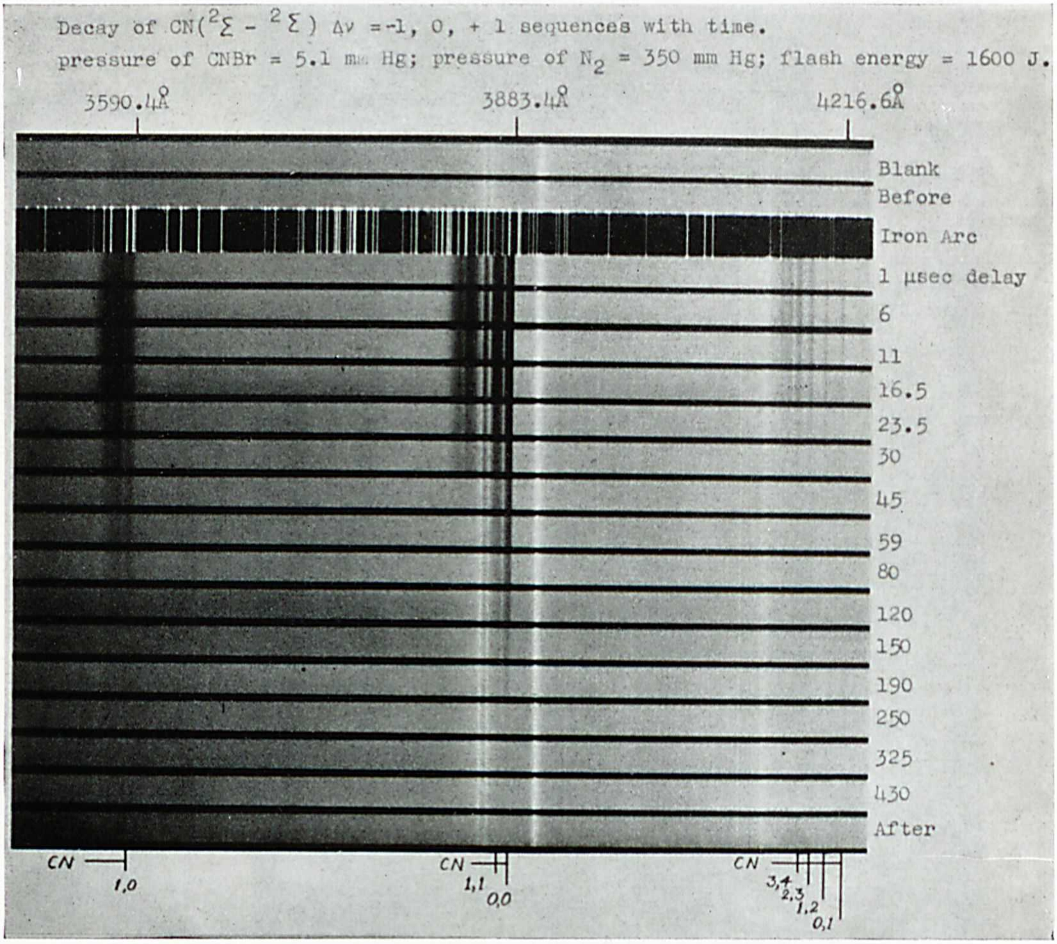


Fig. 10. — Vibrational excitation of CN from CNBr.

Photolysis of cyanogen and cyanogen halides.

It may be added that the flash photolyses of C_2N_2, CNBr and CNI (which will be referred to generically as CNR) yield results which appear to be very similar to NOCl and NOBr.(13) These substances absorb in the short end of the quartz ultraviolet below 2300 Å, and on flashing in the presence of high pressures of inert gas yield vibrationally excited CN radicals up to $v = 6$ which are observed spectroscopically in absorption in the $\Delta\nu = 0, \pm 1$ and -2 sequences of the violet $(B^2\Sigma - X^2\Sigma)$ system at 3590, 3883, 4216, and 4606 Å. Typical decay sequences with time of CN* are shown in Figures 9 and 10 (see pp. 117 and 118). At all except the highest pressures where only the decay is observed, all the vibrational levels rise to a maximum and then decay. At the lowest pressure of CNR the maximum for the highest levels is at about 30 μsec and for the zeroth level at about 90 μsec, persisting to ca. 90 μsec and ca. 600 μsec respectively.

Photometry of the plates emphasises that the lower the pressure of CNR the slower the decay of all levels, and the greater the population of the higher excited levels relative to the zeroth level. This suggests the preferential production of CN* in the higher excited vibrational levels in the primary process and their deactivation by collision with CNR. The population of the higher levels appears to follow the profile of the flash, the only levels to survive the flash being the zeroth and the first levels of the $X^2\Sigma$ ground state. The bond dissociation energy of cyanogen CN — CN may be taken as 112 kcal/mole and the dissociation energies CN — R for CNI and CNBr may be estimated as 64 and 75 kcal/mole respectively : there is thus ample energy for primary excitation of the CN radical. However, the mechanism appears to be otherwise : evidence afforded by the use of colour filters of acetic acid, and nickel sulphate surrounding the reaction vessel indicates that not more than 6% of the excitation is primary. The remainder is due to secondary population of CN* by absorption of light in the region 3500 Å - 4500 Å, far outside the photolytic wavelengths of CNR. This arises from the fact that the extinction coefficient of the CN radical is extremely great so that it can suffer many reversible excitations during the flash, — e.g.

$$\mathrm{CN}\ X^2\Sigma(v = 0, 1, 2\ ...) + h\nu \rightleftarrows \mathrm{CN}\ B^2\Sigma(v = 0, 1, 2\ ...)$$

the reverse reaction taking place either by fluorescence or collision. This process which differs from the nitric oxide mechanism because of the great difference between the extinction coefficients of NO and CN leads to a situation where all vibrational levels of CN are populated (ideally to an equal extent; corresponding to an infinite vibrational temperature) during the period of the flash, — but at the end only $v = 1$ remains as before.

Relaxation of $NO_{v=1}$ by carbon monoxide.

Reference to Table I shows that the probabilities of relaxation of $NO(v = 1)$, by CO and N_2 differ by a factor of about 100. In view of the isoelectronic character of the two gases this was regarded as somewhat of an anomaly and further work by Basco, Callear and Norrish (14) has investigated this point. By carrying out kinetic spectroscopic experiments involving detection of the products by their absorption in the vacuum ultraviolet it was shown that a very strong enhancement of the carbon monoxide absorption as measured at 1650 Å occurred in a mixture such as 5 mm NO + 100 mm CO + 650 mm N_2 (Fig. 11, see p. 121). Comparative experiments showed no appreciable enhancement of the CO absorption in the absence of NO. The concentration of CO was measured by photometering the unresolved 0.1 band of the fourth positive $A^1\Pi \rightarrow X^1\Sigma^+$ system at 1650 Å. As with NO, this band is observable in the spectrum of CO at atmospheric pressure and so the photometric results can be calibrated in terms of absolute concentrations of the first vibrational level of the ground state.

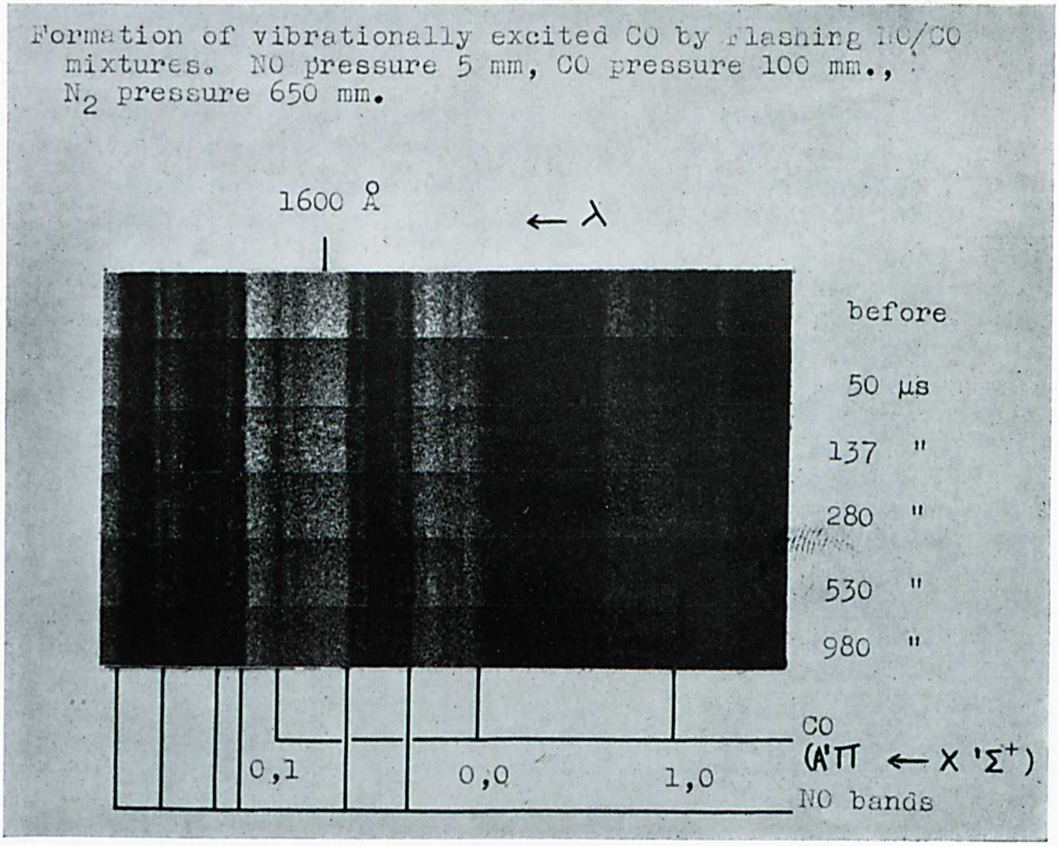
Thus there is indicated a vibrational exchange between $NO(v = 1)$ and $CO(v = 0)$ represented by

$$NO(v = 1) + CO(v = 0) = NO(v = 0) + CO(v = 1).$$

The fundamental vibration frequencies of N_2, NO, and CO are shown in Table III.

TABLE III

Substance	Fundamental
N_2	2350 cm^{-1}
NO	1904 cm^{-1}
CO	2170 cm^{-1}



Formation of vibrationally excited CO by flashing NO/CO mixtures. NO pressure 5 mm, CO pressure 100 mm., N_2 pressure 650 mm.

Fig. 11. — Production of CO($v = 1$) by resonance with NO($v = 1$).

It may therefore be calculated that in an equal mixture of NO and CO at 20 °C there are 3.7 vibrationally excited NO molecules for each vibrationally excited CO molecule. If a predominantly high pressure of CO is present with a few millimeters of NO the vibrational energy thus leaks away into the CO and by the time equilibrium is established the concentration of $NO(v = 1)$ is too small to be detected. Thus the probability P_{1-0} of 2.5×10^{-5} for the relaxation of $NO(v = 1)$ by CO cited in Table I is the probability of the vibrational exchange reaction.

By comparing the rate of relaxation by N_2 with that of He and Kr it was concluded that relaxation by nitrogen also proceeds by vibrational exchange and that 4×10^{-7} represents the probability of the reaction

$$NO(v = 1) + N_2(v = 0) = NO(v = 0) + N_2(v = 1).$$

It is therefore suggested that the exchange reaction of NO and CO is much faster than that of NO with N_2 because the energy discrepancy as shown by Table IV is less. Both reactions being endothermic will require activation, but that with CO very much less, and the achievement of vibrational equilibrium with CO will therefore occur in a time very much shorter than with N_2 as is indeed the case.

Table IV gives the observed values of exchange probabilities compared with the theoretical indications of the theory of Herzfeld and his collaborators.(15)

TABLE IV

Reaction	P (obs)	P (calc)
$NO\ (v = 1) + CO\ (v = 0)$, etc.	2.5×10^{-5}	1.7×10^{-6}
$NO\ (v = 1) + N_2\ (v = 0)$, etc.	4×10^{-7}	1.5×10^{-7}

It was further shown that the inclusion of CO in a mixture of NO and N_2 greatly facilitates the attainment of equilibrium between the species to an extent in agreement with the observed kinetic factors.

IV. Vibrational excitation by secondary photochemical processes.

Reactions of oxygen atoms.

The vibrationally excited species which have been so far considered originate, one way or another, directly from the primary photochemical process. The methods of kinetic spectroscopy have however, also brought to light a wide range of secondary reactions resulting from the transient products of photolysis which give rise to highly vibrationally excited products, but which are otherwise cold as regards translation and rotation. In 1955 McKinley, Garvin and Boudart (16) demonstrated that the reaction between hydrogen atoms and ozone gives rise to vibrationally excited hydroxyl radicals which they detected by infra-red emission. Almost simultaneously, Lipscomb, Norrish and Thrush (17) examined the well known photolytic reactions of chlorine dioxide and nitrogen dioxide by kinetic spectroscopy and showed the production of highly vibrating oxygen molecules, with up to eight quanta. The quantum yield for the nitrogen dioxide reaction is a maximum of 2 (18) and of the same order of magnitude for chlorine dioxide.(19) The excited oxygen can only have its origin in the secondary reactions of the schemes

$$
\begin{aligned}
&\mathrm{ClO_2} + h\nu &&= \mathrm{ClO} + \mathrm{O} && && (1)\\
&\mathrm{O} + \mathrm{ClO_2} &&= \mathrm{ClO} + \mathrm{O_2^*} && (+\ 61\ \mathrm{kcal}) && (2)\\
&\mathrm{ClO} + \mathrm{ClO} &&= \mathrm{Cl_2} + \mathrm{O_2} && && (3)\\
&\mathrm{NO_2} + h\nu &&= \mathrm{NO} + \mathrm{O} && && (4)\\
&\mathrm{O} + \mathrm{NO_2} &&= \mathrm{NO} + \mathrm{O_2^*} && (+\ 46\ \mathrm{kcal}) && (5)
\end{aligned}
$$

with vibrational levels of eight quanta corresponding to considerably more than half of the exothermic energy of the reactions. More recently Basco and Norrish have observed the 9th, 10th and 11th vibrational levels of O_2^* produced in the photolysis of nitrogen dioxide, corresponding to the whole of the exothermic output of the reaction. In Figure 12 (see p. 125) is shown the decay of vibrationally excited O_2^* produced by the photolysis of ClO_2. The oxygen spectrum observed consists of an extension of the Schumann Runge spectrum into the quartz ultraviolet. The reactions are entirely isothermal and the rotational fine structure shows that the vibrationally excited molecules are cold rotationally and therefore translationally, while the vibrational structure indicates a temperature of many thousands of degrees K. We thus have a unique source of highly vibrating molecules uncomplicated by the effects

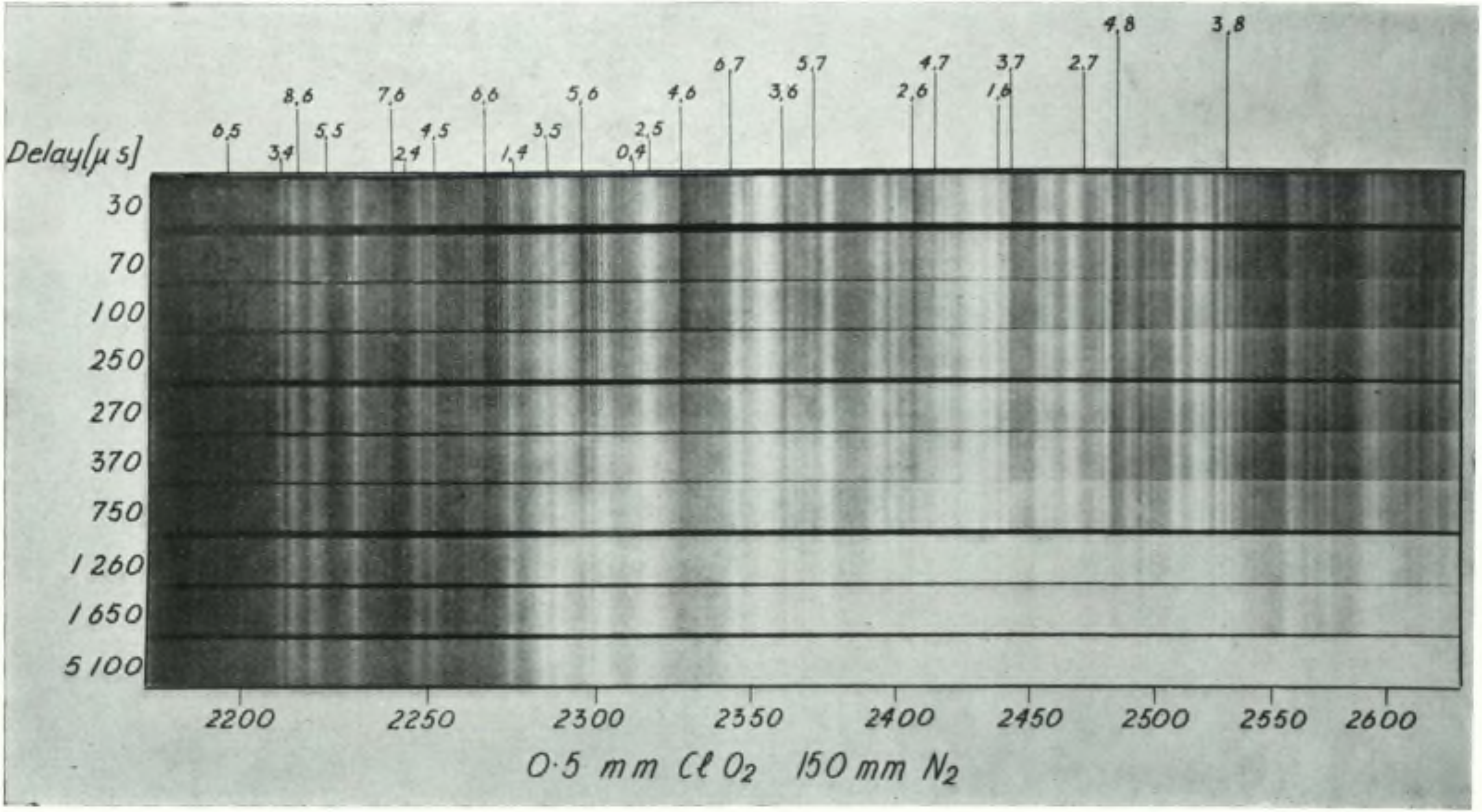


Fig. 12. — Formation and decay of vibrationally excited oxygen by photolysis of ClO_2, shown in absorption by Schumann Runge bands.

of high temperature which naturally invites the study of molecular relaxation by collision. In preliminary experiments of this kind, using chlorine dioxide the effect of added gases on the rate of decay of the vibrationally excited oxygen molecules from the 6th to the 5th level was estimated photometrically, the analysis of the results involving also the effects of reactant and the product ClO. In Table V are given the results compared with those of Kneser for the 1→0 transition which were obtained by ultrasonics.(20)

TABLE V

Deactivating molecule	Number of collisions for deactivation	Number of collisions for deactivation	Nearest vibration frequencies (cm^{-1})
	6→5	1→0	
He	—	1.5×10^5	—
Ar	10^7	—	—
N_2	10^7	10^5	2359
O_2	—	5×10^5	—
CO_2	7000	25000	1286, 1388
ClO	2000	—	868
ClO_2	2000	—	945, 1106
NO_2	500	—	1320, 1621
CO	—	8500	—
H_2O	—	400	—

Oxygen frequency interval 6→5 = 1440 cm^{-1}.

There seems to be some correlation between probability of deactivation and closeness of corresponding vibration frequencies in the case of CO_2 and NO_2 and possibly some specific action of the radical ClO, and the ClO_2 molecule, which may be due to unsaturation. These conclusions can only be tentative as the data are approximate and incomplete; they suggest however that resonance with the deactivating species may play its part.

The results with ClO_2 and NO_2 suggested that by analogy the photolysis of ozone might well give rise to vibrationally excited oxygen molecules. This proved indeed to be the case; using pure ozone with added inert gas McGrath and Norrish (21) found it to give up to 17 quanta of vibration, with no rise of rotational temperature (Fig. 13, see p. 129).

Ozone is photolysed both by orange light and by ultraviolet light below 2500 Å. In the former region the quantum yield is 2,(22) while in the ultraviolet a short chain reaction is observed with quantum yield up to 8.(23) Classical studies had indicated the following scheme for photolysis in the ultraviolet : (24)

$$O_3 + h\nu = O_2 + O \qquad (6)$$

$$O + O_3 = O_2^* + O_2 \qquad (7)$$

$$O + O_2 + M = O_3 + M \qquad (8)$$

$$O_2^* + O_3 = O_2 + O_2 + O \qquad (9)$$

$$O + O + M = O_2 + M \qquad (10)$$

$$O + \text{wall} = 1/2\, O_2 \qquad (11)$$

The simplicity of the system uniquely requires this formal scheme for propagation, in which the excited oxygen molecule plays an essential part but the nature of the excited oxygen molecule was not specified, though it was generally assumed to be some electronically excited state. On the basis of flash photolysis it is now identified as the vibrationally excited oxygen molecule containing more than 17 quanta. This conclusion is based upon the deduction that the oxygen atom generated in reaction (6) must be in the ^1D state — the first excited state lying 45 kcal above the ^3P ground state, as will appear later; and also that the chain reaction in the ultraviolet is propagated by ^1D oxygen atoms, because no chain reaction occurs in the photolysis by orange light where magnitude of the light quantum is only sufficient for the generation of ^3P atoms. Reaction (9) involving ^1D oxygen atoms is 69 kcal endothermic so that the excited oxygen molecule must bring 69 kcal or more to the reaction. More recent work of Basco and Norrish (25) has shown that vibrationally excited O_2^* molecules may be seen faintly up to 20 quanta corresponding to 73 kcal. The agreement is sufficiently close; we should expect that all oxygen molecules with 17 quanta or less of vibration to be ineffective in energising reaction (9) : they must therefore decay by normal relaxation processes and are visible by kinetic spectroscopy. Higher vibrational levels, however, which carry sufficient energy for reaction (9) react so

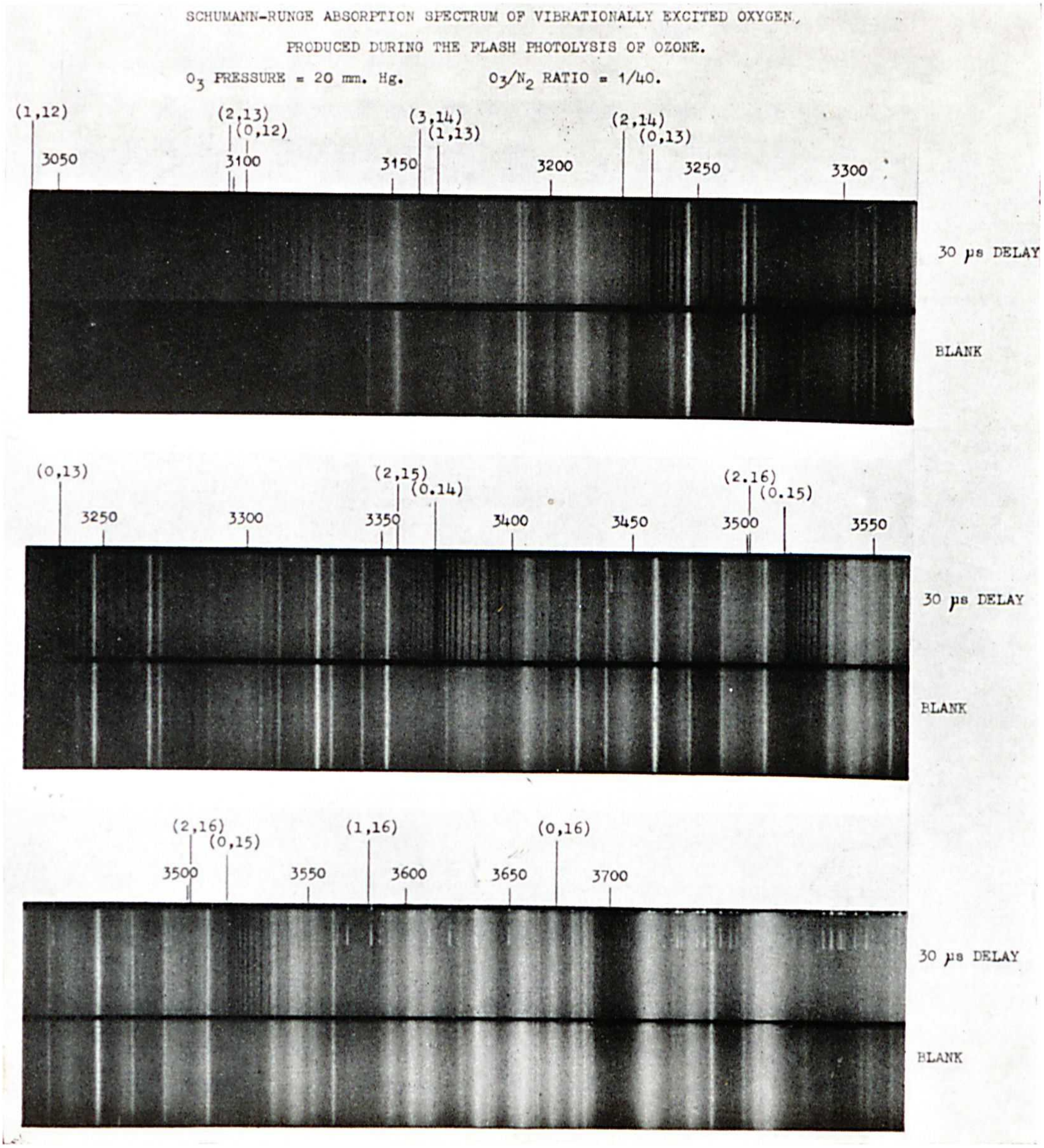


Fig. 13. — Vibrationally excited oxygen produced by the photolysis of ozone.
Flash energy : 2000 J.

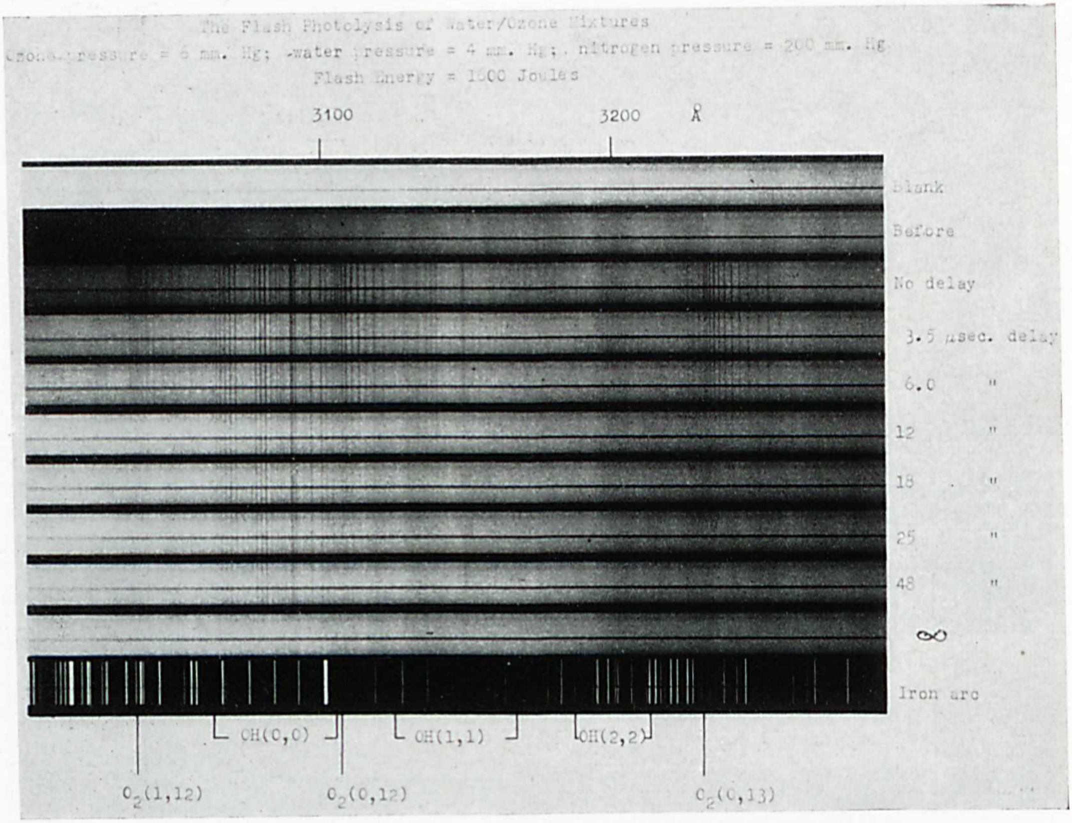


Fig. 14 — Production of excited hydroxyl by reaction of O^1D with water.

rapidly that they are not seen, except that the threshold between 17 and 20 quanta is slightly diffuse as the probability of reaction (9) rises from zero to unity.(26) It is significant that reaction (7) involving ^1D oxygen atoms is exothermic to the extent of 138 kcal so that vibrational levels of O_2^* up to the limit of dissociation of oxygen can theoretically be generated.

The chemical proof that the oxygen atom in the above reactions is in the ^1D state lies in the fact that when ozone is flash photolysed in the presence of increasing small quantities of water vapour, the spectrum of the vibrating oxygen molecules is progressively suppressed and replaced by the absorption spectrum of OH (Fig. 14, see p. 130). Heidt and Forbes (27) had shown by classical methods that the quantum yield for the photolysis of ozone in the presence of water could be as high as 130, as compared with a maximum of 8 for dry ozone. Clearly the mechanism of chain propagation is altered, and on the basis of the observation of the hydroxyl radical in our experiments we may postulate the chain mechanism

$$\begin{array}{llll} O_3 + h\nu = O_2 + O & & & (6) \\ O + H_2O = OH + OH & & & (12) \\ OH + O_3 = HO_2 + O_2 & \left.\right\} & \text{Propagation} & (13) \\ HO_2 + O_3 = OH + 2O_2 & & & (14) \end{array}$$

followed by chain ending by intercombination of radicals.

This scheme satisfies the kinetic findings of Heidt and Forbes and explains the appearance of the OH radical in the flash photolysis results. But if reaction (12) is to take place it must be exothermic and this is only possible if the oxygen atom is in the ^1D state. We have

$$\begin{array}{lll} O^3P + H^{\prime}O = 2\,OH & -11\ \text{kcal} & (12a) \\ O^1D + H^1O = 2\,OH & +34\ \text{kcal} & (12b) \end{array}$$

The appearance of OH thus clearly proves the excited character of the oxygen atom and shows the reaction with water to involve a competition between reactions (7) and (12*b*) with the latter predominating as the pressure of H_2O increases and a progressive replacement of the spectrum of O_2^* by OH. It is significant that water has no effect on the ozone photolysis in the orange where only ^3P oxygen atoms can be generated; the quantum yield remains unchanged at 2.

Further reactions of O^1D.

The experiments described above with ozone and water suggested other possibilities for the reaction of the O^1D atom. Basco and Norrish (28) studied the following, using pure O_3 at 4-6 mm, highly diluted with nitrogen to maintain the reaction isothermal and varying low pressures of the second reactant. The following reactions were readily demonstrated :

$$O^1D + H_2 = OH + H \qquad + 44 \text{ kcal} \qquad (15)$$

$$O^1D + HCl = OH + Cl \qquad + 45 \text{ kcal} \qquad (16)$$

$$O^1D + NH_3 = OH + NH_2 \qquad + 45 \text{ kcal} \qquad (17)$$

$$O^1D + CH_4 = OH + CH_3 \qquad + 46 \text{ kcal} \qquad (18)$$

The OH radicals produced in these reactions, as in the reaction between ozone and water are maximally excited vibrationally to the extent of 2 quanta as seen in the example shown in Figure 15 (see p. 133).

$A + BCD = AB^* + CD$.

Added to the photolysis of ClO_2, NO_2 and O_3 described above, and with the following reactions demonstrated by McGrath and Norrish (29)

$$Cl + O_3 = ClO^* + O_2 \qquad + 19 \text{ kcal} \qquad (19)$$

$$Br + O_3 = BrO^* + O_2 + O_2 \qquad + 40 \text{ kcal} \qquad (20)$$

in which ClO^* is vibrationally excited to the level of 5 quanta and the BrO^* to the level of 4 quanta, they formed the basis of our generalisation (25) (30) that in the reaction between an atom and a molecule, which may be represented by

$$A + BCD = AB^* + CD$$

the molecule AB with the newly formed bond, may take a high proportion of the exothermic energy of reaction in the form of unequilibrated vibrational energy.

This generalisation is confirmed by the work of McKinley, Garvin and Boudart (16) referred to above, and by the work of Cashion

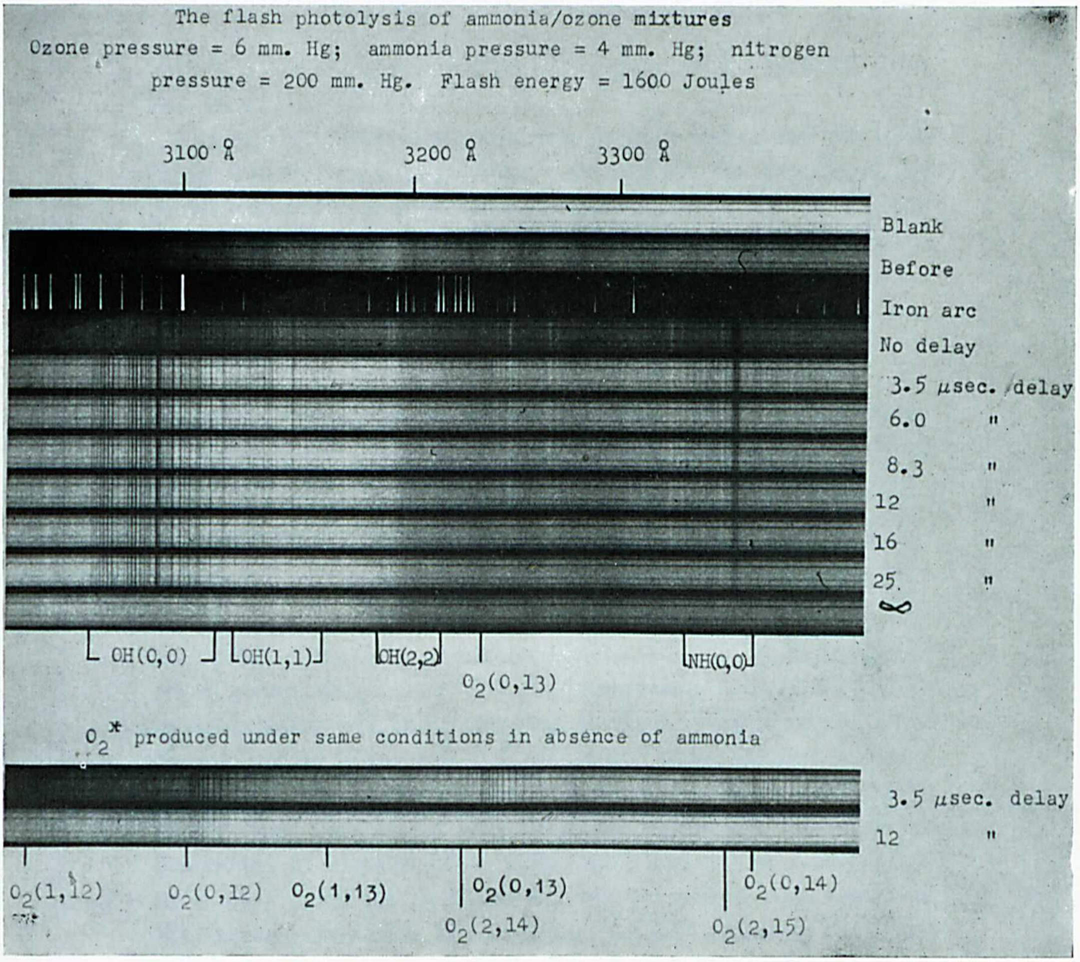


Fig. 15. — Production of excited hydroxyl by reaction of O^1D with ammonia.

and J.C. Polanyi (31) (32) who using the same method of observing the infra-red emission spectrum claim the reactions

$$H + Cl_2 = HCl^* + Cl \qquad + 45\ \text{kcal} \qquad (21)$$
$$H + Br_2 = HBr^* + Br \qquad + 41\ \text{kcal} \qquad (22)$$
$$H + HO_2 = OH^* + OH \qquad + 38\ \text{kcal} \qquad (23)$$

with 6, 5 and 1 quanta of vibration respectively for the HCl, HBr, and OH.

These results invite theoretical examination and so far two fruitful approaches have been made. Polanyi (33) has considered the problem from the point of valence bond resonance, and for reaction between an atom and a diatomic molecule his hypothesis is suggestive. He concludes that for the reaction

$$A + BC = AB + C$$

almost the entire heat of reaction will appear as vibrational energy in the bond AB. The transition complex is considered to be most stable when the two resonance forms

$$AB - C$$
$$A - BC$$

have equal energy. In an exothermic reaction the bond strength of AB is greater than that of BC, the internuclear separation (A — B) in the complex will be greater than in the isolated molecule, while the internuclear distance B — C will be that of the isolated molecule. Since the energy of the complex is considered to be only 5 ± 5 kcal greater than that of the two resonance forms and assuming the probability of transfer of an appreciable amount of energy to C to be very small the molecule AB will be formed with nearly all the energy of reaction in vibration. Besides indicating molecules of AB possessing nearly all the heat of reaction as vibrational energy, the hypothesis requires all the molecules to be formed in the highest observed vibrational state. Polanyi considers that the energy distribution observed corresponds to a system relaxing from a high vibrational state, and restricted to the cases $H + Cl_2$ and $H + Br_2$ as well as $H + O_3$ his conclusions appear plausible. They are not confirmed however by the reaction $O + H_2$ where only about half the exothermic energy can be observed in vibration. Nor is it apparent to what extent the model applies to the more general case

$$A + BCD = AB + CD$$

where the probability of energy transfer between AB and CD may well be higher, resulting in the production of some molecules AB with appreciably less than the maximum possible vibrational excitation. We need also to know more about the process and speed of relaxation of highly vibrating molecules produced exclusively at a single level : evidence presented earlier in this paper indeed suggests that this is a comparatively slow process and observable by kinetic spectroscopy.

For a non linear molecule BCD one would expect that some fraction of the energy would appear as rotational energy of AB and CD, as also should be the case for an oblique collision of an atom with a linear triatomic molecule, but since rotational relaxation is so rapid it could not be observed by any method at present at our command.

Smith's approach (34) to the problem postulates a definite maximum value for the transfer of heat of reaction to vibration which is limited by a kinematic factor $\sin^2\beta$ where β is the angle of rotation required to take a co-ordinate system describing the reactants into one describing the resultants. This depends only on the masses M_A, M_B, M_C, M_D of the atoms and was calculated for the reactions

$$A + BC \rightarrow AB + C \quad \text{as} \quad [\tan^2\beta = \frac{M_B}{M_A} + \frac{M_B}{M_C} + \frac{M_B^2}{M_A M_C}]$$

and

$$A + BCD \rightarrow AB + CD \text{ as } [\tan^2\beta = \frac{M_B}{M_A} + \frac{M_B}{M_C + M_D} + \frac{M_B^2}{M_A(M_A + M_C)}]$$

This model predicts accurately for the reactions $H + O_3$ and $H + Cl_2$. It was claimed to predict for the reaction $O + NO_2 \rightarrow O_2^* + NO$, but now that we have observed the 9th, 10th and 11th vibrational levels its agreement with the 8th level must be considered inadequate. Similarly the agreement of the theory with experiment in the case of ozone cannot be accepted since the exothermicity of the reaction was calculated for the reaction of the O^3P atom, whereas we have seen that it is the O^1D which is involved. Further, our evidence described above is strong in favour of oxygen molecules with more than 17 quanta reacting so rapidly with O_3 by the reaction

$$O_2^* + O_3 = O^1D + 2O_2$$

that except for a trace of vibrational levels 18, 19 and 20 they do not appear in the flash photolysis experiments rather than their not being produced.

It would further appear that the values of $\sin^2\beta$ for reactions of the type

$$O^1D + RH \rightarrow OH^* + R$$

described above are insufficient except in the case of H_2 for the observed production of the excited OH radical.

In a recent private communication from Dr. D.L. Bunker involving a more generalised treatment of Smith's approach, he states "... that when the Smith treatment is generalised by lifting the restriction that collisions be collinear, it becomes apparent that the fraction being calculated [i.e. of energy transferred to vibration of AB in the reaction A + BC] is more nearly a lower limit than an upper", he concludes "that observations concerning these reactions must therefore be reinterpreted as follows. Appearance of vibrational energy in excess of the amount calculated from the one dimensional Smith model is always to be expected if the reflexion approximation for the motion of the representative point is a realistic one. Appearance of vibrational energy less than the amount calculated may mean that the reflexion approximation is a poor one or that not all the heat of reaction is released as kinetic energy during the approach of the reactants, or that the observations have been made after some vibrational relaxation of the observed species has occurred".

Here the matter may be left for the present.

V. Electronic excitation and deactivation.

In 1921 Klein and Rossland (35) following the experimental studies of Franck and Hertz (36) on atomic excitation in gaseous discharge lamps distinguished inelastic collisions of the "first" and "second" kinds. The former conception was derived from the observation that collisions between electrons and atoms in the discharge tube remain perfectly elastic until a certain critical potential gradient is reached, when radiation characteristic of the first excited electronic state of the atom is emitted. For the mercury discharge lamp this potential gradient corresponds to an electronic energy of 4.9 ev, for the helium discharge lamp 21 ev. The whole of the translational energy of the electron is absorbed by the atom, and corresponds precisely to the light quantum emitted by the excited atom. If the energy of collision is greater than the critical, the excess remains as translational energy of the atom and electron. The concept of such inelastic collisions of the first kind was extended to include critical collisions between atoms radicals and molecules which can give rise similarly to molecular or atomic electronic excitation.

By the principle of microscopic reversibility Klein and Rossland postulated inelastic collisions of the second kind, in which an electronically excited species on collision can transfer its energy. Cario and Franck (37) showed that excited mercury atoms in the $^3P_1$ state can transfer their energy to thallium atoms producing electronically excited thallium or can bring about the dissociation of hydrogen on collision :

$$Hg^* + H_2 = Hg + H + H.$$

There is close agreement between the energy of the excited mercury atom, and the energy of dissociation of hydrogen.

Such reactions form the basis of a large number of photosensitised reactions. The deactivation of such excited species by collision is often found to depend on the ability of the colliding body to take up the energy as vibration but this in turn may be influenced by the forces of chemical affinity, and by the possibilities of resonant exchange. We will now consider some examples of processes to which I have referred above.

Inelastic collisions of the first kind.

The simplest case must occur when electronic excitation or ionisation accompanied by radiation is produced in simple gases at high temperatures and which becomes apparent when sufficient thermal collisions reach the critical value. Such temperatures in general must be very high and though they may be generated in detonation waves of explosion and in shock waves it is not always easy to distinguish such thermal radiation from chemiluminescence.

Apart from the study of gaseous discharge lamps, a more promising opportunity for the study of collisions of the first kind is afforded by the production in flames of electronically excited species in amounts exceeding those corresponding to thermal equilibrium. This is done by the addition of traces of metallic elements as salts to premixed flames of hydrogen or hydrocarbons with air or oxygen, and has been studied quantitatively over the past ten years by Sugden (38) and his collaborators. Chemiluminescent emission in the visible or ultraviolet results, and three main mechanisms of excitation have been revealed :

(i) The burnt gases of these types of flame contain hydrogen and hydroxyl radicals and these can excite metallic atoms by

$$H + H + M = H_2 + M^*$$
$$H + OH + M = H_2O + M^*$$

the former reaction providing 103 and the latter 118 kcal/mole for the excitation of the metallic atom M.

(ii) Simple molecular species may be produced in electronically excited states under similar conditions, e.g.,

$$Cu + H + X = CuH^* + X$$
$$Mn + OH + X = MnOH^* + X$$

where X is any third body.

(iii) Very highly excited species can be produced in the reaction zones of hydrocarbon flames with energies of excitation up to at least 170 kcal/mole. These are thought to arise from reactions such as

$$CH + O + Fe = CHO + Fe^*$$

with nearly 200 kcal/mole available for excitation.

All excited electronic species are quenched by collision in flames with an efficiency of not less than 1 in 100, but accurate and comparative measurements have yet to be achieved.

Inelastic collisions of the second kind.

The simplest way in which the processes of deactivation of electronically excited species may be investigated, dissociated from the complications of chemical reaction, is by the study of the quenching of the resonance radiation of a monatomic gas, for in such systems there is one process which is independent of collision, namely the re-emission of the excitation energy as resonance radiation, while by a suitable choice of the quenching substance we can limit at will the processes dependent upon collision, to the degradation of electronic energy to thermal energy or to chemical reaction.

Work of this type has been done on the quenching of the resonance radiation of several atomic vapours, particularly that of mercury (Stuart (39); Noyes (40); Mitchell (41); Bates (42); Zemansky (43); Evans (44)) and sodium (Mannkopff (45); Winans (46); Terenin and Prisleshajewa (47); Kisilbasch, Kondratiev and Leipunsky (48); Norrish and Smith (49)). We shall compare here the results for the two metals based in the case of mercury on the results of Zemansky and of Bates, and in the case of sodium on the work of Norrish and Smith. Until the work of the last two authors the data for sodium were restricted to a few unrelated compounds : it is now possible to make an extensive comparison.

Quenching of mercury in the first excited level $^3P_1$ probably occurs more often through transfer to the near metastable $^3P_0$ rather than to the ground level $^1S_0$. In contrast with mercury the first excited level of the sodium atom is not associated with any metastable state and quenching must of necessity result in a transition direct to the ground state. The magnitude of the energy change is so great that we may expect to find considerable difference in these quenching processes and possibly some indication of the factors in molecular structure which most influence the degradation of electronic to thermal energy.

The effective cross section for quenching is a convenient quantitative measure of the quenching efficiency of a gas. It may be defined as follows. The number of collisions per second per excited atom, is given by the expression

$$Z_Q = 2n\sigma^2 \sqrt{\{2\pi RT\,(^1/M_1 + {}^1/M_2)\}}$$

where n is the number of molecules of foreign gas per cc, M_1 is the molecular weight of the atomic vapour, M_2 the molecular weight of the foreign gas and σ is the minimum distance between centres at which collision occurs. The value of σ^2 which must be used in this relation to give the number of collisions per excited atom per cc required to account for the observed quenching assuming every collision to be efficient is called the effective cross section.

The quantity measured experimentally in investigations on quenching is the quenching ratio Q which is the ratio of the amount of radiation emitted in the presence of foreign gas to that emitted in the absence of it. Z_Q and consequently σ^2 may be simply related to the quenching ratio if it be assumed that the presence of foreign gas does not affect the amount of radiation absorbed and if the radiation emitted is proportional to the concentration of excited atoms.

These conditions hold if the vapour pressure of the absorbing atoms is so low that only primary resonance radiation is emitted and if the effect of Lorentz broadening on the absorption line is negligible and if there is no appreciable absorption or emission stimulated by collision.

The ratio of the concentration of excited atoms in the presence of foreign gas to that in its absence is controlled completely under these circumstances by the probability of deactivation relative to that of emission of radiation in unit time. This ratio is the quenching ratio and in terms of the collision frequency Z_Q and the life time τ of an excited atom is given by the Stern-Volmer relation

$$Q = 1/(1 + \tau Z_Q).$$

Since Z_Q is proportional to the pressure of added gas a linear relationship between $^1/Q$ and pressure is indicated and σ^2 can be obtained in terms of Q, n, and τ.

The experimental methods depend on the use of resonance lamps to irradiate the fluorescence cell, and a double beam photometric method involving visual or photometric recording to measure the intensity of fluorescence in the presence of various pressures of added inert gas. Under the conditions of strong quenching only small additions of quenching gas are necessary, and accurate values of Q and σ^2 may be obtained, the absence of appreciable effects due to trapping of radiation and Lorentz broadening being shown by the linearity of $^1/Q$ against pressure.

With weakly quenching gases, however, the values of σ^2 are less accurate due to the incidence of appreciable pressure broadening at high pressures of quenching gas. The following table gives a comparison of the results obtained for mercury and sodium.

TABLE VI

Comparison of quenching diameters for mercury and sodium.

Quenching gas	Effective cross section $\sigma^2 \times 10^{16}$ cm^2		
	Hg (Zemansky)	Hg (Bates)	Na (Norrish and Smith)
Inert gases	Zero	Zero	Zero
Methane	0.0596	0.059	0.11
Ethane	0.415	0.421	0.17
Propane	—	1.60	0.2
Butane	4.11	4.06	0.3
n-Heptane	—	24.0	—
233 Trimethyl butane	—	19.7	—
Cyclohexane	—	—	0.4
Methyl cyclohexane	—	—	0.55
Iso-octane	—	—	0.8
Nitrogen	0.192	—	14.5
Hydrogen	6.01	—	7.4
Carbon monoxide	2.48	—	28
Benzene	—	41.9	75
Hexadiene	—	—	76
Styrene	—	—	78
Pyridine	—	—	104
Trimethyl amine	—	—	6.5
Water	1.00	—	—
Ammonia	2.94	—	—
Carbon dioxide	2.48	—	—
Ethylene	—	—	44.0
Propylene	—	—	52
Butene 1	—	—	58
Butene 2	—	—	58
Heptene 1	—	45.8	—
Heptene 2	—	55.9	—

Zemansky has concluded that in all the cases cited by him except that of hydrogen the quenching of mercury takes place from $^3P_1$ to the $^3P_0$ metastable level, the energy difference of these two levels being 0.218 ev. This energy difference he correlates with the energy of the two lowest vibrational levels of the quenching molecule. In all these cases there is a fair agreement — within 25% and usually much closer. There also seems from the results of Bates as well as of Zemansky to be an increase in quenching probability with molecular mass. In the case of hydrogen however quenching occurs to the ground state with the dissociation of the H_2 molecule. To this must also be added the quenching by higher hydrocarbons such as *n*-Heptane and 223 Trimethyl butane where photosensitised dissociation to give H atoms and free radicals is known to occur.

With sodium on the other hand quenching must occur directly to the ground state involving a change of energy of 2.094 ev. There is no possibility here of resonance with vibrational modes of the molecules and quenching gases can be divided into two groups — the weakly quenching gases including the rare gases and the saturated hydrocarbons, and the strongly quenching gases including nitrogen, carbon monoxide, hydrogen and still more strongly the unsaturated hydrocarbons, and benzene, and pyridine.

The various values of the energy discrepancy for the saturated hydrocarbons cannot be sufficiently different from those of the unsaturated hydrocarbons to explain this pronounced difference in quenching efficiency for sodium. It may be noted that the molecules of the first group are inert and possess small external fields while those of the second being unsaturated possess large external fields. Apparently the sphere of " quenching influence " is somehow related to the magnitude of the external field in the case of sodium. This is in contradiction to Zemansky's conclusion that the nature of the external field has little influence on the cross section for the quenching process, but he was dealing with the case of mercury where as we have seen the quenching mechanism must be different in view of the small energy transfer involved, and he had then no experience of the effect of highly unsaturated molecules.

On the border of the second group of efficient quenching agents for sodium may be placed hydrogen, nitrogen and carbon monoxide. Nitrogen and carbon monoxide may be regarded as possessing potential unsaturation which will be made operative by the proximity of a sodium atom. Along with hydrogen they probably suffer greater distortion on the approach of a sodium atom than any other molecule of the group as both hydride and azide are easily formed. While this interaction brings about the conditions necessary for the transition process it is considerably less effective than the unsaturation conferred by the presence of a double carbon to carbon linkage.

The process of quenching has been considered theoretically from a quantum mechanical stand-point.(50) It has been calculated on the basis of hypothetical curves representing the potential energy of the interacting particles that the effective cross section of the process depends on the nature of the interaction of the colliding particles, on the relative velocity before collision and on the change of relative energy on collision — that is on the difference between the amount of energy the excited atom has to give and the quenching molecule to receive. As with mercury we would expect the effective cross section to increase with decrease of the discrepancy between the difference of energy levels in the colliding molecules. In the case of sodium the nature of the interaction between the colliding particles would seem to be the predominant factor, and dependent on chemical constitution, for there can be no resonance with the vibrational modes of the deactivating molecule.

The problem of the devising of models involving hypersurfaces may be left for further discussion.

The relaxation and reactions of metastable electronic states observed by kinetic spectroscopy.

The application of kinetic spectroscopy to the study of the growth and decay of electronic states is limited to those metastable states whose life times come within the operational time scale of the apparatus. The life time of a normal electronically excited state is of the order 10^{-8} sec, so neither its growth nor decay can be observed. But with metastable states, of life times varying between 100-1000 μsec we have a ready means of observation. The most extensive work in this field has been done by Porter and his collaborators (51) in connection with the metastable triplet states of organic (mainly aromatic) compounds in solution, but because of the fundamental simplicity of the reactant we shall first refer to the work of Callear and Norrish (52) on the study of the reactions of the metastable triplet state of mercury — Hg $6(^3P_0)$. By flashing mercury vapour at 20 °C with continuous light Callear was readily able to populate this metastable state and to observe its growth and decay in the presence of inert gases and other reactants by its absorption spectrum. Since the excitation occurs by continuous light the addition of a high pressure of inert gas was necessary to pressure-broaden the atomic lines. Thus by absorption of light on the wings of the 2537 Å line an approximately homogeneous production of $^3P_1$ atoms was achieved in the reaction vessel, which by collision with the inert gas were transformed to the metastable $^3P_0$ state. By adding other gases approximate values were obtained for the rate constants of their reactions with Hg $6(^3P_0)$.

The metastable atoms were detected by the following spectral lines in absorption.

TABLE VII

λ Å	Transition
4046	$7(^3S_1) \leftarrow 6(^3P_0)$
2967	$6(^3D_1) \leftarrow 6(^3P_0)$
2753	$8(^3S_1) \leftarrow 6(^3P_0)$
2535	$7(^3D_1) \leftarrow 6(^3P_0)$
2378	$8(^3D_1) \leftarrow 6(^3P_0)$

The strong line at 2967 was chosen for plate photometry and an example of its growth and decay is shown in Figure 16 (see p. 147). The mercury lines at 4047 and 2967 Å appear weakly at first, build up in intensity as the flash develops, and reach a maximum just before the end of the flash. The decay occurs in the next few hundred microseconds. At this stage the other lines listed above are also observed fairly strongly.

Metastable atoms were detected in mixtures of mercury vapour with nitrogen, water, carbon monoxide, and argon (very weakly). With nitrogen the decay is unimolecular and independent of nitrogen pressure. It was concluded that deactivation is entirely due to collisions with ground state mercury atoms since there is no time for diffusion to the walls, and the forbidden line 2637 Å $(6(^3P_0) \rightarrow 6(^1S_0))$ was not observed. The unimolecular constant k_3 is thus equal to $k_4[\mathrm{Hg}]$ and knowing the concentration of mercury vapour the bimolecular constant could be calculated. From this may be derived the cross section for deactivating collisions as $22 \times 10^{-16}\ \mathrm{cm}^2$, which is to be compared with 18×10^{-16} cm^2 found by Coulliette for the diffusion cross section of Hg $6(^3P_0)$. This corresponds to deactivation at almost every gas kinetic collision, and may possibly be related to the formation of a vibrationally excited triplet Hg_2 molecule.

Metastable atoms were not produced by flashing mixtures of mercury vapour in the presence of any one of the gases hydrogen, carbon dioxide, oxygen, ethane, ethylene, nitric oxide, nitrous oxide, and it is to be concluded that in most cases these gases react directly with $^3P_1$ atoms producing chemical dissociation and ground state mercury atoms, as is indeed known to be the case from the occurrence of a wide variety of photosensitised reactions based on the products. In the case of carbon dioxide and ethylene however triplet states are probably produced, for triplet CO_2 has an energy level close to 4.86 eV corresponding to 4.9 eV for Hg $6(^3P_1)$. With oxygen electronic excitation is highly probable.

By adding the above gases at low partial pressures to mixtures of nitrogen and mercury vapour, approximate values for their rates of reaction could be determined, the order of reactivity being $N_2O > C_2H_4 > NO > H_2 > O_3 > C_2H_6 > H_2O > CO_2 > N_2$. The reactivity while following the same pattern as with $Hg(^3P_1)$ is very much less, yielding "quenching" cross sections of the order 0.1 to 1.0×10^{-16} cm^2 except for CO_2 and H_2O which are unexpectedly inefficient and give values of the order of 10^{-18} cm^2. Further work along these lines with more detailed measurements may be expected to yield valuable information relating to the transfer of energy from $6(^3P_0)$ mercury atoms, and electronic deactivation in general.

The triplet state in organic compounds.

The extensive work of Porter (51) and his colleagues using the methods of flash photolysis has clearly established the reality of the triplet or diradical state in a wide variety of organic compounds produced under the influence of irradiations and has made possible the study of their decay and reactions. A normal organic compound is usually in the ground singlet state, with no unpaired electrons or free valency. The triplet states of such compounds may then be

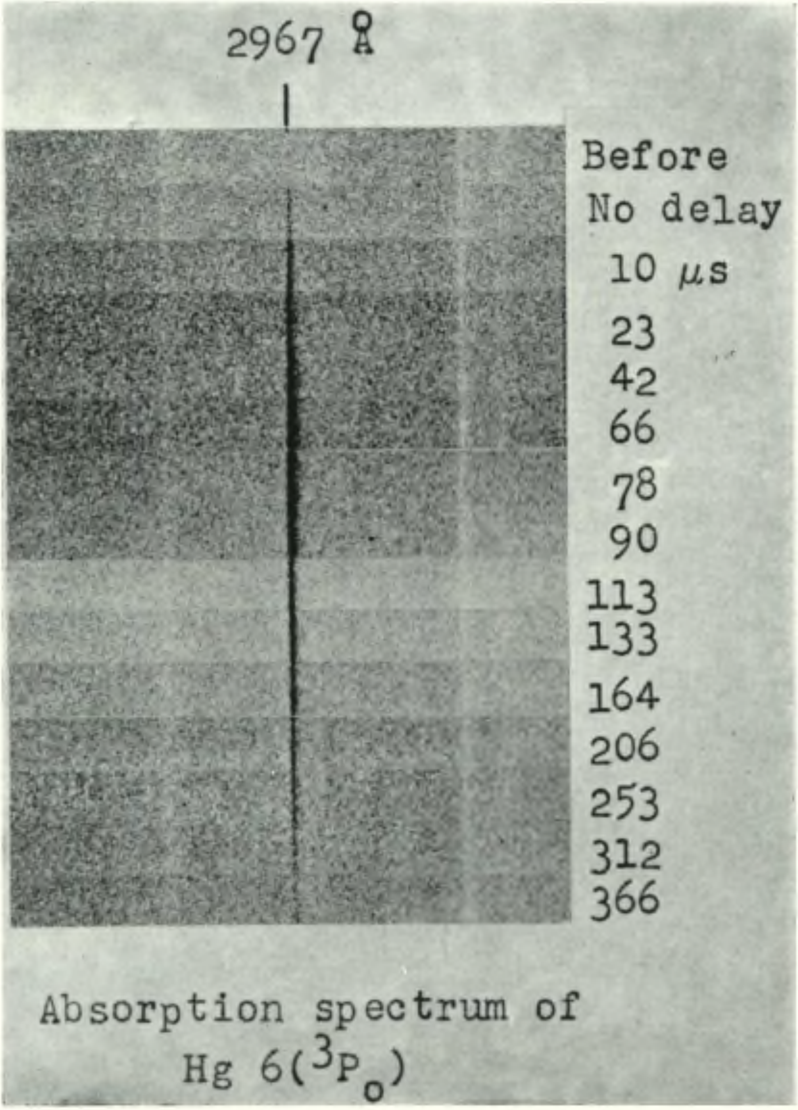
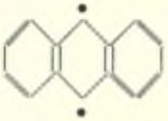
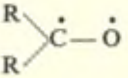


Fig. 16. — Growth and decay of Hg 6($^3P_0$) shown by the 2967 Å absorption line.

represented as generated by the unpairing of electrons to yield diradicals of the type





$R_2\dot{C}-\dot{O}$ $H_2\dot{C}-\dot{C}H_2$

formed from anthracene, quinone, ketones and unsaturated hydrocarbons respectively. The triplet state consists of three levels corresponding to spin combinations of 1, 0, and — 1, and in the case of organic compounds where we are concerned with light atoms, they are so close together that for our purpose we can regard them as a single level.

Excited phosphorescent states of aromatic compounds and dyestuffs in rigid solvents at low temperature had long been known, and the phenomenon was first interpreted by Jablonski in terms of transitions involving a metastable state of the molecule, which later was interpreted by Lewis and his co-workers,(53) and by Terenin (54) in terms of a triplet state. The Jablonski diagram (55 shown in Figure 17 forms the basis of all subsequent interpretation.

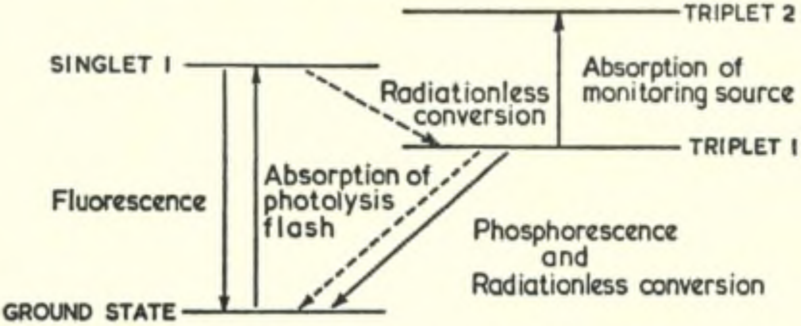


Fig. 17. — Jablonski diagram showing singlet-triplet relationship. (Courtesy Prof. G. Porter).

Absorption of light, accompanied by fluorescence results from a singlet-singlet transition as shown. The metastable lowest triplet state is populated by a radiationless transition which must result from a crossing of the potential curves of the excited singlet and triplet states. The return of the first triplet state to the ground state which as a forbidden transition is slow, is accompanied by phosphorescent emission, but it may also occur by a radiationless transition. Lewis and Kasha observed the absorption spectra of the first triplet state, corresponding to the transition triplet 1 - triplet 2 for a large number of substances, and thus established their energy levels and radiative life times in solid solution at low temperatures.

The importance of the work of Porter and his co-workers lies in the fact that they were able by flash photolysis to establish the existence of the triplet states in solution and the gas phase at normal room temperature. The first successful photograph which they obtained by flashing a thoroughly outgassed 10^{-5} molar solution of anthracene is shown in Figure 18 (see p. 151). The short lived triplet 1 of life time about 200 μsec is seen to be formed at the expense of the anthracene whose concentration as shown by its spectrum (first singlet) is seen to be temporarily depleted, and regenerated as the triplet fades. Similar results have been obtained for a wide range of aromatic hydrocarbons, ketones, quinone and certain dyestuffs and in view of the short life of the triplet at normal temperatures it is clear since no short lived phosphorescence is observed that the return from the triplet to the ground state must be conditioned by some other process, such as a radiationless transfer, or collisional deactivation.

Oxygen is found to be a powerful inhibitor of triplet formation and other inhibitors such as nitric oxide exist so that extreme care in purification and degassing of solutions is essential. Working under such conditions Porter and Wright (56) showed that the decay rate for triplet naphthalene is predominantly first order but that there is some contribution of a second order reaction, involving triplet-triplet collisions. Since the depletion of the singlet state can be readily measured, the absolute concentration of the triplet state at measured intervals after the flash can be derived and the absolute values of the velocity constants obtained. Using solvents of various viscosity it was found that the rate of decay decreased rapidly with increasing viscosity as shown in Table VIII, which is taken from Porter's Tilden (51) Lecture, k_3 and k_4 being the unimolecular and bimolecular constants respectively.

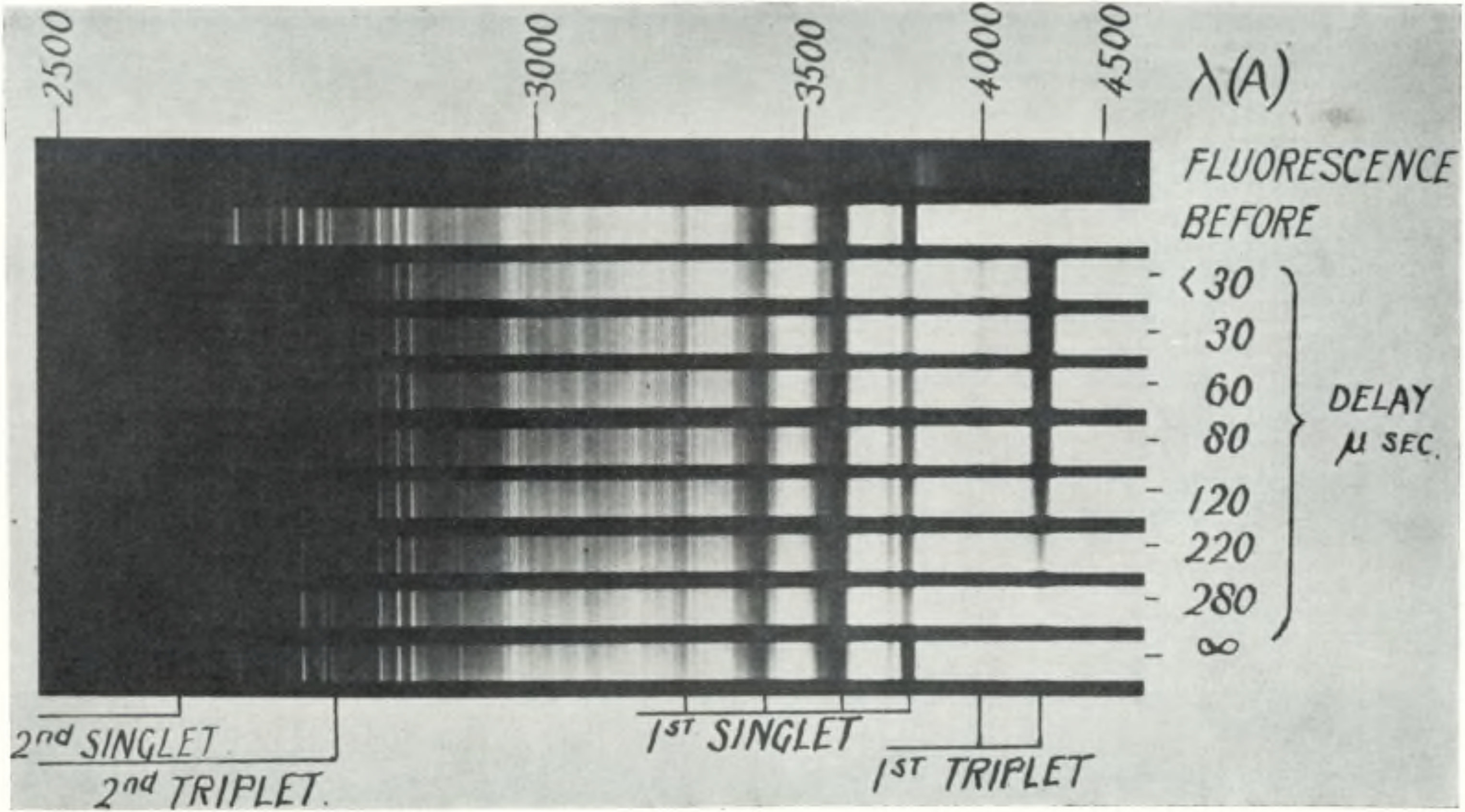


Fig. 18. — The triplet state in anthracene revealed by flash photolysis. (Courtesy Prof. G. Porter).

TABLE VIII

Rate constants of triplet naphthalene decay in several solvents.
Concentration of naphthalene = 10^{-4}M

Solvent	Viscosity (cp	$10^{-3}k_1$ (sec^{-1})	$10^{-9}k_4$ (l.m.$^{-1}$ s.$^{-1}$)
n-Hexane	0.3	12.1 ± 1.3	2.1 ± 0.6
Water	1.1	7.5 ± 0.6	4.1 ± 1.2
Ethylene glycol .	21.1	0.97 ± 0.1	0.22 ± 0.03
Liquid paraffin 1	33.0	1.5 ± 0.1	0.39 ± 0.02
Liquid paraffin 2	167	0.31 ± 0.3	0.08 ± 0.01

Porter concludes :

" (1) The rate determining process of triplet state deactivation in solution and in the gas phase in the absence of specific quenching by other molecules is radiationless conversion to an iso-energetic level of the ground state.

" (2) The transition is inhibited or prevented in viscous or rigid media for the following reason. If a molecule is rigidly held in one particular nuclear configuration it will oscillate back and forth between the two electronic states, but will not be able to lose energy since no conversion into kinetic energy can take place. It will therefore remain in this configuration until energy is lost by radiation. "

He continues, " It is interesting that the appearance of phosphorescence is then dependent, not only on the spin-forbidden nature of the radiative process but also on the configurational forbiddenness of the radiationless transition in rigid media. "

It seems to be established that quenching may take place by chemical reaction, as is probably the case with anthracene which yields with oxygen the trans-annular peroxide, but it has also been found that paramagnetic substances in general such as NO and paramagnetic ions of the first transition series and rare earth series are efficient deactivators. It has been suggested that the process involves a complex formation which dissociates into the ground singlet state and the unchanged quencher without violation of the spin conservation rules.

Finally resonant transfer of electronic energy from one molecule to another of the type

$$A^*(\text{Triplet}) + B(\text{Singlet}) \rightarrow A(\text{Singlet}) + B^*(\text{Triplet})$$

has been identified by Porter and Wilkinson in solution as an efficient process, an example being the transfer of energy from triplet benzophenone to naphthalene in benzene solution.

There can be no doubt that the study of the energy relationships of the triplet states of organic compounds particularly in solution is of paramount importance to the understanding of the mechanism of many reactions. Further work in this direction is proceeding as for example the studies of radiationless transfer from the triplet state by Hoffman and Porter.(57) It seems likely that triplet transients, as do free radicals, may well play their part in thermal as in photochemical processes and if this is so many interesting possibilities will be opened up, as in the case of sulphur dioxide at high temperature.(77)

VI. **Drierstoss. Atomic and radical recombination.**

The recombination of atoms and simple radicals is well known to require the intervention of a third body. In a direct recombination such as

$$X + Y = XY^*$$

most of the energy of recombination is taken up by vibration, so that unless the association complex is stabilised by the intervention of a third body to remove the energy, it will dissociate. In rare cases the complex XY^* may be formed in an electronically excited state which can stabilise itself by emitting a large part of the energy of recombination as radiation — the so-called recombination continuum as described for the reaction

$$CO + O = CO_2^* \rightarrow CO_2 + h\nu$$

by Laidler,(58) and for the reaction

$$S + O = SO^* \rightarrow SO$$

by Norrish and Zeelenberg.(59)

Such continua are possible if the excited complex exists in a repulsive state, so that transitions to the lower stable electronic state involve continuous emission. Cases of this kind may however be more frequent than is realised, and careful examination of atomic or radical reactions for chemiluminescent emission of this kind, especially in the ultraviolet, might well be rewarding.

For the stabilisation of an excited complex by ternary collision the process can be divided into two stages, — the meeting of two particles to form an excited complex, and its subsequent or simultaneous reaction with a third. Since no collision can be regarded as truly ternary, the second stage must occur within the life time of the excited complex, — probably the time of one vibration, say, 10^{-13} to 10^{-14} sec.

The matter has been considered from the kinetic stand-point by Noyes and Leighton,⁽⁶⁰⁾ following Rabinowitch ⁽⁶¹⁾ who distinguish two possibilities. In the first the complex may be formed between the recombining particles, and the stabilisation subsequently effected by the third body according to the sheme

$$\mathrm{X} + \mathrm{Y} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{XY}^*$$

$$\mathrm{XY}^* + \mathrm{M} \xrightarrow{k_3} \mathrm{XY} + \mathrm{M}.$$

This yields the kinetic result

$$\frac{d\,(\mathrm{XY})}{dt} = \frac{k_1 k_3 (\mathrm{X})(\mathrm{Y})(\mathrm{M})}{k_2 + k_3 \mathrm{M}},$$

and it is seen that if k_2 is large compared with $k_3\mathrm{M}$ the reaction will be first order with respect to each of these reactants, but second order if $k_3\mathrm{M}$ is much greater than k_2.

The second process involves the formation of a transitory complex between one of the combining particles and the third body, which then reacts with the second particle, as represented by the scheme:

$$\mathrm{X} + \mathrm{M} \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} \mathrm{XM}$$

$$\mathrm{XM} + \mathrm{Y} \xrightarrow{k_3'} \mathrm{XY} + \mathrm{M}.$$

The rate of recombination is given by

$$\frac{d\,(XY)}{dt} = \frac{k_1{}'k_3{}'(X)(Y)(M)}{k_2{}' + k_3{}'(Y)},$$

and the rate will be first order with respect to M under all conditions and independent of Y if $k_2{}'$ is small.

Assuming 10^{-13} sec as the life time of the excited complex, the "ternary collision" must be achieved within this time and it may readily be shown kinetically that the ratio of such ternary to binary collisions is of the order 1/100 or 1/1000 at 300 °K at one atmosphere pressure, and that this ratio will be directly proportional to the square root of the absolute temperature. The same result was originally obtained empirically by Bodenstein (62) who, with a keen insight into the problem, took the ratio of ternary to binary collisions as equal to the ratio of the binary collision diameter to the mean free path in the gas.

The most available data based on classical methods of kinetics apply to the recombination of bromine and iodine atoms. Ritchie,(63) and Hilferding and Steiner (64) derived their measurements from the kinetics of the photochemical formation of hydrogen bromide from its elements in the presence of added gases. Rabinowitch and Wood (65) studied directly the photochemical equilibrium of the reaction

$$X_2 + h\nu \rightleftarrows X + X$$

in the presence of various third bodies (M) by an optical method. Table IX, derived by Noyes and Leighton,(60) gives the ratio of the number of recombinations to binary collisions as calculated from their results, taking the collision diameters for bromine as 4.5×10^{-8} cm, and for iodine as 5.2×10^{-8} cm.

In general the order of magnitude predicted by the simple kinetic theory is confirmed and the order of efficiency is in general the same as for the quenching of fluorescence, those molecules which can take up energy only as translational energy being much less efficient than those which conceivably absorb it into vibrational degrees of freedom.

TABLE IX

(After Noyes and Leighton.)

Values of ratio $\dfrac{\text{No. of } X_2 \text{ molecules formed}}{\text{No. of bimolecular } X + X \text{ collisions}}$

for $T = 300\ {}^{\circ}K$ and $(M) = 2.45 \times {}^{19}$ molecules/cc.

X	Data of	He	H_2	N_2	HBr	Br_2	CO	CH_4	CO_2	C_2H_6
Br	R: H. & S.	$\frac{1}{4000}$	$\frac{1}{1500}$	$\frac{1}{2200}$	$\frac{1}{850}$	$\frac{1}{650}$	$\frac{1}{300}$	—	—	—
Br	R. & W.	$\frac{1}{1400}$	$\frac{1}{470}$	$\frac{1}{430}$	—	—	—	$\frac{1}{290}$	$\frac{1}{190}$	—
I	R. & W.	$\frac{1}{600}$	$\frac{1}{270}$	$\frac{1}{170}$	—	—	—	$\frac{1}{90}$	$\frac{1}{60}$	$\frac{1}{10}$

R. = Ritchie.
H. & S. = Hilferding and Steiner.
R. & W. = Rabinowitch and Wood.

Other cases of stabilisation by ternary collision may be cited though data are sparse; Griffiths and Norrish (66) studying the decomposition of nitrogen trichoride photosensitised by chlorine showed that the chain length is depressed to a limiting value of 2 by the addition of inert gas. This was interpreted quantitatively by the expression for the quantum yield γ

$$\gamma = \frac{1}{k\,P_{Cl_2} + k_x P_x} + 2.$$

The expression readily explains the course of the reaction on the basis of reaction chains which have their inception from chlorine atoms formed in the gas phase and their conclusions through some ternary collision in which both nitrogen trichloride and a third body participate. This is believed to be the stabilisation of the complex NCl_4 by the reaction

$$NCl_3 + Cl + M = NCl_4 + M.$$

Table X shows the values for k_x when the pressure of chlorine P_{Cl_2} and of inert additive P_x are measured in millimeters Hg.

TABLE X

	k_x
Helium	0.00093
Argon	0.0016
Nitrogen	0.0017
Oxygen	0.0025
Carbon dioxide	0.0038
Chlorine	0.0038

These may be compared with the values of Dodd and Steacie (67) for the reaction

$$CH_3 + CH_3 + M = C_2H_6 + M$$

who by determining the pressure dependence of the reaction deduced with reserve the following relative values for the efficiency of the third body.

TABLE XI

Argon	0.03
Carbon dioxide	0.03
Fluorobutane	0.2
Fluoroheptane	0.3
Acetone	1.0
Ethane	1.0
Acetaldehyde	3.0

With increase in complexity of recombining radicals, the need for third body stabilisation must rapidly decrease, since it is to be expected that stabilisation by internal vibrational degrees of freedom will take its place.

Specificity in ternary recombination.

Finally we may refer to reactions which involve a remarkable specificity of three body collision mechanism, as shown by classical kinetics. The photosensitised decomposition of ozone by chlorine studied by Norrish and Neville (68) is a chain reaction involving the propagating steps :

$$\begin{aligned} Cl + O_3 &= ClO + O_2 \\ ClO + O_3 &= ClO + 2O_2. \end{aligned}$$

This has recently been confirmed by kinetic spectroscopy. The chains are terminated by the reactions

$$\begin{aligned} ClO + ClO &= Cl_2 + O_2 \\ Cl + O_3 + M &= ClO_3 + M. \end{aligned}$$

The latter reaction takes place predominantly when the concentrations of chlorine and oxygen are relatively high and gives rise to the short lived red vapour Cl_2O_6.

The important point is that the third body is represented only by Cl_2 or O_2, the effects of nitrogen and carbon dioxide being unobservable in comparison. This apparent specificity was explained by supposing that short lived complexes (sticky collisions) are formed between chlorine atoms and the third body, represented by Cl_3 and $Cl{\cdot}OO$. Cl_3 as a transient complex has been postulated theoretically by Rollefson and Eyring,(69) and by Lehner and Rollefson (70) in connection with the photosynthesis of phosgene where it may well act kinetically in a specific manner for the propagating reaction

$$Cl + Cl_2 + CO = COCl + Cl_2.$$

The application of flash photolysis to the problem of atom recombination.

The study of the recombination of iodine atoms by kinetic spectroscopy was first made by Christie, Norrish and Porter (71) using a spiral flash lamp surrounding a linear double walled quartz reaction vessel protected by suitable light filters and containing iodine at very low pressure (ca. 0.1 mm), and varying high pressures of inert gases. The molecular iodine concentration was strongly depleted by the flash due to dissociation, and the rate of recombination of iodine atoms could be measured by the rate of return of the I_2 spectrum. This was achieved by a monitoring beam of light from a tungsten lamp which passed through the length of the reaction cell and was recorded by a photoelectric cell and oscillograph. On operating the photoflash the time base of the oscillograph was triggered and the oscillograph trace provided a measure of the growth and decay of iodine atoms. Calibration of the iodine atom concentration in terms of trace deflection was carried out by determining the relationship between a microammeter reading and trace deflection, and between microammeter reading and iodine concentration for each mixture used in the rate determinations. Extension of this work by Christie, Harrison, Norrish and Porter,(72) in which disturbing magnetic effects were eliminated, and the disturbance caused by slight temperature inhomogeneity was allowed for, gave good second order constants for the recombination of iodine atoms, and yielded the third order rate constants for the five inert gases as follow :

TABLE XII

M →	He	Ne	A	Kr	Xe
$10^{32}k_M$ (ml.^{2}mol.$^{-2}$ s^{-1})	0.67	0.92	1.84	2.25	2.99

Measurements by other authors for argon gave confirmatory values for the termolecular recombination at room temperature :

	$10^{32}k$(ml.^{2}mol.$^{-2}$sec^{-1})
Marshall and Davidson (73)	2.32 ± 0.22
Russell and Simons (74)	2.00 ± 0.10
Strong and Willard (75)	1.60 ± 0.05
	1.47 ± 0.04

Comparison of these values with those of Rabinowitch and Wood using the steady state method referred to above was very satisfactory; in the same units they found for argon $3.4 \pm 0.3 \times 10^{-32}$.

From the work of Christie, Harrison, Norrish and Porter however there emerged a further important point, — namely the powerful third body effect of the iodine molecule. Compared with the value of the termolecular constant for helium of 0.67×10^{-32}, that for iodine was found to be 470×10^{-32} and even though the pressure of iodine was very small, it exerted a significant effect on the reaction rate.

This powerful effect of the I_2 molecule may be explained by the formation of an I_3 complex of considerable life : such a complex may be regarded as a " sticky " collision between I and I_2 and greatly increases the probability of stabilising ternary collisions. We have

$$\begin{aligned} I \quad + I_2 &= I_3^* \\ I_3^* + I \quad &= 2I_2. \end{aligned}$$

A specific stabilising effect of the same kind was attributed to bromine in the recombination of bromine atoms by Givens and Willard (78) who later studied the analogous reaction by flash photolysis.

These results of specific stabilisation are to be correlated with the " sticky collisions " of chlorine and oxygen already referred to above in connection with the ozone photolysis and the specific effect of chlorine on the photosynthesis of phosgene.

Temperature effect.

Whereas it has been concluded on kinetic grounds by Noyes and Leighton as stated above, that the ratio of ternary to binary collisions should be proportional to the square root of the pressure, it has been found experimentally that ternary recombination reactions show a small negative temperature coefficient. This was confirmed by Russell and Simons (74) for example, who found that the velocity of recombination of iodine atoms at 127 °C is approximately 0.4 times the velocity at 20 °C for six different additives. The work of Russell and Simons, which covered a wide variety of third bodies and showed an enormous difference in the stabilising power of different molecules (from 0.94×10^{-32} ml^{2}mol^{-2}sec^{-1} for helium to 224×10^{-32} for mesytelene) appears to the writer to emphasise the importance of an increasing number of degrees of freedom within the stabilising molecule. They were however able to correlate their results with the molecular force fields of the stabilising molecule and to show parallelism between the corresponding boiling points and critical temperatures.

In the opinion of the writer however it must be said that where complex hydrocarbons, and other organic species, are considered as third body, much caution must be exercised in view of the possibility of chemical reaction with iodine atoms.

The work of Russell and Simons has been extended more recently by Porter and Smith (76) who have measured the third order constant k and the negative temperature coefficient for a series of third bodies. The following table is extracted from their results, assuming $k = Ae^{-E/RT}$.

TABLE XIII

Quenching gas	$10^{32}k$	$-$ E (kcal/mole)
Helium	0.84	0.4
Argon	1.64	1.3
Oxygen	3.72	1.5
Carbon dioxide	7.41	1.75
Benzene	43.9	1.7
Toluene.	107	2.7
Ethyl iodide.	144	2.4
Mesytelene	223	4.1
Iodine	760	—

Following Russell and Simons, Porter and Smith adopt the second mechanism of Noyes and Leighton, in which the stabilising molecule first makes a transitory complex with one of the combining atoms. If it be assumed that the reverse reaction of

$$I + M \rightleftharpoons IM$$

is so rapid (k_2' is large in Noyes and Leighton's scheme) that equilibrium is maintained, then the negative temperature coefficient, and also the fact, confirmed by them, that higher ternary recombination rates should be associated with more negative coefficients are explained.

However, the van der Waals type interactions in the complex IM envisaged by Russell and Simons are too low to give the bonding energy necessary to account for the magnitude of the negative temperature coefficients of Porter and Smith and the authors are driven to postulate a charge transfer complex between the stabilising body and the iodine atom. They examine their conclusions on a theoretical basis but it seems clear that much more experimental work is required before any generalisation relating to the mechanism of recombination of atoms can be established. It is to be expected that this will be achieved by the application of methods depending on shock wave techniques and kinetic spectroscopy.

It will be obvious to those who have penetrated to these last paragraphs that our approach to the problem of energy transfer between atoms and molecules has been chemical and empirical. In handing on the torch to my younger friends and colleagues, I can only express the hope that some experimental results have been presented which may be worthy of further investigation, both experimentally, intuitively and mathematically. This is in no sense meant to be an authoritative or a complete review, but I hope that the experience of some forty years of photochemistry may have been presented with some measure of integration in so far as our main topic is concerned. In re-reading the manuscript I am hopeful that it has something in common with the " curate's egg ". If that is so and if anything I have written should give rise to further thought and experimentation I am well rewarded.

In conclusion I wish to thank all those collaborators whose work I have cited, and many whose work has not been referred to; if it should appear that I have misrepresented their views, I can only ask them to remember our unresolved discussions. For them tomorrow is another day and the world of research is wide open.

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Discussion du rapport de M. Norrish

M. Herzberg. — I should like to supplement Prof. Norrish's report by a few remarks on the relaxation of electronically excited species, also observed by means of the flash photolysis technique first developed by Norrish and his collaborators. While our interest at Ottawa has been mainly on questions of the structure of free radicals, we have made some qualitative observations on energy transfer involving electronically excited species which may be of interest in connection with Prof. Norrish's account.

We have shown that the free methylene radical (CH_2) has two low-lying electronic states : a triplet state ($^3\Sigma_g^-$) in which it is linear and a singlet state ($^1A_1$) in which it is bent with an angle of about 105°. In the flash photolysis of diazomethane (CH_2N_2), the CH_2 radical is first formed in a highly vibrationally excited singlet state (singlet because of spin conservation) in which it has only a lifetime of a fraction of a microsecond before it decomposes spontaneously into CH + H. The CH_2 radical is observed only if the diazomethane is mixed with a large excess of inert gas (Ar, N_2, He, etc.). Collisions with inert gas atoms or molecules remove vibrational energy in the singlet state and thus stabilize the CH_2 molecules before they have time to decompose. Collisions can further produce a transition of CH_2 from the singlet to the triplet state, but since this transition is spin-forbidden it requires a large number of collisions.

Singlet CH_2 has a discrete absorption spectrum in the red as well as the far ultraviolet part of the spectrum while triplet CH_2 absorbs only in the far ultraviolet, near 1400 Å. By observing the relative intensities of the singlet and triplet features as a function of time and of the mixing ratio, we can judge the way in which the triplet and singlet concentration varies. We find that triplet CH_2 persists longest and that it is strongly favoured by higher mixing ratios, that is, after a greater number of collisions. We conclude therefore that the triplet state is *below* the singlet state. Unfortunately we have not been able to determine the magnitude of the energy difference but it is likely to be fairly small. As yet we have not found any great difference between various gases with regard to their effectiveness in bringing about a singlet → triplet transition. It seems however significant that a singlet-triplet transition can be brought about by a number of collisions of the order of 1000.

A number of chemical experiments have already been made by various investigators showing the different chemical behaviour of triplet and singlet CH_2. For a better understanding of this behaviour a more quantitative study of the triplet-singlet transfer would be desirable.

Another interesting observation in the flash photolysis of diazomethane is the following. Under the conditions which are most suitable for the production of CH_2, an absorption band with a widely spaced fine structure appears near 3000 Å. Dr. J.W.C. Johns and I have recently identified this band as being due to a transition from the excited $^2\Sigma^-$ state to a higher electronic state $^2\Pi$ which was previously observed as the upper state of an absorption band in the vacuum ultraviolet (at 1690 Å). The lifetime of the $^2\Sigma^-$ state is known (1) to be only about 10^{-6} sec, i.e. it is not metastable. It is interesting that this state is formed during the photolysis in sufficient abundance to be observable in absorption in spite of its short life. Moreover during its life it must suffer a number of collisions with the inert gas atoms or molecules without being deexcited.

A related observation is that of absorption from the $^3P_1$ state of mercury (present as an impurity) in spite of its even shorter lifetime of about 10^{-7} sec.

Similar to Prof. Norrish's work on O_2, we have observed in the flash photolysis of diazomethane vibrationally excited CH (or CD) with up to four quanta. These states decay with a half-life of the order of 10 μsec.

A phenomenon similar to the production of singlet CH_2 by the photodecomposition of diazomethane has been observed in the photolysis of hydrazoic acid (N_3H). Here we observe strong absorption from the lowest singlet state ($^1\Delta$) while in the photolysis of hydrazine (N_2H_4) only absorption from the ground state ($^3\Sigma^-$) of

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NH is observed. The observation of singlet NH in N_3H is a striking consequence of the spin conservation rule. If

$$N_3H + h\nu \rightarrow N_2 + NH$$

then since both N_3H and N_2 are in singlet states NH must also be in a singlet state and this is what is observed. It would be interesting to follow the gradual transformation of NH $^1\Delta$ into NH $^3\Sigma$ but this has not yet been done.

M. Norrish. — Dr. Herzberg's observation of the excited singlet state of CH_2 in absorption resulting from the flash photolysis of diazomethane (CH_2N_2) may be related to earlier photochemical experiments on ketene (CH_2CO) [Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933)], when I postulated that CH_2 may be produced in the singlet state. It was shown that in the case of ketene, the magnitude of the quantum is much too small simply to break the double bond to give $>CH_2$ and $>CO$ but that the primary products are CH_2 and CO. It was further shown that what we called the energy of reorganisation of the CO carbonyl to carbon monoxide (involving ~ 100 kcal) is sufficient to account for this discrepency. It therefore may be suggested that CH_2 be formed as a singlet since carbon monoxide is produced in the singlet state itself. The photolysis of diazomethane appears therefore to be quite analogous to that of ketene as CH_2 is spectrospically observed in the singlet state with the simultaneous production of N_2 in the singlet state.

The observation by Dr. Herzberg of the doublet excited state of CH in absorption resulting from the flash photolysis of CH_2N_2 is interesting. The lifetime of an electronically excited species is such that these have not been observed in absorption by the flash photolysis technique except for metastable states involving forbidden transitions. Is the electronically excited CH metastable ? If it is not, the instantaneous concentration produced at any time during the photoflash discharge must be extremely high as there could be only a very small build up in CH concentration in the electronically excited state on account of the rapid decay. In our experience, the time scale of the flash photolysis apparatus makes the observation of species whose lifetimes are of the order of 10^{-7} to 10^{-8} unlikely. If superior time resolution has been obtained in this work, I have nothing further to add.

M. Herzberg. — I can only repeat that the excited electronic state that we found in CH, namely ${}^2\Sigma^-$ is certainly not metastable. It has a lifetime of about one microsecond.

M. Porter. — In connection with Dr. Herzberg's remarks about the relative energies of the excited singlet and ground state triplet levels of methylene, I think perhaps the most important species with which collision results in depopulation of the singlet under the conditions of these experiments are likely to be free radicals, these paramagnetic species being known to be very effective in catalysing spin-forbidden transitions of this kind.

A possible method for at least bracketing the energy of the singlet would be to carry out an energy transfer experiment of the type

$$M_S^* + A_S \rightarrow M_T + A_T^*$$

where M is methylene and A is an accepter molecule with a triplet level of lower energy than M_S^*. A series of acceptors of different triplet energy would establish the energy of M_S^*.

M. Polanyi. — Prof. Norrish has postulated a " rapid resonant deactivation " of vibrationally excited NO by way of

$$NO_{v=n} + NO_{v=(n-2)} \rightarrow 2NO_{v=(n-1)} \qquad (1)$$

However, the overpopulation of $v = 1$, that he observes, is due in the first place to the slowness of

$$NO_{v=1} + NO_{v=0} \rightarrow 2NO_{v=0} \qquad (2)$$

and would, I believe, be observed even if equation (1) were too restrictive and rapid resonant transfer occurred also through collisions between NO molecules having vibrational quantum numbers, v, differing by more than 2. Mis-match due to anharmonicity cannot be large for NO.

In the case of HCl there is some preliminary evidence due to Dr. F.D. Findlay in my laboratory, that the restiction implied by equation (1) is operative, i.e., transfer is predominantly between $HCl_{v=n}$ and $HCl_{v=(n-2)}$. But for HCl the anharmonity is quite large.

The experimental evidence comes from experiments where room temperature HCl, effectively pure $HCl_{v=0}$, is added to a vessel conteining HCl† distributed in a known fashion among vibrational levels $v = 1, 2, 3, 4...$ A decrease in HCl† concentration is observed in excited levels 2, 3, 4..., but the decrease is anomalously large for $v = 2$. No decrease whatever is observed in the concentration in $v = 1$. This certainly suggests a process of type (1) replenishing $v = 1$, while at the same time depleting $v = 2$.

M. Norrish. — I would like to ask Prof. Polanyi to describe the nature of the vibrational distribution resulting from the reaction

$$H + Cl_2 \rightarrow HCl^\dagger + Cl$$

Are the vibrationally excited HCl molecules in a Boltzmann distribution or in the initial vibrational distribution ?

M. Polanyi. — The distribution depends on the pressure of vibrationally excited HCl†.

Dr. F.D. Findlay and I have investigated the $H + Cl_2$ infrared luminescence at 1 mm total reagent pressure. From the emission intensity we know that we have a relatively high concentration of HCl†. Under these circumstances we obtain close to a Boltzmann distribution of HCl† among vibrational states. Moreover HCl† can be observed to be present in levels extending considerably above the maximum level ($v = 6$) in which the $H + Cl_2$ reaction could form them directly. (This, I think, is what Prof. Norrish has in mind.)

To round out this picture I should add that in the experiments that Mr. Charters has carried out at low pressure (several orders of magnitude lower partial pressure of HCl†) a highly non-Boltzmann distribution was obtained. For example, the ratio of populations in vibrational levels 1 and 2 could be characterized by a " temperature " of 8.000 °K, whereas the ratio between levels 1 and 5 was characterized by a "temperature" of 2.930 °K. It was this non-Boltzmann low-pressure distribution that was used in the calculation of R_v, the relative rate of reaction into each vibrational state of the product.

M. Mayer. — Does not the reaction

$$M_{(v=n+1)} + M_{(v=0)} \rightarrow M_{(v=n)} + M_{(v=1)} \qquad \text{(A)}$$

go with nearly the same cross-section as that for

$$M_{(v=n+1)} + M_{(v=n-1)} \rightarrow 2M_{(v=n)} \qquad \text{(B)}$$

since, were there no anharmonicity, the energy match would be as good for (A) as for (B) ? In the case that the population of the zeroth state is very much larger than that of any of the others, I would expect (A) to be the most important process, especially if the anharmonicity is low.

M. Karplus. — When considering the reestablishment of thermal equilibrium among vibrational states after flash photolysis, one must remember with what molecular species the excited molecules can collide.

When NO (plus an inert gas) is photolysed, the resulting vibrationally excited molecules in the electronic ground state will dominantly collide with NO in the vibrational ground state. We can then have the almost resonant exchange

$$(NO)_{v=0} + (NO)_{v=n} \rightarrow (NO)_{v=1} + (NO)_{v=n-1}$$

until all the vibrational energy is in the first excited state. Further collision with NO will not change this situation except by the much slower processes of energy conversion to rotational and translational degrees of freedom. Also, collisions with the inert gas will contribute to further slow relaxation.

If NOCl is photolysed, the resulting NO in the electronic ground state will also be vibrationally excited. Now, however, there is no reservoir of unexcited NO molecules that can serve as collision partners. Resonant energy exchange can occur only in collision with another excited NO. But such interactions result only in a rearrangement of the energy among the excited states, not in a net relaxation of energy out of the vibrational degrees of freedom. One can look at this phenomenon as a diffusion process among the vibrational states that will result in the ultimate population of a wide band of such states. Concurrently with this interaction, there are collisions with NOCl (and any inert gas which is present) that gradually take energy out of vibrational excitation. These collisions are less efficient, but more frequent. It could be interesting to determine the relative rates of these two types of interactions.

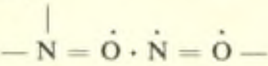
M. Norrish. — Professors Karplus, Mayer and Polanyi have pointed out that the reaction

$$\mathrm{NO}\,(v = 0) + \mathrm{NO}\,(v = n) \rightarrow \mathrm{NO}\,(v = 1) + \mathrm{NO}\,(v = n - 1)$$

corresponds to almost resonant exchange and that the collision cross section should be high as anharmonicity is relatively low. This is not contested. I did not exclude other resonant transfers between more widely separated vibrationally excited NO molecules, but pointed out, what must be true, that the most efficient transfer is to be expected between two molecules differing in vibrational level by two. It is obvious that in any case NO ($v = 1$) will be the final state reached by this mechanism. However small the effect of anharmonicity, a difference of two between the vibrational quantum numbers of the colliding molecules will result in the best match. It is interesting to note that Prof. Polanyi has observed that transfer is predominant between HCl ($v = n$) and HCl ($v = n - 2$), though it is agreed that in his case anharmonicity effects are greater.

As regards the production and decay of vibrationally excited NO from NOCl, I agree with Prof. Karplus's remarks on this point but emphasize that this is basically precisely the same as I said in my paper and, in fact, the hypothesis I advanced to account for the difference in behaviour between NO* from NO and NO* from NOCl. The probability of transfer of a quantum from one molecule to any other molecule will depend on the vibrational distribution at the particular point in time being considered. From the kinetic viewpoint, it will be possible to offset lower collisional cross sections resulting from anharmonicity by higher concentrations. In the case of NOCl, we are concerned with a non-Boltzmann distribution for vibration where the concentrations of the lower levels are relatively small. Thus we may expect that resonant exchange will be limited largely to the upper levels which will tend to produce a localised Boltzmann distribution amongst themselves.

M. Linnett. — Prof. Norrish has shown that NO itself is relatively efficient in the conversion of NO in its first vibrational level to the ground state, the energy being transformed to translational energy (see Table I which shows that it is much more effective than N_2 which, in fact, probably takes up the energy as vibrational energy, the other process being still less efficient). For this to happen there must be a coupling between the potential energy of the NO bond and the NO/NO intermolecular distance. It seems to me that this is a consequence of the fact that NO contains an odd number of electrons. The electronic structure of NO can be represented by $-\dot{N} \overset{\cdot}{=} \dot{O}-$, and that of the collision complex might involve, at least in past, the structure



$$\overset{|}{-N} = \dot{O} \cdot \dot{N} = \dot{O} -$$

If this is so, the formation of the weak intermolecular one-electron bond causes the bond in the molecule (on the left above) to decrease in strength so that its equilibrium length increases. This would provide the necessary coupling for the transfer of energy from the NO vibration to the translational energy of separation of the two molecules.

As regards the production of vibrationally excited NO from the photolysis of NOCl, it is likely that, in the excited state, the NO bond is longer than in the ground states of NO and NOCl, in both of which it is close to 1.15 Å. This is suggested by the work of H.S. Johnston, who showed that in NOF the NO bond becomes weaker and the NF bond stronger on electronic excitation (see also J.W. Linnett, *J.A.C.S.*, 1961). This dissociation would occur from an excited electronic state of NOCl (or NOBr) to NO in the ground state, the equilibrium bond length being different. Consequently, by the Frank-Condon principle, the product will be vibrationally excited.

On the other hand, because the equilibrium NO bond length in the ground state of NOCl is the same as that in NO, the reaction of NOCl with chlorine atoms will be expected to form NO with no vibrational excitation. This fits in with the rule proposed by Prof. Norrish that in the process

$$A + BCD \rightarrow AB + CD$$

the CD is not vibrationally excited.

In general, therefore, we should attempt to see what bond length changes may take place during the processes that are involved to understand whether the products will possess vibrational energy.

By this means we may discover something of the potential energy curves and surfaces in the collision processes, etc.

M. Norrish. — The possible part played by a change in bond length for a process giving rise to a vibrationally excited species or the deactivation of such a species is clearly crucial. Dr. Linnett's suggestion that the explanation for the efficient relaxation of NO $(v = 1)$ to NO $(v = 0)$ by nitric oxide itself can be given in terms of a specific collision complex may well be correct. The relative ease of conversion of vibrational into translational energy for such a model is an attractive one.

The explanation of the production of vibrationally excited NO from NOCl as involving a change in NO bond distance in the excited state of NOCl compared with the ground state of NO is supported by the experiments of Dr. Basco and myself. Our results are consistent with direct vibrational excitation rather than the initial formation of an electronically excited NO molecule (possibly $^4\Pi$) followed by internal conversion to vibration. For more complex molecules, there is a possibility of a change in geometry in going from the ground state to an electronically excited state. Under certain conditions, a free radical might be produced from the fission of an excited molecule which would possess a different shape to that of its ground state.

With respect to Dr. Linnett's question on a change in bond length in CD for the generalized reaction

$$A + BCD \rightarrow AB + CD,$$

the reactions that we had studied have not involved a large change in the CD distance, as in, for example,

$$O + ClO_2 \rightarrow O_2^* + ClO$$

$$O + NO_2 \rightarrow O_2^* + NO$$

$$O + O_3 \rightarrow O_2^* + O_2$$

$$Cl + NOCl \rightarrow Cl_2 + NO.$$

The maximum change in bond length for such cases is ~ 0.06 Å. If an example could be found in which there was a large change in CD, this would be very interesting from both the experimental and theoretical standpoint.

Table of CD bond lengths in the forms BCD and CD for some reactions of the type $A + BCD \rightarrow AB + CD$.

r_{CD} in BCD (Å)		r_{CD} in CD (Å)	
ClO_2	1.49	ClO	1.55
NO_2	1.197	NO	1.150
O_3	1.278	O_2	1.211
NOCl	~ 1.13	NO	1.150

M. Shuler. — As pointed out by Prof. Norrish, it is possible to obtain values for $P_{a \rightarrow b}$, the vibrational-translational (or vibrational-vibrational) transition probability per collision from the analysis of flash photolysis data. If only two vibrational states are involved, as appears to be the case in the experiments on NO, the result of such an analysis is unequivocal and is as accurate as the experimentally determined values of the population of the two vibrational states involved in the transition, i.e., $v = 0$ and 1 for the NO molecule.

If any other vibrational states are however appreciably populated by the primary photochemical process, the analyses of the transition probabilities $P_{a \rightarrow b}$ from the relaxation data can easily lead to inaccurate (and even meaningless) results. Mathematically, the problem is represented by the matrix equation

$$\frac{d\overset{w}{X}}{dt} = \overset{w}{A}\,\overset{w}{X}$$

where $\overset{w}{X}$ is the concentration vector (with components x_0, x_1, ... representing the population in levels 0, 1, ...) and where $\overset{w}{A}$ is the transition probability matrix whose elements A_{ij} are equivalent to the $P_{a \rightarrow b}$ defined above.

Given $\overset{w}{X}(t)$ as experimental data, it is desired to obtain the elements A_{ij} of the matrix $\overset{w}{A}$.

As has recently been pointed out again in a very instructive paper by T. Carrington [*J. Chem. Phys.*, **35**, 807 (1961)], the values of the A_{ij} are *exceedingly* sensitive to the values of the vector components x_0, x_1, ... An error (i.e. experimental uncertainty) $\varepsilon \ll x_i$ in the x_i can, and usually will, produce *very large* errors in the A_{ij} of much larger magnitude than ε. This is a well known fact (and problem) in the machine solution of large number of simultaneous equations, of which the above matrix equation is an example.

Unless, therefore, the population in *all* the appreciably populated vibrational states can be measured with very high accuracy, which is usually not the case, the analysis of the relaxation data to obtain transition probabilities may well be a futile excercice in arithmetic. If attempts at such an analysis are made, it is essential to test the stability of the solution (i.e. of the values of A_{ij}) to small variation in the x_i.

M. Norrish (communicated after the meeting). — *I agree with Dr. Shuler's remarks on the determination of transition probabilities in a multilevel system. In our experiments on the rate of vibrational energy transfer from* $NO_{(v=1)}$, *measurements were made under the conditions under which only the level* $v = 1$ *was observed in absorption above the vibrational ground state. Measurements were made also after the initiation by the photoflash and therefore in the absence of excitation processes. It can certainly be concluded that nitric oxide in the first vibrational level is not being produced by decay processes from higher levels in the ground state for* by the time we observe it *the whole vibrational pattern has collapsed to* $v = 1$. *Its production by chemical processes is not significant here as nitric oxide is not photolysed.*

M. Polanyi. — Prof. Norrish was kind enough to invite my comment concerning the part of his survey that had to do with the distribution of energy among the products of simple exothermic reactions.

Our work on this topic at the University of Toronto was suggested by McKinley, Garvin and Boudart's discovery, in 1955, that the system $H + O_3$ gave rise to vibrationally excited $OH^\dagger$, in its electronic ground state. They had demonstrated this by photographing emission due to high overtone transitions of OH. We set out to look at simpler, three atom, systems (A + BC), and to make our observations of the fundamental emission in the instrumental infrared. After five years we are still studying the infrared emission from the first system we investigated, namely $H + Cl_2 \rightarrow HCl^\dagger + Cl$ (there is no detectable visible emission, in contradistinction to $H + O_3$).

The first analysis of the $HCl^\dagger$ distribution, performed with J.K. Cashion, indicated that contrary to expectation the most probable route for reaction led into median and lower vibrational states of the product. Mr. P.E. Charters, in my laboratory, repeated the experiments in a new type of reaction vessel at much lower pressure. He obtained a result which was qualitatively similar to the earlier one : from $v = 6$ (the highest vibrational state accessible to the reaction; the heat of reaction is 45 kcal/mole) down to $v = 3$ the rate of reaction into the specified vibrational states increased rapidly, flattening out to some sort of a plateau for $v = 3$, 2 and 1. These three levels that are populated with high probability, represent

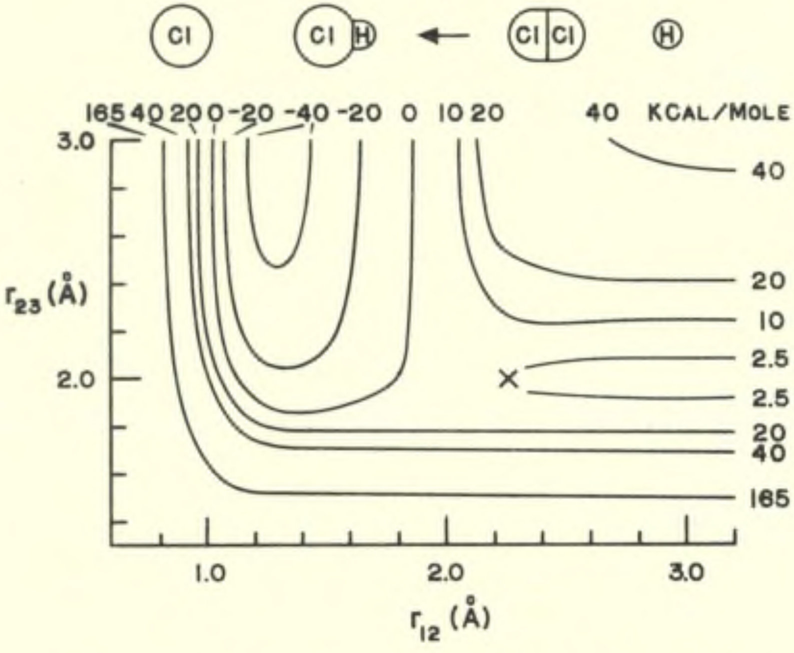


Fig. 1. — L.P.E.S. potential surface for linear approach of H to Cl_2.

17-50% of the available energy turning up in the form of vibration.

M. David Rosner and I have made a calculation (very much on the lines of Wall, Hiller and Mazur's work on the thermoneutral reaction $H + H_2$) to see whether we can account for this energy distribution among reaction products, on the basis of three atoms, H, Cl and Cl, moving freely and classically in a plane, subject to a London-Polanyi-Eyring-Sato interaction potential. Figures 1 and 2 show the (L.P.E.S.) potential surface for linear and for perpendicular approach of H to Cl_2. Actually, of course, the movement takes place along neither of these constrained paths, but across a potential hypersurface $V(r_{12}, r_{23}, r_{13})$. Figure 3 (*a*) shows the symbols used to describe the configuration of the system. Figure 3 (*b*) gives the details of a particular reactive collision (the

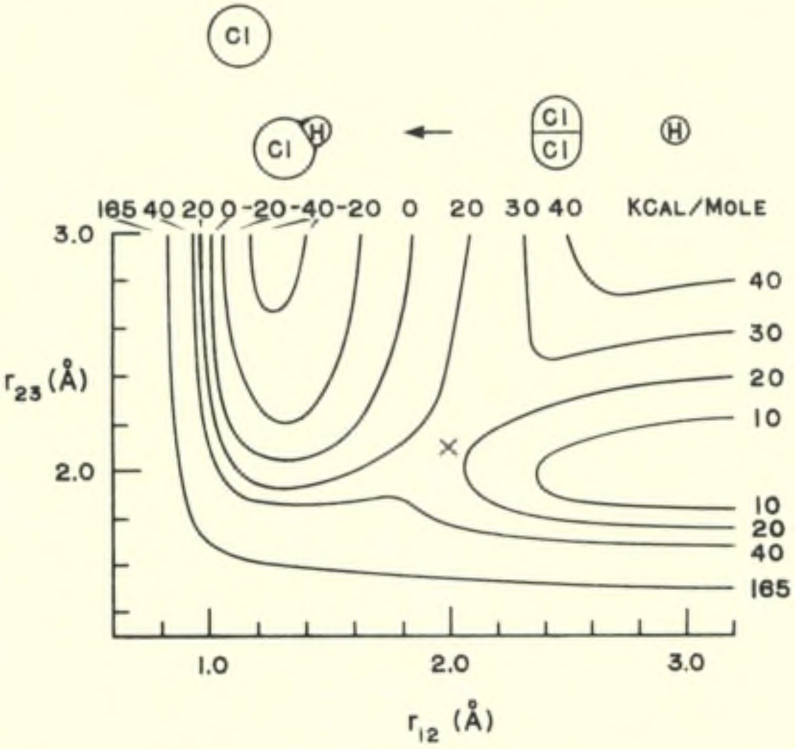


Fig. 2. — L.P.E.S. potential surface for perpendicular approach of H to Cl_2 (Cl retreats along a path perpendicular to the H → Cl axis).

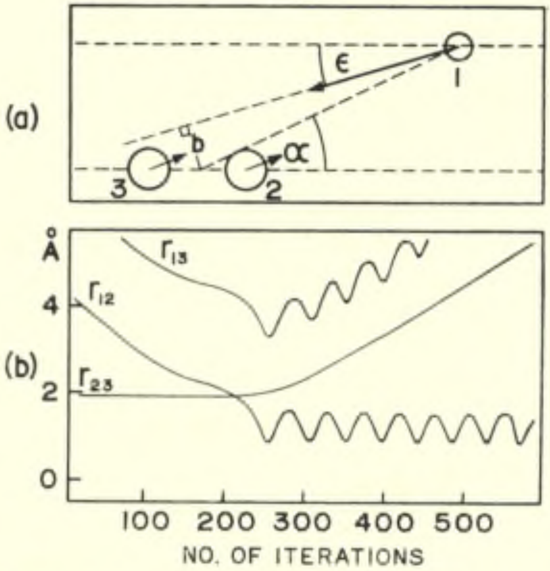


Fig. 3. — (*a*) Atom 1 is H, atoms 2 and 3 are Cl; (*b*) Variations of internuclear separations during a reactive collision for which the initial state parameters were $\alpha^i = 20° 54'$, $\varepsilon^i = 25° 55'$, $b = 0.437$ Å, relative translational energy $E^i_{TRANS} = 2.662$ kcal/mole. In the transition state $\alpha^{\ddagger} \approx 15°$. In the final state, energies of vibration, translation, HCl-rotation, and orbiting of the system about the centre of mass, were: $E^f_{VIB} = 30.04$, $E^f_{TRANS} = 21.22$, $E^f_{ROT} = 0.0156$, $E^f_{ORBIT} = 0.00055$ kcal/mole.

curves were printed out by a 7090 computer). In the last figure the energy distribution among the products is recorded for a number of reactive collisions. The range of ε^i (and b) in the abscissa represents the range over which computations were made; points have, however, only been shown in the range of ε^i where reaction occurred.

The calculation predicts 50-60% of the energy in vibration in the product molecule, and the balance as translation. There is only a negligible amount of rotation. The system appears to pass without delay through the activated state. This accords with observations made by Herschbach and co-workers in their crossed molecular beam experiments on $K + CH_3I$. Within the limits of ε^i (and b) for which reaction is possible, the reaction probability does not oscillate but remains consistently high; as Ross and Greene have it in figure 14 of their paper which reports on a detailed investigation of $K + HBr$ in crossed molecular beams (energy distribution among the products could not, however, be measured in their experiments).

The percentage of energy going into vibration on this model is somewhat high, and the range of percentages is a good deal too small, compared with our experiments.

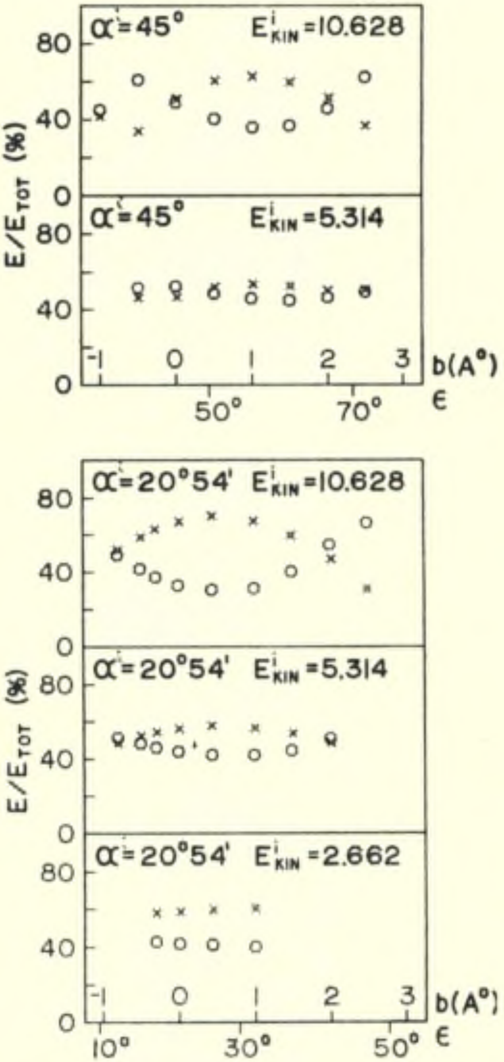


Fig. 4. — Percentage vibrational energy (*x*) and translational energy (*o*), among the reaction products.

This could be due to failure of the L.P.E.S. potential function, which has never been put to such a test before. It would, indeed, be remarkable if it gave quantitatively the correct answer, since its theoretical basis is flimsy. This is especially true in the present application, which involves atoms with directed orbitals (Cl).

Alternatively the fault could lie in our use of the classical equations of motion.

We are continuing to investigate the systems $H + X_2$ under a variety of conditions. At the same time we are exploring the effect on our theoretical energy distributions of variations in the form of the potential function.

ON THE POSSIBLE IMPORTANCE OF EXCITED STATES IN THE KINETICS OF CHAIN REACTIONS

by **N.N. SEMENOV,**

Member of the U.S.S.R. Academy of Sciences, F.R.S.

The chain reaction concept appeared first in 1913 in a work of Bodenstein (1) who observed a huge quantum yield (up to a million) in the photochemical reaction of hydrogen with chlorine. In 1916 he proposed the following reaction mechanism (2)

$$0)\ \mathrm{Cl_2} + h\nu = \mathrm{Cl_2^*} \qquad \text{chain initiation}$$

$$\left.\begin{array}{l} 1)\ \mathrm{Cl_2^*} + \mathrm{H_2} = \mathrm{HCl^*} + \mathrm{HCl} \\ 2)\ \mathrm{HCl^*} + \mathrm{Cl_2} = \mathrm{HCl} + \mathrm{Cl_2^*} \\ 3)\ \mathrm{Cl_2^*} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{HCl^*} \end{array}\right\} \text{chain propagation}$$

Here Cl_2^* and HCl^* are molecules of chlorine and hydrogen chloride excited at the expense of the reaction heat

$$\mathrm{H_2} + \mathrm{Cl_2} = 2\mathrm{HCl} + 45\ \text{kcal.}$$

This is how the first concept of an energy chain arose. In 1923 Christiansen and Kramers (3) brought forward this concept as one explaining a number of pecularities of the kinetics of unimolecular decomposition : $A = B + C$. The primary activation is accounted here by thermal motion

$$A \rightleftharpoons A^* \qquad \text{chain initiation}$$

$$\left.\begin{array}{l} A^* = B^* + C \\ B^* + A = B + A^* \end{array}\right\} \text{chain propagation}$$

However, it was discovered soon that the explanation for the pecularities of unimolecular decomposition is different and there is no need in introducing the energy chain concept. On the other hand, it became more and more evident that the products of B* readily dissipate their energy as heat. Towards the end of nineteen twenties it was ascertained that energy chains, if any, may occur but in very rare cases.

In 1918 Nernst (4) proposed a more clear and simple mechanism of hydrogen photochlorination involving H and Cl atoms as chain carriers. These atoms are very reactive due to their free valences

$$
\begin{aligned}
&0)\ Cl_2 + h\nu = Cl + Cl \\
&1)\ Cl + H_2 = HCl + H \\
&2)\ H + Cl_2 = HCl + Cl \\
&\text{etc.}
\end{aligned}
$$

Later on, the Nernst mechanism obtained direct experimental confirmation with respect to every reaction step. This was the first appearance of the concept of a material chain carried on by active atoms and radicals as intermediates. It is the basis of modern ideas on chain reactions. All the chain reactions studied, with the exception of ozone decomposition, are believed to involve material chains.

BRANCHED CHAIN REACTIONS AND THE MECHANISM OF BRANCHING

Branched chain reactions were discovered in the second half of nineteen twenties by my coworkers and myself for phosphorus oxidation (5) and, soon after, by Hinshelwood with coworkers for hydrogen oxidation.(6) A mathematical theory for branched chain reactions was worked out at our Institute at the beginning of nineteen thirties.

Let us consider in what do the branched chain reactions differ from those unbranched. A new radical carrying the chain is formed at every elementary step of an unbranched chain reaction, along with a product molecule. The chain terminates through disappearance of the free radical which is taken up by the wall or by an inhibitor molecule, or else recombines with another free radical. The reaction rate is $w_{unbranch} = n_0 \nu$, where n_0 — is the number of formed (and, consequently, terminated) chains per second and ν is the chain length (the number of elementary steps from start to termination of the chain).

With branched reactions two more radicals may appear at every link of the chain with a probability δ. These radicals will start two new chains. Branching may occur by a strictly chemical mechanism. An example of it would be the raction $H + O_2 = OH + O$ in the oxidation of hydrogen involving the formation, along with the OH radical, of an O atom capable of yielding two additional radicals by reaction $O + H_2 = OH + H$ (material branching).

The two other types of branching were proposed by me as far as 1934(5). Branchings increase the chain reaction rate in the ratio

$$\frac{w_{branch}}{w_{unbranch}} = \frac{1}{1 - \nu\delta}.$$

The $\nu\delta$ value is a function of many parameters of the system : gas pressure, vessel dimensions, wall condition, dilution with inert gases, inhibitors, etc.

With $\nu\delta \geqslant 1$ a stationary branched chain reaction becomes impossible and its rate starts increasing with time in avalanche, resulting in chain explosion. Contrary to thermal explosion, chain explosion may occur under isothermic conditions, often at low temperatures. When the number of primary chains is negligibly small (as is often the case), the remarkable phenomenon of reaction limits takes place. For example, when the pressure drops or the vessel dimensions are smaller than a certain critical value (limit) there is practically no reaction, but as soon as any of these parameters attains or overcomes the limit, there occurs a chain explosion often terminated within fractions of a second.

Another unexpected result was the formation of great over-equilibrium amounts of free atoms and radicals in the course of a fast branched reaction. This result was obtained in our Institute on the basis of theoretical and experimental information(7,8). For example, up to 10% of initial H_2 were converted into atoms in the cool flame of an $H_2 + O_2$ mixture under low pressure. Within the last year Voevodskii(9) and Nalbandyan(10-13) obtained direct confirmation for this, by using the ESR technique. The first step of this process may be described by the overall reaction

$$3H_2 + O_2 = 2H_2O + 2H + 15 \text{ kcal/mole}.$$

The second step involves disappearance of hydrogen atoms, mainly be recombination at the wall $H + H = H_2 + 103$ kcal/mole. The low heating up observed for cool flames is connected to a considerable extent with the heat of the first reaction step.

The concept of branched chain reactions appeared to be very fruitful. Nuclear branched reactions are known to have been discovered towards 1940, and this resulted in the advent of atomic energy. The essence of this phenomenon certainly differs from that in chemistry, but the kinetic mathematical laws governing the nuclear process, especially so the occurrence of limits, proved to be quite similar to those for the chemistry of branched chain reactions. From the standpoint of these laws similar are also the processes taking place in the recently discovered sources of coherent radio and visible light radiation namely in maser and lasers

ENERGY BRANCHING

(through vibrational excitation)

Let us consider now the possibility of energy branchings through use of the vibrational energy of products for the dissociation of initial molecules into atoms and radicals. For instance, in the chlorination of hydrogen by reaction $H + Cl_2 = HCl + Cl + 45$ kcal/mole, a certain part X of the energy liberated by the reaction $(X < 45)$ is imparted to the HCl molecule. The latter loses this energy but slowly, on the average during 10^4 collisions. Collision with a $Cl_2{}^*$ molecule possessing (due to the Maxwell-Boltzmann distribution) a vibrational energy higher than or equal to $D - X$ kcal/mole, may result in dissociation of this molecule into two Cl atoms that would start two additional chain $[D(Cl - Cl) = 57$ kcal/mole$]$.

$$HCl^* + Cl_2{}^* = HCl + Cl + Cl\,.$$

The rate of branching is

$$w_{branch} = 2Z(\underset{X}{HCl^*})\,(Cl_2)\exp\left[-(D - X)/RT\right].$$

The rate of deactivation is

$$w_{deact} = 10^{-4}Z\,(\underset{X}{HCl^*})\,(Cl_2)\,.$$

Hence, the probability of branching is

$$\frac{w_{branch}}{w_{branch} + w_{deact}} = 2 \times 10^4 \exp\left[-(D - X)/RT\right].$$

This equation was obtained by us in 1934(5).

By virtue of the function $\exp[-(D - X)/RT]$ branching will be realized only when $X = 45$ kcal/mole (the sixth vibrational level, $v = 6$) and $D - X = 12$ kcal/mole. The amount of molecules is

$$(HCl^*_{v-6}) = \frac{1}{n} \sum_{v-0}^{v-6} (HCl^*),$$

and according to Polanyi(14)

$$\frac{1}{n} = \exp(-45{,}000/RT_o)\cdot$$

T_o is the calculated vibrational temperature of HCl^*.

Hence

$$\delta = 2 \times 10^4 \exp(-12{,}000/RT) \exp(-45{,}000/RT_o)$$

which gives

$$\delta_{600^oK} = 10^{-4},\ \delta_{300^oK} = 5 \times 10^{-9}.$$

The 2700°K temperature is attained in the case when, on the average, only 10% of 45 kcal are in the form of vibrational energy of HCl^*. This value and, consequently, the temperature might appear to be three times higher, and T_o will then be 8100°K. Under this assumption $\delta_{300^oK} = 1.2 \times 10^{-6}$. It will be remembered that in the hydrogen-chlorine reaction the chain length amounts to 10^6.

However, we have, in fact, admitted in this calculation that Cl_2 dissociation occurs at every collision of an HCl^* with a Cl_2^* molecules (possessing energies of 45 and 12 kcal, respectively). And yet, according to Nikitin's calculations, the probability Π of such energy transfer is very low. Nikitin (Institute of Chemical Physics, U.S.S.R.) calculated to a first approximation of the perturbation theory the probability for the occurrence of the reaction studied, allowing for the electronically excited chlorine level. The probability for branching was found to be $\Pi \simeq 10^{-9}$ to 10^{-10}. Thus the true probability for branching will be $\delta_{tr} = \delta\Pi$. For 600°K this gives a value of 10^{-13} to 10^{-14}, i.e. $\nu\delta_{tr} \simeq 10^{-7}$ to 10^{-8}.

If the estimation of Π is correct, the energy branching considered is of no importance for the hydrogen-chlorine reaction.

An essentially different result was obtained for the reaction between hydrogen and fluorine. An elementary step of this reaction $H + F_2 = HF + F$ yields 97 kcal, while the F_2 dissociation energy is 36 kcal only.

According to Nikitin, in this case $\delta_{tr} = \Pi\delta \simeq 10^{-8}$ and is independent of temperature. When the chain length in a reaction between fluorine and hydrogen is 10^8, chain explosion appears to be possible even at very low temperatures.

It was shown by experiment (15) that under routine conditions hydrogen could never be mixed with fluorine without explosion, even at very low temperatures. Under very specific conditions the explosion may sometimes be prevented, but not always, and uncontrolled explosions were observed to occur even upon complete removal of organic admixtures. This information, incomplete as it is, suggets the occurrence of chain explosion in $H_2 + F_2$ mixtures.

Branching through vibrational energy may appear to be especially effective for addition reactions. For instance in acetylene chlorination

1) $\dot{Cl} + CH = CH \rightarrow ClCH = \dot{C}H + \sim 56$ kcal/mole,

2) $ClCH = \dot{C}H + Cl_2 \rightarrow ClCH = CHCl + \dot{Cl} + \sim 33$k cal/mole.

The 56 kcal emitted in the first reaction are stored as vibrational energy of the radical formed. In the given case this energy succeeds in being distributed over all degrees of freedom before reaction (2) occurs. The energy stored in the second reaction is not always converted into vibrational motion of dichlorethylene, but there is a certain probability of it, and then the dichlorethylene molecule will be energized to 56 kcal + 33 kcal = 89 kcal/mole.

But the C — Cl bond energy is approximately equal to this value and the dichlorethylene molecule may, consequently, dissociate into a chlorine atom and a $ClCH = \dot{C}H$ radical that would start two new chains, i.e. branching would occur.

The energy of ethylene chlorination is insufficient for branching. This seems to account for smooth ethylene chlorination, while that of acetylene is accompanied with uncontrolled explosions, probably of a chain nature. In the case of fluorine chlorination the energy is more than sufficient for branching, and uncontrolled explosions are also observed.

Since transfer of vibrational energy from one molecule to another does not take place in the reactions considered, the value $\delta_{tr} = \delta$ does not include the small Π value.

Returning to reaction $H_2 + Cl_2$, I would suggest that the conclusion as to the low probability of branching should not be considered as final. First of all this calculation was made to a first approximation of the perturbation theory. In other words perturbation in electronic shells of HCl and Cl_2, that were caused by collisions, were not allowed for. The whole set of energy levels in these molecules is supposed to be similar both for individual and for colliding molecules. However, the stronger the interaction by collision, the higher the probability for energy transfer, and, consequently, for branchings.

I would like to draw attention to a trivial fact. When speaking of exchange reactions such as $H + Cl_2 = HCl + Cl$, or $Cl + H_2 = HCl + H$, i.e. of collisions involving strong interaction of electronic shells, no doubt ever arises in the high probability of multiquantum vibrational transitions. A reaction is considered to be very probable when the energy of particles exceeds the activation energy for a process. A considerable part of the former energy is concentrated in vibrating Cl_2 and H_2 molecules. Thus, when a Cl_2 molecule in a normal electronic state is converted adiabatically in the presence of an H atom into an HCl molecule in a normal state in the presence of a Cl atom, then the multiquantum vibrational transition will occur without hindrance. The activation energy as such known to be roughly determined by intersection of potential curves for the initial and final states. I am no specialist in energy transfer problems and I would like to hear from the eminent scientists present, whether I am justified in suggesting that at a strong interaction of colliding particles multiquantum vibrational transitions are no more difficult ? However, certain conclusions may be drawn even without detailed analysis of this theoretical problem.

Indeed, we may suggest that the formation of Cl atoms under the action of energy of vibrationally excited HCl^* proceeds by a mechanism similar to that for the exchange reaction :

$$1)\ HCl^* + Cl_2 = HCl \cdot Cl + Cl,$$

$$2)\ HCl \cdot Cl = HCl + Cl.$$

It would only be necessary to allow for the occurrence of a short-lived complex $HCl \cdot Cl$, which is very probable.

When there is an $HCl \cdot Cl$ radical, the difficulty of multiquantum vibrational transitions falls off, as in the case of the above mentioned exchange reaction, and, consequently, the branching probability value δ becomes close to that calculated under the assumption of ready transfer of energy from HCl^* to Cl_2.

It will be noted that suggestions of this kind are made at present also with respect to hydrogen dissociation under the action of the electronically excited Hg'.

$$Hg' + H_2 = HgH + H;\ HgH = Hg + H.$$

The HgH radical bonding seems to be similar to that of $Cl_2 — H$, if the latter radical exists.

There is yet another possibility that would eliminate the difficulty of multiquantum vibrational transition in the branching reaction $HCl^* + Cl_2 = HCl + Cl + Cl$. This is the probable occurrence of the $HCl \cdot Cl_2$ complex, the lifetime of which would be sufficiently long for complete exchange of energy within this complex, and the consequent possible dissociation of Cl_2 with a probability calculated from the theory of unimolecular reactions. Dodgen and Libby (16) suggested in 1949 the occurrence of such complexes, when making experiments on isotopic exchange. Energy exchange within the complex would be ensured even at a very short lifetime. The only thing important is that it be long enough compared with the collision time (10^{-13} sec), or, better to say, with the period of atomic vibrations in the complex.

ENERGY BRANCHING THROUGH ELECTRONIC EXCITATION

In chemiluminescence reactions one or another part of the chemical energy will be accumulated as electronic excitation. An example of it would be the reaction between phosphorus and oxygen. This reaction proceeds by the chain branching mechanism. I have suggested before(5) that the main chain in phosphorus oxidation propagates materially, and molecules of various oxides, excited to highest electronic levels, are formed as intermediates. Towards the end of nineteen twenties Leipunskii (17) observed electrons of an energy by 10 eV higher than that of the initial electrons, when passing a beam of slow electrons through phosphorus undergoing oxidation at low pressures. Thus the molecules involved excited levels such as could transfer this high energy by collisions of the second kind. Excited particles are known to be capable of dissociating molecules by collisions of the second kind. This was the ground for suggesting that the mechanism of branching in phosphorus oxidation is accounted for by dissociation of the oxygen molecule into two atoms through transfer of the electronic excitation energy of the phosphorus oxide molecules by collisions of the second kind, upon collision with O_2. In this case the branching probability δ will be sufficiently high, as it will be accounted for by the ratio of the transfer rate for excitation energy inducing dissociation to the rate of excitation removable by collision with other molecules. As to the emission of light it will be sufficiently slow due to the metastable nature of the level. It would be of interest to obtain a better insight into the theory of these processes.

ENERGY CHAINS

1. Photodecomposition of ozone.

The energy branchings considered above become important for the kinetics of chain reactions when the probability of these branchings is of the order of $1/\nu$ (ν is the chain length). This is the reason for suggesting that in certain events, especially so with electronically-excited reaction products, energy branchings of this kind will actually occur.

Things are different when it comes to energy chains as such. In this case the chain length will be

$$\nu = \frac{\alpha}{1-\alpha} \text{ whence } \alpha = \frac{1}{1 + 1/\nu}.$$

With long enough chains the probability of chain propagation α or, in other words, of the utilisation of energy products for the activation of initial reagents, would be close to unity. In the majority of cases this is, certainly, impossible. Even for a very short chain involving only three links, α would be 0.75, i.e. in 75 cases out of 100 the total amount of vibrational or electronic energy would be required for a reaction of initial products to occur. Thus, energy chains as such were discarded by chemical kinetics long ago. Same as with branching, the lowest probability would be that of an energy chain utilizing the translational and vibrational energies of products.

However, at present a similar concept arose again with respect to ozone decomposition under UV light, involving short chains with 5 to 6 decomposed ozone molecules per one quantum of light absorbed. Norrish (18), and also McKenney and Laidler (19) proposed the following mechanism of this chain reaction :

$$0)\ O_3 + h\nu = O_2 + O' \qquad \text{chain initiation}$$

$$\left.\begin{array}{l} 1)\ O' + O_3 = O_2 + O_2' \\ 1')\ O_2' = O_2^* + h\nu \\ 2)\ O_2^* + O_3 = O_2 + O_2 + O' \end{array}\right\} \text{chain propagation}$$

Here O' is the electronically-excited oxygen atom with an energy store of 46 kcal/mole. O_2' is an electronically-excited oxygen molecule with an energy store of 142 kcal/mole. O_2^* is a strongly vibrating oxygen molecule in a normal electronic state. It was shown experimentally by Norrish (18) and by Laidler (19) on the basis of the Franck-Condon principle that O_2^* molecules were excited to different vibrational levels v, the greatest amount being excited to $v = 13$ (53.5 kcal/mole). Molecules excited to $v = 17$ (69 kcal/mole) were observed experimentally, but the number of these is considerably smaller than that of molecules excited to the

$v = 13$ level. It will be seen by using these data that reaction (1) is practically thermoneutral, and reaction (2) for O_2^* molecules, excited to the 13th vibrational level, is endothermic by 17.6 kcal/mole. This, certainly, makes reaction (2) and, consequently the scheme proposed by the above scientists, impossible. For O_2^* molecules excited to the 17th level reaction (2) appears to be practically thermoneutral. But these molecules are few and the probability of chain propagation thus appears to be considerably lower than the 0.75 value necessary for obtaining a chain of 5 to 7 links in the given case. I should think that the scheme of an energy chain propagating by means of electronically-excited O' and O_2' particles would be more probable. It was already mentioned that the probability for dissociation of initial molecules through electronically-excited molecules of products is considerably higher than with vibrationally-excited molecules. But most essential is the fact that in this case reaction (2) appears to be strongly exothermic. We suggest the following scheme of ozone decomposition

0) $O_3 + h\nu = O_2 + O'$

1) $O' + O_3 = O_2 + O_2'$ thermoneutral reaction

2) $O_2' + O_3 = 2O_2 + O' + 71$ kcal/mole.

Reaction (1′) of the Laidler-Norrish scheme, $O_2' = O_2^* + h\nu$, certainly occurs but it does not enter into the chain propagation mechanism. On the contrary, it terminates the chain, as it results in the disappearance of the O_2' carrier by conversion to an O_2^* molecule that is, I think, of no use for reaction. The O_2' molecule looses electronic excitation by spontaneous emission of light (reaction 1′) on the average after a time period of $\tau = 2.5 \times 10^{-9}$ sec. Under the conditions of Norrish's experiments half of the O_2' molecules disappear by reaction (1′), and the remainder participate in chain propagation (reaction 2). Thus the probability of chain propagation would be at best 0.5. However, this would be the case if reaction (2) were to occur at gas-kinetic cross-sections for the collision of oxygen and ozone molecules. In reality the electronic excitation resulting in resonance dipole interaction between O_2' and O_3 considerably increases the effective cross-section for the collision of these molecules leading to reaction (2), and the probability of chain propagation is thus increased. Moreover, when the light emitted in reaction (1′) is absorbed by ozone and results in the formation of O′ atoms, reaction (1′) will never cause chain termination.

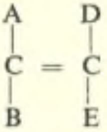
As to the vibrationally-excited O_2^* molecules observed by Norrish, these are probably formed as intermediates in reaction (2). The heat (71 kcal/mole) emitted in this reaction is capable of exciting vibrations in the O_2 molecule up to $v = 17$(*).

The above analysis seems to show that the energy chain of ozone decomposition is accounted for by electronically- and not vibrationally-excited particles. Same as with branching, electronic excitation appears to be more effective than vibrational excitation. But even with electron excitation energy chains would be capable of propagating in gases or liquids under exceptionally favourable conditions only. Things seem to be different for solids, and especially for crystalline bodies at low temperatures.

2. **Chain polymerization reactions.**

Polymerization of liquid and of dissolved monomers is a typical chain reaction occuring by the radical or ionic mechanism under the action of substances capable of relatively ready dissociation into radicals ($\dot{X}$) or ions (Y^+ and Z^-) (**).

Let us take as an example the polymerization of ethylene derivatives



$$\begin{array}{ccc} A & & D \\ | & & | \\ C & = & C \\ | & & | \\ B & & E \end{array}$$

or, for the sake of simplicity, $C = C$. Radical polymerization occurs by a number of consecutive elementary steps

$$\dot{X} + C = C \rightarrow X\text{-}C\text{-}\dot{C} \qquad \text{chain initiation}$$

$$\left.\begin{array}{l} X\text{-}C\text{-}\dot{C} + C = C \rightarrow X\text{-}C\text{-}C\text{-}C\text{-}\dot{C} \\ X\text{-}C\text{-}C\text{-}C\text{-}\dot{C} + C = C \rightarrow X\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}\dot{C} \end{array}\right\} \text{chain propagation}$$

etc.

It will be noted that a radical $\sim$C-$\dot{C}$ participates in every elementary step of chain propagation (here the sign $\sim$ denotes a

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(*) O_2 molecules excited to the 20th vibrational level 73 kcal/mole were observed lately by Norrish (20). However, it was stated during this discussion by Voevodskii and myself that this would bring no change in the ideas I brought forward.

(**) We shall not discuss here the polymerization induced by complex catalysts.

more or less long polymer chain attached to the end-radical). The effect of this chain on the end-radical properties is negligible, and it may be considered that the $\sim C\text{-}\dot{C}$ radicals possess the same levels and the same energies of activation for every step of chain propagation.

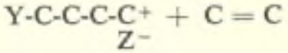
In the case of an ionic mechanism (for example, cationic) the chain will propagate as follows

$$Y^+ + C=C \rightarrow Y\text{-}C\text{-}C^+ \qquad \text{chain initiation}$$

$$\left.\begin{aligned} &Y\text{-}C\text{-}C^+ + C=C \rightarrow Y\text{-}C\text{-}C\text{-}C\text{-}C^+ \\ &Y\text{-}C\text{-}C\text{-}C\text{-}C^+ + C=C \rightarrow Y\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C^+ \end{aligned}\right\} \text{chain propagation}$$

etc.

Although the number of polymerization processes of an ionic nature is great, the mechanism of ionic polymerization is not sufficiently established. A suggestion was made that an anti-ion Z^- accompanies the $C\text{-}C^+$ ion, so that the end group of a growing polymer may be represented as a complex



$$Y\text{-}C\text{-}C\text{-}C\text{-}\underset{Z^-}{C^+} + C=C$$

When the next monomer molecule is added, the positive charge will attract the electrons of the $C=C$ molecule, as a result of which it becomes neutral and, consequently, the positive charge passes to the extreme carbon atom of the polymer radical chain formed. The anti-ion Z^- will migrate simultaneously towards the same atom, thus giving $Y\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}\underset{Z^-}{C^+}$. In the liquid phase this migration will be hindered, especially so when the Z^- ion is solvated, and this is apparently the reason why an activation energy is necessary for ionic polymerization to occur. If it were not for these complicating circumstances (the anti-ion, solvation shells, etc.), the process of monomer addition as such, with migration of electrons and displacement of the charge along the carbon chain, would probably require no activation energy. A certain ground for it may be provided by Talrose's experiments (Institute of Chemical Physics, U.S.S.R.) (21), and by those of Stevenson *et al.*, U.S.A. (22). They have studied diverse reactions between ions and molecules in vacuum in a mass-spectrometer chamber.

It appeared that practically for all exothermic reactions of this kind the activation energy was zero. At the same time ionic reactions in solutions always require an activation energy due to the presence of solvation shells and the interactions with oppositely-charged ions.

With solid crystalline monomers the migration of positive and negative charges at low temperatures and under certain polymerization conditions seems to proceed without hindrance. Consequently chain propagation would require no activation energy. We connect this with the existence of excitons, i.e. with the migration of an electron-hole pair within the crystal, the pair suffering no destruction for a considerable lengths.

In polymerization the migration of a hole is equivalent to that of the positive charge along the carbon chain, and the respective migration of electrons to the movement of the negative anti-ion in the above mentioned scheme for ionic polymerization in the liquid phase. However, in the case considered, i.e. in the solid phase, the migration of the electron-hole pair is not hindered.

Since excitons decrease the activation energy for an elementary act of polymerization, the migration of these results in growth of the polymer chain. However, it will be noted that the polymerization process is connected with certain displacement of the carbon atoms, and this makes exciton migration more difficult, decreasing its rate to 10^{-5} cm/sec.

On the same ground the exciton-induced polymerization may be considered also as a reaction of the electronically-excited $\sim C\text{-}\dot{C}'$ group with simultaneous transfer of electronic excitation to the newly formed end-group

$$\sim C\text{-}\dot{C}' + C=C \rightarrow \sim C\text{-}C\text{-}C\text{-}\dot{C}'.$$

This mechanism corresponds to a typical energy chain. It was said above that the properties and energy levels of the $\sim C\text{-}\dot{C}'$ group are practically independent of the length of the polymer chain attached to this group. Thus the states of the initial and final system are in resonance. This would make the probability for energy transfer in the above reaction very close to unity, and, consequently, might ensure a greater length of the energy chain, provided the activation barrier is zero, or low.

The range of action of electronically-excited particles may be higher than those for non-excited particles, and this would lead to a decrease in the activation energy. Ionization is the limiting case of electronic excitation and if the above considerations are true, the activation energy of the latter should be zero. Every polymerization step liberates 15 to 20 kcal of heat, as vibrational energy. This heat would be soon dissipated in a solid, and would scarcely result in the surmounting of the activation barrier and in the appearance of long enough chains. However, in reactions involving electronically-excited radicals this heat may help in surmounting a low activation barrier, if any.

Let us use the following simple model for discussing in more detail the mechanism of energy chain propagation involving electronic excitation. Let us imagine a reaction between an electronically-excited atom A′ with a molecule BC, where all atoms A, B and C are identical, and A′ and C atoms are fixed at a certain distance L from each other, while the B atom may move between the two. In principle, three reaction paths are possible :

1) $A' + BC = AB^* + C$ (the excitation energy A′ is converted into the vibrational energy of AB);
2) $A' + BC = AB + C'$ (excitation is transferred to the C atom);
3) $A' + BC = AB' + C$ (the excitation energy of A′ is transferred to AB′).

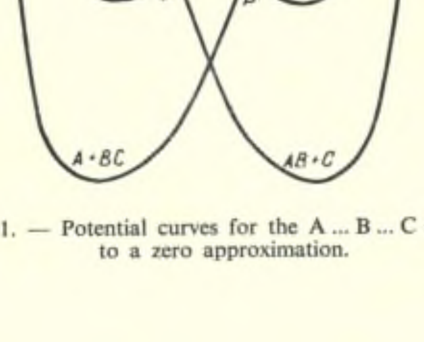


Fig. 1. — Potential curves for the A ... B ... C system, to a zero approximation.

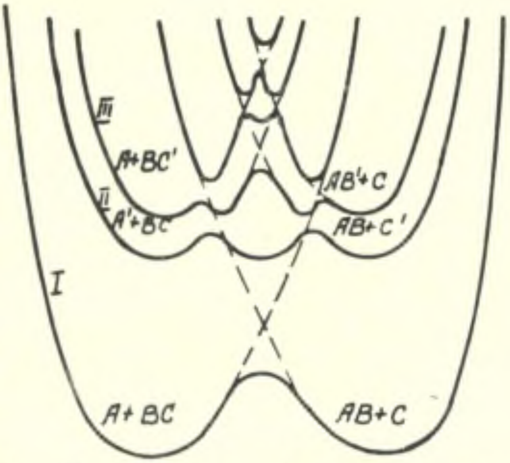


Fig. 2. — True potential curves for the A ... B ... C system.

In reaction (3) the excitation energy of AB′ is, as a rule, higher than that of A′ and, consequently, this process is practically impossible. When reactions (1) and (2) compete, the latter seems to be more probable than (1), since reaction (2) involves strict resonance between the initial and final states.

Let us make a qualitative analysis of the three reactions by plotting curves for potential energies of systems A + BC, AB + C, A′ + BC, AB + C′, A + BC′, AB′ + C, as functions of the B atom position between the A and C atoms fixed at a distance L. It will be noted that $L = X + Y$ (here X is the distance between B and A, and Y between B and C. The potential curves for the six systems are, strictly speaking, the cross-sections for respective potential surfaces along the straight line $X + Y = L$.

The curves for potential energies of the six states mentioned are shown in Figure 1, no allowance being made for interaction between these systems.

The same curves allowing for interaction are shown in Figure 2. It is essential here that due to splitting of terms transitions from state II (A′ + BC = AB + C′) to states I (A + BC = AB + C) and III (A + BC′ = AB′ + C) may be only non-adiabatic. It follows that the probability of these transitions is low, and thus reactions (1) and (3) practically cannot occur. Then there will be only the adiabatic reaction (2) (A′ + BC = AB + C′).

It will be seen from Figures 1 and 2 that due to the interaction of excited states $A' + BC$ and $AB + C'$ (points of intersection P and P′ in Fig. 1) the activation energy for process (2) (Fig. 2, curve II) appears to be considerably lower than that for the reaction of non-excited atom with the BC molecule (curve I).

Thus :

First, the energy for electronic excitation of the A′ atom by reaction with the BC molecule is readily transferred to the C atom.

Second, the activation energy for this reaction is low, in any case considerably lower than for the reaction $A + BC = AB + C$.

The model reaction $A' + BC = AB + C'$ differs from the elementary polymerization act $(\sim\text{C-}\dot{\text{C}}\text{-}\overset{+}{\text{C}}{}' + \text{C} = \text{C} \rightarrow \sim \text{C-C-C-}\dot{\text{C}}{}'$, or, which is the same, $\sim A' + B = C \rightarrow \sim\text{A-B-C}')$ only in that there occurs an addition reaction with breaking of the π bond, instead of the exchange reaction. But this brings no qualitative changes into the nature of potential curves. Of importance is the fact that A, B and C atoms are identical in polymerization as well, and, what is still more important, identical are the electronic levels of the A′ and BC′ end-groups. For this reason the treatment of the model system is valid for elementary polymerization acts as well. Here also the electronic excitation will be readily transferred to the end-group added, and at a low value of the activation energy this would ensure quick development of a long energy chain.

To a certain extent, the above considerations might be taken as ground for substantiating the possibility of coordinated migration of the exciton and of carbon atoms within the solid monomer, the activation barrier being, so to say, eliminated by the exciton which leaves behind a track, as the polymer chain.

Goldanskii, Enikolopyan *et al.* (23) of our Institute studied the polymerization of acrylnitryl, vinyl acetate, and methylmetacrylate in the solid state, under irradiation by fast 1.6 MeV electrons, within a temperature range from the freezing point of the monomer down to −196°C. The reaction rates were rather high, about the same as for the liquid phase close to the freezing point. However, while with liquids the radiation-induced polymerization rate was strongly temperature-dependent, no change in the reaction rate was observed for solids at a change in temperature almost by 100°.

The activation energies for radiation-induced liquid-phase polymerization of the four monomers, as determined by the above mentioned and other scientists, were found to range from 3 to 5 kcal/mole. This was in agreement with the data on activation energies required for an elementary act of chain growth in catalytic polymerization.

The results obtained for solids may be interpreted as evidence that under these conditions the elementary acts of chain growth proceed without activation energy. If this is so, then the only explanation possible would be the assumption of readily growing energy chains of polymerization.

Besides the radiation induced free radicals, free ions, and electrons trapped by various matrices, it seems that the irradiation leads to the formation of electronically-excited C-C′ radicals, that start initiation of the above mentioned energy chain without any activation energy. Termination of the energy chains discussed may be due to loss of excitation energy, for example by emission of a quantum of light.

Calorimetric determination of the heating up of irradiated monomers and the recording of ESR signals in the course of irradiation and after it, as conducted by Goldanskii, Enikolopyan *et al.*(23), provide a convincing argument in favour of the possible great importance of short-lived excited states in the solid-phase radiation-induced polymerization. It appears that polymerization of vinyl acetate and acrylonitryl proceeds only in the course of irradiation and terminates after the latter is switched off, though the form and intensity of the ESR signal persists. Thus, radicals as such do not induce polymerization in the solid phase after irradiation. Ions that may form in the solid phase are also known to persist at low temperatures for a long time after irradiation (24), but it is evident now that they carry the reaction no more. Thus, it should be natural to suggest that short-lived states favouring the propagation of energy chains in polymerization may be formed in the course of irradiation.

Investigations are being carried out in our Institute with the aim to obtain more direct evidence for the existence of such energy chains.

If I succeeded, to any extent, in reviving the interest in problems connected with branched chain reactions and in promoting new investigations in this field, I shall consider as justified this paper of mine, which certainly has many defects, first of all in that it contains many questions and few answers.

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Discussion du rapport de M. Semenov

M. Norrish. — If the hydrogen — chlorine reaction is a branching chain reaction, then in the reaction

$$H + Cl_2 \rightleftharpoons HCl^* + Cl \qquad + 45 \text{ kcal},$$

even if the total exothermicity appears in vibration, it is insufficient to cause branching by the reaction

$$HCl^* + Cl_2 \rightleftharpoons HCl + Cl + Cl - 57 \text{ kcal}.$$

Activation energy would be required. I do not think that at present there is sufficient evidence to bear upon this point. At the same time, it may well be postulated that the explosion limits of the hydrogen — chlorine reaction are conditioned by a purely thermal mechanism.

(Communicated after the meeting.)

I regret that judging from the transcript of his paper which was only available to me after the meeting, Prof. Semenov seems to have misunderstood the mechanism of the ozone photolysis which I have proposed. First, I do not subscribe to the scheme which he describes as the Laidler-Norrish scheme and never have done. I believe the first product of the reaction

$$O^1D + O_3 \rightleftharpoons O_2^* + O_2$$

is a vibrating O_2 *molecule in the ground state in accord with our generalization*

$$A + BCD \rightleftharpoons AB^* + CD$$

when much of the exothermic energy of the reaction appears as vibration in the newly formed bond. I have never suggested the primary formation of an electronically excited O_2 *molecule which degrades to a vibrationally excited molecule in the ground state. This scheme must be attributed to Laidler and is not part of my conception. I regard the vibrationally excited* O_2^* *molecule with* *vibrational energy greater than that corresponding to 17 quanta as the chain carrier. This is supported by the experimental facts. All molecules with less than 17 quanta do not react but are degraded by relaxation processes and hence are seen by flash photolysis.*

Prof. Semenov has proposed that chain propagation in the hydrogen-fluorine reaction is propagated by vibrationally excited HF^* *molecules.*

I would ask him if there is any formal distinction between the two following schemes, i.e., his for $H_2 + F_2$ *and mine for* O_3 :

$$\begin{array}{lr}
H + F_2 = HF^* + F & + \ 97 \text{ kcal.} \\
HF^* + F_2 = HF + F + F & - \ 36 \text{ kcal.} \\
O^1D + O_3 = O_2^* + O_2 & + 137 \text{ kcal.} \\
O_2^* + O_3 = O_2 + O_2 + O^1D & - \ 69 \text{ kcal.}
\end{array}$$

If he believes in the mechanism of chain propagation in the first case, why not in the second ?

Let me now deal with my proposed scheme in greater detail. The evidence for vibrationally excited oxygen molecules as chain carriers in the decomposition of ozone, which has been mentioned in my paper, can be briefly summarized as follows : O^1D atoms are shown to be produced as a result of the photolysis of ozone in the ultraviolet, according to the reaction

$$O_3 + h\nu \rightleftharpoons O_2 + O^1D \qquad - 69 \text{ kcal.} \tag{1}$$

The chemical proof of the electronic state of the oxygen atom is shown by its reactions with a number of compounds of formula RH, such as H_2O, NH_3, H_2, HCl and CH_4 in which vibrationally excited hydroxyl is produced. The hydrogen abstraction reactions with oxygen atoms are only thermochemically favoured in the case of O^1D for such molecules. The electronic states of oxygen that can be produced on photolysis are limited to $O_2{}^1\Delta_g$ and $O_2{}^1\Sigma_u{}^-$. The others can be ruled out on the grounds of spin correlation rules and of thermochemistry.

The two possible propagation reactions with oxygen atoms can be examined :

$$O^1D + O_3 \rightleftharpoons O_2 + O'_2 \text{ (electronically excited)} \quad + 138 \text{ kcal.} \tag{2}$$

$$O^1D + O_3 \rightleftharpoons O_2 + O_2^* \text{ (vibrationally excited)} \quad + 138 \text{ kcal.} \tag{3}$$

Vibrationally excited O_2 molecules with $v > 17$ are thought to propagate the chain. Reaction (3) is 138 kcal exothermic with respect to the zeroth vibrational level in the ground state of O_2. There is therefore sufficient energy to dissociate oxygen molecules according to

$$O^1D + O_3 \rightleftharpoons O_2 + O^3P + O^3P \qquad + 21\ \text{kcal}, \quad (4)$$

taking

$$O_2 \rightleftharpoons O^3P + O^3P \qquad - 117\ \text{kcal}. \quad (5)$$

In this case, light of sufficient energy can give rise to explosion, possibly because the O^3P atoms still possess high translational energy (up to $138 - 117 = 21$ kcal). Hence branching may take place under such conditions. The strongest vibrational level observed corresponds to a maximum in the region $v = 13$ to 15. It is contended that O_2^* is produced with energy up to the dissociation limit and that the levels that are *observed* disappear by relaxation processes. It is assumed that levels beyond $v = 17$ are removed by instantaneous reaction with ozone. It would therefore appear that there is competition between the reaction giving rise to the fission of ozone :

$$O_2^* + O_3 \rightleftharpoons O_2 + O_2 + O^1D \qquad - 69\ \text{kcal} \quad (6)$$

and the fast relaxation processes of the higher levels. The remarkable correlation between the fission of ozone according to reaction (6) and the observation of vibrational levels above $v = 17$ only very weakly must be stressed. A strong comparison can be made between the case of the photolysis of ozone and other cases involving exothermic metathetical reactions of oxygen atoms, for example,

$$NO_2 + O \rightleftharpoons NO + O_2^*$$

$$ClO_2 + O \rightleftharpoons ClO + O_2^*$$

$$OO_2 + O \rightleftharpoons O_2 + O_2^*.$$

The vibrational levels observed in the oxygen molecule are very high. Are all these to be explained in terms of the initial formation of an electronically excited oxygen molecule in each case and if so how ? Indeed, it may be stressed that the ozone results were entirely predicted and discovered by analogy with the two above reactions.

M. Semenov. — The explosion quoted by Prof. Norrish in the case of photochemical dissociation of ozone would be of a very great interest if it has really a chain character and is not a thermal explosion. This could be proved directly, as it was shown many years ago, by calculating the values of an appropriate parameter depending on the reaction rate, reaction heat and thermal relaxation in conditions near the limit.

M. Norrish. — I would like to ask Prof. Semenov to present the evidence for electronically excited O_2 as the molecular chain carrier in the photochemical decomposition of ozone.

M. Semenov. — I do not agree with Prof. Norrish that his scheme for the ozone photodecomposition is in better agreement with his own experimental data than the scheme proposed in my paper. The main fact, a sharp change in the concentration of O_2 molecules with $v > 15 - 17$, follows directly from my scheme. On the other hand this scheme leads also to the possibility of α being $\simeq 0{,}8$ that must occur to account for the experimental chain length $\simeq 7 - 8$. Norrish's scheme does not give any possibility to calculate α, and I cannot see how it would lead to values so close to unity.

M. Norrish. — The following points can be made with respect to the observed and expected vibrational levels of the O_2 molecule based on thermochemical considerations, in the ozone photolysis.

1. I have presented the evidence for vibrationally excited oxygen as the chain carrier in terms of the effective cut-off in the spectrum at $v = 17$.
2. Smith's calculation [*J. Chem. Phys.*, **31**, 1352 (1959)] for the vibrational distribution in the oxygen molecule was based on the exothermicity of the reaction between O_3 and O^3P atoms. In the case of O^1D atoms, the expected maximum of the distribution would be shifted to a higher vibrational quantum number.
3. The effect of relaxation and chemical reaction of the higher levels must be stressed. This accounts for our not observing the initial vibrational distribution.

4. In the case of the reaction

$$O + NO_2 \rightleftharpoons O_2^* + NO,$$

it has been possible to observe vibrationally excited oxygen molecules with up to the entire heat of reaction. It is suggested that the case of ozone is similar except that the higher levels beyond $v = 17 - 18$ are removed by chemical reaction.

In the method of flash photolysis, there is an inherent time delay in the circuit at a nominal delay of zero and this is of the order of at least 5 microseconds. One has also to consider that the observations are not instantaneous and that the spectroscopic flash discharge takes the order of 3 microseconds to reach its maximum. Spectra taken under such conditions may therefore be regarded at the maximum of the spectroscopic flash discharge.

I wish to emphasize that the maximum of $v = 15$ in the vibrational distribution of oxygen molecules derived from the photolysis of ozone was observed after a nominal delay of 30 microseconds. These data do not refer to the earliest possible observations nor do they necessarily represent a true instantaneous distribution at the moment of production. Higher levels will tend to relax more rapidly than lower levels. (For a continuation of this discussion see remarks made in connection with the discussion of Prof. Kondratiev's communication, p. 472.)

M. Goldfinger. — With reference to the reactivity of the activated C_2H_2Cl radical formed according to

$$C_2H_2 + Cl \rightarrow \cdot CH = CHCl + 56 \text{ kcal}$$

mentioned by Prof. Semenov, it may be of interest to discuss the similar reaction

$$C_2H_4 + Cl \rightarrow C_2H_4Cl + 23 \pm 1 \text{ kcal} \qquad (1)$$

for which the heat of reaction is reasonably well known [P. Goldfinger and G. Martens, *Trans. Faraday Soc.*, **57**, 2220 (1961)]. Specific reactions of the primarily formed „ activated " or „ hot " $C_2H_4Cl^*$ or similar radicals have been described (P.B. Ayscough, A.J.Cocker and F.S. Dainton, *Trans. Faraday Soc.*, **58**, 284 (1962); P.B. Ayscough, A.J. Cocker, F.S. Dainton and S. Hirst, *ibid.*, **58**, 295 (1962); F.S. Dainton, D.A. Lomax and M. Weston, *ibid.*, **58**, 318 (1962)]. Also the so-called ,, well-known '' kinetics of the photochemical $C_2H_4 + Cl_2$ reaction [R. Schmitz, H.J. Schumacher and A. Jäger, *Z. Physik. Chemie*, **B51**, 281 (1942)] can only be understood assuming slow equilibration

$$C_2H_4Cl^* + M \rightarrow C_2H_4Cl + M \qquad (1a)$$

A severe kinetic test consists in the study of the competition of (1) with

$$C_2H_6 + Cl \rightarrow C_2H_5 + HCl \qquad (2)$$

(G. Huybrechts, G. Martens, T. Montenez and A. Verhasselt, in preparation).

Simple kinetics show that

$$v_2/v_1 = \{k_2(C_2H_6)/k_1(C_2H_4)\} \, [1 + k/(Cl_2)],$$

where k is related to the reverse of reaction (1). If the decomposition of the hot radical is observed, the activation energy is small and $k/(Cl_2)$ is large compared to unity. The results of the latter authors yield a value of k more than 100 times smaller than necessary for the Schumacher or Ayscough mechanism. This must therefore be dismissed : the equilibrium (1a) is established rapidly; a collision formula with 8 square terms and a collision yield of about 0.01 is adequate to explain this equilibration. I do not believe that this problem is settled at the present time and that ,, hot radicals '' do not take a part as chain carriers in chlorine addition to olefin derivatives.

What I whish to emphasize here is that reactions of " hot radicals " are often proposed to explain complex kinetic results. It may happen often, as in the case mentioned above, that a severe kinetic analysis throws doubt on the results and their interpretation in terms of " hot radicals ". Thus J.H. Knox [*Bull. Soc. Chim. Belg.*, **71**, 764 (1962)] has shown in a similar case that kinetic results explained by the assumption of ,, hot radicals '' were simply due to interfering wall effects.

M. Cottrell. — Is the chlorination reaction certainly homogeneous ?

M. Goldfinger. — In reply to Prof. Cottrell's question I would like to answer that for this and many other photochlorination reactions numerous tests of homogeneity have been performed and adequate experimental precautions taken to reduce the incidence of wall reactions to a negligible amount. We are however well aware of Dr. Knox's results (*loc. cit.*) on perturbations by wall reactions and agree that great care must be taken and adequate verifications made.

M. Semenov. — The dissociation of the radical $(ClC_2H_4)^* \rightarrow C_2H_4 + Cl$ cannot be regarded as a branching since it leads only to the transformation of one radical in another, and the chain remains unbranched. In the scheme discussed in my report for the chlorination of acetylene, the dissociation of the excited $(ClCH = CHCl)^*$ molecule leads to the formation of two new radicals and that is a real branching act.

M. Duchesne. — I should like to ask whether the trans-compound occurs predominantly in the addition reaction of acetylene with chlorine, as I would tend to expect. This is important to know in relation with the reaction mechanism to be chosen. If indeed the trans-compound is predominant, the mechanism through which the reaction proceeds should be in relation with the following model.

Preliminary quantum mechanics calculations performed in my laboratory by Dr. L. Burnelle, developing in this particular case general ideas put forward by me some twelve years ago (*), reveal that the first excited electronic state of acetylene, which is known to be trans-bent, might be determinant in the reaction, as already suggested by Prof. Ingold. Indeed, if we treat as a perturbation the coulombic interaction between the approaching reagent and the substrate, it is found that the effect of the reagent is to produce a mixing of the ground state wave function of acetylene with that of its excited state, which would be forbidden by orbital symmetry in the unperturbed molecule. As a consequence, the presence of the reagent favours the bending of the molecule in its trans-shape, and thus orients the reaction towards a trans-addition.

(*) J. Duchesne, *J. Chem. Phys.*, **18**, 1120 (1950); *Bull. Acad. Roy. Belg., Cl. Sci.*, **58**, 197 (1952).

M. Semenov. — The proportions of cis and trans-compound in the addition reaction of acetylene with chlorine have not been measured.

M. Van Tiggelen. — Pure isothermal chain explosions in gas mixtures are only possible if the chain carriers (free radicals) concentration continues to increase far beyond the equilibrium concentration which is to be finally reached in adiabatic conditions; otherwise a considerable heating up would ensue and the system would no more be isothermal. This condition is essential and it makes no difference whether the disappearance of free valencies occurs by a first order (wall), or by a bimolecular (recombination) process.

Even if a *supposed* stationarity equation leads *formally* to a real positive solution for the radical concentration, an isothermal explosion is still possible. The only condition will be that this calculated radical concentration is found sufficiently large. This is the natural consequence of the strong exothermicity of all the chemical reactions leading to explosion. For example, isothermal conditions in H_2/O_2 explosion could almost theoretically be attained if the overall reaction occured by one or more of the following schemes :

$$H_2 + O_2 \rightarrow 2OH \pm \sim 0 \text{ kcal},$$

$$2H_2 + O_2 \rightarrow H_2O + H + OH \pm \sim 0 \text{ kcal},$$

$$3H_2 + O_2 \rightarrow 2H_2O + 2H \pm \sim 0 \text{ kcal, etc.}$$

Of course exothermal recombination of radicals cannot be neglected and this leads to some contribution of thermal explosion which, however, might eventually not play an important role in the *onset* of the explosion.

The same considerations as explained here above are also valid when energy chains are taking part in the reaction : the only difference will be that excited species will play the role of the free radicals.

REVIEW OF COLLISION THEORY

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Our appreciation of the significance of collision theory has increased immensely in the post-war years. This appreciation has not yet had an adequate effect on the textbooks for courses in quantum mechanics and the evident need for learning the subject has created a veritable flood of treatises and reviews. As a result, the same basic ideas and applications have been described many times and there is a certain repetitiousness in the literature. This will apply also to the present review, the purpose of which is, as I understand my assignment, to serve as a background for the deliberations of this conference. Collision theory is one of the pillars which support the structure of transport theory. However, one may as well admit at the outset that, from the point of view of first principles, this pillar is not fully integrated into the structure. Transport theory should be a many body theory both in classical and in quantum physics, i.e., one should at least start from the many body Hamiltonian and many body wave functions. The reduction of the many body problem to the problems we commonly consider is plausible, in fact practically surely correct in the case of a dilute gas. However, it has not been carried out rigorously to date (1) and it is surely impossible to carry it out rigorously except in the limiting case of a dilute gas.

The problem which I just touched upon will not be part of this review, which will deal, rather, solely with collision theory. It will consist of three parts : a shorter first part dealing with the fundamental aspects of collision theory, and a somewhat longer third part dealing with its methods and applications. Sandwiched between these two parts will be some remarks on R-matrix theory.

I. FUNDAMENTAL CONCEPTS

The conceptual significance of the collision matrix, originally introduced by Wheeler (2), was recognized by Heisenberg (3). In order to define the collision matrix, it is not necessary to give the wave function for those parts of the configuration space in which the colliding particles are in intimate contact. Rather, it suffices to specify the state of the system long before, and long after, the collision. Equivalently, one can specify the wave function asymptotically, i.e., for those parts of the configuration space in which the colliding particles, and the collision products, are well separated. In this region, the wave function for a stationary state will have two parts : that describing the incident beam and that the separating collision products. Let us denote the incident beam which contains particles of the type c by ψ_{ic}. The letter c describes the nature of the colliding particles (whether H and Cl_2, or H and an electron) and their state of excitation. The wave function in the aforementioned part of the configuration space then has the form

$$\psi_{ic} - \sum_{c'} S_{cc'} \psi_{oc'} \tag{1}$$

where $\psi_{oc'}$ is an outgoing wave, describing separating particles, the nature and state of excitation of which is characterized by the index c'. The quantities $S_{cc'}$ form the collision matrix. It has as many rows and columns as there are states c' which can be produced by the collision of the particles characterized by c. It is a function of the energy E of the system and also the directions into which the particles which constitute the pairs c and c' travel. As far as the end result is concerned, the collision matrix describes the collision completely, and it describes it not only for the collision in which the particles c collide but also for collisions in which any of the possible collision products of this collision collide. The row index c can assume the same values which the column index c' can assume.

Heisenberg's early publications do not provide a method for calculating the collision matrix without considering the whole process of the collision, i.e., the state vector at times at which the colliding systems are in intimate contact. As a matter of fact, the development immediately following Heisenberg's suggestion led first to Dyson's formula (4) for the S matrix

$$S = \sum_{n} (i\hbar)^{-n} \theta \int \ldots \int V(t_1) \ldots V(t_n) dt_1 \ldots dt_n / n!. \tag{1a}$$

Here $V(t)$ is the operator of the interaction, in the interaction (or Dirac) representation, between the colliding bodies; θ signifies that the time ordered product of the ensuing expression has to be taken. The integrations have to be extended over all time. In field theory, $V(t)$ is an integral of the interaction operator over all space so that the term on the right side of (1a) contains, effectively, a space-time integral over n quartets of variables. Hence, (1a) can be written in such a way that its relativistic invariance is at once evident. Clearly, (1) is but another form of the Born series ⁽⁵⁾, i.e., the expansion of the scattering and collision amplitudes (which are essentially the matrix elements of S) into a power series with respect to the interaction operator. There is only one such power series and, even if they have different forms, two power series for the same amplitude must be equal term by term.

The principal significance of (1a) derives unquestionably from the fact that it lends itself to calculations, transformations and modifications in which the relativistic invariance is never lost sight of. However, (1a) became a milestone in another way also : it marks the renewal of the attempts to use the Born series both for the actual calculation of scattering and collision amplitudes, and also for the derivation of general theorems concerning these amplitudes. Prior to the establishment and detailed investigation of (1a), it was commonly believed that the first term of the Born series (the so-called Born approximation) may be useful for the calculation of cross sections in particularly simple cases, or that it may serve as a general orientation, that the use of the whole series would be, however, impracticable and may also yield incorrect results.

There is one particular transformation of (1a) which, though perhaps not of conceptual significance, is sufficiently important to be mentioned at this point. It represents a return from (1a) to a form more closely resembling the Born series. Since

$$V(t) = e^{iH_0 t/\hbar}\, V\, e^{-iH_0 t/\hbar} \tag{2}$$

the matrix element of $V(t)$ between two states $\psi_i = \int a(E)\, \psi(E, \alpha) dE$ and $\psi_f = \int a'(E')\, \psi(E', \alpha') dE'$ (where α refers to the quantum numbers which are needed, in addition to the energy, to characterize the state completely), becomes

$$\begin{aligned} &< \psi_i | V(t) | \psi_f > \\ &\quad = \int e^{iE' t/\hbar}\, a'(E')^*\, e^{-iEt/\hbar}\, a(E) dE dE' < E', \alpha' | V | E, \alpha >. \end{aligned} \tag{3}$$

Hence, the integration over t can be carried out and gives for the $n = 1$ term of (1a)

$$\mathrm{B}_1 = (2\pi/i) \int \delta(\mathrm{E} - \mathrm{E}')a'(\mathrm{E}')^* a(\mathrm{E})d\mathrm{E}'d\mathrm{E} < \mathrm{E}', \alpha'|\mathrm{V}|\mathrm{E}, \alpha>. \tag{3a}$$

This is the first significant term of the Born series, the so-called Born approximation. Similarly, the integrations over all the variables $t_1, \ldots, t_n$ can be carried out in the nth term and one obtains for this term the limit $\varepsilon \rightarrow 0$ of

$$\mathrm{B}_n = 2\pi i \sum_{\alpha_i}(-)^n \int d\mathrm{E}_1 \ldots d\mathrm{E}_{n-1}\, d\mathrm{E}d\mathrm{E}'\; a'(\mathrm{E}')^* a(\mathrm{E})\, \delta(\mathrm{E}-\mathrm{E}') \\ <\mathrm{E}', \alpha'|\mathrm{V}|\mathrm{E}_1\alpha_1> \\ \frac{<\mathrm{E}_1\alpha_1|\mathrm{V}|\mathrm{E}_2\alpha_2>}{\mathrm{E}_1 - \mathrm{E} - i\varepsilon}\; \frac{<\mathrm{E}_2\alpha_2|\mathrm{V}|\mathrm{E}_3\alpha_3>}{\mathrm{E}_2 - \mathrm{E} - i\varepsilon} \cdots \frac{<\mathrm{E}_{n-1}\alpha_{n-1}|\mathrm{V}|\mathrm{E}\alpha>}{\mathrm{E}_{n-1} - \mathrm{E} - i\varepsilon}. \tag{4}$$

The expression $<\psi_i|\mathrm{S}-1|\psi_f> = \Sigma \mathrm{B}_n$ is called the Lippman-Schwinger series.(6) The individual terms B_n for which (4) gives a convergent result are relativistically invariant if V is the interaction of a relativistic field theory, but this is not evident any more in the form (4).

Heisenberg's suggestion to calculate the S matrix without considering the process of collision in detail was realized more nearly by the dispersion theoretic approach.(7) This was considered, in some detail, at last year's conference, Goldberger and Mandelstam having been the main reporters. Since that time, we have learned a great deal more about the Regge poles, which are also an outgrowth of dispersion theory. The subject has been summarized so often that I feel a bit embarrassed to give yet another review.

The most symmetric coordinates for the description of a collision are the four-momenta of the colliding particles and the *negative* four-momenta of the particles *resulting* from the collision. In collisions of two particles which result again in two particles, there are four such momenta which may be denoted by p_1, p_2, p_3, p_4. The time components of two of these are positive, those of the other two negative. The sum of the four-momenta

$$\Sigma p_i = 0 \tag{5}$$

because of the conservation laws for linear momentum and energy. Because of its relativistic invariance, S depends only on the invariants which can be formed from the p_1. Because of (5) and

$$p_i{}^2 = m_i{}^2, \tag{6}$$

where m_i is the mass of the particle i, there are two independent invariants. (The square of a four-vector will always denote its Lorentz product with itself.) The most symmetric set of invariants are the Lorentz-lengths of the four vectors which contain two of the p_i with positive, two with negative, sign. It is customary to write

$$[(p_1 + p_2 - p_3 - p_4)/2]^2 = (p_1 + p_2)^2 = (p_3 + p_4)^2 = s \quad \text{(6a)}$$

$$[(p_1 - p_2 + p_3 - p_4)/2]^2 = (p_1 + p_3)^2 = (p_2 + p_4)^2 = t \quad \text{(6b)}$$

$$[(p_1 - p_2 - p_3 + p_4)/2]^2 = (p_2 + p_3)^2 = (p_1 + p_4)^2 = u. \quad \text{(6c)}$$

The three invariants s, t, u are not independent but obey the identity

$$s + t + u = \Sigma m_i^2 \quad \text{(7)}$$

The s, t, u are the variables used most conveniently to formulate the dispersion relations. If the p_i are the four four-vectors of an actual collision, one of the variables s, t, u is positive, the two others negative. If p_1 and p_2 are the four-momenta of the colliding particles, s is the positive one and gives the square of the energy in the center of mass coordinate system $(p_1{}^0 + p_2{}^0)^2$; t and u are negative squares of differences between final and initial momenta so that one of these is the square of the " momentum transfer ".

In order to formulate the dispersion relations, the definition domain of S(s, t, u), in which s, t, u are real and obey the preceding equations, is extended to all complex values of its variables. The dispersion relations are then postulates concerning the region of analyticity of S and its behavior as s, t or u go to infinity. In addition, S must be unitary for physically possible s, t, u, i.e., for real s, t, u which satisfy the aforementioned requirements. It is surmised that these postulates, coupled with some information concerning the low or high energy (s, t, or u) behavior of S suffice to determine S completely.

Since we are interested principally in the low energy (that is, non-relativistic) behavior of the scattering cross sections, it is not necessary to use the full apparatus of dispersion theory and Mandelstam representation to obtain significant results. The variables commonly used for describing low energy scattering are the wave number k, giving the kinetic energy $\hbar^2k^2/2\mu$ in the center of mass system (μ is the reduced mass of the colliding particles) and the momentum transfer p, giving the scattering angle ϑ by $p = 2k\hbar \sin \vartheta/2$. Hence, one can write

$$S(\vec{k}, \vec{k}') = \delta^3(\vec{k} - \vec{k}') + \delta(E - E')S(k, p). \tag{8}$$

The postulate of the dispersion theory is, then, that for fixed, real p, the scattering function $S(k, p)$ is analytic in the upper half plane of the complex variable k, except that it can have poles on the imaginary axis corresponding to possible bound states. Further, $S(k, p)$ tends to the same value $S_1(p)$ no matter how k tends to infinity in the upper half plane. The limit, $S_1(p)$, is given by the first term of the Born series. One has, further,

$$S(k, p) = S(k, -p) = S(-k^*, p^*)^*. \tag{8a}$$

If there are no bound states, it follows from the behavior of S in the upper half plane that

$$\begin{aligned} S(k, p) &= S_1(p) + \frac{1}{\pi i} \, P \int \frac{S(k', p)}{k' - k} \, dk' \qquad (9) \\ &= S_1(p) + \frac{1}{\pi i} \int_0^\infty S(k + x, p) - S(k - x, p) dx/x \end{aligned}$$

where $P\int$ denotes a principal value integral which is to be extended from $-\infty$ to ∞. Its meaning is evident from the second line of (9). Together with the requirement that S be unitary, (9) suffices to determine $S(k, p)$ if $S_1(p)$ is known. Gell-Mann has given a method to construct $S(k, p)$ from $S_1(p)$ on the basis of (9) and the unitary condition.(8)

Actually, (9) has been proved only for two particular types of potentials : (a) those which decrease with increasing distance faster than any exponential (9), and (b) for a sum of Yukawa potentials with arbitrary ranges and strengths.(10) It is known that (9) is not valid for certain other potentials.(11) It should be possible, however, to approximate any reasonable potential by a potential of the type (a) or (b) so that (9) should be of practical usefulness. To my knowledge, however, no practical use has been made of (9) in actual calculations of atomic collisions (12) so that we lack practical experience in the use of this relation.

The third important development of a conceptual nature is Regge's theory of complex angular momentum. The relation of this theory to the Mandelstam representation is not yet quite clear and, for reasons which will become evident, I wish to postpone its discussion to the next section. This section will deal with a semi-phenomenological theory in which I was very greatly interested some years ago and on which I wish to relate a few new results. Some of these are elaborations of Regge's theory.

II. R-MATRIX THEORY

R-matrix theory (13) describes collisions in configuration space. It is necessary to subdivise this space into two regions: the so-called inner and external regions. In the latter, the colliding particles or the separating reaction products are either not interacting with each other any more, or their interaction can be described by a potential. The wave function and its normal derivative can be developed on the surface dividing internal and external regions into a set of orthogonal functions ψ_c; the expansion coefficients will be denoted by v_c and d_c. The R matrix, which is a function of the energy, gives the linear relation between these sets of quantities

$$v_c = \sum_{c'} \mathrm{R}_{cc'} d_{c'} \; . \tag{10}$$

The orthogonal set ψ_c is so chosen that it describes a definite pair c of colliding or separating particles. As a result, the wave function in the external region becomes

$$\Psi = \sum_{c} r_c^{-1}[a_c \mathrm{I}_c(r_c) - b_c \mathrm{O}_c(r_c)]\psi_c \tag{11}$$

where I_c and $\mathrm{O}_c = \mathrm{I}_c^*$ are incoming and outgoing waves in the " channel " c; they depend on the energy and on the separation r_c of the pair c. The factor r_c^{-1} is introduced so that the condition that the radial functions I_c and O_c carry unit flux have the simple form

$$\mathrm{I}_c \frac{d}{dr_c} \mathrm{O}_c - \mathrm{O}_c \frac{d}{dr_c} \mathrm{I}_c = \frac{2im_c}{\hbar} \tag{11a}$$

where m_c is the reduced mass of the pair c. The first essential equation of the theory is then the expression for the collision matrix

$$\mathrm{S} = (\mathrm{I} - \mathrm{I}'\mathrm{R})(\mathrm{O} - \mathrm{O}'\mathrm{R})^{-1} \tag{12}$$

valid in this simple form if the surface between internal and external regions is so located that the wave function already vanishes at this surface in closed channels.(14) The I, I′, O, O′ are diagonal matrices; the diagonal elements of I are $I_c(a_c)$ where a_c is the separation of the pair c at the surface dividing internal and external regions and I′, O = I*, O′ = I′* are similar matrices with diagonal elements dI/dr_c, O, dO/dr_c, all at $r_c = a_c$. The second essential equation of the theory is the expression for the elements of the R matrix

$$R_{cc'} = \sum_{\lambda} \frac{\gamma_{\lambda c}\ \gamma_{\lambda c'}}{E_\lambda - E} \tag{12a}$$

where the $\gamma_{\lambda c}$ and E_λ are energy independent constants, the so-called reduced widths and resonance energies.

R matrix theory has two principal weaknesses. The first of these is the necessity to introduce a largely arbitrary dividing surface between internal and external regions. Since the constants $\gamma_{\lambda c}$ and E_λ depend to some extent on the location of this surface, they are not truly characteristic of the collision system. This dependence of the $\gamma_{\lambda c}$ and E_λ on the surface is, naturally, compensated by the dependence of the I, I′, O, O′ in (12) on the a_c since S does not depend on the surface. The second weakness became evident when the dispersion relations were developed. These are sharper conditions on the analyticity of S than can be obtained from R matrix theory.(15) The reason is that the collisions are described, in dispersion theory, by energy (or wave number k) and momentum transfer p, whereas R matrix theory is formulated in terms of energy (or k) and angular momentum. The validity of dispersion theoretic relations made it evident that there must be interrelations between the E_λ and $\gamma_{\lambda c}$ for various angular momenta. However, prior to Regge's work, there appeared no means to discover such interrelations.

As to the first problem, the results of the arbitrariness of the surface dividing internal and external regions, there is no complete answer. Several attempts (16) have been made to eliminate this arbitrariness, but they have achieved only partial success. However, the investigation of this problem has led to a precise formulation of the so-called sum rules (17) which appeared only as an approximate relation in earlier calculations

$$\sum_{\lambda}\Bigl(\sum_{\mu\neq\lambda} \frac{(\gamma_{\lambda c'}\gamma_{\mu c''} + \gamma_{\mu c'}\gamma_{\lambda c''})\gamma_{\lambda c}\,\gamma_{\mu c}}{E_\mu - E_\lambda}\Bigr) = \frac{\hbar^2}{2m_c}\,\delta_{cc'}\ \delta_{cc''}. \tag{13}$$

The detailed derivation of (13) will be published elsewhere. It shows a certain similarity to the Born-Heisenberg-Jordan formulation of the Reiche-Thomas-Kuhn sum rules inasmuch as the sum on the left is conditionally convergent and contains oppositely equal terms. Hence, if the order of summation is reversed, i.e., if one sums first over λ, then over μ, the result is oppositely equal to the right side of (13). Similarly, the commutation relation $pq - qp = \hbar/i$, which was derived from the optical sum rule, gives a non-zero (in fact infinite) value to the trace of a commutator which also contains pairs of oppositely equal terms. The point which is remarkable about (13) is that it is valid for all locations of the aforementioned surface in configuration space. It may be worthwhile to repeat here the equations which give the dependence of the constants E_λ, $\gamma_{\lambda c}$ on the location of the dividing surface, as characterized by the a_c. These are

$$\frac{\partial E_\lambda}{\partial a_c} = \frac{2m_c}{\hbar^2}(V_c - E_\lambda)\gamma_{\lambda c}{}^2 \tag{13a}$$

where V_c is the potential energy acting between the pair c at $r = a_c$ and

$$\frac{\partial \gamma_{\lambda c'}}{\partial a_c} = -\frac{m_c}{\hbar^2}\gamma_{\lambda c'}\gamma_{\lambda c}{}^2 + \frac{2m_c}{\hbar^2}(E_\lambda - V_c)\sum_{\mu \neq \lambda}\frac{\gamma_{\lambda c}\gamma_{\mu c}\gamma_{\mu c'}}{E_\mu - E_\lambda}. \tag{13b}$$

The second point which I wish to mention is a generalization of the R matrix formalism which appears to be relevant also for Regge's theory.(18) This will be sketched only for the one-dimensional case, i.e., for pure scattering. Let us consider the *double* characteristic value problem

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V\right)\psi = Ev^2\psi + Lw^2\psi\,. \tag{14}$$

In the application of the method which one has in mind, $v = 1$, $w = 1/r$, $L = -(\hbar^2/2m)\,l\,(l+1)$. The only relevant limitation of the development which follows from the mathematical point of view is that E and L are the coefficients of positive definite self-adjoint operators; ψ is a function of r but depends also on E and L. The essential point is that, if we again define R by (10), that is, in the present case as the reciprocal logarithmic derivative of ψ at $r = a$, the expansion (12a) remains valid for E (even though its coefficient is not 1 but v^2) and a similar expansion is valid in terms of L. In order to obtain this result, one has to modify the derivation of (12a) but slightly. One defines X_λ by the equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V - Lw^2\right)X_\lambda = E_\lambda v^2 X_\lambda \tag{14a}$$

and the boundary condition $(d/dr)X_\lambda = 0$ which is supposed to leave v and w self-adjoint. The vX_λ are then the characteristic functions of a self-adjoint operator $v^{-1}Qv^{-1}$ where Q is the operator on the left of (14a) which is, however, a function of L. If this has only a discrete spectrum, any function, and in particular $v\psi$, can be expanded in terms of the vX_λ. If $v^{-1}Qv^{-1}$ has also a continuous spectrum — this is the case if $L > \hbar^2/8m$ in the example mentioned after (14) — an integral has to be added to the usual linear sum of characteristic functions. However, we shall disregard here this possibility. The expansion coefficients b_λ of the vX_λ in the expansion of $v\psi$ then can be obtained by the usual manipulation of (14) and (14a) and become

$$b_\lambda = \left(\frac{\hbar^2}{2m}\right)^{1/2}\frac{\gamma_\lambda}{E_\lambda - E}\left[\int|vX_\lambda(r, L)|^2 dr\ \right]^{-1/2}\frac{d}{dr}\psi(a, L). \tag{15}$$

The factor in the brackets is necessary because we have not normalized the X_λ. The $\gamma_\lambda{}^2$ are the reduced widths of the usual theory; they are given by

$$\gamma_\lambda(L) = \left(\frac{\hbar^2}{2m}\right)^{1/2}\frac{X_\lambda(a, L)}{[\int|vX_\lambda(r, L)|^2dr]^{1/2}}. \tag{15a}$$

Hence,

$$R(E, L) = \sum_\lambda \frac{[\gamma_\lambda(L)]^2}{E_\lambda(L) - E} \tag{16}$$

so that, for real L, the R(E, L) is an R function of E. Similarly,

$$R(E, L) = \sum_\lambda \frac{\beta_\lambda(E)^2}{L_\lambda(E) - L} \tag{17}$$

and R(E, L) is also an R function of L for real E. Furthermore, since, when deriving (17) one uses the same X_λ as when (16) was derived,

$$E_\lambda[L_\lambda(E)] = E \quad \text{or} \quad L_\lambda[E_\lambda(L)] = L \tag{18}$$

for all E and L respectively. Similarly

$$\gamma_\lambda(\mathrm{L})[\int |v\mathrm{X}_\lambda(r, \mathrm{L})|^2 dr]^{1/2} = \beta_\lambda(\mathrm{E}_\lambda(\mathrm{L}))[\int |w\mathrm{X}_\lambda(r, \mathrm{L})|^2 dr]^{1/2} \qquad \text{(18a)}$$

and there is a similar relation in which E and L are interchanged

Equation (18) simply means that the poles of R occur for the same E, L combinations in both expansions (16) and (17). Similarly, (18) gives the relation between the residues of R, depending on whether they are considered as functions of E or L. There are some further interesting properties of $\mathrm{E}_\lambda(\mathrm{L})$ and of $\mathrm{L}_\lambda(\mathrm{E})$ which will not be discussed, however. What one would like to obtain is, of course, a joint expansion of R in terms of E and L of which (16) and (17) are specializations. This does not seem to be quite easy, however. Such an expansion might well give the relation between the R(E) for different L, the absence of which was mentioned as the second failing of R matrix theory. At any rate, the preceding discussion can be amplified considerably and shows that at least some of the properties of the complex angular momenta of Regge are shared by a great variety of other parameters.

The question naturally arises concerning the minimum information, in two-particle scattering, which determines all the scattering cross sections. This question was solved, from one point of view, already by Levinson, Jost and Bargmann (19) who showed that if there are no bound states, the scattering cross section for any single angular momentum already determines the interaction potential. The situation is only slightly more complicated if there are bound states. Once the potential is determined, the scattering for any angular momentum can be obtained. The opposite question, that of obtaining the potential if the phase shifts for all angular momenta but only a single energy are given, was first raised and partially answered by Wheeler.(20) The result recently obtained by Regge (21) in this connection is truly surprising : the scattering cross sections, for every value of the energy and angular momentum, are determined once the phase shifts for a single energy and any infinite arithmetical series of angular momenta are given. It is most unlikely that this follows from R matrix theory, even if it is extended in the way indicated. The reason is, probably, that R matrix theory remains valid if the interaction cannot be described by a potential but is a more general integral operator. Regge's result is, most likely, conditioned on a potential type interaction, i.e., an interaction operator which commutes with the position operators.

III. METHODS AND APPLICATIONS

By methods of collision theory one means approximation methods which then can be applied to specific problems. It is almost tautological to say that no approximation method is perfect and it is usually not difficult to find a case in which it fails grossly. What is surprising, rather, is the wide applicability of approximation methods and the often almost uncanny instinct which some physicists have in the choice of these methods.(22) Some of the methods to be discussed were suggested by the mathematical structure of the basic theory, some were designed to meet particular conditions. There are three principal areas in which collision theory plays a decisive role : atomic collisions, nuclear collisions, and collisions between " elementary particles ". Methods have been developed to meet the conditions in each of these fields. These methods have found, however, applications also outside the area of their origin.

The choice of approximation methods to be discussed in a short review may be as difficult as the choice of a method suited to a particular problem. I am well aware that my discussion will appear dilettantish to those who have worked with the method under discussion. However, before proceeding with the discussion, it may be well to make another remark.

As a result of the development and increasing use of computing techniques, the straight two-particle scattering problem, for a definite angular momentum, can be solved for any definite angular momentum with sufficient accuracy. This assumes, of course, that the interaction between the particles is known. Hence, the only significant two-particle problem which remains concerns the high angular momenta and there will be some remarks on this question. The other significant problems are, then: scattering of composite, particles and transmutations. It would seem logical, then, to devote the rest of this report to these questions. However, a detailed discussion of these necessarily more specialized questions would render the remainder of this report too diffuse. Since, further, most of the points to be made can be well illustrated on simple two-body scattering, all examples have been taken from this most elementary field.

(a) The Born approximation (5)

This is the first term of the Born series, discussed before, and it is surprising how close it often comes to reality. The most noted case in point is, of course, the unrelativistic Coulomb scattering.

It should be noted, nevertheless, that the Born approximation often does give very inaccurate results. This will be the case, in general, if the actual wave function differs considerably from a plane wave. This will occur if the interaction is strong enough to distort the incident plane wave appreciably. In regions of configuration space in which the potential is strongly repulsive, the actual wave function will have a much smaller value than the plane wave. Hence, the scattering and reaction due to the interaction in these regions will be much smaller than calculated for an undistorted plane wave, that is, using the Born approximation. A strongly attractive potential affects the amplitude of the wave function less drastically and is less likely to lead to gross errors. Nevertheless, section (d) contains implicitly an example for this opposite behavior : it calculates the Born approximation for the scattering by an r^{-p} potential in order to obtain the scattering by a potential which behaves as r^{-p} at infinity but has no singularity at $r = 0$. This latter singularity does not affect the Born approximation for the higher angular momenta although it would affect the actual scattering. However, in practice, strongly repulsive potentials are much more likely to cause a failure of the Born approximation than attractive ones: they give a too-large cross section. In fact, the most common sign for the inaccuracy of the Born approximation is that it gives a very large cross section.

Whether or not the cross section is very large can be judged more easily if one uses the Born approximation for the spherical waves with definite angular momenta. In this case there is a natural measure, the maximum possible cross section $4\pi(2l + 1)/k^2$, with which to compare the approximate cross section. This is given by

$$\sigma = 4\pi(2l + 1)m^2 I_l^2/\hbar^4 k^4 \tag{19}$$

$$I_l = \int_0^\infty 2V(r)[j_l(kr)]^2 dr \tag{20}$$

the j_l being kr times the spherical Bessel functions: $j_0(kr) = \sin kr$, etc. One will expect the Born approximation to be valid or to fail, depending on whether or not $2mI/\hbar^2 k$ is small as compared with one. However, this is not a safe criterion as it seems altogether not easy to give general criteria for the accuracy of the Born approximation. Thus, the scattering in a Coulomb field in a given direction is correctly given by the Born approximation even though the integral for I diverges in this case. In this case, the total cross section is infinite and it is this circumstance that is reflected in (20) becoming infinite. On the other hand, in the case of a rapidly decreasing potential (19) is surely grossly inaccurate if $2mI/\hbar^2k$ is of the order of 1 or larger. Conversely, if $2mI/\hbar^2k$ is small, one can reasonably assume that (19) is accurate. There is one well-known exception to this : a resonance is not reproduced by (19) so that (19) surely can give far too small cross sections over narrow energy intervals.

A further point worth remembering is that, for a potential which is attractive in some, repulsive in other, regions, I, and hence the Born cross section, may well vanish for a definite k. This is a consequence of the real nature of I and is a rather general occurrence in Born approximation. The actual cross section, however, vanishes only under exceptional circumstances (23) and both theoreticians and experimental physicists have learned to view with suspicion the zeros in the cross sections, or in the angular distributions, predicted by the Born approximation and some of its generalizations.

It hardly needs to be repeated that the preceding discussion, restricted as it was to the simplest possible case, does not do justice to the immense area of applicability of the Born approximation. In fact, the principal value of Born's method may well lie in the ease with which it gives, for almost every collision problem, at least some guidance on what to expect. This is only indicated by the simplicity of the formula (19) which, however, could well serve to illustrate its strengths as well as its weaknesses.

(b) Distorted wave Born method (24)

The Born approximation becomes inaccurate if the potential modifies the wave function considerably. Thus, in the hard sphere case ($V = \infty$ for $r < a$) the Born approximation gives an infinite cross section even if a is small, so that the actual cross section is quite moderate. The reason is evident : the calculation assumes that the incident wave penetrates to $r < a$ and is very strongly scattered there. Evidently, the accuracy of the method could be improved considerably if at least the bulk of the effect of the potential could be taken into account to begin with. This is the idea of the distorted wave Born approximation.

The distorted wave method can be used to calculate scattering; more commonly it is used to calculate reaction cross sections. The scattering amplitude consists of two parts : the one inherent in the distortion, and the other due to the part of the interaction which is not taken into account by the distortion. Thus, in the aforementioned case of a hard sphere, the $l = 0$ part of the distorted wave would be $\sin k(r - a)$ for $r > a$, and this would completely describe the effect of the hard sphere. However, if the potential extended beyond the $r = a$ point, this could be taken into account approximately by the first term of the power series development of the solution of the wave equation, in terms of the residual potential.

The most important areas of applications of the distorted wave method are, however, problems of reaction and transmutation. When calculating these, it is important not to permit the incident wave to have a considerable amplitude in regions of configuration space where the interaction causing the reaction is strong but where the incident wave can hardly penetrate. If one wants to preserve symmetry between initial and final state (and hence preserve the principle of detailed balance), not only the wave function of the colliding particles but also that of the reaction products must be distorted, that is at least crudely adjusted to the prevailing potential.

The method as described in the preceding paragraph assumes that the interaction can be separated into a part which modifies the wave function of the colliding particles (and may have a similar effect on the wave function of the reaction products) but does not affect their identity, and another part which is responsible for the reaction or transmutation processes. The simplest way to obtain an expression for the first part of the interaction is to calculate its expectation value for the wave function of the colliding particles (or of the reaction products) as function of their distance and use this expectation value as distorting potential. The starting point for the Born series is, then, the scattering wave function in this potential. From what was said about the hard sphere case it should be evident that this will give a considerable improvement over the undistorted wave method and will be, in fact, a good approximation if the second part of the interaction, leading to reactions, does not modify the wave function seriously.

If the wave function is considerably modified by the part of the interaction which leads to reaction or transmutation, it may be possible to bar the incident particles from the region which they cannot reach, because they are transmuted before, by introducing an absorptive (complex) potential. This is a rather customary procedure in nuclear physics and has proved very fruitful.(25) However, no motivation from first principles seems to be available.(26) It is clear, in particular, that there must be a consistency condition between the magnitude of the absorptive part of the distorting potential and the result of the subsequent calculation of reaction probability. Similarly, in order to preserve the principle of detailed balance, the reaction products should also move in a complex potential. Consistency conditions of this nature have been applied in the past only sparingly and it is even customary to treat the distorting potential as an adjustable quantity. This is justifiable if one wishes to obtain a first orientation, but not in a definitive theory.

The distorted wave Born approximation has played an important role in the theory of atomic collisions much before its recent use for nuclear phenomena. In particular, Zener's calculation (27) of the excitation of vibrations in molecules by atomic impact is based on this method, as are also various modifications and refinements of his work. In this case, the method seems to give satisfactory results which is, unquestionably, at least in part due to the fact that the cross sections are small, i.e., the transfer of translational energy to vibrations is often a notoriously slow process. However, the distorted wave Born method has been used also to calculate the excitation of rotational degrees of freedom and applied also to some other processes to which it is, probably, less applicable. It is almost as easily handled as the straight Born approximation and is unquestionably more accurate. The report of O.K. Rice reviews these applications.

(c) **Classical path, quantum interaction**

This is, in fact, a variant of the previous method, based on the fact that in many cases the motion of the colliding bodies can be better described by classical theory than by a crude approximation to the solution of the distorted wave equation. Recently, this method, originally devised for describing chemical processes (28) has been applied with great success to transmutations occurring in the course of heavy ion collisions.(29)

If the paths of two atoms cross at a reasonable distance and with sufficient relative velocity so that the energy transfer cannot be expected to affect the paths substantially, the paths can be calculated by means of classical theory with reasonable accuracy. One then obtains the interaction operator affecting the internal coordinates of the two atoms as function of their position or, on the basis of the preceding calculation, as function of time. The transitions caused by this time-dependent interaction can then be calculated by means of first order perturbation theory.

The method is particularly adapted to calculate electronic excitations or vibrational or rotational transitions. The use of classical theory for the calculation of orbits is unquestionable if the impact parameter is so large that the orbits could be traced out by the motion of wave packets. In order to have appreciable transition probabilities in spite of large impact parameters, the interaction energy must decrease slowly with increasing distance of the particles. This condition is satisfied most accurately if one of the particles is charged and its field, varying at the site of the other particle, induces transitions therein. The calculation of this effect is probably the most important application of the method in the theory of heavy ion collisions. However, it can be expected also to give a good description of the collision excitation of molecules with dipole moments.

(d) **The WKB method**

This method is intermediate between the distorted wave Born approximation and the preceding method, inasmuch as it takes the quantum character of the motion of the colliding particles at least approximately into account. The principles of the method, as usually applied (30), are probably too well known to need further comment. There is a number of subtle points in connection with the replacement of $l(l+1)$ by $(l+1/2)^2$ and the behavior of the wave function near the classical turning point. I would like to call attention, however, to a modification of this method, using the semi-classical distribution function.(31) It is possible, apparently, to avoid some of the ambiguities in this way. However, as far as known to me, the method has been applied so far only to two-body scattering.

There is a remarkable difference between the classical and the quantum theory of scattering which has not been much emphasized, perhaps because it has no obvious visualization. In classical theory, the cross section is always infinite if the forces have an infinite range, no matter how fast they go to zero with increasing distance. The reason is that two particles, no matter at what distance they pass by each other, suffer some deflection. Hence, the cross section is always infinite for very small scattering angles, and it is often infinite also (32) for a scattering angle π. In quantum mechanics this is not the case; if the potential drops fast enough, the total cross section remains finite; for an even faster drop, even the differential scattering cross section at very small angles is finite. It may be of some interest to ascertain how fast the potential must drop so that these conditions are satisfied.

The total cross section is

$$\sigma_t = \sum_l \frac{4\pi}{k^2}(2l + 1)\sin^2\eta_l \tag{21}$$

where η_l is the phase shift of the partial wave with angular momentum $l\hbar$. The forward scattering cross section is

$$\sigma(\mathrm{O}) = \frac{1}{2k^2}\sum_l \left|(2l + 1)(e^{2i\eta_l} - 1)\right|^2. \tag{22}$$

Hence, since at any rate $\eta_l \to 0$ for large l, the total cross section will be finite if the series $\Sigma\,(2l + 1)\eta_l^2$ converges, the zero angle differential cross section will be finite if $\Sigma\,(2l + 1)\eta_l$ converges.

It is not difficult to show that, for large l, the Born approximation gives a correct phase shift. This follows essentially from the magnitude of the Born scattering cross section.

$$\sigma_l = 4\pi(m^2/\hbar^4k^4)(2l + 1)\mathrm{I}_l^2 \tag{23}$$

where I_l is given by (20). Hence, one will write

$$\sin\eta_l = -(m/\hbar^2k)\mathrm{I}_l. \tag{24}$$

If this is very small, the condition for the validity of the Born approximation is satisfied and one can prove its actual validity also more rigorously. We shall use a potential r^{-p} because the calculation is easiest for this potential. Actually, this potential gives infinite scattering, because of its singularity at $r = 0$, but it can be shown that I would be asymptotically the same for all potentials which become r^{-p} at large distances. Hence, we calculate (33)

$$\begin{aligned}\int_0^\infty \frac{[j_l(r)]^2}{r^p}\,dr &= \frac{\pi(p-2)!\,(l-p/2+1/2)!}{2^p[(p/2-1)!\,]^2(l+p/2-1/2)!}\\ &\approx \frac{\pi}{2}\left(\frac{p-2}{p/2-1}\right)(2l+1)^{-p+1}.\end{aligned} \tag{25}$$

Hence, the total cross section will be finite if the potential decreases faster than r^{-2}; the differential cross section at zero angle will be finite if it decreases faster than r^{-3}. It is interesting that, in the present case, the Born cross section is essentially correct where it is largest, namely at zero angle. Actually, for a potential which goes to zero as r^{-p}, the differential cross section at a very small scattering angle ϑ is proportional to ϑ^{2p-6} as long as $1 \leq p < 3$.

(e) Variational principles

The great accuracy of the variational calculation of discrete energy levels, particularly that of the normal state, suggests the use of this principle also for collision processes. The early investigations of Hulthén (34) and of Tamm (35) were concerned only with scattering but Lippmann and Schwinger (36) extended the method to arbitrary collision processes.

There is at least one great difference between the application of the variational principle to the calculation of the energy of the normal state and its application to obtain scattering cross sections: the sign of the error which is positive in the former case remains unknown in the latter. As a result, in the case of collisions it is, as a rule, not possible to tell which of the trial functions gave the more accurate result. This impairs the usefulness of the method to some extent : its effectiveness is so striking in many cases that it is surprising that it is not used more generally.

The problem is to find an expression for the phase shift, or the collision matrix element, or something equivalent, in terms of a trial wave function suggested by simplicity or physical intuition. This expression should be, furthermore, insensitive to deviations of the trial wave function from the accurate one. More precisely, it is demanded that the error in the wave function enter only quadratically into the error in the phase shift or collision matrix element. This can be always accomplished by adding the first correction to the original value of the physical quantity in question. The remaining error will then be of second order. Let us consider a simple scattering problem

$$(\mathrm{H} - \mathrm{E})\psi = (-\hbar^2/2m)\psi'' + \mathrm{V}\psi - \mathrm{E}\psi = 0 \qquad (26)$$

and assume that ψ assumes, for large r, the form $\sin kr + c \cos kr$. The constant $c = \tan \eta$ can then be regarded as the tangent of an angle η which is called the phase shift because, for large r, the wave function becomes proportional to $\sin(kr + \eta)$. Similarly, let us consider a trial wave function ψ_t which we hope is not too different from ψ. At large r, it should approach the form $\sin kr + c_t \cos kr$, corresponding to a trial phase shift η_t for which $c_t = \tan \eta_t$. If ψ_t is inserted into (26), the right side will not vanish; we denote it by e_t

$$(\mathrm{H} - \mathrm{E})\psi_t = -(\hbar^2/2m)\psi_t'' + \mathrm{V}\psi_t - \mathrm{E}\psi_t = e_t. \tag{26a}$$

One then easily derives the equation

$$(\hbar^2/2m)k(c - c_t) + \int_0^\infty \psi e_t dr = 0. \tag{27}$$

The integral converges because ψ_t is a solution of (26) for large r so that e_t goes to zero. One can give (27) the form

$$(\hbar^2/2m)(k \tan \eta - k \tan \eta_t) + \int_0^\infty \psi_t e_t dr = \int_0^\infty (\psi_t - \psi) e_t dr. \tag{27a}$$

Both integrals converge. The expression on the right side is indeed second order in the deviation of ψ_t from ψ so that it can be assumed to be small.

If one believes that the trial wave function is already reasonably close to the true wave function, (27a) gives directly

$$\tan \eta = \tan \eta_t - (2m/\hbar^2 k) \int_0^\infty \psi_t e_t dr \tag{27b}$$

this being correct to the second order in the deviation of ψ_t from ψ. This is the simplest and most common way to use the variational expression (27a).

If one is not ready to assume that a trial wave function of sufficient accuracy can be guessed, one can use an analysis which shows a certain similarity to the application of the variational principle to the determination of the energy of stationary states. Nevertheless, there are significant differences which render the variational principle for scattering less effective than for the determination of the energy of bound states. The principal reason for this is that the latter principle represents, at least for the normal state, a minimum principle whereas the sign of the right side of (27a) can be positive as well as negative. Similar to the trial wave function for bound states, one assumes for the scattering problem also a trial function of considerable flexibility

$$\psi_t(r) = \sin kr + c_t f(r) \cos kr + \sum_1^N t_n u_n(r) \tag{28}$$

where $f(r)$ is some function, such as $1 - e^{-\alpha r}$, which vanishes at $r = 0$ and approaches 1 at large r. The $u_n(r)$ also vanish at $r = 0$ so that ψ_t satisfies the boundary condition $\psi_t(0) = 0$. At large r, the $u_n(r)$ approach zero since these functions are square integrable and the asymptotic behavior of ψ_t becomes $\sin kr + c_t \cos kr$. The functional form of $f(r)$ and the u_n, as well as their number N, are dictated by physical intuition; the u_n are introduced to permit the trial function to approach the real Ψ also for small r.

If $\psi_t(r)$ happens to be the true ψ, both sides of (27a) will vanish. If the t_n and η_{lt} differ from the values which give the true ψ by small amounts, the two sides of (27a) will differ from zero by an expression which is second order in $\eta_l - \eta_{lt}$ and the deviations of the t_n from their real values. It is reasonable, therefore, to determine the t_n and η_{lt} by the condition that

$$\mathrm{L} = (\hbar^2/2m)k\, c_t - \int_0^\infty \psi_t e_t dr \tag{29}$$

be an extremum. This will, indeed, lead to correct equations whenever $\psi(r)$ can be expressed in the form (28) with suitably chosen t_n and η_{lt}.

If one calculates the integral in (29), one obtains terms which are second order in the c_t and t_n, something like $ac_t^2 + c_t \Sigma a_n t_n + \Sigma a_{nm} t_n t_m$. In addition, however, one also obtains linear terms in c_t and the t_n, coming from the $\sin kr$ term in (28), and even a term which is independent of the c_t and t_n. Hence, if one sets the derivative of (29) with respect to the c_t and t_n equal to zero, one obtains $\mathrm{N} + 1$ linear inhomogeneous equations for the c_t and t_n which have, in general, a unique solution. This is different from the case of the application of the variational principle to the discrete spectrum, that is to bound stationary states. This leads to homogeneous linear equations and a secular equation for E to assure the compatibility of these homogeneous equations. In the present case, of course, the energy need not be adjusted. Once the t_n and c_t are obtained, the corresponding value of $\tan \eta = c$ can be obtained by evaluating L and using (27)

$$\tan \eta = c = (2m/\hbar^2 k)\mathrm{L}. \tag{30}$$

Again, this is different from the stationary case for which the energy is obtained as $\int \psi_t \mathrm{H} \psi_t$. The calculation of the parameters (c_t and t_n in the scattering case) is in principle simpler for the scattering than for the stationary case. On the other hand, whereas one can show by the minimum principle that the addition of further terms to the trial wave function of the stationary case always improves the result (lowers the energy), the addition of further terms $t_{\mathrm{N}+1} u_{\mathrm{N}+1}(r)$, ... may render the value (30) for η less accurate. One can, of course, say that the earlier, better value was more accurate fortuitously, but the fact is that it is difficult to judge the accuracy of the η, obtained by the variational method, unless $e_t = 0$ in which case, of course, $\eta = \eta_t$ and the trial wave function was accurate.

There are other variational methods (37) which permit an estimate of the error in η. These are based on the calculation of the expression

$$\int[(\mathrm{H} - \mathrm{E})\psi_t]^2 dr \tag{31}$$

which, of course, does obey a minimum principle. However, the calculation of this expression seems to be very cumbersome, just as in the stationary case. Under certain conditions (e.g., at very low energy), the L of (29) also obeys a minimum principle.(38) In such a case, it should be on a par with the variational method for the energy of stationary states. However, no systematic theory could be developed so far to obtain general variational expressions of this nature.

Kato, and also Spruch and Kelly (37) observed that the phase shift increases if the potential is decreased (or made more negative). This suggests the use of a method similar to Bazley's (39) to obtain upper and lower limits for the phase shift, by approximating V, both from above and below, by potentials for which the scattering problem can be solved accurately. Unfortunately, there are few such potentials.

The variational method, as all other methods, was discussed in its application to simple scattering. However, most of the preceding considerations can be extended also to problems of reaction and energy transfer. Unfortunately, one often has the impression that the variational principle is used more often to demonstrate its power than to solve new problems. It is surprising how often (27b) gives a close value for η_l, even for a very simple ψ_t.

THE IMPULSE APPROXIMATION (40)

Dr. Karplus drew attention during the meeting to the impulse approximation. This approximation is particularly simple to apply to the collision of a single particle with a system of other particles, the latter forming a bound state. It was originally devised to describe the collision of a single nucleon with a complex nucleus. It could be used also to describe the collision of an electron, or of a proton, or perhaps even of an atom, with an atom or a molecule.

The impulse approximation is somewhat similar to the Born approximation inasmuch as it is particularly useful at high energies. There are n terms in the potential energy between an incident particle and a complex containing n particles. These correspond to the interactions of the incident particle with each of the particles of the complex. Each term in the potential energy gives rise to a term in the scattering amplitude of the Born approximation. This is true also of the impulse approximation, the only difference being that the terms of the Born approximation are approximate expressions for the scattering by a single particle whereas the impulse approximation uses the accurate expressions for these quantities. However in both approximations the total scattering amplitude is simply a sum of the scattering amplitudes due to the particles of the complex. One reason for this not giving the accurate value is that the incident particle can be scattered by two or more particles in succession and the second and higher members of the Born series indeed contain terms which correspond to such events. Another reason is that the particle which scattered the incident particle will continue to interact with the other particles of the complex also after having collided with the incident particle, and the impulse approximation does not take this interaction into account. In fact the properties of the bound state of the complex enter the calculation only by determining the momentum distribution of the constituents. The total scattering amplitude is the superposition of the scattering amplitudes which correspond to the momentum spectra of the constituents.

It follows from the preceding description of the impulse approximation that it can be used only if the scattering of the incident particle by the individual constituents of the complex is already known. However, if this is the case, it can be used just about as easily as the Born approximation. Unfortunately, no very detailed and conclusive discussion of the impulse approximation is available but the consensus is that it gives useful results only if the energy of the incident particle is much higher than the binding energies of the constituents of the complex. Only if this is the case, can the scattering by bound particles be treated as if they were free; as was mentioned before, the bound nature of the scattering particles manifests itself only by their having a spectrum of momenta, rather than a single momentum.

The impulse approximation has not played a significant role so far in the theories of atomic or molecular collisions.

ACKNOWLEDGMENT

I wish to express my appreciation of the friendly criticisms of Drs. Blankenbecler, Engelsberg, Goldberger and Treiman. They were most helpful.

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Discussion du rapport de M. Wigner

M. Karplus. — I should like to emphasize Prof. Wigner's reference to the way properties of the bound state are treated in the impulse approximation. Because of the binding, the single particle in the bound system which acts as target is not in a state of known linear momentum (at rest, for example). Instead it is in a superposition of momentum states, a superposition which is described by the fourier transform of the target particle's spatial wave function. The total scattering amplitude from this one target particle, then, is obtained by superposing the amplitudes which correspond to the various momenta in the momentum spectrum of the target particle, each weighted by the amplitude for occurrence of this momentum. The total amplitude for scattering by the bound system is finally obtained by adding the impulse approximation amplitudes for each of the particles in the system considered as target. As Prof. Wigner has mentioned, many other important effects of binding are neglected.

The impulse approximation in nuclear physics has been particularly useful when the momentum transferred to one target particle in the collision is large compared to the momenta in the initial distribution. In atomic and molecular problems this relationship usually does not hold.

M. Shuler. — Prof. Wigner has just given us a beautiful and lucid talk on scattering theory. As he has pointed out, all the successful applications are in the fields of quantum electrodynamics, nuclear physics and electron-atom (or molecule) scattering. As far as I know from my own work and from the literature, there have been essentially no successful applications of modern quantum scattering theory to inelastic molecular collisions such as, for instance, the dissociation reaction

$$AB + M \rightarrow A + B + M.$$

I wonder if one of the practical problems in the calculation of inelastic atomic and molecular scattering is not the absence of a convenient and reasonable expansion parameter. In most of the successful applications of scattering theory, such as scattering of electrons or photons from atoms or molecules, there is such an expansion parameter — either the mass ratio of the scattering centers (m_e/m_{atom}) or an energy ratio. I would appreciate to hear Prof. Wigner's views on that.

M. Wigner. — Perhaps in my desire to report on the general aspects on collision theory, I have underemphasized the theoretical treatment of phenomena of particular interest to our conference. As for these problems, interesting results have been obtained not only on the theory of the excitation of vibrational motion but also on the electronic excitation by atomic collisions and a number of other phenomena which I am sure will be discussed in the course of our conference.

As to the main point made by Dr. Shuler, I agree fully. Except for the very simplest systems, all successful approximation methods are based on the circumstance that some parameter or quantity is small. In addition to those enumerated by Dr. Shuler, I might call attention again to the case in which the only process of high probability is that of scattering. Furthermore, it may be possible to treat this accurately. All the other processes, such as vibrational or electronic transitions, are then unlikely and their probability is effectively Dr. Shuler's small parameter. I realize that I have now restated the conditions for the validity of two of the approximation schemes which I discussed : the distorted wave Born approximation and the classical path, quantum interaction method. However, the validity of the other approximation methods, with the possible exception of that of the variational method, can also be shown to depend on the small value of some parameter.

As to Dr. Shuler's first question, it is true that the most recent theoretical treatment of the association reaction with which I am familiar, that of Keck, is not based on collision theory, but uses the transition state method. As a matter of fact, I consider it the main result of the transition state method that it shows that rate processes can be calculated without a detailed description of the collisions. This was so far possible only in classical, that is non-quantum, theory and quantum effects could be taken into account only approximately. Theoretically, this is a serious limitation in our treatment of association reactions. In practice, the limitation is less significant because quantum effects are, as a rule, not very important in association reactions.

M. Widom. — The Born series goes in inverse powers of Planck's constant. One knows the practical usefulness, however, of expressions for the cross-section which go in increasing powers, the leading term of which is the classical theory. The question then arises, whether the analytical properties of such series might not lead to results which sumplement in a valuable way the conclusions based on the analytical properties of the Born series.

M. Wigner. — Dr. Widom's suggestion seems to me to be a very interesting one. As a matter of fact, some hint in the direction which he mentions is contained in the written report which I presented, even though I omitted this part in my verbal presentation. $\hbar^2$ is the coefficient of a positive definite operator in the Hamiltonian so that some of the remarks contained in the section on R matrix theory apply to it. However, this point has not been worked out to date. Further, lest too much significance be attributed to the considerations in my report to which I am referring, I wish to re-emphasize that the behavior of S in the complex plane at infinity, which plays such an important role from the point of view of the dispersion relations, does not follow from R matrix theory.

SHOCK TUBES
FOR HIGH TEMPERATURE GAS KINETICS

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SUMMARY

The adaptation of the shock tube to the production of high temperature gases has provided a powerful tool for the study of gases at temperatures beyond those obtainable in furnaces. The essential advantages of shock tubes over electrical discharge devices is the capability to produce a homogeneous gas sample (HGS) with enthalpy and pressure which can be dependably calculated from the measured shock velocity and the conservation laws. This paper is concerned with setting forth the variety of conditions which can be reached and the precision and dimensions of the HGS which can be produced. Diaphragm type shock tubes are capable of heating gases to temperatures sufficient for the study of all chemical reactions and many electronic processes. The enthalpy and pressure of the gas sample can be calculated from the conservation laws with precision falling from 1 to 10% as we move from lower to higher temperatures. Knowledge of the gas state in shock tubes has allowed the development of numerous diagnostic devices and their application to a tremendous variety of problems in gas kinetics.

The advent of electromagnetically driven shock tubes opens up the possibility of achieving similar advantages at temperatures up to millions of degrees. An assessment is made in this paper of the

degree to which an HGS has been produced in this temperature range. It is concluded that in some cases evidence exists for this achievement. This will accelerate the study of very energetic excitation and ionization phenomena. It will also contribute to the study of completely ionized plasmas in which at high temperatures, collisions become a very rare process. The understanding of collision free plasmas is basic to astrophysics and to the design of thermonuclear fusion reactors.

I. INTRODUCTION

It was first pointed out by Vieille (1899) that waves moving faster than the speed of sound could easily be created in straight tubes by bursting a diaphragm separating regions of high pressure, driver, gas and low pressure, reagent, gas. Payman and Shepherd (1946) used a similar device, which has since become known as a shock tube, to study the aerodynamics of shock waves. During and subsequent to the war, shock tubes received considerable development as an instrument for the study of the aerodynamics and diffraction effects of shock waves and as an economical substitute for transonic and supersonic wind tunnels. In the work of Bleakney and his co-workers (1949), the shock tube was refined to a precision instrument for aerodynamic research (see monograph by Wright 1961, also Glass and Hall, 1959).

The adaptation of the shock tube to the production of high temperature gases for study was begun about a decade ago in the laboratories of Laporte (Hollyer *et al.*, 1953) at the University of Michigan and the present author at Cornell (Resler *et al.*, 1952). This work was based on the observation that using high pressure ratios across the diaphragm combined with large ratios of the driver to the reagent speed of sound made it possible to reach very high temperatures (e.g., 18,000 °K) while retaining many of the advantages of the aerodynamic shock tube. Since this work, the high temperature shock tube has received extensive development for the study of the kinetics of gases. This has been greatly stimulated by the need for such information in the design of vehicles to re-enter the earth's atmosphere from velocities up to and exceeding the satellite velocity. The most comprehensive review of gas kinetics results in shock tubes was made by Losev and Osipov (1961) who give a bibliography of 191 papers. The present paper will not attempt to review the results but rather will attempt to exhibit the variety of gas conditions which can be produced in a shock tube and to assess the precision with which high temperature shock tubes have produced a homogeneous gas sample HGS with enthalpy and pressure calculable from the shock velocity measurement.

The shock tube is unique in its ability to create a homogeneous sample of gas which has been suddenly heated to an enthalpy and pressure calculable (Section II) from the undisturbed gas state, the measured shock velocity and the laws of conservation of mass, momentum and energy. The homogeneity of the gas sample produced (Section III) is limited by the boundary layer along the tube walls and by the accuracy with which the shock speed remains constant. The HGS, is in high temperature shock tubes usually only a fraction ($\sim 1/2$) of the reagent gas which has passed through the shock. The interface between the driver and HGS is usually turbulent and the onset of this turbulent region (which has absorbed part of the heated reagent gas) can usually be easily identified. When the HGS has extended to a tube diameter or more the shock is not disturbed by the turbulent region and typically becomes very plane and normal to the tube walls. The achievement of a plane shock followed by a homogeneous gas sample is essential for the validity of the conservation law calculation of the gas state. Much confusion in the literature, particularly in electric and electromagnetic shock tubes, has resulted from investigations in which this demonstration has not been performed.

The use of hydrogen drivers is capable of producing high temperatures, e.g., in argon up to 12,000 °K and, thus, this type of device has been most useful in studies of chemical kinetics. Reflection of the shock from the closed end of a shock tube produces a gas with about twice the enthalpy available following the incident shock (15,000 °K in Argon). However, the extent and precision of the HGS is sometimes much reduced in this case by boundary layer effects (Mark, 1957). The maximum gas enthalpy available in shock tubes can be increased by increasing the speed of sound of the driver gas and, therefore, considerable effort has been devoted to producing shock tube drivers with sound speeds above room temperature hydrogen. These methods will be discussed in Section IV and include the admixture of oxygen and helium and ignition which can be used to increase the driver sound speed by 75%. Numerous proposals have also been made to heat the driver gas by adiabatic compression and by shock waves. The highest shock speeds (1.3 cm/μsec) achieved with diaphragm type shock tubes are produced by heating the driver gas with an electric discharge from a condenser bank. These drivers are capable of achieving more than an order of magnitude higher gas enthalpies than H_2 with some sacrifice of precision and the length of the HGS.

Lord Rayleigh (Fowler *et al.*, 1951) observed that the production of a sudden electric discharge in a glass vacuum system frequently produced brilliantly luminous shock waves which travelled down the tubing connecting the discharge tube with the pump. Fowler and his co-workers have exploited this phenomenon to produce a so-called electric shock tube which has the important advantage of not requiring diaphragm replacement between runs. Many attempts have been made to construct shock tubes in which the driver gas is a portion of the reagent gas heated by an electrical condenser bank discharge. To achieve high shock velocities it has been necessary to operate close to the discharge (because of rapid driver cooling) rather than the hundred or more tube diameters downstream characteristic of diaphragm shock tubes. The inevitable inhomogeneities in driver sound speed produce violent turbulence as the gas expands into the low pressure region. Until the turbulence level subsides below a critical value no HGS is created. No case of electrically heated shock tube drivers (without diaphragms) in which this turbulence had been supressed or an observable HGS produced has come to the author's attention. In these cases no information on the state of the gases in the shock vicinity can be calculated from the measured shock velocity sacrificing the essential advantages of the shock tube over electric discharges for the production of high temperature gases for study.

The acceleration of rarefied gases (plasmas) by electromagnetic forces is capable of producing very high plasma velocities (Bostick, 1956). Various people, Colgate (1957), Kolb (1957), Janes and Patrick (1958), etc. have suggested that the moving plasmas produced in this way could be used to drive very high speed shock waves. To realize this possibility and preserve the validity of the conservation law calculation of the gas state, i.e., produce an HGS, it is necessary that the driver gas electromagnetically shield the reagent gas from the heating and disturbing effects of the driving currents. A resultant lower bound to the minimum shock tube length necessary for the appearance of an HGS is estimated for various gases as a function of temperature in Section V. Satisfaction of this requirement is feasible for a one meter shock tube in hydrogen at temperatures $> 20{,}000\,^{\circ}K$. Apparently only Patrick's Magnetic Annular Shock Tube (MAST) experiments satisfy this requirement. At temperatures greater than about a few electron volts increases in diffusion speed necessitate the use of containing magnetic fields and these have been incorporated in the MAST. There is evidence that he has produced shock velocities up to 60 cm/μsec and an HGS with enthalpy corresponding (after equilibration) to temperatures beyond $10^6\,^{\circ}K$. The extension of the shock tube to the plasma region where particle collisions become infrequent and other dissipative mechanisms must be explored, opens an exciting area for study.

II. IDEALIZED SHOCK TUBE OPERATION *

The construction of a pressure driven diaphragm type shock tube is illustrated schematically in Figure 1 (*a*). It consists essentially of a high pressure driver and a low pressure chamber separated by a thin diaphragm. The burst diaphragm flattens against the tube walls very rapidly when the material is highly stressed prior to rupture. After the material bursts, a compression wave which rapidly steepens to form a shock moves into the low pressure gas. Simultaneously an expansion wave moves into the high pressure gas and broadens with time. The surface separating the two gases is called a contact discontinuity. Generally the "contact discontinuity" broadens out into a region in which the gases are mixed by the turbulence produced during the diaphragm burst. The conventional method of representation of the flow is shown in the distance-time, x-t diagram of Figure 1 (*b*). In this diagram the waves created by the diaphragm burst can be traced in time. Figure 1 (*c*) shows a typical pressure distribution along the tube at the instant of bursting and at a time t_1 later.

It can be made clear from a rough calculation of the enthalpy of the gas behind the incident and reflected shock waves [regions 2 and 5 of Fig. 1 (*b*)] that very high temperature gases can be produced in a shock tube. For simplicity the limiting case of infinite pressure ratio across the diaphragm will be considered first. It is known from the usual theory ** (Courant, *et al.* 1948 and Kantrowitz,

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* This section follows Resler, E.L., Lin, S.C., and Kantrowitz, A. (1952) closely.

** Applying Newton's second law of motion $F = m du/dt$ to a one-dimensional fluid element of thickness dx under the action of a sound wave travelling at velocity a, we get (p = pressure and ρ = density)

$$-dp = \rho dx \frac{du}{(1/a)dx} = \rho a du.$$

The isentropic law can be written

$$\frac{dp}{p} = \frac{C_p}{R}\frac{dT}{T} = \frac{2C_p}{R}\frac{da}{a};$$

by combining these equations with $a^2 = \gamma p/\rho$ we get

$$\frac{2\,C_v}{R} da + du = \frac{2}{\gamma - 1} da + du = 0,$$

which integrates to $(2/\gamma - 1)\, a + u = \text{constant} = P$.

1958) of one-dimensional wave propagaiton in perfect gases with constant heat capacity that the quantity $P = (2/\gamma - 1)\, a + u$ is

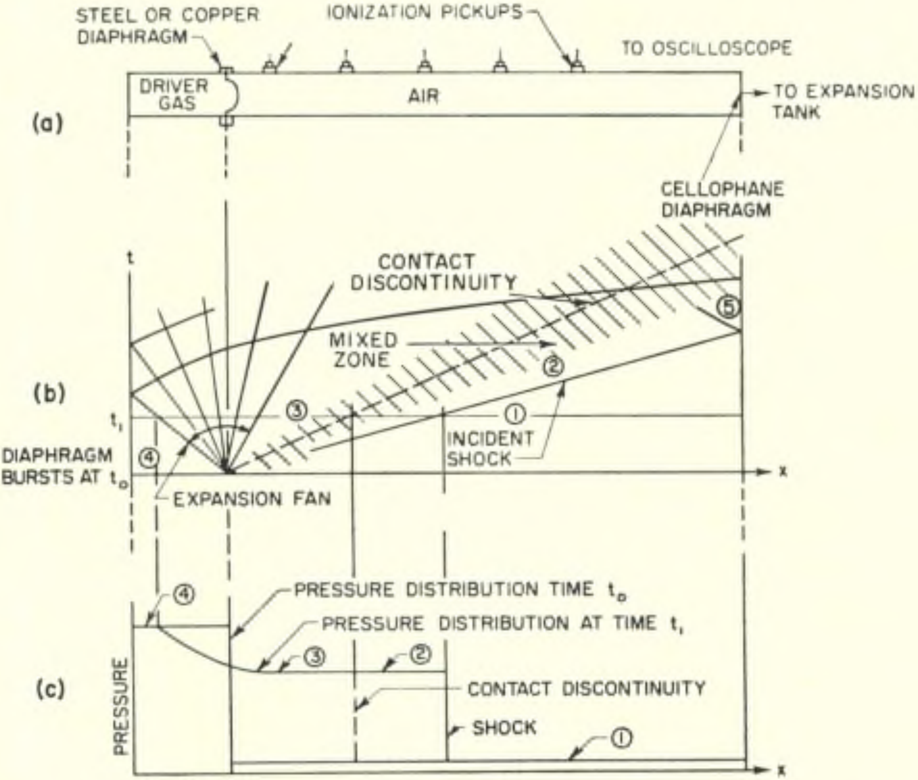

Fig. 1. — (*a*) Schematic drawing of a conventional shock tube. (*b*) *x*-*t* diagram showing the progress of shock and expansion waves following the diaphragm burst. The gases which were originally in the high and low pressure portions of the shock tube are separated by the contact discontinuity. The expansion fan reflects from the back end of the driver and eventually overtakes and decelerates the shock. The driver must be made long enough so that this effect does not reduce the HGS. (*c*) The pressure distribution along the shock tube at times t_0 and t_1.

constant across the simple isentropic wave between regions 4 and 3 in Figure 1(b), where γ is the ratio of the heat capacities, a is the speed of sound, and u is the particle velocity. If the ratio of the pressures p_4/p_3 is sufficiently large, the ratio of the sound velocities

$$\frac{a_4}{a_3} = \left(\frac{p_4}{p_3}\right)^{(\gamma - 1)/2\gamma}$$

will also be large, thus as the pressure ratio approaches infinity the velocity of the gas 3 approaches $2a_4/(\gamma_4 - 1)$. The velocity of the gas 2 is identical with that of gas 3, while the velocity of the shock wave, U_S, is a little larger than [$(\gamma_1 + 1)$ 2 times as large] the velocity of the gas behind it when the gas 1 ahead of the shock wave is at rest (see below). Thus, the shock velocity for infinite pressure ratio across the diaphragm will be

$$U_s = \frac{\gamma_1 + 1}{\gamma_4 - 1} a_4 . \tag{1}$$

The ratio of the shock velocity to the velocity of sound ahead of the shock will be

$$\frac{U_s}{a_1} \equiv M_1 = \frac{\gamma_1 + 1}{\gamma_4 - 1} \frac{a_4}{a_1} . \tag{2}$$

Conservation of energy across the shock wave,* in a coordinate system moving with the shock front so that the flow is reduced to a steady flow, gives

$$H_1 + \frac{U_s^2}{2} = H_2 + \frac{(U_s - u_2)^2}{2} , \tag{3}$$

where H is the enthalpy per unit mass. For a very strong shock the enthalpy of the gas ahead of the shock is negligible and the term $1/2\,(U_S - u_2)^2$ is small (about 5%) compared to $U_S{}^2/2$. Thus approximately for strong shocks,

$$H_2 \approx \frac{U_s^2}{2} . \tag{4}$$

By combining Eq. (4) with Eq. (1) the enthalpy of the gas in region 2 for the case when the diaphragm pressure ratio is infinite is

$$H_2 \approx 1/2 \left(\frac{\gamma_1 + 1}{\gamma_4 - 1} a_4\right)^2 . \tag{5}$$

If the gas 2 (which is the same as gas 1) is a perfect gas with constant heat capacities, the temperature ratio T_2/T_4 will be

$$\frac{T_2}{T_4} \approx \frac{\gamma_4 (\gamma_1 - 1)}{2\gamma_1} \left(\frac{\gamma_1 + 1}{\gamma_4 - 1}\right)^2 \frac{\mu_1}{\mu_4} , \tag{6}$$

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* For a steady flow, if no energy is transmitted across the walls of a stream tube, the total energy (internal energy E plus kinetic energy per unit mass $u^2/2$) plus the work done by pressures pV must be the same at any cross section of the tube; that is

$$E + 1/2\, u^2 + pV = H + (1/2\, u^2) = \text{constant.}$$

where μ is the molecular weight. For example, if the gas 1 is argon and the gas 4 is hydrogen, one obtains $T_2/T_4 \approx 250$ (ignoring the ionization energy). The gas in region 5 [Fig. 1 (*b*)] which has been traversed by both the incident and the reflected shock has an enthalpy more than twice as large as the gas in region 2.

The idealized analysis for finite pressure ratios and for reagent gases with known constant heat capacities has been done in many places (Resler *et al.*, 1952, Glass and Hall, 1959 and Wright, 1961) and will not be reproduced here. However, in Figure 2 we reproduce idealized calculations published by Camm and Rose (1962) for air driven by a monatomic driver gas.

Production of a homogeneous gas sample.

The shock tube is unique in its ability to produce a homogeneous sample of high temperature gas. The idealized theory presented in this section would indicate that the region 2 of Figure 1 (*b*) would be a region of constant gas conditions (provided no chemical reactions were taking place). According to the idealized theory the region 5 following the reflected shock in Figure 1 (*b*) is also a homogeneous region. These regions, which will be called the HGS, have been called the test time measured vertically in Figure 1 (*b*), or the hot gas slug measured horizontally. In the production of such a homogeneous region the shock tube excels for two reasons in comparison with other devices, for production of high temperature gases for study. First, the difficulty of unfolding information applicable to a single temperature from observations taken over a sample of variable temperatures is avoided. This unfolding procedure, while it has been done on occasion, has been sufficiently difficult to seriously inhibit the study of the properties of high temperature gases before the advent of the high temperature shock tube. Second, when an HGS is produced the conservation laws allow dependable information on the gas state to be obtained from measurements of the shock velocity. This information has been important in the development of diagnostic devices for the study of high temperature gases.

When the reagent gas undergoes a reaction after passing through the shock, heat releases and molecular weight changes alter the gas state in a calculable way. Thus, the gas state will no longer be

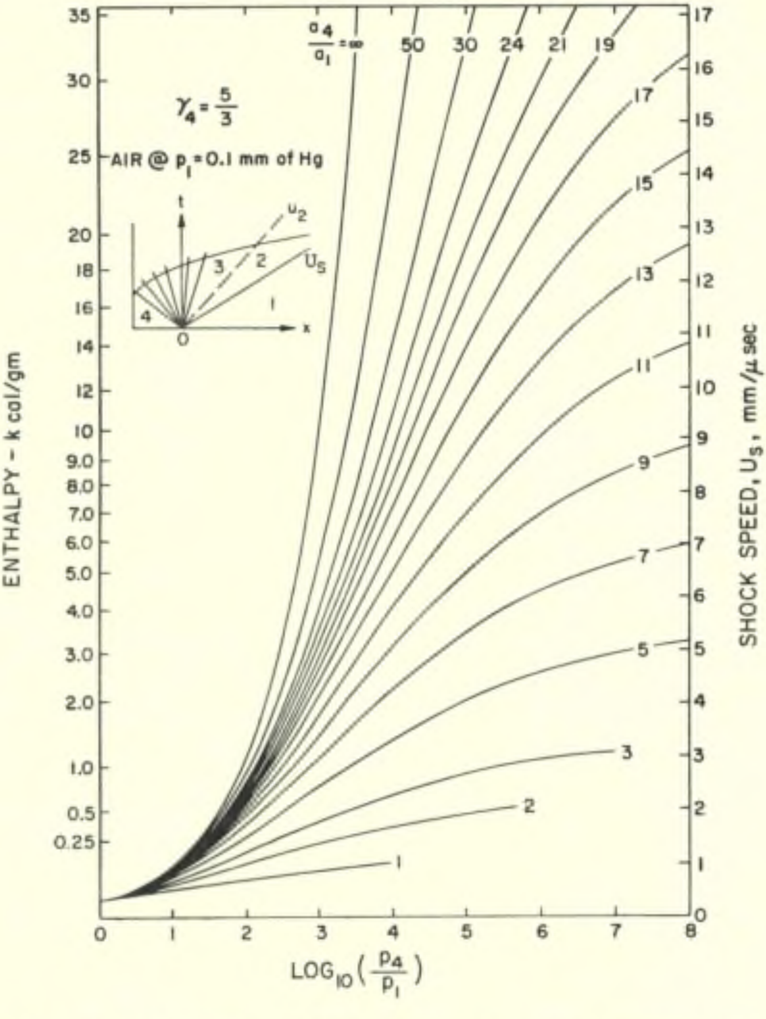

Fig. 2. — Idealized calculations of the shock speed from Camm and Rose (1962) and rough enthalpy per gram estimates from Eq. (4) of shock tubes of varying pressure ratio. The actual shock speeds produced (Restler *et al*, 1952) for hydrogen drivers in argon are typically about 10% below this calculation.

homogeneous strictly speaking, however, such gases will be referred to as HGS since the gas state is still calculable from the measured shock velocity and the degree of completion of the reaction. These effects have in many investigations been greatly reduced by adding a large amount of inert diluent gas to the reagent.

The utility of the shock tube for the study of high temperature gases is related to the ease with which a precise HGS can be created and the range of conditions over which this is possible. The precision with which an HGS can be created in diaphragm type shock tubes is the subject of Section III.

III. DEPARTURES FROM IDEAL DIAPHRAGM SHOCK TUBE PERFORMANCE

The idealized shock tube theory assumes that the gas conditions along the shock tube are one-dimensional, i.e., that the state of the gas is a function of x and t only and that the shock propagates at a constant velocity. This neglects the turbulence which invariably exists at the interface between the driver and reagent gases. It neglects also the boundary layer effects due to the transfer of heat and momentum at the shock tube walls. These effects have a variety of consequences for shock tube operation which will be briefly sketched below.

Recognition of an HGS.

During the opening time of the diaphragm a supersonic jet which only partially fills the shock tube will mix with the reagent gas. This will drive a shock wave ahead of it but the shock will not be even approximately plane until the jet spreads to fill the whole cross-section of the shock tube. As the diaphragm opening increases this jet will enlarge and compression waves will continuously overtake the shock. Thus, typically the shock will accelerate for the first forty diaphragm diameters of its progress down the shock tube. The reagent gas is typically compressed in high temperature shock waves by factors of the order of 10. Therefore, in coordinates moving with the shock wave the rate of accumulation ($U_S - u_2$) of compressed reagent gas is only a fraction ρ_1/ρ_2 ($\sim \cdot 1$) of the relative velocity between the compressed reagent gas and the shock tube walls, u_2. The turbulent velocities produced during the diaphragm break are certainly larger than $U_S - u_2$ during the early period following the diaphragm break. However, after the shock has progressed many diameters down the shock tube the appearance of an HGS unaffected by turbulence can be recognized. Various techniques for the measurement of the HGS are shown in Figure 3. In Figures 3 (*a*), and 3 (*b*), the driver gases which contain metal vapors are much more luminous than the compressed pure air in the HGS. The characteristic sharp and very rough boundary between the two can be seen. The sharpness of the boundary between the HGS and the turbulent interface is very important in shock tube

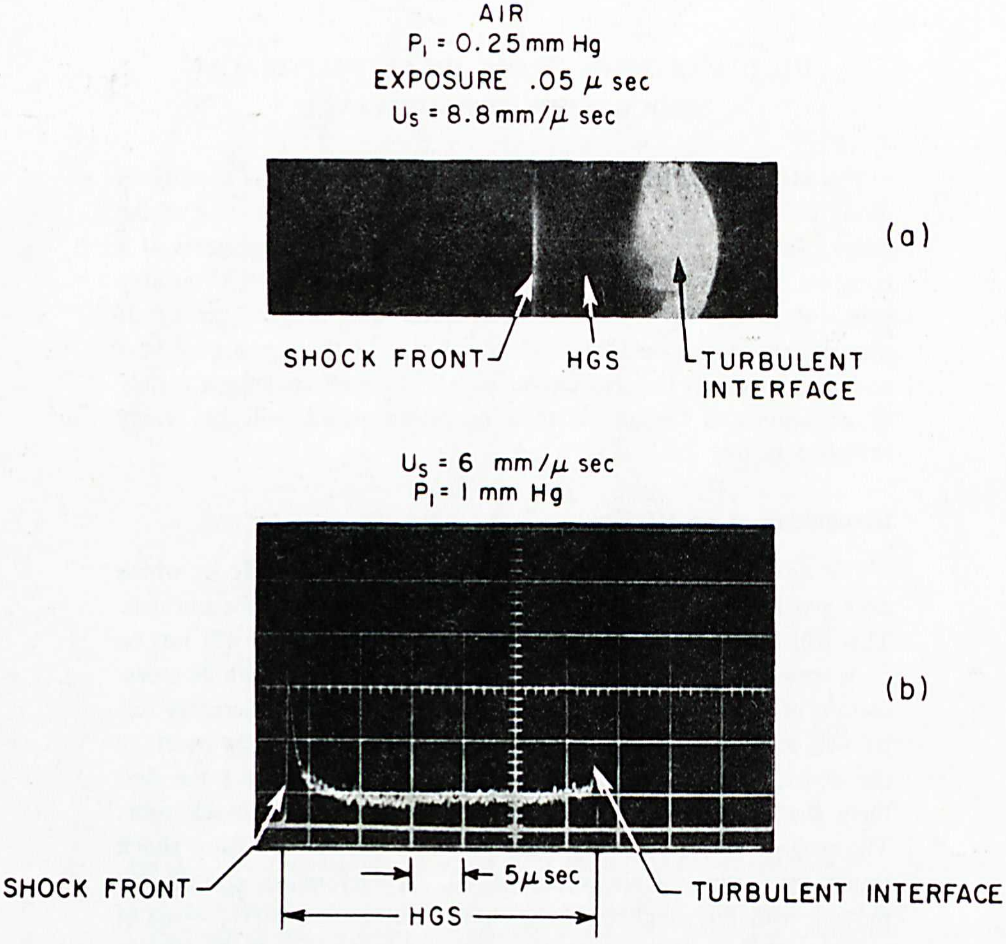

Fig. 3. — Evidence for the existence of an HGS in diaphragm type shock tubes.
(*a*) An image converter photograph of the flow in the arc driven shock tube (Camm *et al.*, 1962). This photograph was taken in a condition where the shock front itself has a very high luminosity. A sharp decline in luminosity accompanies the rapid drop in temperature associated with dissociation. The HGS is clearly visible and is followed by a turbulent interface with a characteristic luminosity increase. The horizontal striations are an image converter artifact.
(*b*) Photomultiplier trace taken with the ADST.

technique. It permits easy recognition of the end of the HGS, e.g., by photomultiplier traces. The high luminosity (characteristic of arc driven shock tubes, ADST) of this interface and its relative sharpness has sometimes produced a certain amount of confusion between the interface and the shock.

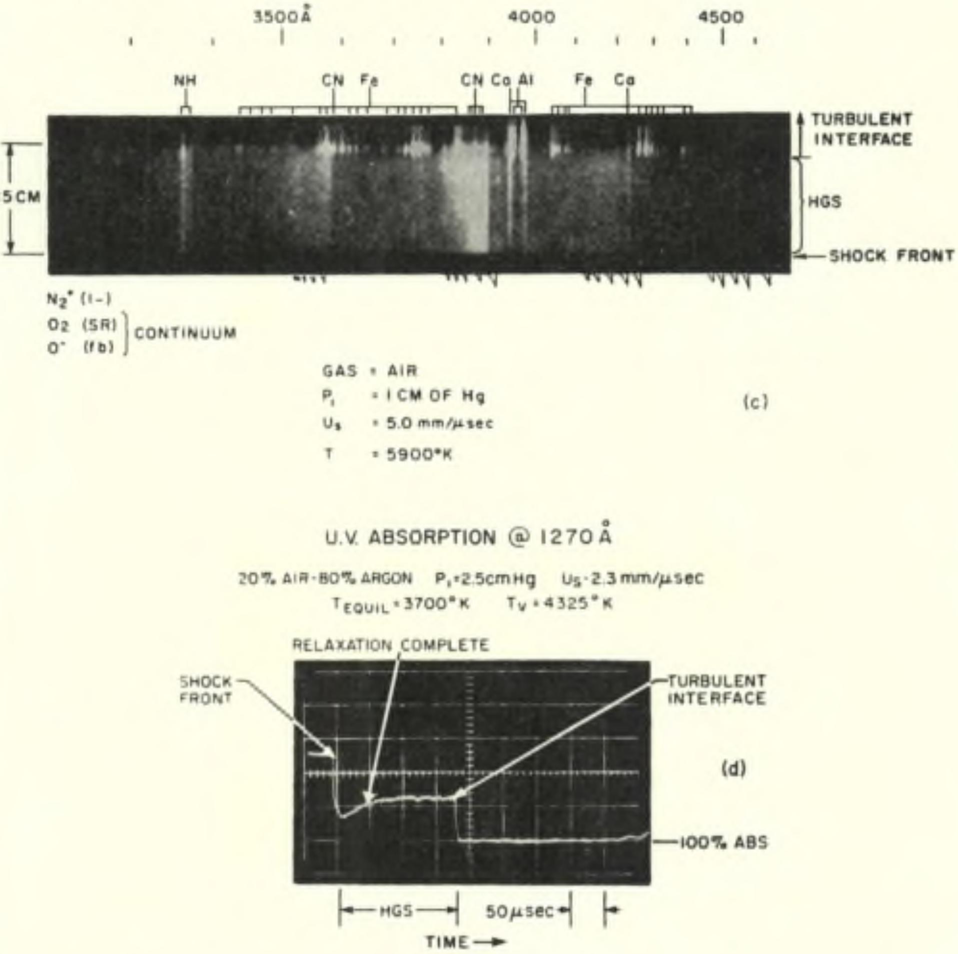

Fig. 3.

(*c*) Time dependent spectrum taken with a combustion driven shock tube (Camm, private communication) again showing the shock, the HGS, and the turbulent interface observable by the sharp enhancement of impurity spectrum.

(*d*) Absorption at 1270 Å showing the HGS in NO absorption. Note that at the turbulent interface the absorption changes very sharply. (Wray, private communication). Thus, all four of these techniques and, in fact, others such as electrical conductivity can be used to identify the onset of the turbulent interface.

Boundary layer effects.

Heat and momentum will be transferred from the HGS to the shock tube walls. The gas directly affected by these phenomena is confined to a region near the walls known as the boundary layer. For sufficiently low pressures below in air about $p_1 = 1$ cm hg (more accurately for Reynolds number less than 5×10^6 (Hartunian *et al.*, 1958) this boundary layer will be laminar, i.e., its thickness can be estimated by simple diffusion theory which to illustrate the order of magnitude of effects will be reproduced here very crudely. This effect spreads into the HGS by diffusion of cold decelerated molecules from the shock tube walls. Molecules leaving a wall will diffuse a distance proportional to an average mean free path λ in the boundary layer and to the square root of the number of collisions. At a time $\tau = \Delta x/u_2$ after the shock has passed a point, a molecule evaporating from the wall will have time for $\tau\,\bar{c}/\lambda$ collisions ($\bar{c}$ mean thermal speed) and, thus, would have diffused a distance

$$\delta \propto \lambda \sqrt{\frac{\tau \bar{c}}{\lambda}} \;\; \propto \sqrt{\lambda \Delta x \frac{\bar{c}}{u_2}}\,.$$

The distance δ is a measure of that fraction of the HGS which has been lost by contact with the walls. If λ and $\bar{c}$ are measured in the gas adjacent to the wall then the constant of proportionality can be obtained from the boundary layer calculations of Mirels (1961) and Kemp (private communication) which give the mass flow of gas in the boundary layer point Δx equal to $\rho_w u_2 \delta$ where

$$\delta = K\sqrt{\lambda \frac{\bar{c}}{u_2} \Delta x}$$

and K is a factor for which representative values for air are given in the accompanying table :

Weak Shocks	$U_s \sim 1$ mm/μsec	$K \sim 0.65$
Medium Shocks	$U_s \sim 3$ mm/μsec	$K \sim 0.50$
Strong Shocks	$U_s \sim 10$ mm/μsec	$K \sim 0.30$

The boundary layer is decelerated and cooled so that it quickly passes into the turbulent interface region. Boundary layer effects, therefore, also result in dimunition of the HGS. It will be seen that for given shock tube conditions and shock velocity there is a maximum HGS which could be achieved even if the shock propagated at constant speed down an infinitely long tube. When this maximum HGS has been achieved, the fresh reagent gas flowing through the shock is equal to the reagent gas flowing into the boundary layer and back through the interface.

In Figure 4 the comparison of the idealized HGS with the HGS which should result from laminar boundary layer effects is plotted. It will be noticed that the experimental points all show the HGS smaller than that which can be accounted for by boundary layer

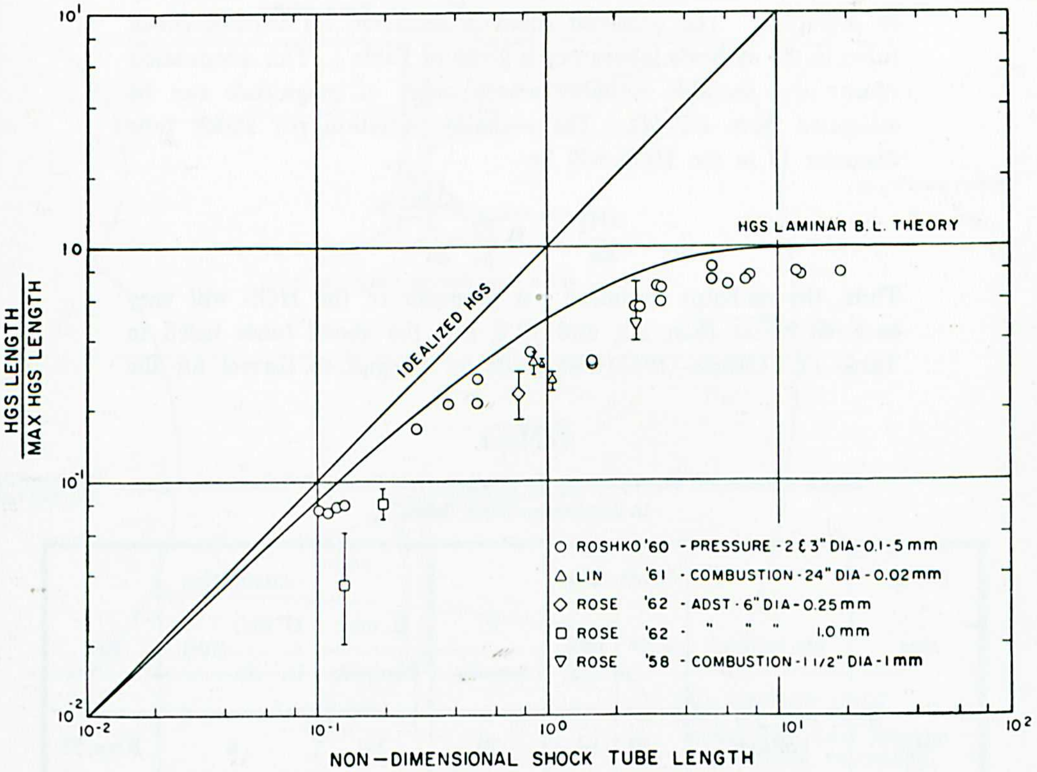

Fig. 4. — Comparison of the idealized HGS, length $= L\rho_1/\rho_2$ with laminar boundary layer theory (Roshko, 1960, with boundary layer thicknesses from Mirels, 1961) and with experiments. For short shock tubes it will be seen that the loss through the laminar boundary layer is small, and the major loss is to interface turbulence. For long shock tubes, the boundary layer becomes the dominant loss. Some of the techniques for establishing the experimental HGS length are illustrated in Figure 3. The shock tube length is made non-dimensional by dividing by the length of the shock tube required in the absence of boundary layer effects to produce an idealized HGS equal to the maximum obtainable HGS including boundary layer effects.

effects. Presumably, the discrepancy is due to the entrainment of reagent gas in the turbulent interface. In general, the discrepancy which must be attributed to the turbulent interface is larger for high temperatures shock tubes than for aerodynamic shock tubes.

The idealized shock tube theory yields a shock velocity which is constant until expansion waves reflected from the back end of the driver reach the shock [Fig. 1 (*b*)]. It would be expected that as the HGS, the turbulent interface and the high speed driver gas all increase in length, the momentum loss to the wall would continuously increase and, thus, the shock would continuously decrease in velocity or attenuate. The observed shock attenuation for various shock tubes in the author's laboratory is given in Table 1. This attenuation results in a variable enthalpy whose order of magnitude can be estimated from Eq. (4). The enthalpy variation per shock tube diameter D in the HGS will be

$$\frac{dH_2}{dx} = D\,\frac{\rho_2}{\rho_1}\,\frac{d\frac{U_s^2}{2}}{dx}$$

Thus, the enthalpy variation per diameter of the HGS will vary between better than 1% and 10% (for the shock tubes listed in Table 1). Camac (1961) has made an attempt to correct for the

TABLE 1.

Shock attenuation experience at the Avco-Everett Research Laboratory in diaphragm shock tubes.

Driver		Shock tube				Attenuation	
Gas	Mechanism	L/D	DIA. / IN.	P_1 / mm.Hg.	U_s max / mm/μsec	$\frac{D}{U_s}\frac{dU_s}{dx}(10^4)$	Ref.
H_2	Pressure	150	1-1/2	10	3.0	6	Rose 58
H_2, O_2, He	Combustion	150	1-1/2	10	4.7	12	Rose 58
H_2, O_2, He	Combustion	150	1-1/2	400	2.5	21	Rose 58
H_2, O_2, He	Combustion	25	24	0.02	5-6	0 → 34	Lin 61
He	ADST	60	1-1/2	1	11.0	14	Camm *et al.* 62
He	ADST	60	6	0.25	7.-12.0	40 → 58	Camm *et al.* 62

effects of attenuation. This effect limits the precision of shock tube studies and it would be well to design a shock tube so that the idealized theory would predict an accelerating shock wave, e.g., by tapering the driver, thus, compensating for the wall interactions.

The boundary layer growth behind the shock wave also results in the shock being convex (Fig. 5) toward the undisturbed reagent gas (Lin *et al.*, 1961 and Duff *et al.*, 1961). The bowing will depend on the ratio of the tube radius R, to the boundary layer thickness

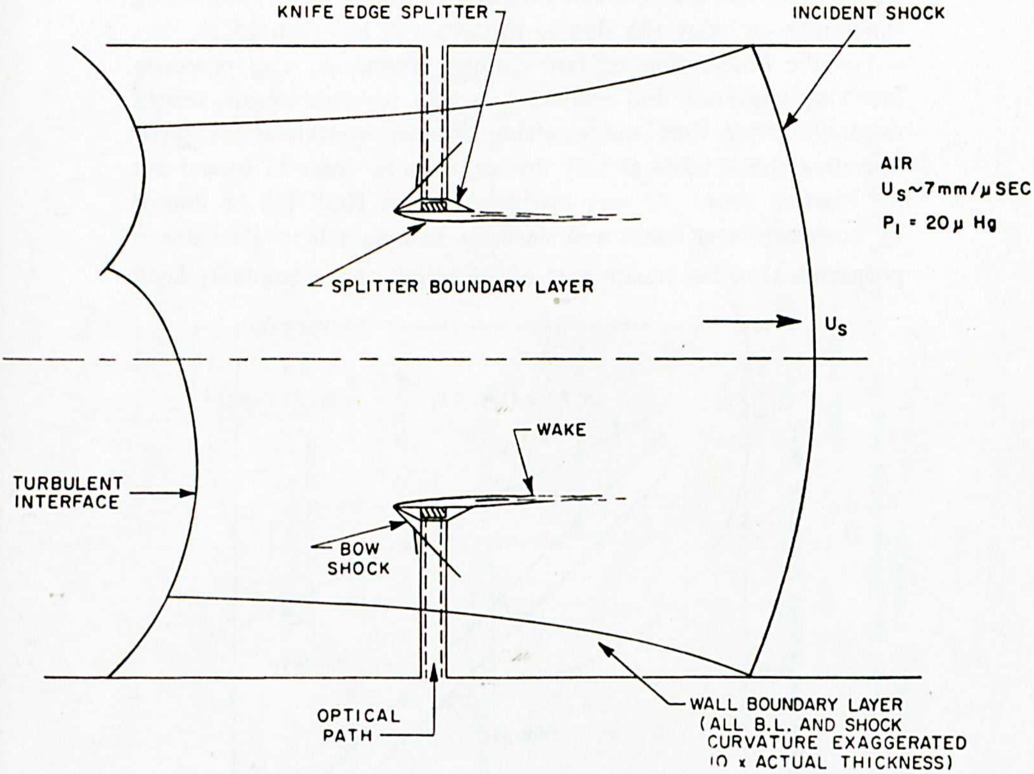

Fig. 5. — Illustrating some of the effects of boundary layers on shock tube performance. The drawing is schematic and illustrates calculated boundary layer thicknesses and measured shock curvatures (Lin and Fyfe, 1961) for shock moving into 20μ hg air in the 24-inch low density shock tube at 7 mm/μ sec. The boundary layer produces a noticeable curvature of the shock wave at low densities. The boundary layer thickness through which observation must be made can be reduced by use of the splitter technique shown here schematically. An actual apparatus employing the splitter technique is shown in Figure 7.

after the boundary layer has developed for a distance comparable to the tube radius. This effect results in an apparent shock thickness measured for example by the absorption of ultraviolet light which is considerably greater than the theoretical shock thickness. It will be noticed from Figure 6 that the apparent thickness varies inversely as the square root of the initial pressure (in agreement with the boundary layer hypothesis) rather than the first power as would be required from shock theory.

It should be remarked that the thickening of the boundary layer results in a slight pressure and enthalpy rise in the HGS. For strong shocks the enthalpy rise due to this effect is less than 2%.

For the observation of fast chemical reactions, e.g., processes involving ionization and excitation in high temperature air, instrumental resolving time and resolving distance considerations favor operating shock tubes at very low densities in order to spread out the reaction zone. At very low densities the HGS will be limited by boundary layer losses and since the boundary layer thickness is proportional to the square root of the length of the boundary layer

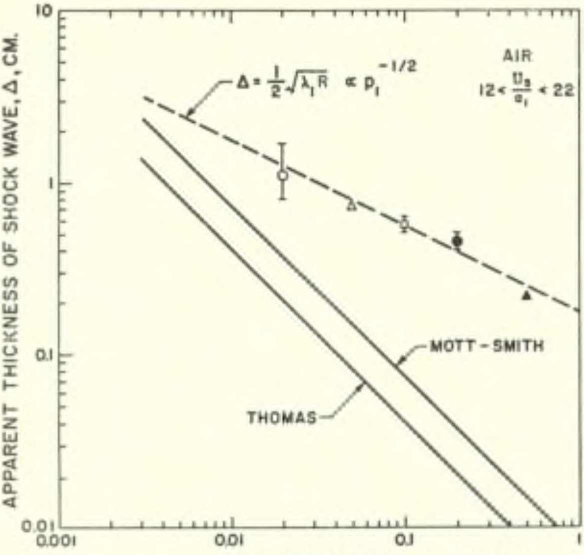

Fig. 6. — The apparent thickness of the shock wave as measured in vacuum UV absorption by Lin and Fyfe (1961). It will be seen that the apparent thickness is considerably larger than that anticipated for plane shocks. This thickness correlates very well with rough estimates of the shock wave bowing due to boundary layer effects at the shock tube wall (the dashed line).

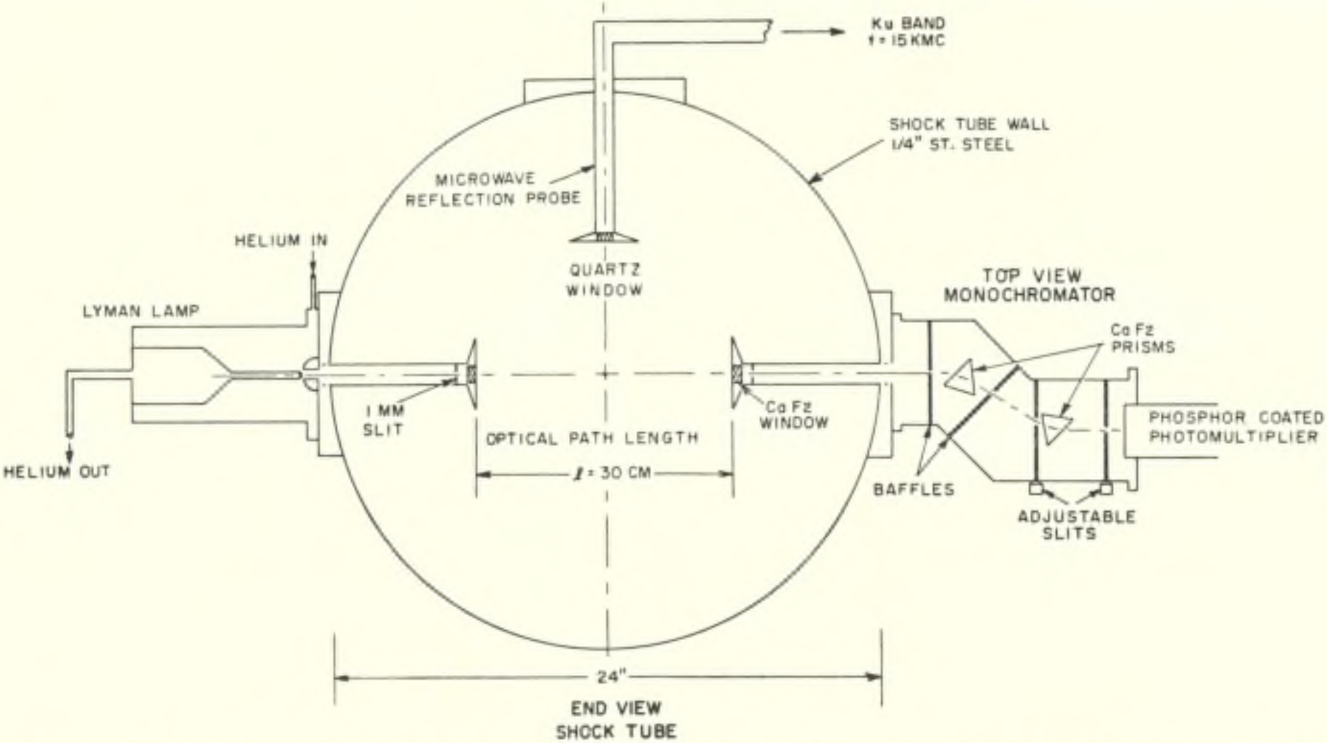

Fig. 7. — Typical instrumentation of the 24-inch shock tube for observation of the rates of ionization by 4 mm microwave reflection and chemical reactions by vacuum UV absorption.

run, the HGS will be proportional to the square of the shock tube diameter. Therefore, considerable gains can be made by using large diameter shock tubes as has been done by Lin *et al.* (1960) with a 24-inch diameter shock tube. For such shock tubes it is desirable to use a relatively small diameter diaphragm since, apparently, the shock travel before interface turbulence has decayed to a point which permits the appearance of an HGS is proportional to the diaphragm diameter rather than the shock tube diameter.

In order to make observations on emission or absorption of radiation, it is necessary to remember that these observations must be made through the wall boundary layer. The depth of gas through which the observations must be made can be minimized by the splitter technique (Lin, *et al.* 1960 and Lin 1961). This is shown schematically in Figure 5 and examples of its application to vacuum ultraviolet absorption and to microwave reflection measurement is shown in Figure 7.

If the incident shock wave is reflected from a closed end shock tube the kinetic energy of the HGS is converted into gas enthalpy when it is brought to rest by the reflected shock. Since this kinetic energy is comparable with the gas enthalpy behind the incident shock, the enthalpy of the gas after reflection is roughly doubled. This technique has frequently been employed to achieve higher temperatures than can be achieved with a given driver following the incident shock. It was pointed out (Mark, 1957, 1958) that this technique sometimes suffers from more serious boundary layer problems than those encountered with the incident shock. These problems are associated with the fact that the boundary layer air is accelerated back toward the driver by the pressure rise in the reflected shock.

IV. HIGH SPEED SHOCK TUBE DRIVERS

It has already been made clear that the maximum enthalpy * which can be produced in a shock tube (Eq. 5 or Fig. 2) depends

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* It should be noted that higher temperatures can sometimes be reached by the addition of appropriate diluents to the reagent gas. The use of high molecular weight inert diluents can reduce the reagent speed of sound and increase the temperatures reached with a given shock speed, i.e., a given enthalpy per unit mass. Inert diluents have also been used to allow the use of more rarefied reagent gases and to provide a heat bath to reduce the effect of reactions in altering the gas state in the HGS.

on the driver speed of sound. This section will survey briefly various techniques for increasing the speed of sound beyond that obtainable in pure hydrogen.

It has already been noted that turbulence at the interface between the driver and reagent gases reduces and may even eliminate the

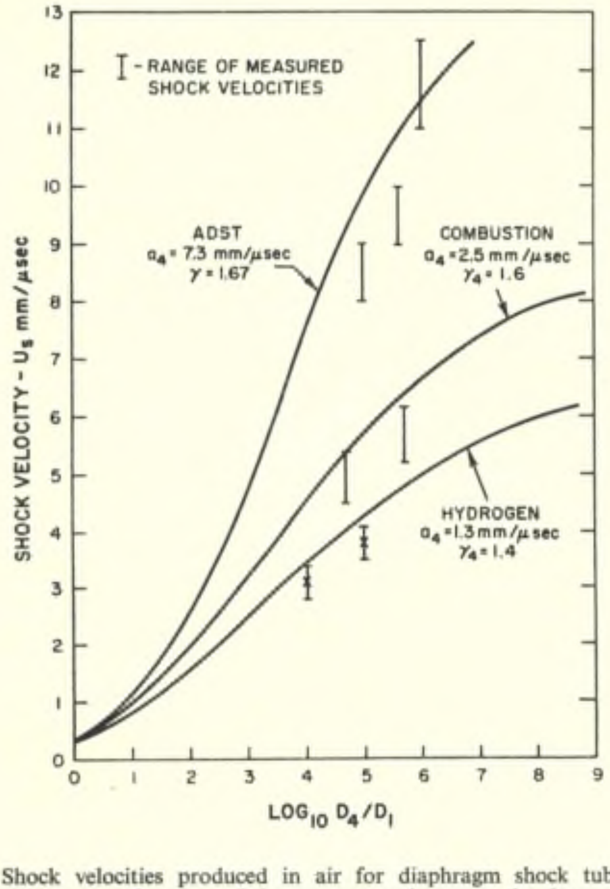

Fig. 8. — Shock velocities produced in air for diaphragm shock tubes with various drivers as a function of the pressure ratio across the drop. For the combustion driver 20% hydrogen, 10% oxygen and 70% helium were used. For the arc driver helium was heated by the addition of electrical energy in a pulsed condenser discharge initiated by a fine aluminium wire. Note that in the ADST of Camm and Rose (1962) a 20 to 1 area expansion occurs between the driver and the low pressure section resulting in effective a_4 reduction of 30%. The theoretical curve presumes a temperature of 16,000 °K, pure helium and a 30% a_4 drop in the expanding region. Actually, of course, the gas was probably hotter than this but also contained some high molecular weight contamination from material ablated from the walls during the intense discharge. The vertical bars represent experimental points obtained with various shock tubes at the Avco-Everett Research Laboratory.

HGS. One cause of turbulence is the opening process of the diaphragm. Another cause of turbulence which will be prominent in the high speed drivers considered in this section is inhomogeneity of density in the driver gas. When an element of gas accelerates through a pressure drop the acceleration produced is inversely proportional to the gas density. Thus, the use of a driver gas with density inhomogeneities results in shear between regions which have been accelerated to various velocities. The resultant increased turbulence has reduced HGS for all of the high speed drivers reported in this section (see Fig. 4) and only those drivers where pains have been taken to assure a degree of homogeneity have been successful in producing any HGS at all.

The most widely used high speed driver gas is a stoichiometric mixture of hydrogen and oxygen diluted with about 70% helium. After ignition this mixture produces shocks about 70% faster than those which can be produced by room temperature hydrogen (Resler, *et al.*, 1952). This technique is considerably safer than the pure hydrogen driver since the quantities of hydrogen used are reduced typically by a factor of about 50. The shock speeds (Fig. 8) and gas enthalpies (Fig. 9) which can be produced with combustion drivers are considerably higher than with H_2 drivers. The shocks produced, however, are not quite as reproducible in velocity and the attenuation is somewhat greater than that of the pure hydrogen drivers (Table 1). Also the HGS produced is not quite as long as that produced for the pure hydrogen drivers (Fig. 4).

In the use of combustion drivers it is important to avoid the production of detonation waves which frequently cause portions of the diaphragm to fly down the tube rather than flatten against the tube walls. One technique for preventing detonation is to provide distributed ignition throughout the driver by the explosion of a series of long fine wires inside the driver or by multiple spark plug ignition (Nagamatsu *et al.*, 1959). The distributed ignition is also important in helping to provide the homogeneous drivers necessary to suppress interface turbulence.

Another technique for increasing the driver sound speed in a diaphragm shock tube is the sudden addition of electrical energy to the high pressure driver, e.g., helium, by the discharge of a large condenser bank (Resler *et al.*, 1952). A shock tube based on this principle has been developed by Camm and Rose (1962). This device is known as the arc driven shock tube (ADST). Their driver is 1.3″ I.D. and 1 ft. long. The low pressure section is 6″ I.D. and 30 ft. long and connected to the driver by a conical diverging region 18″ long. The large diameter low pressure region allows the use of lower reagent pressure, but the expansion in the diverging region reduces the effective driver sound speed by about 30%. Shock velocities up to 13 mm/μsec (Fig. 8) have been produced in this way by adding 230 joules/cu. cm to helium at 14 atmospheres. In this technique the diaphragm described is set to burst at 700 atmo-

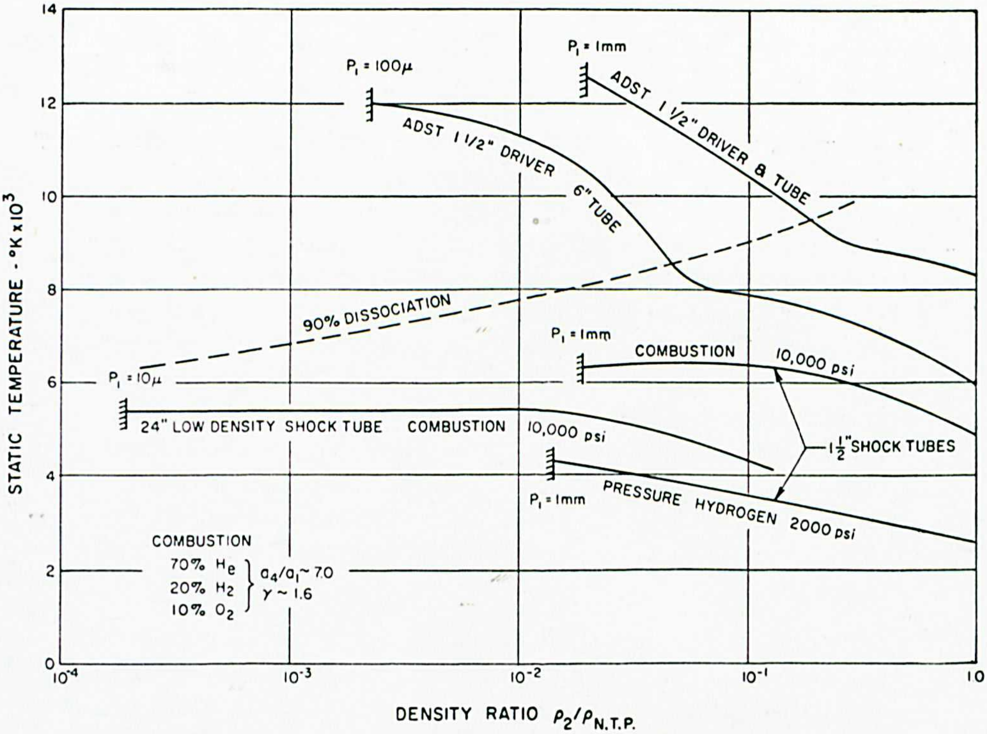

Fig. 9. — Temperatures and densities (after equilibration) obtainable in air behind the incident shock for various diaphragm shock tube drivers. The driver pressure in all cases is limited to 10,000 PSI for the ADST and the combustion drivers and to 2000 PSI for H_2. The minimum densities which can be used are those at which the HGS becomes unusably small. Note that the dissociation and ionization processes " thermostat " the temperatures so that, e.g., with the combustion driver for $\rho < \cdot 1$ NTP somewhat lower temperatures are reached with higher shock velocities (Fig. 8) as we increase dissociation by moving to lower densities.

spheres. The diaphragm does not open until about 40 μsec after the discharge is complete. The 40 μsec dwell time combined with the fact that the mixing velocities in the driver must be of the order of magnitude of sound speed about .73 cm/μsec and 1.3 cm diameter of the driver should allow enough time for mixing to achieve considerable driver homogeneity. It has, in fact, been observed (Fig. 4) that the HGS obtained with this type of driver is only slightly inferior to those obtained in combustion driven shock tubes. As can be seen in Figure 8, temperatures in air up to about 12,500 °K behind the incident shock have been achieved. It seems likely that with further development shock velocity might be increased by another factor of 2 or the gas enthalpy by a factor of 4. Figure 9 shows the temperatures and density behind the incident shock which are available for hydrogen, combustion and arc driven shock tubes.

The use of modifications in shock tube geometry, in particular, the application of two diaphragms to produce the so called buffered shock tube (Resler *et al.*, 1952 and Russo and Hertzberg, 1958) can provide perhaps a 20% increase in available shock velocity with a given driver. Improvements in driver performance have also been sought by the adiabatic compression of the driver gas with a rapidly moving piston and the application of external heat to the driver container. These techniques, in general, have resulted in small increases in performance which do not match that obtained with a combustion driven shock tube. However, some advantage in the reproducibility and the reduction in attenuation is claimed for these devices. Schreffler and Christian (1954) created very strong shock waves in argon at atmospheric pressure with the use of a high explosive driver.

It is well-known that shock waves can be produced by sudden electrical discharges. This phenomenon was exploited by Fowler and his co-workers (1951) to produce high speed shock waves by initiating a powerful electric discharge in a glass tube. In these devices the pressure ratio equivalent to p_4/p_1 of Figure 1 is of the same order of magnitude as the temperature ratio produced in the discharge. Thus, considerably higher temperatures are required to produce shock waves of the strength which can be produced in the ADST (Fig. 2). For example, to produce a shock with a speed of 10 mm/μsec in helium, it is necessary to produce a driver temperature of about 25,000 °K. At these temperatures radiation and/or rapid wall cooling produces a rapid decay of the driver pressure. It has accordingly always been observed that the velocity of the shock produced in these devices rapidly decays with time. In the diaphragm type shock tubes which have a high pressure ratio before heating begins, the production of 10 mm/μsec shock velocity can be accomplished with He driver temperatures of about 10,000 °K, and the cooling is much slower. Thus, with arc driven shock tubes, it has been possible to use large length to diameter ratios.

When the diaphragm is omitted it has been possible to obtain much higher speeds in the luminous front. Thus, luminous front speeds up to perhaps 10 cm/μsec have been reported very close to the discharge (Josephson *et al.*, 1961). However, it is clear that in some cases, the shock waves have been partially driven by electromagnetic effects which is the subject of Section V. It is striking that in no case with diaphragmless electrically heated shock tube drivers has there been any evidence of the production of an HGS. Photographs of the flow, McLean *et al.* (1960) and Fowler and Turner (1961) exhibit the effects of turbulence and oblique shock waves. Attempts to correlate spectroscopic measurements of the gas temperatures and density of the gas behind the shock with calculation from the conservation laws and shock velocity measurements have not been successful. McLean *et al.* (1960) exhibited luminous front photographs showing turbulence at the leading edge and they found spectroscopic indications that the enthalpy of the gas produced was more than twice as large as could be accounted for from the measured shock velocity and the conservation laws. It is clear in their case that the effects of the turbulence in the driver gas extend to the shock front. Probably some effects due to the presence of magnetic field were also present but these again must produce considerable non-uniformities. The observations referred to were made 2 diameters from the discharge region. In the work of Fowler and Turner (1961) who used an axial magnetic field to reduce diffusion to the shock tube walls, a finite luminous region was observed. No attempt, however, was made to establish correlation between the shock velocity and other observables. The occurrence of oblique shocks would probably make the attainment of an HGS impossible.

To summarize the situation with diaphragmless electrically driven shock tubes, it seems at the present time that the high level of turbulence produced in the driver combined with the necessity for using short shock tubes has prevented the attainment of an HGS with state variables calculable from the measured shock velocity. Thus, these devices must be considered together with other electrical discharge devices which can also produce high temperature gases but which do not possess the essential advantage of a shock tube in knowledge of the gas state obtainable from fluid mechanics.

V. ELECTROMAGNETICALLY DRIVEN SHOCK TUBES

It is well known that intense magnetic fields can easily be produced with condenser discharges. When these intense magnetic fields are used to propel rarefied plasmas, extremely high velocities can be reached. Employment of these very high speed plasmas to drive shock waves and to produce a homogeneous gas or plasma sample in the sense that these words have been used in previous sections, will be explored in this section.

At the present writing considerable interest has been generated in the study of plasmas at very high temperatures one, two or more orders of magnitude beyond those that can be reached with diaphragm shock tubes. It will be useful to make a brief statement on the sources of this interest to enable a discussion of the contributions possible from an extension of shock tubes to this area. The temperature range just above that accessible to the ADST is the interesting range where gases become fully ionized and the phenomena associated with multiple ionization enter. The mean free path in a fully ionized plasma varies (at constant density) as the square of the temperature. Therefore, at extremely high temperatures collision processes become very rare and the approach to a maxwell distribution via collision processes becomes very slow. One of the fundamental questions then is the study of the operative dissipative mechanisms in so called collision free plasmas which are beyond the temperatures where collision processes can dominate. Many astrophysical phenomena are connected with the dynamics and dissipation mechanisms of the collision free plasma. The central problem in the production of a controlled thermonuclear fusion reactor is the magnetic containment of collision free plasmas. The inhibition of the collisional dissipation mechanism has resulted in the appearance of a tremendous variety of instabilities which must be understood before a high temperature plasma can be contained. Finally, the propulsion of space vehicles by electrical acceleration of very high temperature plasmas has been receiving an increasing amount of interest and will be of practical importance in the future.

Various people (Bostick, 1956, Colgate, 1957, Janes and Patrick, 1958, Kolb, 1957) have demonstrated that rapid intense condenser discharges can accelerate plasmas to velocities ranging up to about 20 cm/μsec. In most of these early experiments the driver currents are imbedded in the shock heated gas and the heating effects of these driver currents make it impossible to identify an HGS.

Some general requirements for electromagnetic shock tubes.

It might be well to set down some of the conditions necessary for electromagnetically driven shock tubes to achieve at very high temperatures the advantages which have been achieved at lower temperatures with diaphragm shock tubes. In order to prepare an HGS, it is first necessary that the shock be shielded from the driving magnetic field to prevent electrical heating of the gas immediately behind the shock. Isolation from the shock tube walls will become increasingly difficult as we move to higher temperatures. However, some advance in enthalpy capabilities should be possible in magnetic driven shock tubes without insuperable wall losses. To achieve very high gas temperatures and with them very large mean free paths, some form of magnetic containment from the walls must be used.

The first requirement is that the skin depth for the penetration of the drive current into the plasma be less than the idealized HGS length. It is easy to make a one-dimensional calculation which determines the order of magnitude of the shock tube length required to satisfy this condition.* At a time t seconds following the sudden application of a magnetic field to the plane surface of a thick conductor with conductivity, σ, it penetrates a skin depth, δ, given by

$$\delta = \sqrt{\frac{t}{2\pi\sigma}}. \tag{7}$$

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* A more accurate analysis similar to but independent of this one has just been given by Falk and Turcotte (1962).

On the other hand the length of the idealized HGS is

$$\Delta = \frac{\rho_1}{\rho_2} U_s t \, . \tag{8}$$

Since the idealized HGS increases with the first power of the time and the skin depth only as the square root, there is a critical time required before the shock heated gas will shield the shock from the driving magnetic field. Thus, the condition $\Delta = \delta$ will provide a crude lower bound for the minimum shock tube length after which it is possible to create an HGS. Presuming that the gas has reached equilibrium, and that the interface diffusion is not enhanced by turbulence, we can readily calculate the electrical conductivity of the gas behind the shock wave (Spitzer and Härm, 1953). The density ratios and the temperatures produced behind the shock waves have been tabulated for many gases. It is now possible to calculate the minimum shock tube length required and such calculations made by Dr. Frank Fishman are given in Figure 10, where the minimum shock tube length is plotted as a function of the temperature behind the shock wave. It should be remarked that many of the earlier attempts to drive shocks magnetically did

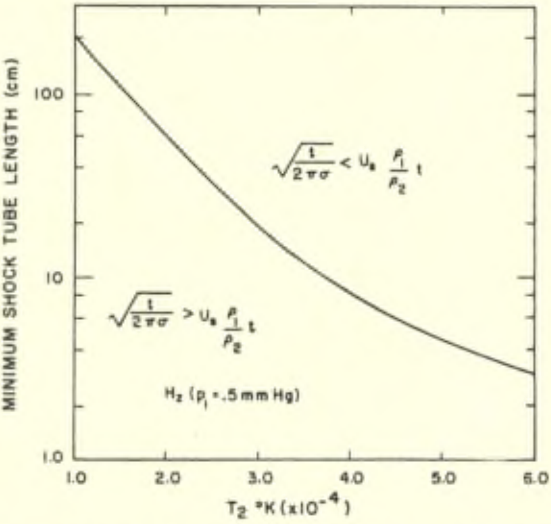

Fig. 10. — A crude estimate of a lower bound to the shock tube length necessary for the achievement of an HGS in electromagnetically driven shock tubes. This curve exhibits the minimum shock tube length at which the shock wave is barely shielded from the drive field by the gas behind the shock wave which has been assumed to possess the electrical conductivity appropriate to thermodynamic equilibrium. It is assumed here that the flow is one-dimensional.

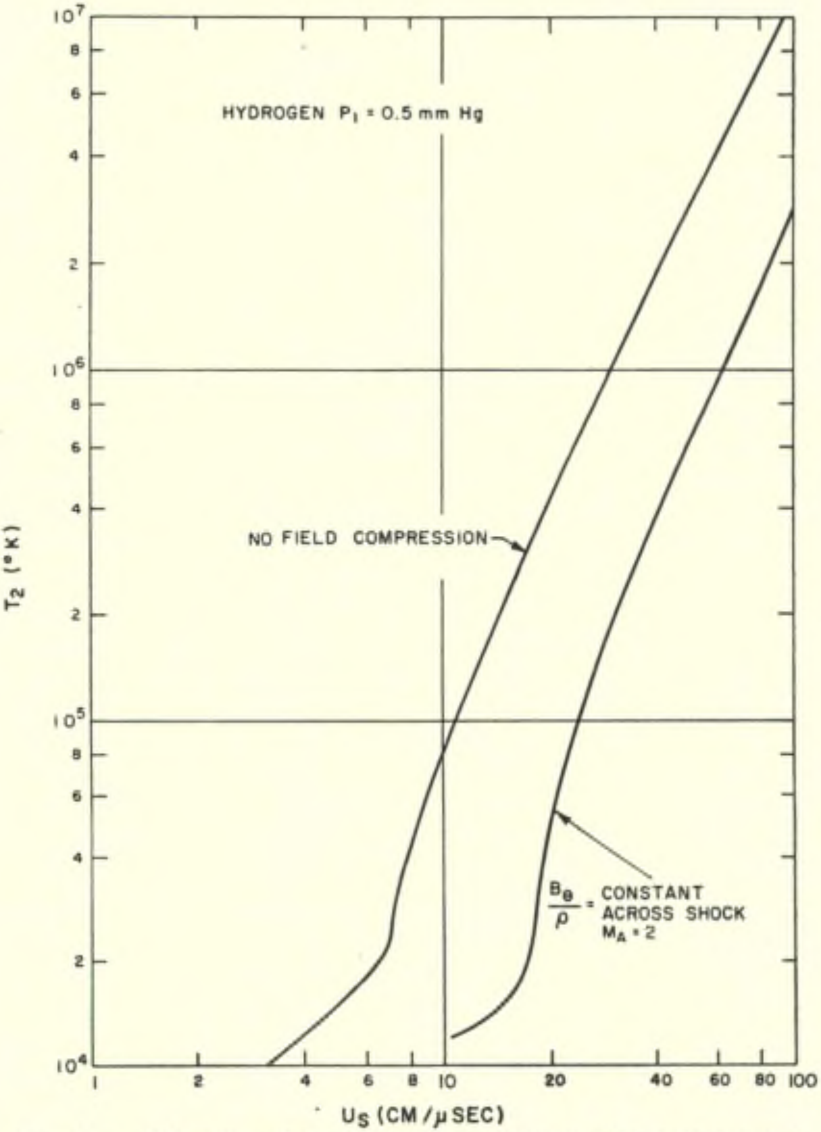

Fig. 11. — Calculation of the equilibrium temperature behind shock waves. The curve on the right assumes sufficient conductivity in the shock wave so that the component of the magnetic field (B_θ) in the plane of the shock front remains proportional to the gas density. This curve is drawn for the case where the magnetic field is adjusted so that the initial Alfven velocity $\frac{B}{\sqrt{4\pi\rho}}$ is half the shock speed (Alfven Mach No. $M_A = 2$). The temperatures achieved with a given shock velocity are very much lower when magnetic compression exists because most of the kinetic energy of the gas entering the shock is used to compress the magnetic field.

not satisfy the simple skin depth requirement (e.g., McLean *et al.*, 1960), therefore, it is not surprising for this reason alone, that it was not possible to identify an HGS. The calculations given above have considered the case where no initial magnetic fields are present, but are not affected if the magnetic fields are parallel to the gas velocities.*

There is one simple case in which the adequacy of shielding against magnetic drive fields can be readily demonstrated. This is the case where a component B_θ of the magnetic field lies in the plane of the shock wave and where the gas conductivity becomes very large before the gas is appreciably accelerated by the shock. In this case it can readily be shown that the B_θ/ρ is a constant through the shock wave (de Hoffman and Teller, 1950). The application of the conservation laws in this case is again simple.

It should be noted that when an appreciable magnetic field compression occurs several phenomena takes place which drastically alter the situation. In the first place, the density ratio across the shock is usually much reduced compared to that with no magnetic field (or with a magnetic field in the direction of the gas velocities). This leads to a greatly increased rate of accumulation of HGS and, thus, this is very helpful. Secondly, the gas temperatures reached (Fig. 11) are much lower than those that would be reached following a shock at the same velocity in the absence of a magnetic field. Third, when the magnetic pressure is large compared to the gas pressure the diffusion of gas is driven only by the gas pressure and, thus, the effective conductivity is increased by the ratio of the magnetic to gas pressure. Calculations were made for the case (Alfven Mach number = 2) where the magnetic pressure behind the shock is six times the gas pressure. Computing the minimum shock tube length as in Figure 10, the lengths obtained for $T > 12{,}000\,°K$ are less than 1 mm. Thus, the achievement of magnetic compression in the shock front will insure shielding of the shock from the driver currents. When this does not occur the minimum length calculated in the absence of magnetic field (Fig. 10) applies.

A second requirement for the achievement of an HGS is that of containment from the shock tube walls. As was pointed out in

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* Note : " Switch on " shocks (Kemp and Petschek, 1959) are an exception.

Section III, the achievement of an HGS in a channel requires that the diffusion mean free path (λ) be at least an order of magnitude less than the channel diameter. This requirement has necessitated the use of large diameters in diaphragm type shock tubes where densities less than 1 mm have been used. For fully ionized gases where $\lambda \sim T^2$, the necessary diameters to achieve adequate containment become impossibly large since, for energetic reasons, it is necessary to work at very low densities. Therefore, the achievement of temperatures in excess of a few electron volts necessitates the use of magnetic containment. Magnetic fields parallel to the shock tube walls must be provided initially so that the shock heated gas will contain magnetic field which hopefully will inhibit its diffusion to the walls.

It should be borne in mind that any contact between very high temperature plasmas and the containing walls can result in the evolution of the large amount of gas compared to that initially in the shock tube. If the mean free path is greater than the typical dimensions in the problem, then without any containment the energy impinging on a sq. cm from the plasma is

$$2\,\frac{n\bar{c}}{4}\,\frac{3}{2}\,kT$$

For plasma density $n = 10^{16}$ protons/cc. and $3/2\,kT$ the average energy per particle $=$ 100 EV ($\sim 10^6$ °K at equilibrium) and the average proton thermal velocity $\bar{c} = 2.4 \times 10^7$ appropriate to protons at 10^6 °K, the energy deposition is the order of 2000 kw/sq. cm. The time required (simple heat conduction theory) to raise the surface of various substances to their melting or decomposition point with this heat flux is given in Table 2. It would be expected

TABLE 2.
Time to reach melting temperature.

Material	Melting temperature	Time for $Q=2\times10^6$ watts/cm^2 in μ sec
Tungsten	3370 °C	10
Copper	1083 °C	4.0
Stainless steel	1515 °C	1.0
Quartz	1470 °C	10^{-3}
Lucite	135 °C	6.0×10^{-6}

that considerable gas evolution occurs long before these temperatures are reached. It is worth noting that there have been many observations that insulators in the presence of a high temperature plasma frequently exhibit good conductivity on their surface. This observation may be related to gas evolution since the evolved gas rapidly becomes ionized and a good conductor and in many cases would be much more dense close to the surface than the initial plasma. Thus, in many experiments this evaporated gas could be expected to behave much like a rigid conductor.

The magnetic annular shock tube (MAST).

It will be apparent that the achievement and recognition of an HGS for electromagnetically driven shock tubes would constitute an important advance. It seems quite likely that this achievement would open the way to a large variety of researches on plasmas in the temperature range starting at about the temperature which can be reached with arc driven diaphragm shock tubes and extending to millions of degrees K or higher. In achieving this advance two developments must proceed simultaneously. First, the design and development of "shock tubes" so that after taking into account all the known properties of high temperature plasmas such as those discussed briefly above, that one could expect the achievement of an HGS. The second is the development of diagnostic tools and understanding of the high temperature plasma so as to verify the supposed experimental conditions. The development of diagnostic tools has been severely handicapped by the fact that spectroscopy which was so useful in the development of diaphragm shock tubes is not as nearly so powerful a tool at the high temperatures, low densities and short exposure times usually encountered. Gas evolution from surfaces has also complicated the use of probes inserted into the gas for the measurement of magnetic and electric fields and plasma densities. The achievement of containment in attempts to produce thermonuclear fusion has been beset with instability problems. Wall containment in shock tubes should be simpler since only short containment times are required and since the proximity of rigid conducting walls inhibit many instabilities. Instability problems at the interface may present more serious problems.

The only systematic attempt which has been made with electromagnetically driven shock tubes to achieve an HGS has been made by Patrick and his co-workers with a magnetic annular shock tube which is illustrated schematically in Figure 12. It will be instructive to review first the degree to which this device meets the requirements stated above and, secondly, the degree to which the diagnostic developments presently available have been able to identify an HGS.

This coaxial design immediately achieves one important objective in that it makes possible the driving of shock waves for comparatively long distances with relatively modest energy requirements. Thus, it becomes relatively easy to satisfy the condition that the

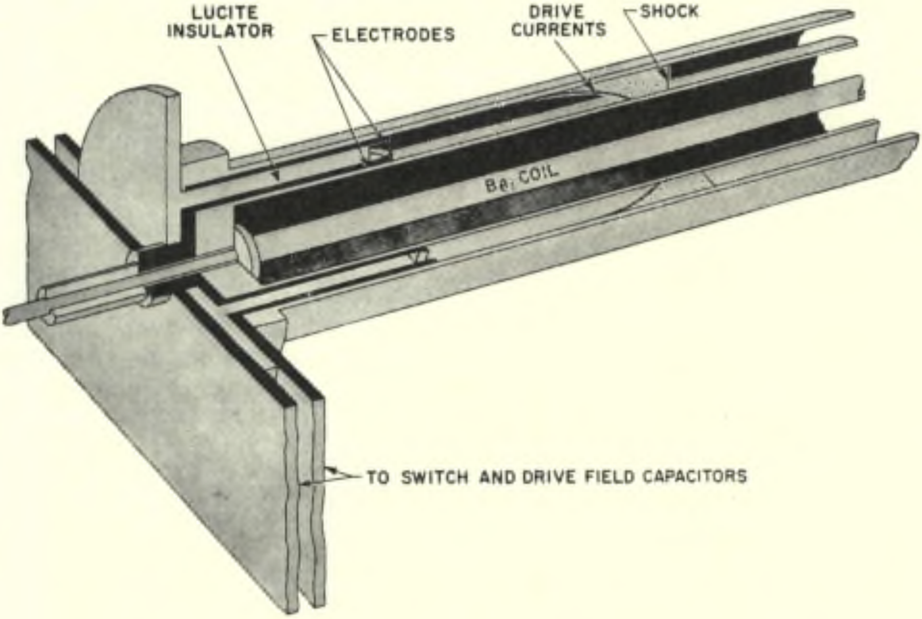

Fig. 12. — A schematic drawing of the magnetic annular shock tube (MAST) as developed at the Avco-Everett Research Laboratory. This device consists essentially of two coaxial cylinders between which a radial electric field is imposed suddenly by switching on a condenser bank. The gas at the left and adjacent to the lucite is preionized by devices which are not shown (Patrick and Camac, 1961). Following preionization the switch is closed and ideally a radial drive current sheet uniform around the annulus is formed. The magnetic field generated by this current sheet drives the gas in the shock tube and a shock wave precedes ahead of the driver currents. The tilting of the current sheet is due to the higher magnetic pressure at smaller radii. The rod down the center line can be used to produce an aximuthal magnetic field (B_θ) which serves to contain the plasma which has been compressed and heated by the shock. Provision is also made for the use of solonoids surrounding the MAST which make possible the use of axial containing fields (B_z).

gas heated by the shock wave shield the shock from the driver field (Fig. 10). This geometry also achieves a driving magnetic field which does not intersect the shock tube walls. This avoids some problems with surface currents and associated gas evolution.

The coaxial geometry of the MAST is especially favorable for the important consideration of the design of containing magnetic fields. The inclusion of a central axial conductor and of external solenoids allows the use of various types of containing fields which are driven by relatively slow condenser banks separate from the main bank which supplies the driver current.

The idealized theory of operation of this type of shock tube has been given by Bazer (1958) and by Kemp and Petschek (1959), where the phenomena occurring with various combination of B_z and B_θ containment fields are discussed. Presuming that the flow is one-dimensional and that the electrical conductivity is infinite and that the drive current is a step function, they calculate the flow.

With this type of device it must be noticed that neglecting axial currents in the gas B_θ must vary inversely as the radius R from the axis. The resulting non-uniformity in the magnetic drive pressure will produce a departure from one-dimensional flow which has been treated by Fishman and Petschek (1962 *a*). Thus, it would be expected that the current sheet will be more advanced near the inner electrode than near the outer one (Fig. 12). This effect is especially prominent when there is no initial B_θ. In this case for $\gamma = 5/3$ an annulus spacing less than 1/6 of average radius is required to prevent the leading inner edge of the current sheet from overtaking the shock. Many experiments with coaxial accelerators, e.g., Dattner, private communication and Keck (1962) have demonstrated that when smaller inner electrodes are used that the current sheet is sharply tilted. This work has demonstrated that in this case nothing like an HGS appears in the flow.

The use of a strong initial B field allows larger annulus spacings before the leading edge of the current sheet intersects the shock. For this case the distortion of the strong magnetic field by the relatively small gas pressures is tolerable. (For $M_A = 2$, $\frac{B_\theta^2}{8\pi p} = 6$ if $\gamma = \frac{5}{3}$.) Also note that the greater HGS length reduces the effect of current sheet distortions on the shock front. However, appreciable (of the order $\sim 30\%$ for Alfven Mach No. 2 and ratio of inner and outer radii of 5/6) temperatures and pressure non-uniformities will still occur due to variations in magnetic field ahead of the shock.

In the MAST experiments reported below the rise time of the driver current is comparable with the time of travel of the shock. The calculated shock position for conditions in the 12-inch MAST (M_A at drive current maximum is 2.2) is given in Figure 13. The theoretical interface between the HGS and the drive currents is also shown for both the one-dimensional flow case and for the conditions which correspond to the ideal two-dimensional flow

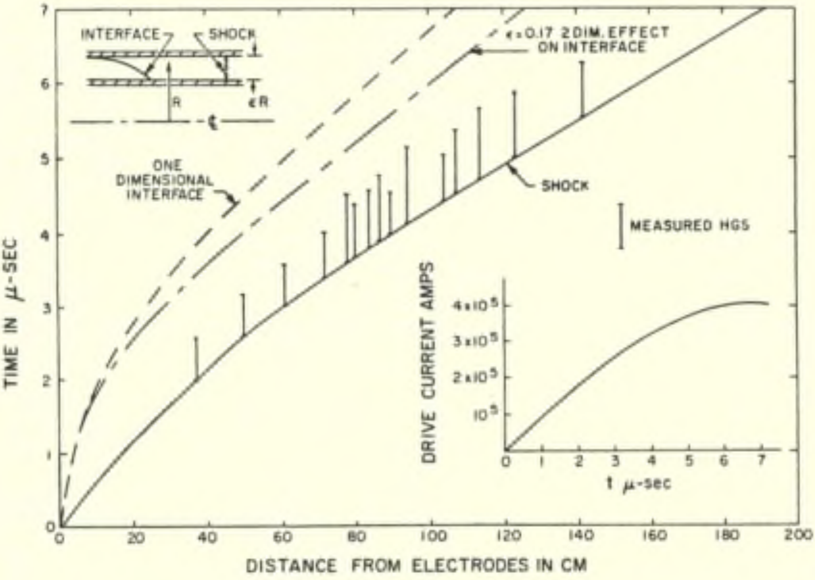

Fig. 13. — The calculated shock position and drive current interface in a MAST are plotted versus time after the initiation of the main discharge. These calculations correspond to a shock velocity at drive current maximum equal to 33 cm/μsec, the initial Alfven speed equal to 15 cm/μsec, and a quarter cycle time for the drive magnetic field equal to 7 μsec. The drive current interface is shown for both the one-dimensional case and the two-dimensional case (Fishman and Petschek, 1962*a*). The two-dimensional effect on the interface is due to the nonuniform drive magnetic pressure in the annulus, and the calculation was done for the particular case where $\varepsilon = 0.17$. The measured test times were obtained from the plasma radiation in the visible (Fig. 13) and the B field (Fig. 16), and the test time was defined as the time for which the measured plasma density of B field was constant within 10% of the value behind the shock.

according to Fishman's and Petschek's calculation (Fishman and Petschek, 1962 *a*). Note that no interaction between these two effects has been considered in this calculation.

Attainment of an HGS in the MAST.

In this section we will not attempt to summarize the experimental problems and developments which have been reported elsewhere (Patrick, 1958; Patrick, 1959; Kantrowitz *et al.*, 1959; Camac *et al.*, 1961; Patrick *et al.*, 1961). Rather, we will be concerned with those elements which supply evidence concerning the mode of operation of this device and the attainment of an HGS. It has been possible with the MAST to generate shock waves with velocities in excess of 60 cm/μsec which would be calculated to produce an enthalpy corresponding to 10^6 °K after equilibration if an HGS has been produced. One characteristic of these shock waves is that the velocity is fairly close to that anticipated from momentum considerations (Kemp and Petschek, 1959). The correspondence between the shocks obtained in the case where B_θ field was used and the theoretical predictions are shown in Figure 14. The correspondence between the calculated and theoretical velocities is significant evidence of some understanding of the operation of this device. However, it cannot be taken as evidence of an achievement of an HGS since the momentum considerations which govern the speed of the shock are relatively insensitive to non-uniformities, turbulence, energy loss to the walls, etc., which could easily destroy the HGS.

Patrick has monitored the light in various wave length regions emitted by the heated plasma and a sample oscillogram is shown in Figure 15. It is seen that the light rises steeply indicating the presence of a sharp " shock front ". The thickness of this shock region varies with density and temperature in a manner reproducible to a factor of two. These variations have been in the past correlated to a theory of a shock front based on wave wave interactions which will not be treated here (Kantrowitz *et al.*, 1959). More recently, this thickness has received a simpler and more plausible explanation (Petschek and Gerry, to be published) but related to the ionization rate in the shock front. The latter theory shows striking similarity to the measured thicknesses which supports the supposition that the steep rise in light intensity is indeed a shock wave. The radiation behind the shock front is attributed to free free bremsstrahlung from the completely ionized gas. Note for electron temperatures greater

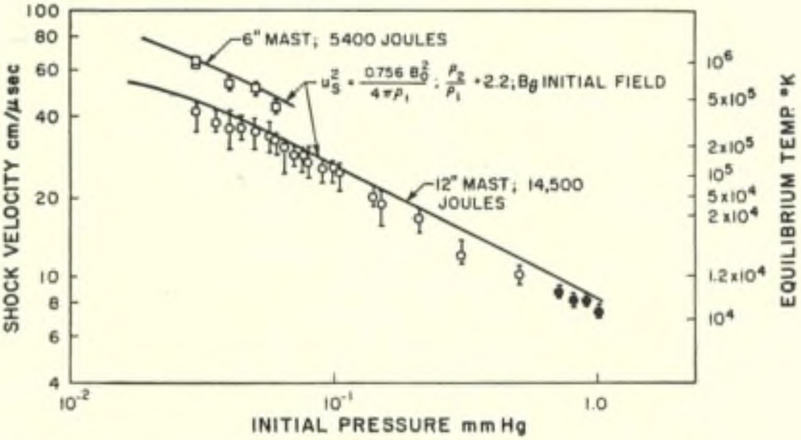

Fig. 14. — Measurements of the shock velocities produced in the MAST as a function of the initial pressure. Curves are taken with a constant driving energy and a constant $M_A = 2$. The temperatures which would be obtained if equilibration was complete are exhibited as the right hand ordinate. The blacked in points refer to those cases where no evidence for the existence of an HGS was obtained. The theoretical shock velocities are taken from Kemp and Petschek (1959) and it will be noticed that the agreement is as good as that usually obtained in high temperature diaphragm type shock tubes.

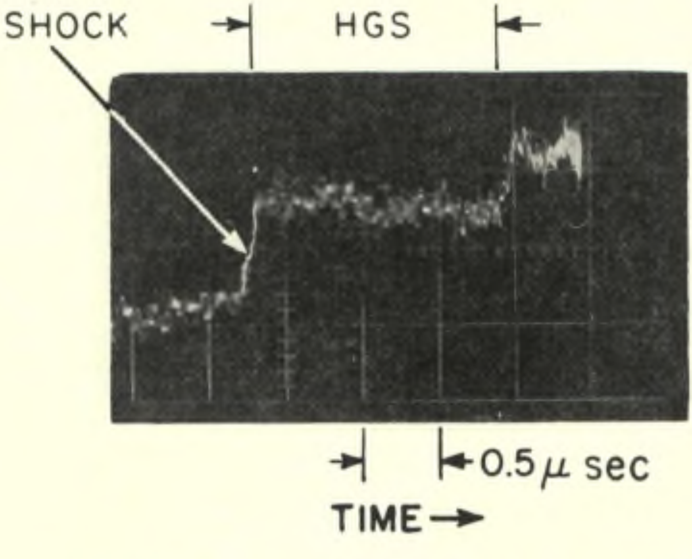

Fig. 15. — Light intensity observed near 4500 Å at a station 38 cm downstream from the electrodes in a 12-inch diameter MAST. The measured shock velocity was 28 cm/μsec and the initial pressure was 60 μ Hg of hydrogen. An initial containing B_θ field of 4000 gauss yields $M_A = 2$.

than 10^5 °K, the contribution of the free bound radiation is not important in the visible. Observations have been made of the emission in the far ultraviolet indicate that the electron temperature must be in excess of 10^5 °K for the fast shocks.

In many, although not all of the shocks observed, a constant light intensity for a considerable period of time is observed as in Figure 15. The duration of constant light intensity is plotted on Figure 13. The light intensity produced for high shock speeds correlates very well with the expected gas density. Note that the free free radiation in the visible from a fully ionized gas has little dependence on the gas temperature so this radiation can be used as a density measurement. The densities which are obtained from these radiation measurements agree very nicely with those expected from the shock theory as exhibited in Figure 16 where cases with both B_z and B_θ are plotted.

In the MAST the current buildup occurs over several μsec so that the shock is accelerated through the first part of its passage through the device (Fig. 13). The measured shock velocity and visible light intensity at various times as it passes down the shock tube are exhibited in Figure 17. It will be seen that at first the measured velocity corresponds more closely to that predicted for the interface. Note that the predictions plotted presume that the gas in the shock wave is a good enough conductor to compress the magnetic field. When this is not the case, the density ratio is much larger and the shock velocity should be close to u_2. Also, the light intensity under these conditions should be much higher as it varies as the square of the gas density. It seems to be rather strikingly indicated that the shock does not compress the magnetic field until velocities of the order of 12 cm/μsec are obtained and after this time the agreement with the expected density and the expected shock velocity are achieved. The values exhibited previously in Figures 14, 15 and 16 were those obtained after this " breakaway " had occurred.

The technique of probing plasmas with magnetic field measuring devices is widely used (Burkhardt *et al.*, 1958, Colgate *et al.*, 1958). Early attempts to measure the magnetic field change across the shock tube with conventional magnetic coils enclosed in a glass or quartz envelope (Keck, 1962 *b*, Patrick *et al.*, 1961) did not give understandable results. It was found that by use of an open loop and especially one in which the wire was bare rather than insulated gave much more understandable results. With coils of this type magnetic field compression in shock fronts has been measured. A typical pair of oscillograms giving both dB/dt and after integration the change in B is exhibited in Figure 18. Here again a measurable shock thickness is exhibited and this correlates very closely with a measured rise time for the light intensity supporting the indication that a shock wave does, in fact, exist in this device. It can be noticed also from Figure 18 that the magnetic field changes following the

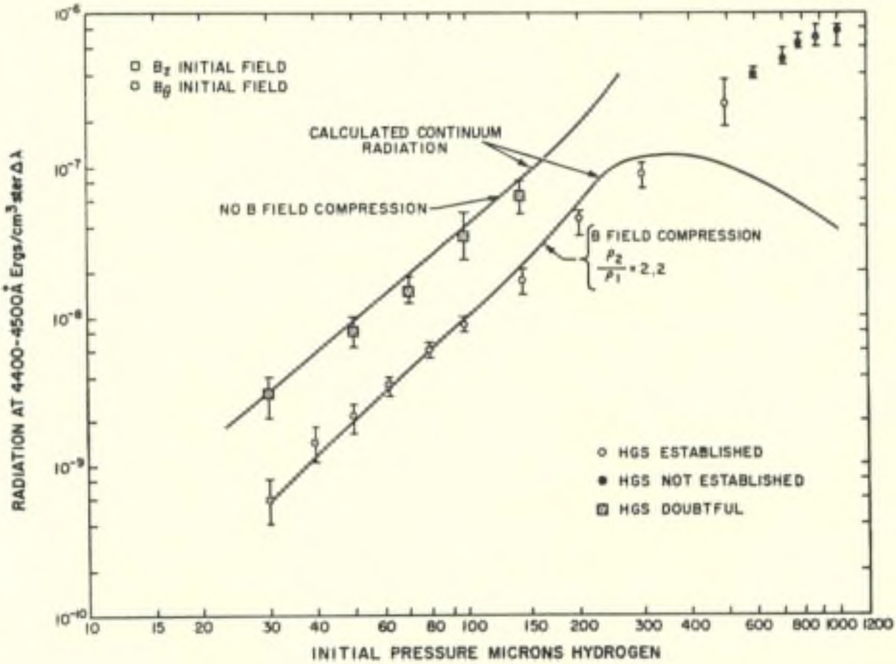

Fig. 16. — Comparison of the measured continuum radiation with a theoretical calculation assuming complete equilibrium. Note that this radiation is independent of the electron energy distributions corresponding to an electron temperature greater than 10 EV. Therefore, it is not to be taken as evidence that the gas has reached thermodynamic equilibrium. It does, however, indicate that the electron density (the radiation is proportional to the square of the electron density) is close to that expected. The square points measured with a B_z containing field are shaded because some doubt exists that an HGS should have been formed in this case. However, it should be noted that the light intensity traces exhibited constant values within 10% for several channel widths behind the shock. The theory of Fishman and Petschek (1962*a*) would indicate a deviation from the one-dimensional model for these cases. The blacked in points are those where the magnetic compression was incomplete for the B_θ case. The data obtained with B_θ correspond to those plotted on Figure 14 for the total drive energy of 14,500 joules.

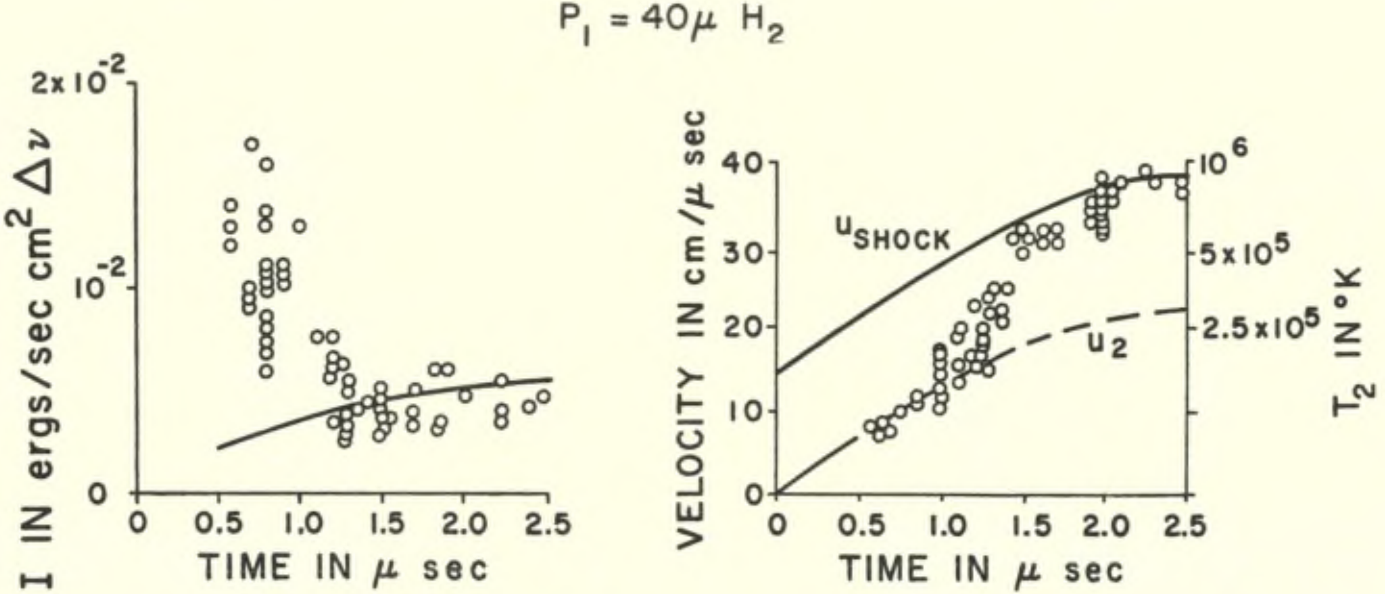

Fig. 17. — Comparison of the light intensity and shock velocity measured at various axial stations along the shock tube. The density is plotted vs. the time from initiation of the main discharge. The 1/4 cycle time of the drive current is about 2.5 μsec. These data were made with a B_θ containing field in a 6-inch diameter MAST. It will be noticed that when the front velocity exceeds about 12 cm/μsec both the front velocity and the light intensity approach those calculated (Kemp and Petschek, 1959) for an infinite conductivity shock wave which are shown as the solid lines.

shock are much slower and that a fairly flat magnetic field region in agreement with the idealized theory has been obtained. In Figure 19, a comparison between the measured and calculated change in B_θ is plotted against shock velocity. It is strikingly exhibited here for velocities greater than 12 cm/μsec the magnetic field is, in fact, compressed in the shock wave according to the law B_θ/ρ constant. Thus, for these high velocity shock waves the effective electrical conductivity must be very high during the acceleration in the shock front.

Camac (Patrick and Camac, 1961) has developed a heat transfer gauge which depends on the infrared measurement of the temperature of a thin film of carbon exposed to the plasma. This instrument

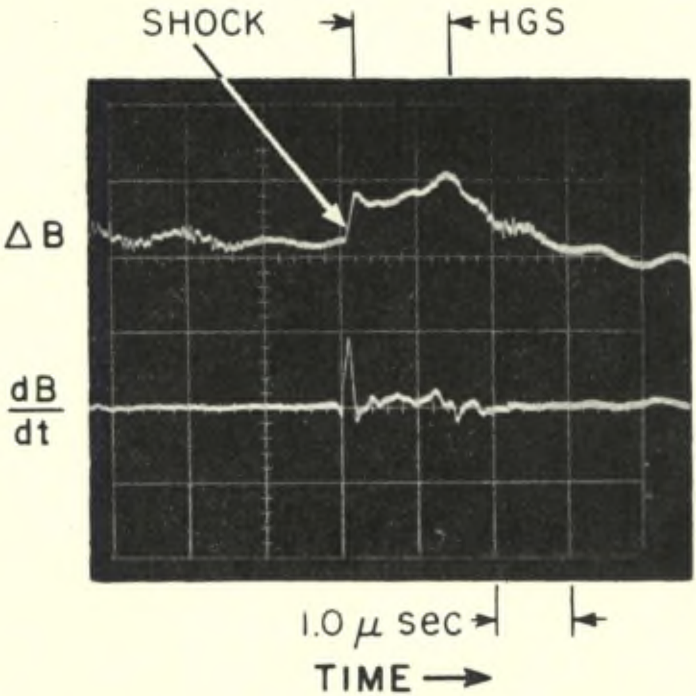

Fig. 18. — The B_θ field 53 cm from the electrodes for the same view as Figure 15. It is exhibited that the magnetic field changes steeply through the shock wave as required for high conductivity in the shock and that the magnetic field following the shock is relatively flat. The slow decline after the end of the HGS is related to the time constant of the integrating circuit used to exhibit ΔB. The upper curve is processed from the lower curve in which the oscilloscope is directly connected to the coil terminals.

has been used to measure the heat transfer to the outer wall of the MAST. It has been exhibited that the heat transferred to this film indicates a heat deposition corresponding to the energy contained in less than 10% of the plasma heated by the shock. This would tend to indicate that the containment (at least at the outer wall) is indeed quite good for the whole of the HGS indicated by light intensity and ΔB measurements. Some questions remain concerning the possible influence of evaporated gas on these measurements.

Calculations of the energy transfer between protons and electrons show that during the time a plasma sample is in the HGS, considerable sharing of the energy between the protons and electrons should occur due to particle collisions. If electron temperatures greater than about 20 volts were achieved, it would be anticipated that considerable X-ray emission would occur. Attempts to observe X-ray emission at 44 Å were made and failed to indicate electron temperatures greater than 20 volts. The reason for this discrepancy is not understood.

To summarize the general position regarding the production of an HGS, indications have been obtained from the shock velocity, the steep and calculable rise in light intensity and the corresponding

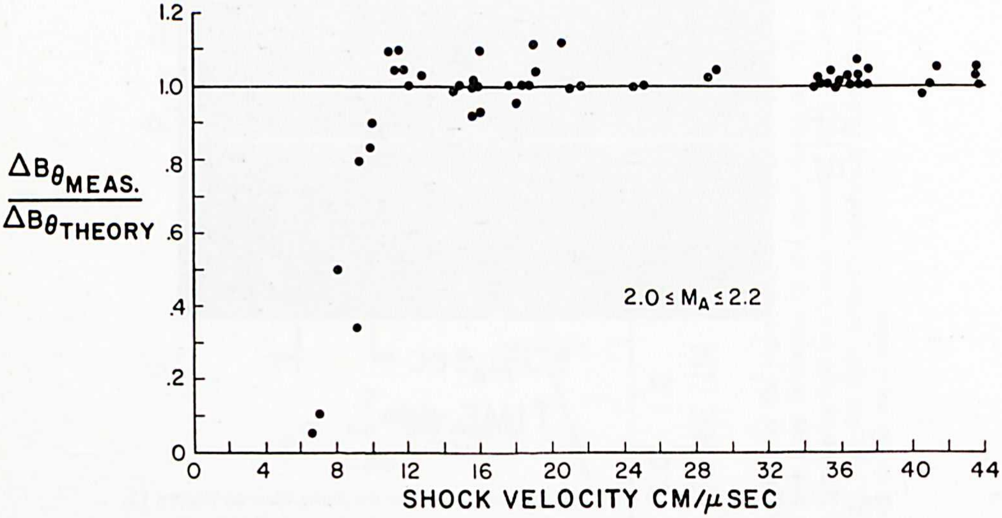

Fig. 19. — The comparison of the measured and calculated change in B_θ with shock velocity. It will be noted that the conductivity is apparently high enough at a shock velocity at 12 cm/μsec, so that the theoretical magnetic field compression for infinite gas conductivity is obtained.

steep and calculable changes in magnetic field that, in fact, plane MHD shock waves with velocities exceeding 60 cm/μsec have been obtained and the MAST does provide a good device for the study of these shocks. Regarding the formation of an HGS, the evidence is less clear. The light intensity is fairly constant and exhibits the expected values for shocks of velocity greater than 16 cm/μsec. For shocks with velocities less than this, i.e., pressures greater than 300 μ on Figure 16, the measured light intensities fall above the theoretical value assuming full magnetic compression in the shock front. The theoretical intensity decreases at higher initial pressures where ionization is no longer complete. At still lower speeds, around 10 cm/μsec (Fig. 19) magnetic compression falls below that expected for infinite conductivity which is anticipated due to the fact that the temperature assuming magnetic compression would now be down to 12,000 °K (Fig. 11).

It should be remarked that in view of the fact that the visible light intensities are theoretically expected to be independent of the temperature, they do not provide the complete story on the gas state. Regarding the magnetic field increase, the verification of the constancy of B_θ/ρ provides further support for the existence of shock waves. However, the measured B values behind the shock are not sensitive to the gas state since the gas pressure is very small (the order of 1/6) of the magnetic pressure. The attempt to establish the existence of an HGS in very high temperature plasmas suffers from difficulties associated with the non-attainment of complete thermodynamic equilibrium (i.e., equalization of ion and electron temperatures) which would not occur through particle collisions in the time available here. It will be recalled that the recognition of the attainment of equilibrium in an HGS in diaphragm type shock tubes was very important in their development. Thus, finally, it is clear that useful studies of the shock front can be made with the present apparatus. Improved diagnostic techniques must be developed before the promising indications of the achievement of an HGS can be developed to a certainty.

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Discussion du rapport de M. Kantrowitz

M. Ross. — Alder and Wainwright have calculated, with high speed computers, the translational relaxation time of a system of hard spheres and find the establishment of a Maxwellian distribution of speeds from various non-equilibrium distributions with a few collisions per particle.

M. Herzfeld. — The relaxation of the translation distribution function was already discussed by Maxwell for special cases and has recently been considered in a general manner by H. Grad and by Offerhaus. It turns out to be always not longer than a few collision times. Actually in the discussion of the previous days it has always been assumed that the translational relaxation time is much shorter than any other relaxation time involved, Maxwell distribution for the translation being presumed.

M. Norrish. — In connection with the interesting methods of initiating and studying shock waves described by Dr. Kantrowitz, I would like to stress that it is possible to generate shock waves by adiabatically heating an isolated section of a gas sample by flash irradiation. For example, if a mixture of hydrogen, oxygen and a trace of NO_2 as sensitizer with no added coolant gas, be subjected to a high intensity flash at one end of a quartz tube, the rest of the tube to the extent of, say, five sixths being blacked out, a shock wave is produced by the explosive reaction of the charge which travels down the tube. This is to be correlated with detonation in explosion. Dr. Thrush [*Proc. Roy. Soc.*, **A223**, 147 (1956)], has followed the passage of such a shock wave by placing photomultiplier monotoring stations at different positions along the tube and observing the emission resulting from sharp thermal compression. It is also observed longitudinally when the shock wave hits the end of the reaction vessel and gives rise to a sharp peak of emission lasting one to two microseconds. Work on knock and antiknock has shown, using amyl nitrite, etc. as a sensitizer, that knock in the internal combustion engine is identical with homogeneous detonation and that when the antiknock, such as lead tetraethyl, is added to the mixture, the sharp peak of emission is smoothed out to a curve characteristic of slower burning and the suppression of detonation.

Another more simple example which can be cited in this context is that of the flash irradiation of chlorine. A quartz reaction vessel containing chlorine gas at a pressure of half to one atmosphere disintegrates by explosion when flashed with an energy of about 2000 Joules. By using such a tube of chlorine or other simple reactant flashed at one end, it should be possible to initiate a sharp adiabatic shock wave which would readily lend itself to the study of fast chemical processes.

M. Kantrowitz. — I believe this technique could be used to produce shock waves and an HGS. It would have the advantage of not requiring diaphragm replacement which would be especially valuable when the gas returns to its initial state after it settles down. The application of this idea is of course limited to a restricted class of gases.

M. Hornig. — If one does not need quite such exotic conditions as those described by Dr. Kantrowitz, for instance, if temperatures of less than 3000 °K are adequate, the problem of obtaining a homogeneous gas sample and maintaining uniform conditions is much less severe. The problem of the boundary layer, however, is always there but it is doubtful if the effects it produces have introduced serious errors in dissociation measurements. For example, if the homogeneous gas sample is heated to 1500 °K, the boundary layer which is at the temperature of the tube wall, 300 °K, is about five times more dense. Since its thickness is of the order of 0.2 mm, the effective sample thickness would be changed by just over 1% in a 75 mm tube.

There is one circumstance, though, in which its effect can be catastrophic, namely if the sample can be condensed at 300 °K and the pressure of the shock. In that case a liquid film which is highly scattering is produced on the wall and the measurements are strongly distorted. We have observed such effects in CCl_4 and nitromethane.

M. Porter. — I am not clear why the boundary layer problem is relatively unimportant in shock studies compared with flash photolysis. In both cases the gas temperature is raised instantaneously above that of the container and this is followed by a cooling of the gas near the wall which, since pressures must equalize, results in a higher concentration near the wall than at the center of the vessel. The distribution changes with time and for air at N.T.P., for example, and an initial temperature difference of 100 °K, there is a 10% maximum reduction in concentration at the center of a 2 cm diameter cylindrical vessel. In sensitive measurements like those in atom recombination even a 2 °C intitial temperature difference can cause significant errors. How can shock tubes experiments tolerate differences of 1000 °C or more ?

M. Kantrowitz. — Boundary layer effects will be present in most cases where reactions are studied in closed vessels. As far as shock tubes are concerned the splitter technique allows us to achieve a steady and easily calculable boundary layer quickly.

M. Norrish. — The effect of temperature gradient between the centre and the walls of the reaction vessel in the flash technique must not be overemphasized. As far as kinetic spectroscopy is concerned, the observation times are short enough for the effect of condensation on the walls to be neglected. For example, the disappearance of a given spectrum on flashing is attributed to the formation of a different chemical form rather than the denuding of the reactants along the central axis of the reaction vessel. In the case of sulphur dioxide, it has been shown that the spectrum of SO_2 completely disappears on flashing and only returns in the course of a few milliseconds. That this was not due to the condensation of the reactant on a surface zone is shown by the fact that a new absorption spectrum appears in place of the original and disappears as the former returns. Such phenomena which can be observed in the case of formaldehyde, etc. are to be ascribed to the production of high temperature isomers (and in the case of SO_2, possibly a triplet).

SHOCK-TUBE STUDIES OF PROCESSES OF ELECTRONIC EXCITATION IN GASES

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ABSTRACT

It is shown that measurement of the spectrum-line reversal temperature in shock-heated gases can be used to obtain information about efficiencies and processes of electronic excitation of metal atoms at high temperature. For excitation by molecules, the electronic excitation temperature tends to follow the effective vibrational temperature of the molecules, and reversal temperatures may be low near the shock front if the vibrational relaxation time is appreciable. Although excitation of metal atoms by cold inert gases has a very small effective cross-section, it is shown that at 2,500 °K the cross sections for excitation of chromium or sodium by argon or by neon are around 1/20 of the gas-kinetic cross sections. Processes of excitation are discussed, using the concept of crossing of potential energy curves.

INTRODUCTION

The processes by which atoms and molecules become electronically excited are important in determining the radiation emitted by hot gases, and a knowledge of their efficiency is necessary for assessing the validity of some spectroscopic methods of measuring high gas temperatures. In complete equilibrium, the ratio of the population of an atomic or molecular species in an excited electronic state to the population in the ground state is given by the usual Boltzmann factor $e^{-E/kT}$ and the statistical weight term. Under these equilibrium conditions the process of electronic excitation by absorption of radiation will be in balance with electronic deactivation by emission of radiation, and excitation by collision will be balanced by collision deactivation; excitation as a result of chemical reaction will be balanced by the reverse reaction in which the electronically excited species provides the activation energy. However, this perfect equilibrium is only attained in a constant-temperature enclosure such as the ideal black-body furnace, and the radiation must then give a continuous spectrum with unit emissivity. In practice we are more familiar with hot gases emitting discrete spectra, often with rather low emissivity. Under these conditions, depopulation of excited electronic states by emission of radiation must exceed the rate of population by absorption, so that the proportion of atoms or molecules in excited electronic states will tend to fall below the equilibrium value defined by the Boltzmann relationship. The extent by which the population falls below the equilibrium value will depend on the extent to which the collision processes are able to maintain the population, that is on the relative importance of the radiation and the collision processes.

The efficiency of the radiation processes can be determined from measurement of the absorption coefficient, leading to the oscillator strength or f value for the line or band system involved. Many such values are available, and radiative lifetimes for fully allowed transitions in the visible region of the spectrum are of the order 10^{-8} sec.

Some information about the collision processes can be obtained from the quenching of resonance fluorescence. Experimental data by Norrish and Smith (1940) have been particularly useful, and the subject has been well reviewed by Pringsheim (1949). Quenching cross-sections are very variable, being rather greater than the gas-kinetic cross sections for some particular diatomic and polyatomic molecules, but quite low for other molecules and almost vanishingly small for the inert monatomic gases like argon. This quenching work has mostly been done at fairly low temperature (below 800 °C) and only gives information about quenching processes requiring little or no activation energy. There is some evidence that quenching cross-sections may vary with temperature, especially for the inert gases. Thus Pringsheim quotes Oldenberg as finding that the cross-section for quenching of mercury by argon is four times greater at 750 °C than at room temperature; some shock-tube results discussed here indicate that energy transfer to sodium or chromium by argon at about 2,000 °K is fairly efficient.

The strong quenching (and excitation) by molecules is believed to be due to interconversion of electronic and vibrational energy, so that the electronic excitation temperature, which is measured by the spectrum-line reversal and some other spectroscopic methods, tends to follow the effective vibrational temperature of the molecules rather than their translational temperature. Theoretical treatments of the interconversion of electronic and vibrational energy are made difficult because of lack of knowledge about the potential energy surfaces of the collision complexes, and Dickens, Linnett and Sovers (1962) have shown that effects can only be explained by assuming interactions between such surfaces. Thus there is insufficient knowledge of energy conversion processes involving collisions of excited species with both inert monatomic gases and molecules, especially at high temperature. In recent years the shock-tube has been developed as a powerful tool for high temperature research, and the present paper is intended to summarise a continuation of recent work (Clouston, Gaydon and Glass, 1958; Clouston, Gaydon and Hurle, 1959; Gaydon and Hurle, 1961, 1962 *a*) on spectrum-line reversal measurements of temperature in a shock tube, and their bearing on the collision processes.

TEMPERATURE MEASUREMENTS IN A SHOCK TUBE

The bursting-diaphragm shock-tube is a convenient tool for studying a gas heated almost instantaneously to a high temperature. Observation times are, however, limited to a few hundred microseconds. Measurements of the effective electronic excitation temperature of a suitable metallic atom may be made by the spectrum-line reversal method, using a monochromator or interference filter to isolate the required wavelength, a photomultiplier to detect the light signal and a cathode-ray oscillograph to record it. The technique has been described fully in the references already cited.

If the reversal is observed with a single optical beam against a background source of continuous spectrum at known brightness temperature at the required wavelength, then if the shock heated gas is above the temperature of the background the spectrum line will be in emission so that the oscillograph trace will be deflected positively during the flow period. If, however, the shock-heated gas is cooler than the background lamp, then the spectrum line will be absorbed and a negative deflection will be recorded. Thus a single-beam system gives information whether the gas is hotter or less hot than the known background.

With a double-beam system in which two photomultipliers are set to view background sources of different effective temperatures through the shock-heated gas, it is possible actually to measure the temperature, and its time-variation, in the gas. For this purpose the photomultipliers and amplification systems must be adjusted to equal sensitivities. When temperature variations with time are small it is convenient to work with backgrounds about 150 °K apart in temperature, one above and the other below the expected shock temperature. The temperature can then be measured from the oscillograph deflections using a linear interpolation. A record of this type, for a shock through nitrogen is shown in Figure 1. When there are big fluctuations in temperature, it is better to use one photomultiplier viewing a bright background lamp through the shock and to use the other photomultiplier to view the emission only from the shock. The calculation of temperature is then made using Wien's law (see Gaydon and Hurle, 1962 *b*).

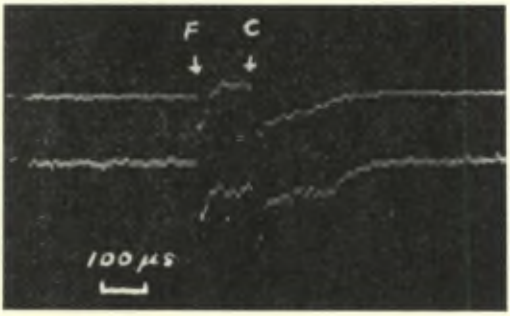

Fig. 1. — Oscillograph trace of sodium-line emission (upwards) or absorption (downwards) for a shock through nitrogen. The background lamp temperatures were 2481 °K (upper trace) and 2625 °K (lower trace). The low temperature near the shock front, F, is obvious, and then the temperature is steady up to the contact surface, C.

The selection of atomic lines which can be used to measure electronic excitation temperatures is very limited. The alkali metals have suitable strong resonance lines in the visible region, and some measurements have been made using the sodium D lines, the sodium being introduced as a smoke in the experimental gas by passing it either through a heated quartz tube containing sodium chloride or sodium iodide or over an electrically heated platinum coil supporting a bead of molten salt. Unfortunately it is not possible to exercise much control on the amount of sodium introduced; the alkali metals do not possess suitable volatile compounds which would enable them to be added as vapours. A few measurements using the blue line of indium have also been made. Russian workers (Sobolev, Faizullov and Kudryartsev, 1960) have made similar measurements using lines of sodium, barium and ionised barium, the metal being introduced by dusting the walls of the shock tube with a salt; this tends to give delayed excitation and to stress the influence of the cool boundary layer. Most substances with volatile organic compounds (e.g. lead ethyl, iron carbonyl) have resonance lines which are of too short a wavelength for the reversal method to give adequate sensitivity, the black-body function being so small at short wavelengths. Recently (Gaydon and Hurle, 1961) some observations have been made using the chromium resonance triplet in the violet, the chromium being introduced in controlled amounts (usually 0.1% by volume) as the volatile chromium carbonyl, $Cr(CO)_6$; this is found to decompose very quickly to free chromium atoms above 1000 °K.

The shock speed is measured by timing the passage of the shock front over a number (usually three) of thin-film platinum resistance detectors. From this speed the equilibrium gas temperature can be calculated from the well-known shock equations, and the measured reversal temperature can then be compared.

EXCITATION BY MOLECULES

Reversal-temperature measurements of the sodium and chromium lines in simple molecular gases, shock heated to temperatures between 2000 and 3000 °K and to pressures between 0.2 and 2 atm., appear to agree excellently with temperatures calculated from the measured shock velocity. This shows that in these cases collision processes are sufficiently rapid to maintain effective equilibrium between the ground state and excited state populations despite radiation losses. This agrees with the results of quenching of sodium fluorescence (Norrish and Smith, 1940) at fairly low temperatures; these indicate quenching cross-sections about the same as the gas-kinetic cross-sections in many cases (e.g. 14.5×10^{-16} cm^2 for N_2, 28.0×10^{-16} cm^2 for CO, 7.4×10^{-16} cm^2 for H_2).

However, the shock-tube work sometimes reveals departures from equilibrium temperature close to the shock front. In some cases (O_2, H_2) the temperature measured by reversal of the chromium or sodium lines is initially above the equilibrium value, and this is attributed to delay in dissociation of the molecules, so that the temperature in translation and in internal degrees of freedom of the molecules is initially too high.

For some molecules (especially nitrogen and carbon monoxide) a low temperature close to the front is observed, this rising fairly quickly towards the equilibrium value. This is well shown by the oscillograph traces in Figure 1; this is of a shock through nitrogen at a calculated temperature of 2530 °K, the effective background temperatures of a pointolite lamp used as background being 2481 °K for the upper beam and 2625 °K for the lower beam; it can be seen that the temperature remains below 2481 °K for the first 40 μ sec. but rises finally to a steady value 2515 °K, only just below the equilibrium value. It appears that this effect is due to the delay in the nitrogen molecules taking up vibrational energy, and indeed the time agrees well with other measurements of the vibrational relaxation time of N_2 interpolated to the conditions of temperature and pressure used in the shock. A similar effect is obtained with carbon monoxide (Gaydon and Hurle, 1962 *a*).

It has been realised for many years that interchange of electronic and vibrational energy is more probable than interchange of electronic and translational energy. Some recent calculations for particular examples by Dickens, Linnett and Sovers (1962) using an ultra-simplified interaction potential showed however, that exchange transfer of electronic and vibrational energy was a very inefficient process except for a near coincidence of vibrational and electronic energy levels. However, although there are a few cases where quenching of fluorescence by molecules is inefficient (e.g. the value of 0.11 × 10^{-16} cm^2 for the cross-section for quenching of Na by CH_4), the generally high quenching cross sections, even when there is no exact coincidence of vibrational and electronic energy levels, suggests that the ultra-simplified theory is inadequate. The experimental work shows that it will probably be necessary to take into account the crossings of the potential energy hypersurfaces of the various electronic states of the collision complexes.

OBSERVATIONS ON EXCITATION BY INERT GASES

The excitation of the sodium lines and the chromium lines in shock-heated argon and neon, shows that the process is much more efficient than might be expected from quenching data in relatively cool gas. Figure 2 shows oscillograph traces of the chromium lines in argon; for this shock the background lamp temperatures were 2500 °K for the upper beam and 2660 °K for the lower. Theie are some initial unexplained temperature fluctuations near the shock front, and then the deflections settle to a steady value so that the lower beam is very near a match, or possibly very slightly in absorption; the observed chromium-line reversal temperature from this record is 2650 °K. This compares with a theoretical translational

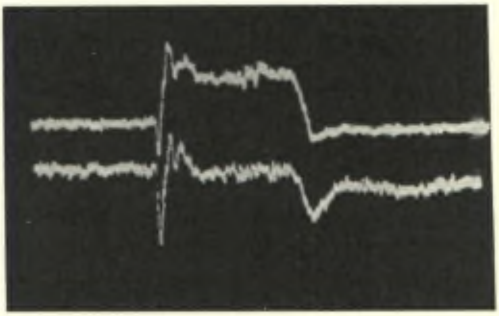

Fig. 2. — Oscillograph trace of chromium-line emission (upwards) or absorption (downwards) for a shock through argon. Background lamp temperatures 2500 °K (upper trace) and 2660 °K (lower trace). The observed line-reversal temperature is clearly about 2650 °K, whereas the true gas temperature is 2800 °K.

temperature calculated from the measured shock speed of 2800 °K. The radiation has thus produced a fall in population in the upper electronic state equivalent to a temperature drop of about 150 °K.

The average result for a number of rather similar shocks shows that the chromium-line reversal temperature in shock-heated argon at a pressure of 0.5 atm. and equilibrium temperature 2500 °K is about 140 °K too low. Under similar conditions the sodium-line reversal temperature is 150 °K low. For chromium in neon at 0.4 atm. and 2700 °K, the observed reversal temperature is about 200 °K below the translational temperature.

It is possible, with certain assumptions, to use these results to calculate the excitation efficiency by collisions. If the population of atoms in the ground electronic state is N_1 and in the excited state N_2 the collision frequency Z, the excitation efficiency E, the theoretical translational temperature T_t and the observed electronic excitation temperature T_e and the radiative frequency (i.e. the reciprocal of the radiative lifetime) is R, then the number of atoms undergoing transitions from the excited to the ground state per second is

$$N_2 \cdot Z \cdot E + N_2 \cdot R$$

and this must be equal to the number undergoing the reverse transition by collisions, which is

$$N_1 \, Z \, E \exp. \, (-\mathbf{h}\nu/\mathbf{k} \, T_t)$$

This ignores excitation by absorption of radiation (see later). Since $N_2/N_1 = \exp. \, (-\mathbf{h}\nu/\mathbf{k} \, T_e)$ it is possible, from knowledge of T_t, T_e, Z and R to eliminate N_1 and N_2 and obtain the collision efficiency E.

Thus for argon/argon collisions the frequency is known, from viscosity data, to be 4.0×10^9 at 20 °C and 1 atm., giving 0.7×10^9 at 2500 °K and 0.5 atm.; we assume a similar value for argon/chromium collisions. For chromium, Ostrovskii and Penkin (1957) have reported an f value of 0.15 for the 4254 Å line; this corresponds to a radiative lifetime of 1.8×10^{-8} sec or $R = 0.55 \times 10^8$. Taking $T_t = 2500$ °K and $T_e = 2360$ °K we obtain the collision efficiency $E = 0.065$. This indicates that the effective collision cross-section for electronic excitation of chromium by argon at 2500 °K is about 0.065, or 1/15, of the gas-kinetic value.

This simple calculation ignores excitation by absorption of radiation, and would only be true for optically thin gas. In the optically thick case, the reversal temperature is mainly determined by the outer layer of gas, on the side towards the spectroscope (see Gaydon and Wolfhard, 1960) where an element of gas is radiating over an angle of 4π and receiving it from only 2π. The radiation loss is thus roughly halved, and in this case the collision excitation efficiency for Cr/A would be 1/30. In the shock-tube experiments, the centre of the line will be near the optically thick case, but the wings of the line will be optically rather thin. The measurements are at present far from precise; some minor statistical-weight terms have also been neglected in the calculations and the actual gas kinetic collision frequency for argon/chromium is unknown. It does, however, appear that the collision efficiency is likely to lie between 1/15 and 1/30.

Similar rough calculations based on the observations for excitation of sodium by argon give an efficiency of between 1/11 and 1/22. For excitation of chromium by neon the value is between 1/17 and 1/34. Dr. Faizullov has informed the author that his observations on excitation of ionised barium lines by argon up to rather higher pressures and temperatures are consistent with an excitation efficiency of about 1/20.

PROCESSES OF EXCITATION BY INERT GASES

It can be seen qualitatively from classical considerations that conversion of relatively large amounts of translational energy of relatively heavy atoms into the energy of motion of much lighter electrons is unlikely. The energy transfer may, however, be explained by assuming that the atom-atom collisions can be treated as the formation of a collision complex in which potential energy curves may cross. If this happens then a radiationless transition from one electronic state to the other may be possible. The various possible electronic states of the diatomic collision complex which can be formed from a pair of atoms in known electronic states can be predicted from the Wigner-Witmer correlation rules. For an inert gas atom in its ground ^1S state interacting with chromium in a ^7S state, only a single electronic state of the CrA complex, a $^7\Sigma$, is possible, and this must certainly be repulsive, i.e. without a potential energy minimum. For argon $(^1S) + Cr(^7P)$, the possible diatomic electronic states are $^7\Sigma$ and $^7\Pi$. If these also give potential energy curves which are strongly repulsive and do not cross that from the ground states, we shall have the situation illustrated in Figure 3 *a*. In this case electronic excitation by collision would be extremely improbable. If, however, one of the upper electronic states is less strongly repulsive, as in Figure 3 *b* and crosses the ground state curve, then it is possible that a collision between argon and chromium atoms with sufficient kinetic energy may lead to the crossing point being reached, in which case a radiationless transition from one state to the other may occur, with the atoms separating as $A(^1S) + Cr(^7P)$.

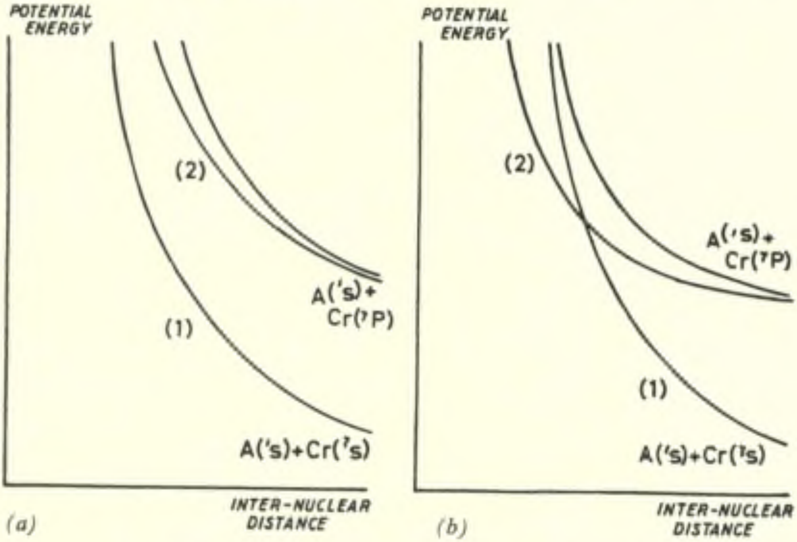

Fig. 3. — Hypothetical potential energy curves for the diatomic collision complex chromium + argon.

If this type of process is assumed to occur, and the collision efficiency of around 1/20 at 2500 °K is interpreted as the activation energy required to reach the intersection point, then this point must lie only about 0.9 e.v. above the limit to $A(^1S) + Cr(^7P)$. The situation with argon/sodium collisions is likely to be similar.

The measurement of the temperature of hot gases by spectroscopic methods, either of the reversal type or from comparison of line intensities, is complicated by the disturbance of the population of electronically excited states by emission of radiation not being compensated for by absorption. When the gas density is around or above atmospheric density, errors will be small for molecular gases, but still not negligible for inert gases. At low gas density errors will be serious. Knowledge of the collision excitation efficiencies, such as that gained from the shock-tube measurements enables the error to be assessed, and possibly corrected.

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Discussion du rapport de M. Gaydon

M. Kantrowitz. — In connection with the anomalous frontal effects in argon, it is important to keep in mind the possible role of impurities, particularly those that may be boiled off the wall and become luminous in the boundary layer. The excitation of the chromium might be by collisions of electrons, the rather low observed temperature being due to the Ramsauer effect.

M. Gaydon. — In reply to Dr. Kantrowitz' suggestion, I should point out that a spectroscopic study did not reveal any impurity features (e.g. CN) in these primary shocks. Deliberate addition of caesium chloride powder on the wall to increase the ionisation dit not affect the reversal temperature. Similar low temperatures were obtained with neon which shows less Ramsauer effect.

M. Norrish. — In consideration of Prof. Gaydon's shock tube observations on the electronic excitation of metals, the quenching of sodium fluorescence by different additives may be compared with his results on electronic excitation by a diatomic gas. The results listed in my paper (Table VI) show that it is not possible to correlate the quenching cross section with the vibrational frequencies in particular hydrocarbons. The difference between the effects of olefins and paraffins on the quenching is striking. The presence of unsaturation in the quenching molecule appears to be very important and clearly some type of specific interaction is involved. In the case of the hydrocarbons, the potential energy is thought to be the dominant factor and not direct correspondence between electronic and vibrational levels. This is to be contrasted with the quenching of Hf^3P_1 to Hg^3P_0 where the energy involved is of much smaller magnitude (e.g. 0.218 eV) and near resonant effects with vibrations may become possible.

M. Kuhn. — The observation that argon does not quench the sodium light emission at ordinary temperature and that it is effective in activating sodium at high temperatures (3000 °K) seems to indicate that the exchange of energy between argon and sodium is depending on temperature. If a certain low value of the distance between the centers of the two atoms is necessary for the energy exchange to take place (intersection of energy-distance curves) it is well possible that the required small distances will be realised in collision at high temperatures, but not in collision at a low temperature, explaining the sodium excitation at high temperatures and the absence of quenching at low temperatures.

M. Polanyi. — Prof. Gaydon's striking results suggest strongly that vibrational energy is being transferred efficiently into electronic energy. This process, and its reverse,

$$M^* + AB \rightarrow M + AB^\dagger,$$

have frequently been involved to account for changing concentration of electronically excited M^*. However, direct evidence of the involvement of a vibrationally excited species, $AB^\dagger$, has been lacking.

Mr. Gabriel Karl in my laboratory has constructed an apparatus in which both M^* and $AB^\dagger$ can be studied simultaneously. M is excited optically, by means of continuous illumination. The concentration of M^* and $AB^\dagger$ in their various excited states are measured, as a function of the pressures of each and of the illumination intensity, by recording the emission in the ultraviolet, visible and infrared regions of the spectrum.

When M is Hg ($\sim 10^{-3}$ mm pressure) and AB is CO or NO (at roughly 10^{-1} - 10^{-3} mm pressure), vibrational excitation is clearly observed. No detailed analysis has yet been attempted in the case of NO. For CO all the variables mentioned above have not yet been explored, but the evidence accumulated up till now suggests a non-resonant transfer of electronic into vibrational energy.

M. Inghram. — I would like to give some experimental results which bear on the question of transfer of translational to electronic energy. The experiments I wish to describe are those of Prof. Clayton Giese of the University of Chicago.

Giese has studied endothermic ion-molecule reactions of the type

$$Ne^+ + CO + \text{energy} \rightarrow Ne + C^+ + O \qquad (1)$$

$$Ne^+ + He + \text{energy} \rightarrow Ne + He^+. \qquad (2)$$

The technique Giese used was to direct a resolved ion beam of known energy into a reaction chamber and to analyze the products of the reaction with a mass spectrometer. Reaction (1) is endothermic by about 0.7 eV. Thus for the reaction to take place 0.7 eV of translational energy must be converted into electronic energy. Giese's experimental results show that as soon as the relative kinetic energy of the $Ne^+ + CO$ reaches 0.7 eV, the cross section rises sharply. It reaches $1 \cdot 10^{-16}$ cm^2 at 1.0 eV, has a maximum value of $3 \cdot 10^{-16}$ cm^2 at about 3 eV, and thereafter decreases very slowly. Giese obtained similar results for A^+ on CO, with a sharp threshold at about 6.7 eV, the endothermicity of the reaction, and a maximum cross section of 10^{-16} cm^2 a few volts above threshold. Clearly, large and efficient energy transfer is possible in collision between ions and molecules.

In contrast to the triatomic complex discussed above, Giese has found the energy transfer between an ion and an atom to be quite inefficient. The cross sections for reaction (2) are at least two orders of magnitude smaller than those for the triatomic cases. Giese has tentatively stated that he believes such cross sections, as well as cross section variations, to be consistent with the quasi adiabatic theories of Massey, i.e. that they increase very slowly above threshold and have a maximum value some hundreds of volts higher.

While the above reactions are between one charge and one neutral species, the question of transition between different electronic states is similar to those encountered in the subject under discussion.

M. Linnett. — Prof. Gaydon has shown, using the sodium line reversal method, that he follows the *vibrational* temperature of nitrogen when it is heated by a shock. This shows that there is a relatively easy transfer between vibrational energy of the nitrogen and electronic energy of the sodium. Dickens, Linnett and Sovers (*Disc. Faraday Soc.*) showed that such an easy transfer could not be understood in terms of a simple interparticle force field. It seems therefore that a special interaction must be involved. Prof. Laidler suggested that the ease of transfer might be accounted for by considering, as a basis for constructing more exact potential energy surfaces, along with the repulsive curves of $N_2 + Na$ (G.S.) and $N_2 + Na$ (E.S.), an attractive one due to the system $N_2^- + Na^+$. This curve would be about 5 eV above the $N_2 + Na$ (G.S.) curve at large separations but would " cross " the others as the separation decreased. On this hypothesis, as the excited sodium atom collided with a nitrogen molecule, it would pass, as the separation decreased, into $N_2^- Na^+$, finally separating into $N_2 + Na$ (G.S.). This will, since the final state is different from the first, clearly necessitate a "jump" from one potential energy surface to another. But the probability is likely to be enhanced because the surfaces are closer. Further, by the fact that, in the collision complex, the nitrogen part of the system is best described by N_2^-, the NN separation in the complex will be greater than in the N_2 molecule. Hence the nitrogen will, by the Franck-Condon principle, have a considerable probability of leaving the collision with vibrational energy.

This type of process cannot happen with a molecule like argon and Table VI of Prof. Norrish's paper shows that inert gases are ineffective in quenching the fluorescence of sodium. On the other hand, ethylene and other unsaturated molecules, in which the N_2 type mechanism above could operate, are very effective. For ethylene itself, the complex would be $C_2H_4^-Na^+$, in which the ethylene part would be expected to be non-planar as well as having a long CC bond. Consequently bending, as well as stretching, vibrations would probably be excited. The saturated hydrocarbons would not so readily form such an "ionic complex", if only because the outside of the molecule is virtually entirely made up of hydrogen atoms so that an electron transfer to the carbon-carbon bond would be more difficult. In the quenching of mercury fluorescence such effects are probably not important because, for N_2, CO, NO, etc., the electronic quantum that is lost matches a vibrational transition. In this case butane is more effective than N_2 or CO. Butane, with its numerous normal vibrations, can match the electronic quantum with a suitable combination of them; methane, with only four, cannot, the magnitude of the bending vibration frequencies being unsuitable.

M. Wigner. — What I am going to say reflects, I hope, not only my own views but also those of Drs. Herzberg and Karplus.

Perhaps I should recall first that it was London who first emphasized that most chemical reactions can be considered to be adiabatic as far as the electronic motion is concerned. The reason is that the electronic motion is so fast as compared with the motion of the nuclei that the electrons always have time to adjust to the position of the nuclei without making a quantum jump. Subsequent investigations, particularly by Teller and Landau, indeed showed that the adiabatic assumption is a very good one. The deviations from this are treated in the "classical path, quantum transition" method of describing collisions, which I discussed in my report. Unless the nuclear motion is extraordinarily fast for a chemical reaction, these transitions should have small probability as long as the energy surfaces do neither cross nor approach each other a good deal more closely than one ordinarily expects electronic levels to do this. In other words, the adiabatic assumption should be very good as long as the spacing of the electronic levels exceeds about 1 eV.

Hence, when it was shown that energy surfaces cannot be expected to cross unless they have different symmetry characters (for instance, in the case of two atoms, one of the energy levels may have Σ, the other Π character) it had to be inferred that electronic excitations are, quite generally, unlikely to result from chemical reactions. This is contradicted, of course, by the numerous reactions leading to chemiluminiscence. Naturally, before one becomes concerned, one has to ascertain whether the electronic transitions are reasonably frequent because London's adiabatic approximation is, after all, only an approximation.

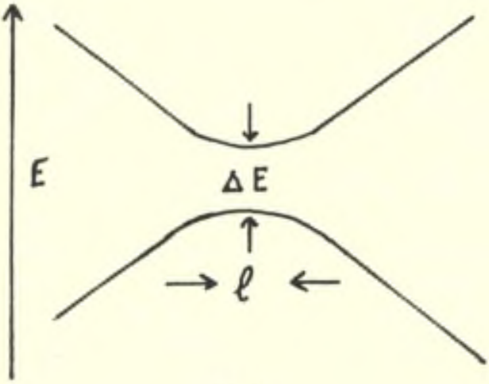

Fig. 1.

The deviations from the approximation, that is the jumps from one surface to the other, should be most marked if the two energy levels nearly cross. In fact, the jump to the other level becomes the likely process if $\Delta E/h < v/l$ where v is the velocity of the atoms toward each other, ΔE and l are illustrated in figure 1. This figure represents two energy surfaces along the path of the motion of the atoms. London already gave examples in which crossing is more probable than the adiabatic motion along the same energy surface. All this is standard material which I thought, however, might well be recalled.

As a rule, the situation in which one would expect the jump from one energy surface to another one to be a likely process, is rare, and the frequency of non-adiabatic reactions has been puzzling us for a long time. There are cases in which the energy surfaces are very complicated and one cannot exclude the possibility of a confused crossing scheme of the very crowded manifold of surfaces. This, however, is difficult to accept, for instance, for a system composed of a noble gas and alkali atom. The matrix element between two different electronic energy surfaces should be of the order of one electron volt and this is then also the ΔE of the figure. The transition probability between two energy surfaces at this distance should be quite small. The only suggestion that occurred to us, and it may have been made and perhaps even refuted many times before, is that the $^2\Sigma_1/_2$ surface, leading to the normal state of the sodium, almost crosses the $^2\Pi_1/_2$ surface leading to the excited state. The transition between the two surfaces, as the separation between them, would then be caused by spin orbit interaction, causing a near crossing.

Let me point out next that, in the case of three or more atoms, a transition to another energy surface can take place by what may be called a topological mechanism, without a jump. The system of three atoms, for instance, has a higher symmetry if the configuration is straight than otherwise. Hence, certain energy surfaces will cross at linear (straight) configurations but remain separated at others. It is as if the two surfaces had, in a certain neighborhood, cone-like shapes, the axis of the cones being parallel to the energy scale and the two cones forming a double cone (see figure 2). At the linear configurations, which are indicated by broken lines in the figure, one of the lines may be a Π state, the other a Σ state. If the total configuration of the three atoms passes through the point of the cones, or goes near to it, the state will pass from the lower to the upper surface, or conversely. If, during the subsequent separation, they do not pass near this point, they will not return to the surface from which they started. This, then, can explain a change in the electronic state without a real jump.

Finally, we all realize that the probability of an electronic transition is in many cases, and perhaps always, much increased if its energy is equal to that of a vibrational transition. In this case, the electronic energy can be transformed into vibrational energy and vice versa, with an increased probability. This indicates that classical theory is no longer adequate for describing this process. In order to describe it quantum mechanically, it would be necessary to use a quantum mechanical picture, not only for the electronic motion but also at least for the particular vibration concerned. Clearly, we have to do here with a resonance phenomenon, but we do not know of a detailed theory which would describe it. Hence, we do not know how to account *in detail* for the phenomenon indicated, that is, for the increased probability of electronic transitions in case of resonance with a vibration.

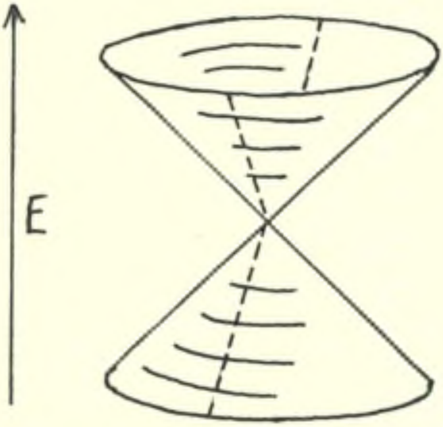

Fig. 2.

As a last point, and in view of many misunderstandings, let me reemphasize that a change in the electronic structure after the collision remains, as a rule, unlikely, even if considerable changes take place during the collision. The electronic structure will be, during a collision, a function of the positions of the nuclei. But, unless there is a jump from one energy surface to another, the changes which take place, for instance, when two atoms approach each other, will be reversed when they again separate. This point is often disregarded by otherwise very knowledgeable people.

M. Karplus. — We are considering the transformation of electronic excitation into energy of nuclear motion, or the motion of ionic cores (vibrational, rotational and translational). In the Born-Oppenheimer treatment, the electronic and nuclear degrees of freedom are treated separately. The results are customarily represented as potential energy surfaces for nuclear motion. The potential energy is just the total electronic energy, estimated for each nuclear configuration, and expressed as function of this configuration. We also know that potential surfaces do not cross, unless there is a degeneracy associated with symmetry of the configuration or unless a selection rule separates the two electronic states associated with the two potential surfaces. Still, there may in general be nuclear configurations where the energy difference between two surfaces is small.

Now the nuclei of course are not really stationary. Their motion results in correction to the B.O. approximation. In the lowest approximation, they move adiabatically, i.e., the electronic states are uncoupled from the nuclear excitation. There will, however, be matrix elements depending on the nuclear velocities that can result in transition among the lowest order states we have chosen, especially when these lowest order states are separated only by a small energy difference. These are the transitions in which we are interested. Especially interesting is the extent to which the transitions depend on the nature of nuclear motion (vibrational, rotational or translational) which is excited in the transitions. There appears to be preferential excitement of vibrations.

M. Gaydon. — If there is strong resonance between the electronic transition and some vibrational transition, then the Born-Oppenheimer approximation may break down, and allow the electronic transition to occur, even when the potential curves are quite far apart.

M. Mayer. — The collision time may be very much longer than that calculated by dividing an assumed ΔR for the range of interaction by the relative velocity, and which is the time we are apt to think about as a collision time. Especially if the colliding species have internal degrees of freedom, the path of the collision may include several waltz turns of the two partners around each other, and have a long time of interaction. These are the " sticky collisions ".

M. Polanyi. — I should like to endorse the remark of Prof. Mayer concerning the probable importance of a " lingering " collision in the electronic-vibrational transfer process. However, it has never been clear to me how long such a collision must last in order that resonance shall become important — 1 vibrational period, 10 vibrational periods... ? Perhaps Prof. Wigner would care to comment ?

M. Wigner. — The situation is similar to that of an elastically bound particle in classical theory. If the frequency of vibration of the particle is ω_0 and is initialy at rest but a periodic force with frequency ω acts on it, the energy of the particle will undergo some fluctuations, but in general show an increase proportional to the square of the time during which the periodic force acted. Furthermore, the factor of proportionality is independent of the closeness of the resonance, that is, it is the same as long as ω_0 and ω do not differ too much. However, the time during which the energy increase continues is $\pi / |\omega_0 - \omega|$, i.e., it depends very much on the closeness of the resonance. Hence, if ω is very close to ω_0, the ultimate energy of vibration of the particle will be high, not because it increases faster than if ω is not so close to ω_0, but because it continues to increase for a longer period. As long as the periodic force acts only during an interval t, it does not matter much how small $|\omega - \omega_0|$ is, as long as it is well below π/t. In other words, the very closeness of the resonance between ω_0 and ω does not lead to a large transition probability as long as the force acts only during relatively short periods. The lingering collisions should be, therefore, more effective than collisions of short duration if there is a resonance between the energies E_1 and E_2 of the degrees of freedom between which the energy transfer is expected. The increase in the lingering time increases the propability of energy transfer as long as it does not much exceed $\pi\hbar / |E_1 - E_2|$. A further increase in the lingering time, beyond this limit, should however, not increase the transition probability substantially any further. The absolute value of the transition probability depends, of course, on the strength of the interaction and there are no general rules for this.

M. Herzfeld. — Perhaps one can understand the problem why transfer to vibration is easier than transfer to translation if one makes use of the so-called semi-classical method of calculating transition probabilities, which is very similar to the method used in calculating electronic excitation by time dependent fields.

If the electronic transition to be excited has an energy $h\nu$, one determines the Fourier component ν in the exciting force; its square is proportional to the excitation probability. If we had an excited single harmonic vibration of frequency ν (case of pure resonance), it would only have a single Fourier component (line spectrum) of the right frequency. This is the case of exact resonance. If we norm according to

$$\int F^2(t)dt \qquad (F : \text{time dependent force})$$

it follows that a motion is the more effective the more its power spectrum is concentrated at the right frequency. For exact vibrational resonance, this concentration is as strong as possible. On the other hand translational motion gives a continuous spectrum with weak components of the right frequency. If we have vibration of not exactly the right frequency plus translation, the force will be of the form

$$F(t) \cos 2\pi\nu' t$$

and the continuous spectrum will extend on both sides of ν' with much higher amplitude than in the absence of vibration.

Of course, all this is standard theory.

M. Cottrell. — The transfer of energy from electronic to vibrational rather than translational nuclear motion is shown not only by Prof. Gaydon's experiments but also, as we were reminded the other day by Dr. Hornig, by the large probability of energy transfer from slow electrons to vibration in diatomic molecules such as nitrogen. If, then, the preferential transfer of electronic energy to vibration is a general phenomenon, however we may explain it, the result of Prof. Gaydon's experiments which is difficult to understand is the surprisingly high efficiency of argon in exciting chromium atoms. If the excitation is here due to electrons, as Dr. Kantrowitz suggested, addition of a species which has a larger cross section than argon for slow electrons might remove the temperature anomaly.

M. Ross. — There is evidence from more than one type of experiment that the probability of vibrational excitation of reaction products, if possible, exceeds the probability of translational excitation.

M. Shuler. — I seem to remember that J.L. Magee made some detailed calculations on the efficiency of electronic-vibrational energy transfer in inelastic collisions. This calculation should be found, I believe, in the *Journal of Chemical Physics* of the 1940's

M. Porter. — The mechanism of intermolecular conversion between electronic and vibrational energy is of more general interest when one considers its relation to the corresponding intramolecular process. When we consider the intermolecular case in terms of complex formation it becomes identical with the intramolecular problem and it is relevant to consider the considerable amount of information which has been accumulated on this problem from fluorescence and photochemical studies of organic molecules.

ENERGY EXCHANGE IN SHOCK AND DETONATION WAVES

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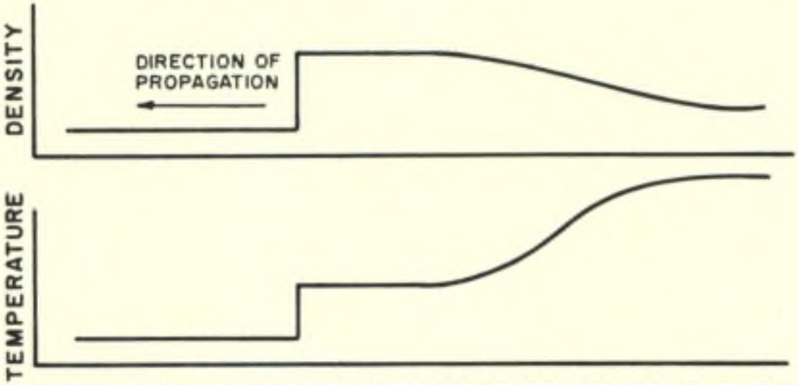
I. INTRODUCTION

Detonation waves, even in gases, involve a series of very rapid events and at atmospheric pressure the entire process may be completed in 10^{-8} sec or less. It is not surprising, then, that questions relating to energy transfer should arise. These questions involve the rate of excitation of external and internal degrees of freedom, the rates of diffusion and heat transfer, the possibility of photochemical energy transport and the rates of chemical reactions.

The classical model of detonation was proposed independently by Zeldovich (1), von Neumann (2) and Doering (3) (ZND). In this model, illustrated in Figure 1, the initial phenomenon is a shock



PROFILES OF DENSITY AND TEMPERATURE ACCORDING TO THE ZELDOVICH-VON NEUMANN-DOERING THEORY OF DETONATIONS

FIG. 1

wave in the reactant gases, compressing them and raising their temperature to 2000 to 3000 °K. Reaction is initiated and proceeds on a much slower time scale, liberating heat to produce the expansion which drives the shock front. Curiously enough, the structure of the wave has little effect on its macroscopic properties since if the reaction proceeds essentially to equilibrium in the Chapman-Jouguet plane, the hydrodynamic theory of detonation (4) derives the detonation velocity from conservation of mass, momentum and energy, together with the equation of state of the reacting gas. To be sure, there are questions relating to the exact form and validity of the Chapman-Jouguet condition (5) but they involve only minor changes in the properties of the wave. It is only when such phenomena as detonation limits as a function of composition or pressure are considered that the hydrodynamic theory breaks down completely, since hydrodynamic solutions are possible outside the limits, and rates become a major factor.

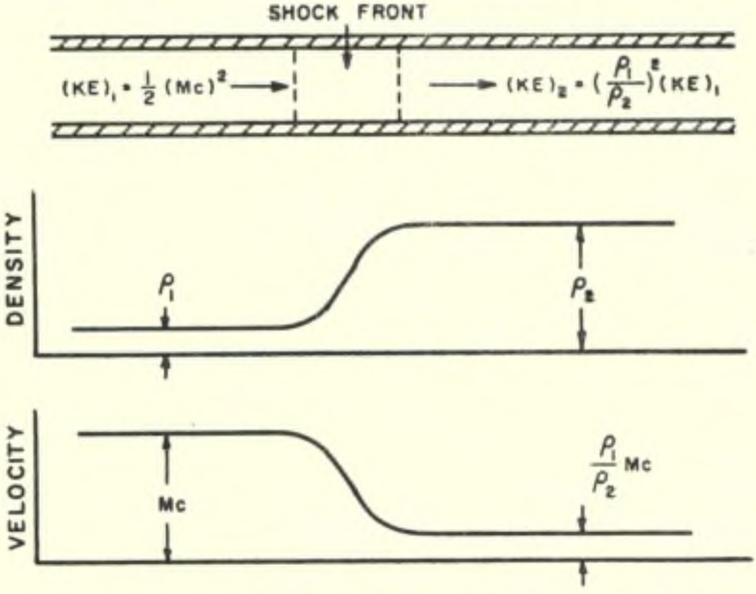
In the ZND model, there is a hierarchy of times and thus of energy transfer problems. The fastest single process is the initial shock compression. In a monatomic gas the compression time is essentially the time to establish a new translational equilibrium in the gas; in a diatomic or polyatomic gas, the initial compression rate depends on the rotational relaxation rate as well. Vibrational relaxation occurs at a much slower pace in an isentropic process following the shock front, followed in turn by chemical reaction and the attendant rate processes. It is this hierarchy of times and processes which we have tried to unsort.

This question has become more pressing in that Hirschfelder and Curtiss (6) have concluded that if the reaction can be represented by a first order Arhennius expression the initial shock and the reaction may be strongly coupled so that, contrary to the ZND model, they cannot be separated at all. More from reasons of mathematical tractability than physical or chemical evidence, this suggestion has been taken up and elaborated by others and adopted as a working model for the detonation process (7).

Finally, all of these questions have been complicated by the experimental discovery by White (8) and others (9) that stable, one dimensional detonations may not exist at all. In that case there are further questions such as the role of turbulent heat transfer or, put differently, of the role of transverse waves and multiple shock interactions.

II. THE EQUILIBRATION OF TRANSLATIONAL MOTION

In order to resolve some of these questions we have undertaken first to measure the rate of compression in shock fronts in monatomic and diatomic gases. This compression process can be expected to occur in a few mean free paths and the nature of the problem is illustrated in Figure 2. In a coordinate system fixed in the shock front, the undisturbed gas flows in at the shock velocity, M*c*, if *c* is the velocity of sound and M is the Mach number. The kinetic energy per gram of gas, $1/2(Mc)^2 = M^2 \gamma RT/2$, is much greater than the mean thermal energy, $3RT/2$, if $M^2 \gg 3/\gamma$, where γ is the ratio of specific heats. In a detonation M is roughly 3-6 so the condition applies. In the shock front, according to the continuity equation, this velocity decreases to a fraction ρ_1/ρ_2 of the incoming velocity and the kinetic energy of flow to a fraction $(\rho_1/\rho_2)^2$. The subscripts 1 and 2 refer to initial and final conditions. Hence if $(\rho_1/\rho_2)^2 \approx 0.1$,



GAS FLOW THROUGH A SHOCK FRONT IN COORDINATES WHERE SHOCK WAVE IS STATIONARY

FIG. 2

a typical case, substantially all of the flow is degraded to thermal energy. The process can thus be thought of as the randomization by collision of the initially parallel flow of molecules.

The thickness of the compression zone is about 10^{-5} cm at atmospheric pressure (thus the time for compression is about 10^{-10} sec).

If the structure of the zone is to be studied, a gauge is required which has dimensions of this order of magnitude; the wavelength of visible light meets this requirement. On these grounds we have developed the optical reflectivity method which, to date, has been the most successful method by which the density profile of shock compressions has been measured.

The only other methods which have been employed are the thin wire gauge of Talbot and Sherman (10) and the electron density probe developed by Duff (11) *et al.* Both rely on increasing the dimensions of the shock front by lowering the gas pressure. The former method relies on heat transport to a wire probe whose diameter is much less than a mean free path when it is placed in a standing shock wave in a low density wind tunnel. Its advantage is that it measures a " wire temperature profile " directly but since the profiles for density, velocity and wire temperature all differ somewhat, the precise relation of the quantity measured to theory is difficult to establish. The electron beam technique is elegant in concept; however, at the low pressures employed, the corrections for shock curvature are bigger than the effect to be measured and the results are badly distorted by secondary effects such as space charge (12).

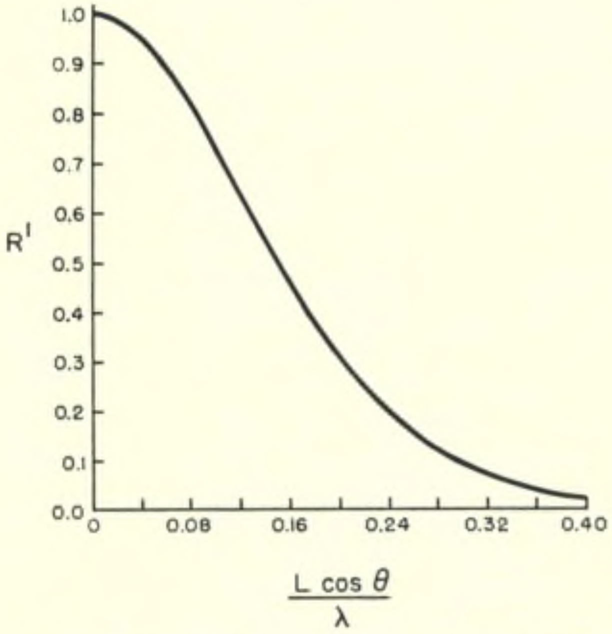
The optical reflectivity of the compression zone is readily shown to be (13)

$$\mathrm{R} = \frac{1 + \tan^4\theta}{4n_1}\left[\int_{-\infty}^{\infty} \frac{dn}{dx} e^{2\pi i x\,(2\cos\theta/\lambda)}\,dx\right]^2 \tag{1}$$

$$= \frac{1 + \tan^4\theta}{4n_1}(\Delta n)^2\,\mathrm{R}'\left(\frac{\cos\theta}{\lambda}\right) \tag{2}$$

if $\mathrm{R} \ll 1$. In these equations θ is the angle of incidence and n the index of refraction as a function of x, the distance perpendicular to the shock front. R' is a function which varies from one when $\lambda/\cos\theta \gg \mathrm{L}$ to zero when $\lambda/\cos\theta \ll \mathrm{L}$, where L is the thickness of the shock front. This behavior, for a typical shock front profile, is illustrated in Figure 3. Since the index of refraction change can be written

$$\Delta n = (n_0 - 1)\,(\rho_1/\rho_0)\,(\Delta\rho/\rho_1) \tag{3}$$



REDUCED REFLECTIVITY CURVE FOR SHOCK WAVE DENSITY STRUCTURE OF EQUATION 5

FIG. 3

where the subscript zero represents some standard state, profiles $n(x)$ and $\rho(x)$ can be obtained by Fourier inversion of Eq. (1) if R is measured over a sufficient range of the variable cos θ/λ.

The basic experimental arrangement we have used is shown in Figure 4. An intense beam of collimated monochromatic light is projected through a shock tube; when the shock wave passes through the beam it sends a pulse of reflected light to the photomultiplier tube. The reflectivity is then determined from the ratio of the intensity of the pulse to that of the monitor signal. The width of the pulse is the passage time of the shock through the light beam,

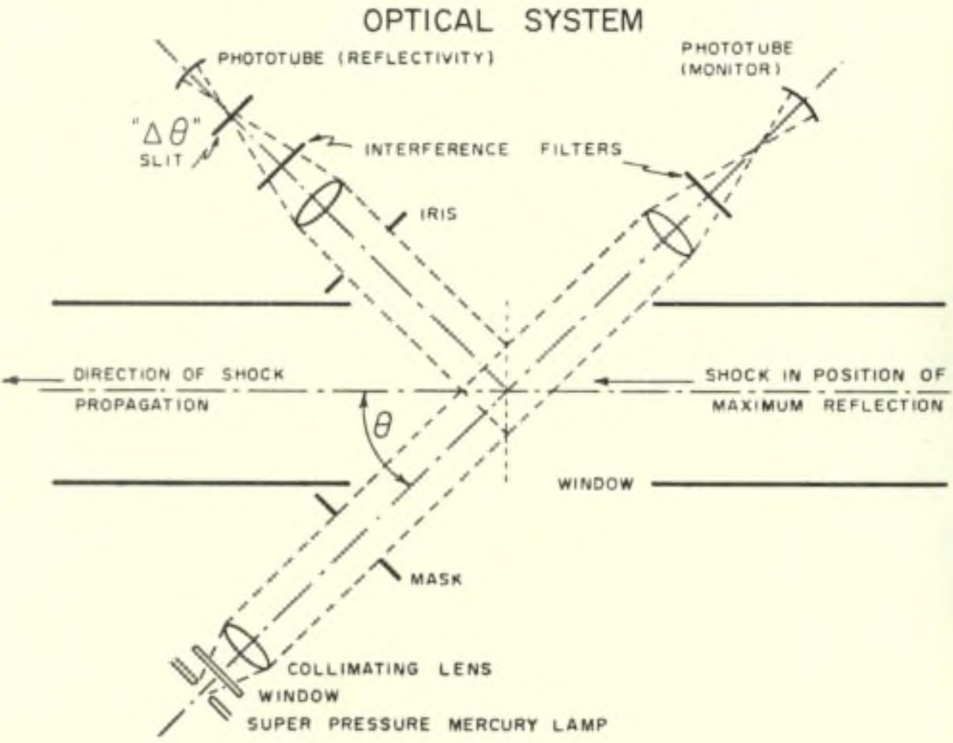


FIG. 4

a few microseconds in typical cases. The magnitude of the reflectivity usually lies in the range 10^{-5} to 10^{-7}. The collimation is usually effected to about $\pm 2^{\circ}$ and λ defined to ± 25 Å. There are, of course, a variety of practical problems in obtaining precise results but these have been described in detail elsewhere (14).

One serious problem is the limited range of the variable $\cos\theta/\lambda$ which is available in practice. This problem can be solved by using the initial pressure as a variable. This is so because the shock phenomenon can be described in terms of non-dimensional variables which are all functions of the non-dimensional distance x/l_1 (where l_1 is a reference mean-free-path ahead of the shock). For a fixed initial temperature l_1 is inversely proportional to p_1 and if M is constant the distance scales as xp_1; i.e. $xp_1 = x'p_0$, where x' is the distance variable for a shock into a gas at a standard pressure p_0, say 1 atm. When this scaling law is introduced into the fundamental reflectivity expression, Eq. (1), it is seen that dx becomes dx', the exponent $2\pi ix(2\cos\theta/\lambda)$ becomes

$$2\pi i\,\frac{x'p_0}{p_1}\left(\frac{2\cos\theta}{\lambda}\right) = 2\pi ix'\left(\frac{2p_0\cos\theta}{p_1\lambda}\right),$$

and the significant experimental variable becomes $\cos\theta/p_1\lambda$. Hence a much bigger range can be obtained by varying p_1 at constant shock strength. Therefore, combining Eq. (2) and (3) with the scaling law one has

$$\mathrm{R} = \frac{1+\tan^4\theta}{4n_1}\left[(n_0-1)\frac{\rho_1}{\rho_0}\right]^2\left(\frac{\Delta\rho}{\rho_1}\right)^2 \mathrm{R}'\left(\frac{p_1\cos\theta}{p_0\lambda}\right) \tag{4}$$

Another problem is that the accuracy of the measurements is not sufficient to use Eq. (1) directly. Instead the data have been fitted to the one parameter function,

$$\rho(x) = \rho_1 + \frac{\Delta\rho}{1+e^{-4x/\mathrm{L}}} \tag{5}$$

in which L is the maximum slope thickness,

$$\mathrm{L} = \Delta\rho/(d\rho/dx)_{max}\,. \tag{6}$$

This function approximates very closely all of the theoretical descriptions of the shock front. For it the function R′ takes the form

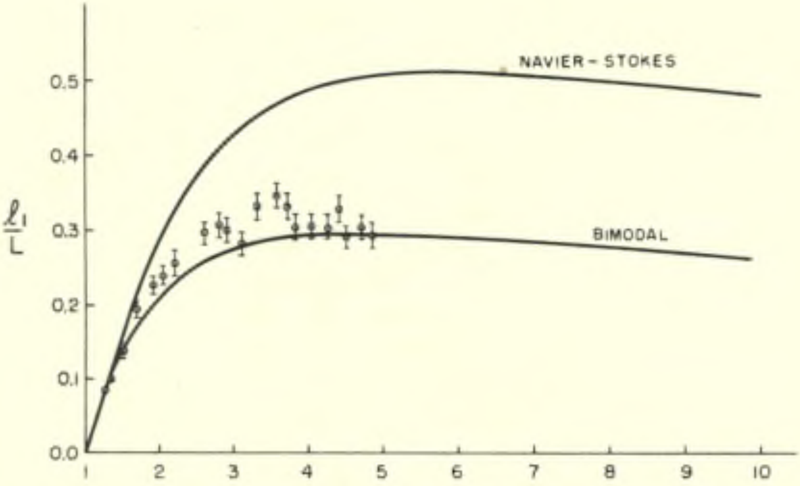
$$\mathrm{R}' = \left[\frac{(\pi^2 y\mathrm{L}_0)}{\sinh\,(\pi^2 y\mathrm{L}_0)}\right]^2$$

if

$$y = p_0\cos\theta/p_1\lambda\,,\quad \mathrm{L} = \mathrm{L}_0\frac{p_0}{p_1},$$

and L_0 is the thickness at the standard pressure p_0. This function is plotted in Figure 3.

The results obtained by a series of investigators (14), notably Linzer (15), are shown in Figure 5 and compared with theoretical curves. The major conclusion is that as the shock strength increases, the thickness declines until in argon it reaches a roughly constant value, about 3 mean free paths of the undisturbed gas. This thickness corresponds to about ten collisions in the shock front.



ARGON SHOCK THICKNESSES BASED
ON LENNARD - JONES 6 - 12 POTENTIAL

FIG. 5

For a gas which is only slightly disturbed from equilibrium the one-dimensional flow is described by the Navier-Stokes equations

$$\rho u = \rho_1 u_1 = a$$

$$P + au - \mu_{eff} \frac{du}{dx} = p_1 + au_1 = b \tag{7}$$

$$aE + bu - 1/2\, au^2 - \lambda \frac{dT}{dx} = aE_1 + bu_1$$

and the equation of state of the gas. In these equations ρ, u, P and E are the density, velocity, pressure and internal energy per unit mass, respectively, while μ_{eff} and λ are the coefficients of viscosity and thermal conductivity. The solution to these equations yields a shock thickness which for weak shocks depends linearly on the viscosity and which is fairly insensitive to the thermal conductivity.

Since in the shock front the gradients are very great and the velocity distribution function changes greatly in a single mean free path the Navier-Stokes equations might be expected to break down. Attempts to study this question theoretically have met with little success so far and the inclusion of higher order kinetic theory terms usually leads to divergent expansions for strong shocks.

For the moment, the best approach to this question is through experimental comparisons of the calculated and predicted properties of strong shocks.

Dr. L. Schwartz has calculated Navier-Stokes profiles, using the method of Gilbarg and Paolucci (16), throughout the region of interest. The viscosity and thermal conductivity of argon were taken from a Lennard-Jones 6-12 potential with $\varepsilon/k = 116\,^{\circ}\mathrm{K}$ and $\sigma = 3.465\,\text{Å}$ which reproduces the experimental viscosity over the temperature range for which reliable measurements exist. The density thickness he calculates is plotted in Figure 5, from which it is clear that the Navier-Stokes solutions do give correct qualitative results but that in the strong shock region the experimental shock thickness is about 50% greater than that calculated from the Navier-Stokes equations. Two other interesting features of his calculations deserve mention : (1) the velocity and density thicknesses are substantially the same when $M < 1.5$ but at $M = 3$ the velocity thickness is about 21% greater than the density thickness, rising to 32% at $M = 7$; (2) the calculated profiles for strong shocks are asymmetric.

If the wave is divided at the point $\Delta\rho/2$, the thickness of the high temperature, high density side is about 2/3 of that of the low temperature low density side in the region $M = 5$ to $M = 6$. If this asymmetry is indeed a property of real shock waves it poses a problem for the method we have used which is based on the symmetrical density function of Eq. (5).

Mott-Smith (17) has proposed an interesting kinetic theory in which he uses a bimodal distribution function which is a linear combination of those appropriate to initial and final states of the gas, i.e.,

$$\rho(x)\,f(x) = \rho_1(x)\,f_1(\mathrm{T}_1) + \rho_2(x)\,f_2(\mathrm{T}_2) \tag{8}$$

$$\rho^1(x) + \rho_2(x) = \rho(x)$$

It leads to the density function of Eq. 5 at all shock strengths. This approach has been elaborated by Muckenfuss (18) and his corresponding theoretical curve, also based on the Lennard-Jones 6-12 potential, is also shown. It agrees quite well with experiment.

For the present purpose the important point is that although our experimental conclusions are based only on argon, both Navier-Stokes and bimodal calculations yield thicknesses of the order of

2-3 mean free paths for Mach three to six shocks in other gases as well. Since these are the conditions characteristic of detonations, we conclude that the initial compression in shocks takes place in about ten collisions. This means that translational equilibration takes place in about ten collisions, even when the temperature changes from 300° to 3000 °K in two or three mean free paths.

Rotational relaxation.

For a diatomic or polyatomic molecule the structure of a shock front may also be affected by the transfer of energy to rotational degrees of freedom. Two limiting cases may be discerned : (*a*) if the rotational relaxation time is long compared to the time for translational relaxation, the usual relaxation theory applies and we expect an initial shock front followed by a slower density increase as rotation is excited or (*b*) if the rotational equilibration time is comparable to that for translation, the effect is to introduce a bulk viscosity $\varkappa$, so that the effective viscosity in the Navier-Stokes equations becomes

$$\mu_{eff} = 4\mu/3 + \varkappa\,, \tag{9}$$

and to change the thermal conductivity through the Eucken correction. Of course, the use of a bulk viscosity implies the same limitations as apply to the Navier-Stokes equations, that the deviation from equilibrium be small. Hence, the augmented Navier-Stokes equations are strictly applicable only to very weak shocks, but in view of their relative success in the monatomic problem, we presume that they may remain accurate to within a factor two even for strong shocks.

Hydrogen (19) is an example of case (*a*). The thickness of shock fronts as well as the compression ratio in the initial shock are characteristic of a monatomic gas and there is no evidence of any rotational excitation in the shock front. It is known from ultrasonic work (20) that rotational relaxation occurs in approximately 350 collisions.

All other gases that we have studied appear to approximate case (*b*). Early data on N_2, O_2, CO, Cl_2, HCl, N_2O, CO_2 and CH_4 showed that the gas immediately behind the shock front reaches the density characteristic of rotational equilibrium (21). The thicknesses of the shock fronts differed little from those expected for translation alone so that in all of these cases it was concluded that the rotational relaxation time (in collisions), given by the equation

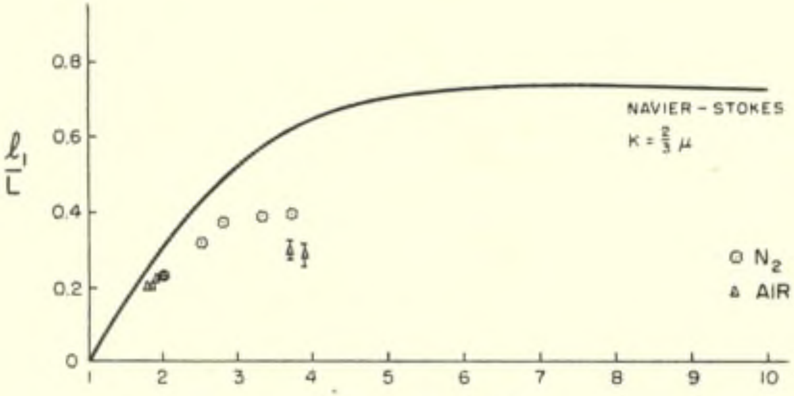
$$\tau' = 8\varkappa/\mu \,, \tag{10}$$

was less than five collisions. This is in agreement with classical theoretical estimates for rough spheres, spherocylinders and loaded spheres.

Nevertheless, a new problem did appear in that the final density was several percent below theoretical when M = 1.55 shock waves were sent through N_2 or CO (19, 21). An even greater discrepancy seemed to show up in a preliminary study of M = 3 shocks in O_2 (22). This raised the question whether the very high J levels which are excited in strong shock waves relax as rapidly as the low J levels involved in weak shocks. There are at least two reasons why this might be the case. In the first place the level spacings are no longer small (e.g. for $J = 80$ in N_2, the spacing $4BJ = 640$ cm^{-1}); in the second place the total ΔJ's needed to populate the upper levels are great so the repopulation must either occur through large angular momentum changes on single collisions or, as is the case in vibrational relaxation, equilibrium must be approached through a series of stepwise transitions.

Linzer (15) therefore undertook to study shock waves in N_2 at velocities ranging from M = 2 to M = 3.7, in which the final gas temperatures ranged from 500 °K to 1100 °K. At first sight his results seemed to show a final density so low as to suggest almost no rotational relaxation in the shock front. However, it became apparent that a systematic error of some sort was present in the measurements when a similarly low final density seemed to occur in strong argon shocks. The source of the difficulty was not established with certainty but the most plausible suggestion was that the reduction in apparent reflectivity was caused by curvature of the shock front. Assuming that this effect, whatever its source, had the same magnitude as in argon, Linzer then concluded that he could find no evidence at all for a discrepancy in the nitrogen limiting reflectivity. Presumably the previous investigators had been misled by the same difficulty.

The existing results for the thickness of shock waves in nitrogen are shown in Figure 6. Navier-Stokes curves computed by Schwartz for $\varkappa/\mu = 2/3$ are included for comparison. A better coincidence



NITROGEN AND AIR SHOCK THICKNESSES

FIG. 6

would be obtained for strong shocks if $\varkappa$ were assumed to be greater; however, since the discrepancy is about the same as in the argon case (Fig. 5), the choice of $\varkappa/\mu = 2/3$ is probably about right. It corresponds to rotational relaxation in 5.5 collisions and the correct result cannot be much different.

We conclude, despite the reservations occasioned by the experimental difficulties mentioned earlier, that even in shocks as strong as those encountered in detonation waves, rotational relaxation occur in parallel with translational relaxation. It apparently is completed during the initial shock compression in something under 10 collisions.

Vibrational relaxation.

Although vibrational relaxation has been extensively studied by ultrasonic techniques at room temperature (23), only a limited number of shock wave studies have been carried out in the temperature range appropriate to detonation. Enough has been done to conclude that over a wide temperature range the theoretical expression of Landau and Teller (30)

$$P_{10} = A_1 T^{-1/3} \exp - [(C/T)^{1/3}]$$

applies. Here P_{10} is the probability per collision of deactivating the first vibrational state. Extrapolation of data taken at temperatures up to 1000° (24) on CO_2 to 2000° yields $1/P_{10}$ equal to 500 collisions. O_2 has been studied over a wide temperature range, most recently and most thoroughly by Camac (25). $1/P_{10}$ for O_2 varies from about 10^4 collisions at 2000 °K to 10^3 collisions at 3000 °K. All of the evidence to date on pure gases supports the notion that vibrational relaxation takes hundreds or thousands of collisions. Nevertheless, it has been observed that at room temperature H_2 is some 25 times and H_2O 1000 times more efficient than a second O_2 in relaxing O_2. This suggests that in mixtures typical of detonations the relaxation may be faster. The trouble is that there is little high temperature data on mixtures. However, the data on $H_2O — CO_2$ (24) suggest that the problem may be less severe at high temperature since the relative efficiency of H_2O and O_2 approaches unity at 1200 °K. One is therefore led to the conclusion that vibrational reaction is much slower than the initial compression, even at these high temperatures. Whether it overlaps the zone of appreciable chemical reaction is an open question, although the work of Schott and Kinsey (26) suggests that this may be the case.

Detonation.

All of the preceding leads to the conclusion that if a shock wave precedes the reaction zone in a detonation, the initial compression, leading to translational and rotational equilibrium in the hot compressed unreacted gas, takes place in 10-20 collisions. Vibrational relaxation is much slower, even at temperatures characteristic of detonation (1500 °K to 3000 °K). It is hard to believe that any appreciable amount of chemical reaction takes place in the region of the shock front, particularly since the initiating steps involve dissociation. All of these arguments suggest that the shock wave should be completely uncoupled in the sense of the ZND model. Nevertheless, one would like to direct experimental evidence for the existence of the shock front and the region of hot, compressed but unreacted gases behind it. There have been a number of previous efforts to detect this zone, notably by Kistiakowsky and coworkers (27), all unsuccessful. It is clear from the computor calculation of Duff (28) that the resolution of the method was inadequate to observe this region, for which he estimates a thickness of 0.4 mm when the initial pressure of the detonating mixture ($H_2 + O_2$) is 30 mm Hg. The space resolution is effectively improved by a factor of about 10^4

in the optical reflectivity method, which should therefore be adequate to detect any initial shock wave.

There are other questions as well. At low pressures (i.e. < 250 mm Hg) it is well established that the front of the detonation wave is not flat (8), that there are bumps and evidences of intersections with transverse waves (9). In addition, the evidence is clear that the flow behind the front is not one dimensional (8). As the initial pressure is raised the scale of all these phenomena decreases so that they have not been observed at higher pressures. The question then arises whether the instabilities have vanished or merely escaped observation. The optical reflection should also yield information on this point since if the front were " rough " on a scale which could not be resolved in pictures or interferograms (e.g. < 0.1 mm) but much greater than the wave length of light (e.g. $> 10^{-3}$ mm), it would reflect the initially collimated light beam through a range of angles characteristic of the degree of "roughness ".

In order to study these questions Levitt and Hornig (22) studied the reflectivity of detonations in $H_2 + 3O_2$ mixtures at pressures ranging from one to three atmospheres. After taking suitable precautions they were able to obtain signals against the background of luminosity from the detonation. The magnitude of the pulses was about that expected and from their fit of the reflectivity *vs* initial pressure curve to the theoretical curve they concluded that the thickness of the shock front was 9.1×10^{-5} cm at 1 atm., also a reasonable value. However, from this same fit they concluded that the density behind the shock front was 20% lower than would be expected if the ZND model held and the gas had reached equilibrium. For reasons which will be discussed, though, these conclusions appear to be incorrect, despite the fact that all of the quantities measured were quantitatively reasonable.

Levitt and Hornig also performed experiments in which the size of the exit aperture (see Fig. 4) was varied. The fact that there was no increase in apparent reflected intensity when it was opened from 3 to 5 mm led them to the conclusion that the initial shock front was smooth and planar at initial pressures of one to three atmospheres, in contrast to the behavior observed by White (8), for example, at lower pressures.

These studies have now been extended by Sastri, Schwartz, and Myers (29), employing light at two wave-lengths (4358 Å and 5790 Å), a series of angles, and a greater range of initial pressures. These results make the situation appear considerably more complicated. The results obtained from measurements on detonations in $H_2 + 30_2$ at an initial pressure of 20 psia are plotted in Figure 7 as apparent

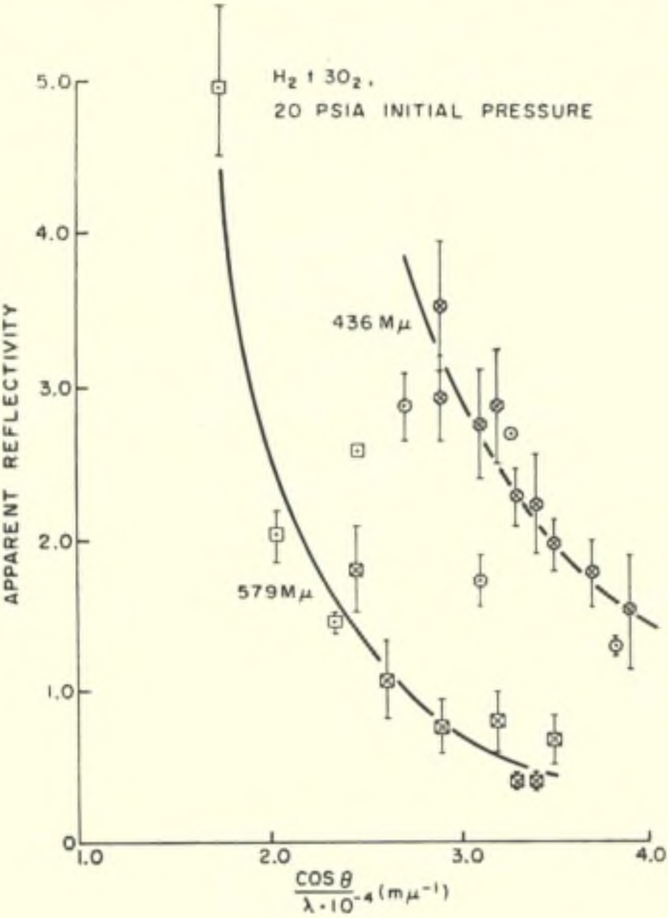


FIG. 7

reflectivity $R'(\Delta\rho/\rho_1)^2$, the known variables having been eliminated by means of Eq. (4). Although the magnitude of the " reflectivity " is close to that expected for reflection from the initial shock front, the data clearly do not fall on a single curve which is a function of cos θ/λ, as expected from Eq. (4). Instead, the 4358 Å points form one curve and the 5790 Å points another.

This situation could reflect a systematic calibration error between the 5790 Å measurements and those at 4358 Å. However, the apparatus was calibrated before and after detonation measurements with weak ($M = 1.4$) shocks in argon whose reflectivity was known. The data plotted were taken in several batches over an interval of two years by two sets of investigators so that the probability of such a systematic error seems very small.

In Figure 8 the same results are plotted as total observed intensity. The " scattering angle " is $2(\pi/2 - \theta)$ in each case. The fact that in all of our experiments on $H_2 + 3O_2$ at 20 psia the 4358 Å signals were more than twice as intense as the 5790 Å signals clearly indicates that the phenomenon observed was not a simple reflection. Even

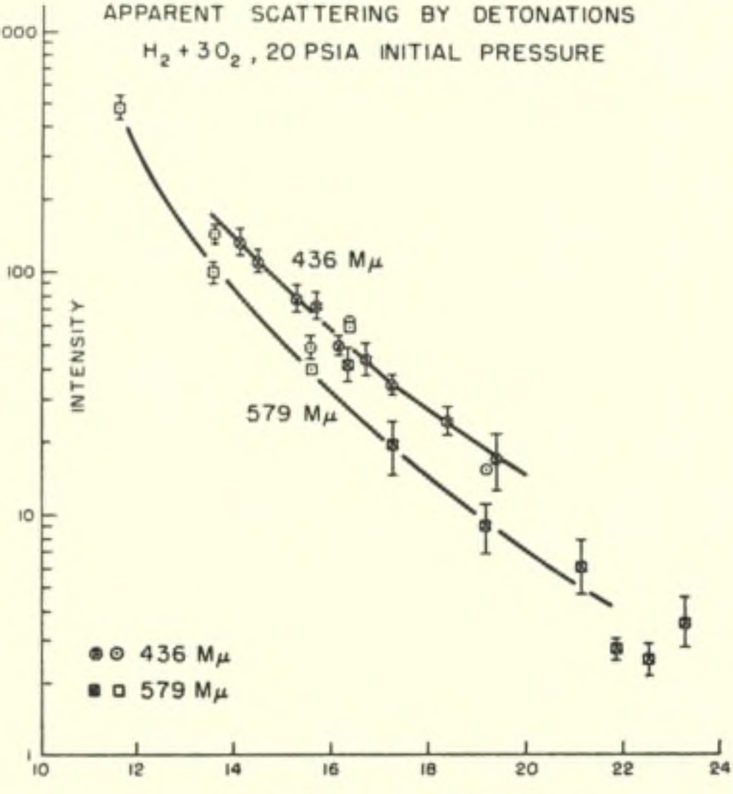


FIG. 8

if the front were irregular the reflectivity should increase as λ increases at any given angle of reflection. The fact that the reverse was observed suggests a major contribution by light scattering.

To check on this conclusion further experiments were carried out in which the angle of incidence was kept constant while the angle of observation was varied. In the case of simple shock waves as shown in Figure 9, reflected light could only be detected when the angle of observation was equal to the angle of incidence to within 2°, a range equal to the angular deviation in the collimation of the light in the optical system. The corresponding observations on detonation waves are shown in Figure 10; a signal is observed over a wide range of observation angle and there is no sign of the maximum at 16° which would have occurred if there had been reflection from a plane front. These experiments show that either the

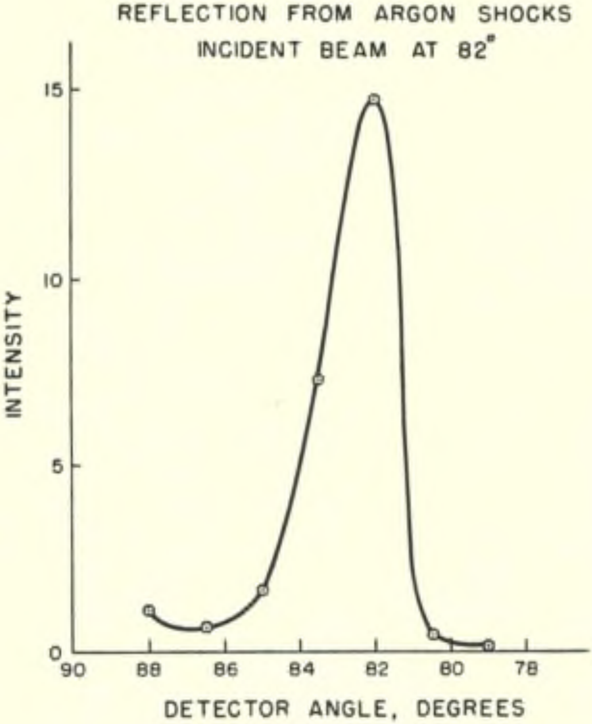


FIG. 9

major effect is scattering or that the reflection occurs from a rough or " bumpy " front.

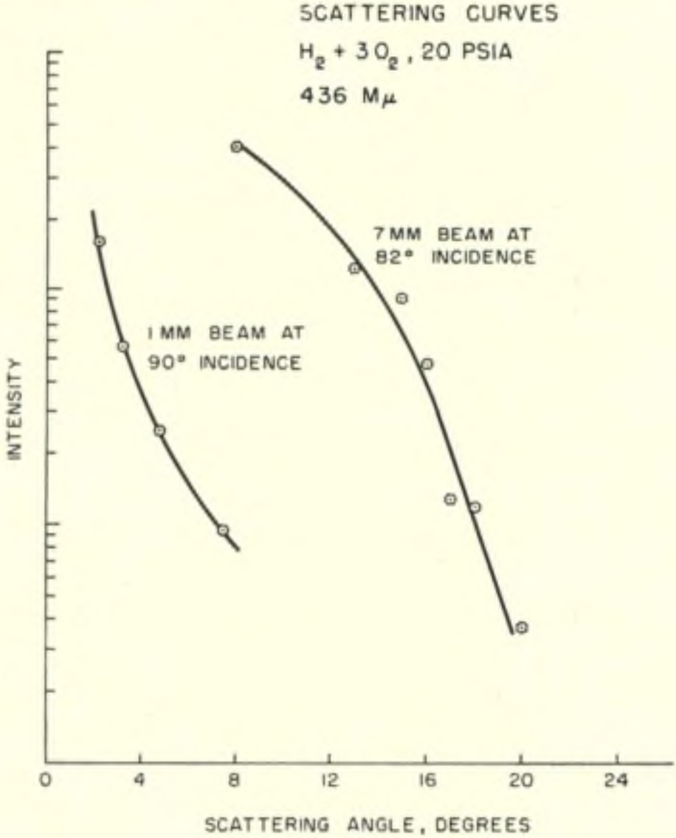


FIG. 10

The intensity is a much more sensitive function of angle than would be expected for Rayleigh scattering, but it could, perhaps, be accounted for in terms of larger scattering centers. However, a " bumpy " reflecting surface might also yield a similar angular distribution of intensity. For example, when the observation angle is θ_2 and the angle of incidence is θ_1, that portion of the surface which deviates from the plane by an angle $\alpha = (\theta_2 - \theta_1)/2$ is observed, and the angle of reflection is $\theta_2 - \alpha$. If a fraction, $\varnothing(\alpha)$, of the surface is inclined at an angle α to the mean, the reflectivity equation becomes

$$R(\theta_2) = \frac{1 + \tan^4(\theta_2 - \alpha)}{4n_1}(\Delta n)^2 \varnothing(\alpha)\, R'\left[\frac{\cos(\theta_2 - \alpha)}{\lambda}\right]$$

$$= \frac{1 + \tan^4[(\pi - \beta)/2]}{4n_1}(\Delta n)^2 \varnothing(\alpha)\, R'\left[\frac{\cos\{(\pi - \beta)/2\}}{\lambda}\right]$$

where $\beta = \pi - (\theta_1 + \theta_2)$ is the scattering angle. This function increases sharply as β decreases until it falls off abruptly at an angle $\beta_{min} = \pi - 2(\theta_1 + \alpha_{max})$, α_{max} being the maximum deviation of the surface from planarity. A signal should be observed to an angle $\beta_{max} = \pi - 2(\theta_1 - \alpha_{max})$. Inspection of Figure 10 shows that in order to account for these observations, $\alpha_{max} > 4°$. However, it should again be noted that if this, and not scattering, were the main source of the signals, the intensity in the preceding experiments would been greater at 5790 Å than at 4358 Å.

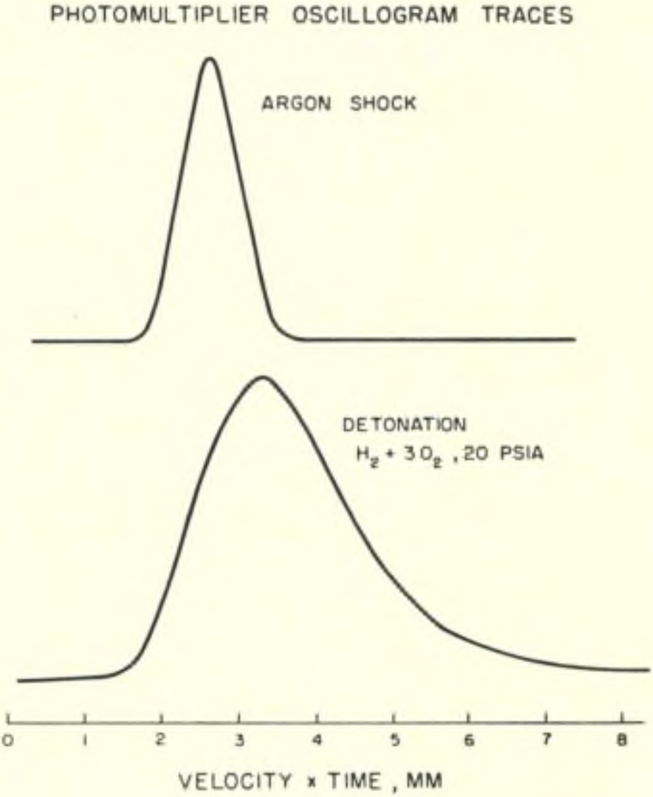


FIG. 11

Whatever their origin, the narrowness of the light pulses observed demonstrates that the signals originate in a narrow zone of the detonation wave. To determine the thickness of this zone, measurements of pulse duration were made with a 1.0 mm wide incident and observing slit system (see Fig. 4). Fig. 11 shows the results obtained. The pulse width for the shock wave in argon is that of the optical beam; the wider pulse from the detonation indicates that the signals originate in a zone approximately 2.5 mm thick. This zone may really be thinner in a local portion of the detonation wave since the measured width includes the effect of curvature of the wave-front. However, it seems unlikely that more than a fraction

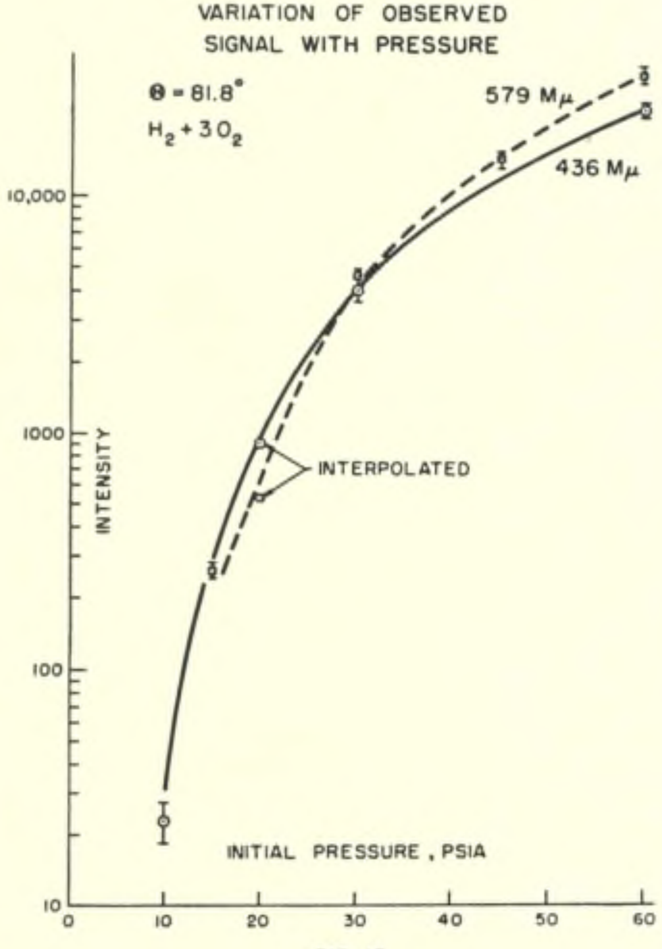


FIG. 12

of a millimeter of the 2.5 mm can be ascribed to curvature so that the signal appears to originate behind the shock front from a region extending at least 2 mm back into the reacting gas.

The pressure behavior of pulses from detonations in $H_2 + 30_2$ and $2H_2 + O_2 + 10$ Ar shown in Figures 12 and 13. They were all measured at a constant scattering angle of 16° ($\theta = 82°$). Their general form can be fitted to the reflectivity equation but, at least for $2H_2 + O_2 + 10$ Ar, the intensity at 4358 Å is greater than that at 5790 Å over the entire range to 4 atm. initial pressure. In $H_2 + 30_2$ there appears to be a cross over at higher pressures, but it is not clearly outside experimental error so that any conclusions must await experimental confirmation of the effect.

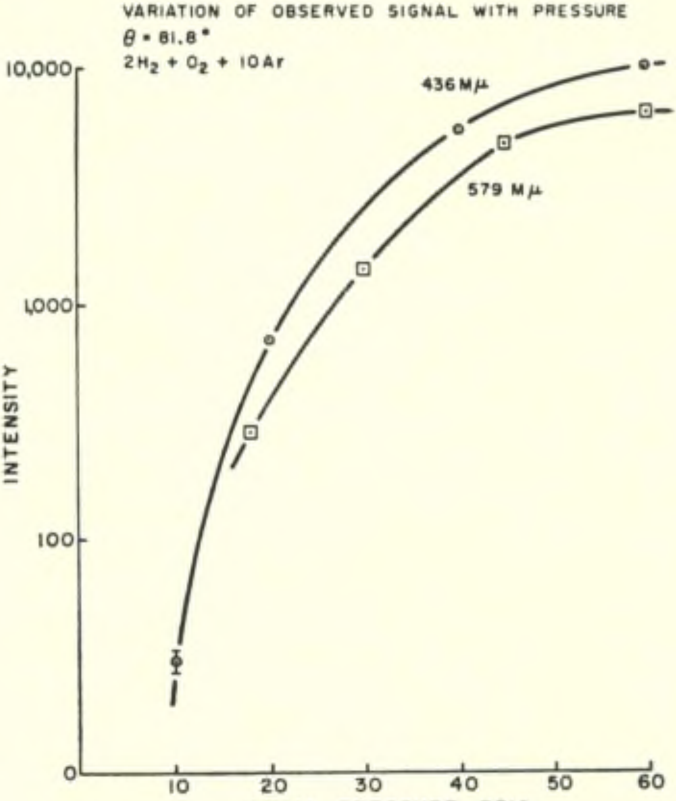


FIG. 13

DISCUSSION

The conclusions to be drawn from this work are not yet entirely clear. In shock waves with strengths and final temperatures equivalent to those in detonations, translational and rotational equilibrium is reached in the initial compression process, i.e. in 10-20 collisions. Vibrational relaxation has not been well studied at the temperatures appropriate to detonation but are certainly much slower, of the order of hundreds or thousands of collisions. On the basis of model calculations, using fairly well established reaction rates, the main part of the heat evolution in hydrogen-oxygen detonations occurs still later. All of this supports the ZND model of a gaseous detonation.

We were unable to observe a signal which could be shown to originate in reflection from the initial compression in $H_2 + 30_2$ detonations. Rather, the observed signal seemed to be caused by scattering from a zone extending about 2.5 mm back into the detonation wave. This observation is consistent with the observation by White and others of a complex wave structure and possibly turbulence in detonations at low pressure. It would mean that such structure or turbulence persists up to several atmospheres initial pressure. In that case the properties of detonations may be largely affected by turbulent heat transfer rather than molecular relaxation processes. Of course, one still expects that some part of the signal is due to genuine reflection from the rough front; one of the principal experimental problems will be to separate it from the scattering components and if this is done it may yet be possible to study the microstructure of a part of the wave.

ACKNOWLEDGMENT

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Discussion du rapport de M. Hornig

M. Ross. — The Mott — Smith solution of the Boltzmann equation may not avoid linearization of that equation as normally introduced in the Chapman — Enskog solution. The reason for this is that there is some theoretical work to show that the streaming terms as usually written suffice only for the *linear* Boltzmann equation (Mori, Oppenheimer and Ross).

M. Hornig. — The two functions involved in the Mott — Smith bimodal solution are equilibrium distribution functions at the initial and final gas temperatures. The general form of the function $\rho(x)$ is then determined by the continuity equation alone but the rate of change of the coefficients comes from the transport equations, usually for v^2.

M. Shuler. — I should like to report briefly on some work which I have carried out with Dr. Knud Andersen of the University of Copenhagen which touches on one of the points discussed by Professor Hornig. Dr. Andersen and I have considered the translational relaxation of a subsystem of heavy structureless particles which is immersed, without spatial gradients, in a heat bath of light structureless particles. The subsystem interacts with the heat bath in hard sphere collisions. This model is commonly known as the Rayleigh gas. If the subsystem is prepared with an initial Maxwellian distribution of velocities with a temperature T_1, and the heat bath has a Maxwellian distribution of velocities corresponding to a temperature T_2, with $T_1 \neq T_2$, then it can be shown that the subsystem will relax to the heat bath temperature through a sequence of Maxwellian distributions which can be characterized by time-dependent translational temperatures. This is quite analogous to the results on the vibrational relaxation of a set of harmonic oscillators obtained previously by Montroll and Shuler. This maintenance of a Maxwellian distribution of velocities during the relaxation may have some bearing on the success of the Mott — Smith bimodal distribution in accounting for the thickness of shock fronts due to translational relaxation.

Another point. If only 10% of the molecules were out of equilibrium, would you be able to detect them ?

M. Hornig — In general yes. The effective rotational heat capacity determines the final density. Hence this question is concerned, not with the measurement of shock front thickness but with the asymptotic reflectivity. That can be measured with quite good precision, and since it depends on $(\Delta n)^2$ it is quite sensitive.

There is still a problem in the measurement I have cited in that one must make a correction for a small curvature of the shock front. This was realized after the measurements were made and it has been assumed that the curvature is the same in nitrogen as in argon. In this case I am not sure what the precision is.

M. Ubbelohde. — Quite a few years ago in connection with the mechanism of transition from quiet thermal decomposition to detonation of unstable solids like lead azide, I put forward a model for the build up of a shock front through the formation of an envelope to numerous small centres of streaming gas. Is it possible to interpret rough shock « macro » fronts as originating in an analogous way from numerous micro-shock waves which themselves originate from local chemical reactions leading to expansive gaseous products ?

M. Hornig. — I believe that in the reaction mixture the instability is fundamental and that there is no smoothing of the sort one finds with shock waves. My picture is this : Suppose one considers an element of gas which has just passed through the shock front, thus being compressed and heated. If as a result of fluctuations the chemical reaction goes faster in that element, the heat generated further increases the temperature and pressure. The pressure pulse then expands laterally, accelerating the reaction in adjacent regions and forming a transverse wave.

One knows that going to the limit of detonation stability by changing the composition will not help matters since the phenomenon of spinning detonations occurs under such circumstances. One then has wave systems whose dimensions are comparable to those of the tube and violent oscillations are observed.

M. Manson. — Je voudrais présenter quelques enregistrements strioscopiques susceptibles de préciser les « instabilités » dont vient de parler Dr. Hornig. Ces enregistrements sont ceux des détonations autonomes dans les mélanges $C_3H_8 + 5O_2 + zN_2$ contenus dans un tube de 20 mm de diamètre sous pression atmosphérique et à une température de 290 °K. Ils ont été décrits en détail dans une communication au International Symposium on Combustion (Cornell University, Ithaca, N.Y., 27 août — 2 septembre 1962) présentée en collaboration avec MM. Ch. Brochet, J. Brossard et Y. Pujol. Ici je voudrais attirer l'attention seulement sur les points suivants :

1) Les « instabilités » peuvent être interprétées en supposant l'existence de phénomènes vibratoires car la fréquence des stries quasi horizontales, visibles sur les enregistrements dans les gaz brûlés, est en bon accord avec la fréquence calculée en supposant que ces vibrations sont transversales; on notera que cette fréquence peut atteindre des valeurs très élevées (plusieurs Mc/sec).

2) Dans les mélanges ($z \simeq 16$) proches de la limite, l'onde de choc et la flamme se séparent momentanément et les gaz derrière le choc sont alors le siège de phénomènes vibratoires non seulement transversaux mais aussi longitudinaux (de même fréquence que dans les gaz brûlés). De ce fait, on peut penser que de tels phénomènes, mais de fréquence bien plus élevée ($\sim$ Mc/sec) existent dans la tranche de gaz séparant l'onde de choc et la flamme des détonations se propageant dans les mélanges dans des conditions éloignées des limites, et qu'ils jouent un rôle important en ce qui concerne le couplage entre l'onde de choc et la flamme.

M. Herzfeld. — In turbulent flames, the flame front is puckered. The normal burning velocity exists normal to the actual flame front, but the velocity of the envelope appears smaller. Would an analogous phenomenon be able to explain the decreased shock speeds reported by Professor Hornig ?

M. Hornig. — If small curved surfaces develop on the detonation front the local velocity may indeed vary. However, mass, momentum and energy must be conserved and these conditions primarily determine the average velocity of propagation. For this reason the average velocity is fairly insensitive to the presence of local curvature.

There may be a small effect on the average velocity because some of the heat of the reaction is consumed in the kinetic energy of turbulent flow, as has been suggested by D.R. White, but no detailed calculations have been carried out. In any case, the experimental velocities are within 1 per cent of those calculated from one dimensional theory.

M. de Boer. — Would the stability of the shock front in a $H_2 + Cl_2$ reaction, where the ultimate number of molecules does not change, be higher than in the case of $H_2 + O_2$?

M. Hornig. — Since the nature of the instability has not been established definitely I am not certain. However, I do not believe it would make any difference since I believe the fundamental source of instability is the rapid increase of reaction rate with temperature and pressure as the reaction in any volume element of the gas progresses.

M. Polanyi. — Why is the probability for v(1-0) deactivation so large for CO_2 ?

M. Hornig. — The efficiency is usually supposed to be the result of the formation of complexes between H_2O and CO_2 and I imagine one might try to relate it to the second virial coefficient in H_2O — CO_2 mixtures. This type of explanation fits well with the fact that whereas H_2O is a 1000 times more efficient in relaxing CO_2 at 300° than another CO_2 molecule, the efficiencies are about equal at 1000°. Since the complexes would dissociate as the temperature is increased, the number of relaxing collisions involving the complexes would decrease.

M. Cottrell. — It was shown some time ago by Eucken, using the ultrasonic method, that the relative effect of H_2O in deactivating vibrationally excited CO_2 diminishes with increasing temperature. Widom and Bauer published an explanation of the effect which-depended on the importance of collisions of high impact parameter when there is an attractive intermolecular interaction.

M. Widom. — When a deep minimum is present in the interaction potential of the collision partners, increasing the average relative velocity by increasing the temperature can cause an increase in the distance of closest approach, which, in turn, leads to a decreased transition probability.

M. Kuhn. — Is there any indication for an optical or other anisotropy in the reaction zone ? Detonation is a highly unidirectional process in space. We might therefore expect that as well as the light emission the polarisability in the reaction zone will be different if the electric vector responsible for the phenomenon (light emission or polarisability) is parallel or perpendicular to the axis of the tube.

M. Hornig. — It is possible to study this question, but the experiments are already involved and I hesitate to complicate them further. However, I had not thought about the possibility that orientation of the diatomic molecules might occur in the front. If the effect were appreciable it would make the index of refraction anisotropic and in that case your suggestion of using polarized light could yield very interesting results. I think we will try it.

I should like on the other hand to call your attention to some very interesting observations by R. Millikan and D.R. White at the General Electric Laboratory. They studied the vibrational relaxation of a mixture of one per cent CO and 99 per cent N_2 after heating to 3000° in a shock wave. The N_2 relaxation was followed by measuring the density *vs.* time with an interferometer; the CO relaxation was followed by the simultaneous measurement of the infrared emission from the $v = 1$ level. The remarkable thing was that although pure CO relaxes four times faster than nitrogen, the two relaxation times were exactly the same. It seems clear that the reason for their result is that the CO vibrational frequency is only 100 cm^{-1} or so beneath N_2. The very fast near resonant transfer of vibrational energy from CO to N_2 keeps the vibrational temperature of the CO equal to that of the N_2 at all times.

This is one of the clearest cases of fast resonance energy transfer I know of.

M. Norrish. — Professor Hornig's reference to the fast vibrational exchange between CO and N_2 resulting from shock tube observations illustrates a principle which ist srongly supported by similar work described in my paper (Fig. 11). The increase in population of the first vibrational level of CO at 1650 Å in the vacuum ultraviolet on flashing mixtures of CO and NO is explained in terms of near resonant transfer from NO($v = 1$) to CO($v = 0$). The attainment of equilibrium in mixtures of CO, NO and N_2 is similarly explained (Table III). In this case, the fundamental frequency of CO lies between that of N_2 and NO and so facilitates near resonant transfer through itself from NO to N_2.

M. Herzfeld. — N_2 and the asymmetrical linear vibration of CO_2 are in resonance. Recently, Professor M.C. Henderson has found in our laboratory that CO_2 is a very effective impurity in deactivating the N_2 vibration. The CO_2 vibration is deactivated stepwise by the other CO_2 modes.

M. Cottrell. — The interesting thing here is that although N_2 and CO are almost at resonance, the N_2 has a higher vibration frequency, that is, the vibrational energy of the CO is relaxing by way of a higher frequency vibration in N_2.

M. Hornig. — It seems worth pointing out that a method is now available by which the relaxation of individual quantum states can be followed. Such a method was provided previously by the spectrophone method, in which individual levels are excited by infrared absorption and their relaxation detected as pressure pulses in the gas, but various practical problems have prevented the spectrophone from realizing its potential. The inverse of this method does appear to be feasible. If a shock wave is used to heat a gas, the heating takes place in a small fraction of a microsecond. The rate of appearance of the molecule in various excited states can be measured by following the infrared emission at appropriate frequencies as a function of time. This method was used by Professor Davidson to follow the relaxation of the second vibrational level of CO but at that time only the slow PbS detectors were available. At the present time we have semiconductor detectors such as doped germanium which are sensitive throughout the infrared spectrum and which respond in about 0.1 microsecond. Using them, Dr. Peter Borrell in my group has studied vibrational relaxation in the first vibrational level of HCl and HBr, the second level of HCl, and the first level of the asymmetric stretching vibration of N_2O and CO_2. It should be possible in this way to study separately the relaxation of the various normal modes of a polyatomic molecule.

M. Kantrowitz. — Vacuum U.V. absorption can also be used.

ULTRASONICS AND ENERGY TRANSFER IN GASES

by **T. L. COTTRELL**

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1. INTRODUCTION

The ultrasonic method of investigating vibrational-translational energy transfer in gases furnished in 1925 the original evidence that in simple molecules this process is very inefficient from a collisional point of view. During the following few years the method yielded considerable information of chemical interest about the great variation of collision efficiency with collision partner. In the last twenty years, the increase in interest in gas dynamics and in the detailed discussion of elementary processes in chemical kinetics has led to the further exploitation of the ultrasonic method and to the development of several new methods of studying energy transfer. This general increase in interest has also stimulated the publication in the last three years of two books (1, 2) largely devoted to the subject. Moreover, the literature on energy transfer in gases up to the end of 1961 has been reviewed (3) so there is no need, in this paper, to write a historical account or a complete literature survey of the-subject. I therefore intend briefly to review the scope and limitations of the ultrasonic method, and consider how far its usefulness can be extended.

2. THE PHYSICAL SITUATION IN THE ULTRASONIC METHOD

The propagation of ultrasonic waves in a gas depends on its thermodynamic properties. If these thermodynamic properties split naturally into groups depending upon different sorts of behaviour at the molecular level, and if these groups equilibrate with one another at finite rates, then it is possible to say something about these rates by studying the propagation of sound of different frequencies. In particular, the velocity of sound in a perfect gas is given by :

$$V^2 = \frac{\gamma RT}{M} = \frac{RT}{M}\left(1 + \frac{R}{C_v}\right),$$

and if :

$$C_V = C_1 + C_2 + C_3 \ldots\ldots$$

where C_1, C_2 and C_3, etc., are heat capacities corresponding to loosely coupled different sorts of motion, then :

$$V^2 = \frac{RT}{M}\left(1 + \frac{R}{C_1 + C_2 + C_3 + \ldots\ldots}\right).$$

If the period of the sound wave is long enough for equilibrium between the different groups to be altered then all the terms in the denominator will contribute to the specific heat and a characteristic low frequency value of the sound velocity, V_o, will be observed. If the period is decreased so that there is no longer time for C_3 to equilibrate with C_1 and C_2, then there will be an increase in velocity with frequency. Similarly if the period is decreased still further, C_2 may no longer contribute and the velocity will be increased again. Finally at very high frequency none of the processes will contribute. Velocity and absorption will both increase and sound will no longer be readily propagated. In practice for diatomic molecules C_3 is the vibrational heat capacity, C_2 is the rotational and C_1 is the translational. For polyatomic molecules with different modes of vibration, there will be specific heat contributions characteristic of each mode, i.e. C_3, C_4, C_5, etc. In some molecules all the vibrational modes relax together : in others they relax independently.

Similar conditions apply to absorption of sound. Each dispersion region is accompanied by a maximum in the sound absorption coefficient per unit wavelength. The height of this maximum depends on the heat capacity contribution of the group concerned, and its position on the frequency at which the group of motions ceases to contribute to the heat capacity.

3. BASIC LIMITATIONS OF THE METHOD

By a basic limitation I understand one imposed by the physical situation implicit in the method, rather than a limitation imposed by purely technical inadequacies. The basic limitation of the ultrasonic method is that it is necessarily concerned with an equilibrium or quasi-equilibrium situation. Equilibrium exists between the different members of a group of motions, even if there is disequilibrium between the groups. Moreover, energy is supplied as translational energy, so that there is no method of preferentially exciting specific internal molecular motions to examine how they relax.

For diatomic molecules with only one vibrational mode (of known frequency) this is hardly a serious limitation, but for polyatomic molecules with a number of vibrational modes the situation is more complicated. This means that if the different groups equilibrate at similar rates we cannot be certain of exactly what is going on.

This limitation is shared with other methods for studying energy transfer, such as the impact tube and shock tube methods. On the other hand, the spectrophone and flash spectroscopic methods do permit more intimate resolution of molecular detail.

4. EXPERIMENTAL LIMITATIONS

In addition to these basic limitations there are other limitations imposed by the limitations of experimental techniques. These limitations are similar in the velocity dispersion and sound absorption measurements, but their detailed analysis is different, and they are dealt with separately here.

4.1 **Velocity dispersion.**

Velocity dispersion is measured in the ultrasonic interferometer. A transducer emits ultrasonic waves which impinge upon a reflector from which they are reflected back to the transducer. When the distance between the source and the reflector is an integral number of half-wavelengths of sound, there is a maximum acoustic impedence at the source. If the reflector is moved to or from the source, positions of resonance occur at half-wavelength separation. If the wavelength is determined and the frequency is known, the velocity follows immediately. Such an apparatus is subject to two types of experimental limitation. The first is the range of operating conditions over which it can be made to function : the second is the accuracy in velocity measurement required to obtain a given accuracy in measurement of relaxation time.

4.1.1 *Limitation of operating conditions.*

There are limitations on temperature, frequency and pressure. The transducer is usually a quartz crystal, which is no longer piezoelectric above 500 °C. This is then an upper limit to the temperature at which the conventional interferometer can be used. Sherratt and Griffiths (4) obtained results for the velocity of sound in carbon monoxide up to 1,800 °C using a quartz crystal kept in a cool part of the apparatus, but moving the reflector in a hot part of the apparatus. This introduction of a temperature gradient must adversely affect the accuracy, and indeed the value of the relaxation time of carbon monoxide derived from their measurements is substantially shorter than that obtained in other ways. However, their work shows that high temperature measurements can be made using a quartz crystal. It seems a pity that this lead has not been followed: but there is the less need to do so, because of the possibility of using the shock tube in this temperature region.

The frequency range can be wide. The conveniently available lower limit to quartz oscillators is about 50 kc/sec, and although lower frequencies have been used, the danger of errors due to diffraction effects at the long wavelengths occurring at low frequencies is considerable. The effective high frequency limit is about 10 Mc/sec Since energy transfer is a collision process, the important variable is f / p, rather than f alone. Although pressures up to 250 atm. have been used in interferometers, absorption in the dispersion region becomes serious pressures above a few atmospheres, and the useful f / p range available for energy transfer studies is from about 5 kc/sec^{-1} atm^{-1} to 1,000 Mc/sec^{-1} atm^{-1}. This corresponds to relaxation times at 1 atm from about 3×10^{-5} sec to about 10^{-9} sec. The upper limit is indeed not so much a functional limitation as due to the fact that 10^{-9} sec is about the period between collisions. This means that limitation of operating conditions restricts the velocity dispersion method to a temperature range of about 60-700 °K, and relaxation times at one atmosphere shorter than about 10^{-5} sec.

4.1.2 *Limitations of accuracy.*

However not all molecules with relaxation times in the above region can be studied, because the relaxing heat capacity may not be sufficiently great to affect the velocity appreciably. This point can be discussed quantitatively in terms of the acceptable error in the measurement of the relaxation time. We have for the relaxation time τ the expression :

$$\tau = \frac{1}{\omega} \cdot \frac{C_0}{C_\infty} \left\{\frac{V_\omega^2 - V_0^2}{V_\infty^2 - V_\omega^2}\right\}^{\frac{1}{2}}$$

where ω is the angular frequency of the sound, C is the specific heat, V is the sound velocity, and the subscript 0 refers to the low frequency end of the dispersion region and ∞ to the high end. The frequency is accurately known, and C_0 and C_∞ are usually known to within a few percent, so that accuracy to which τ is known depends on how accurately we can measure :

$$\{(V_\omega^2 - V_0^2)/(V_\infty^2 - V_\omega^2)\}^{\frac{1}{2}}$$

The most favourable frequency is that at which :

$$V_\omega^2 = (V_\infty^2 + V_0^2)/2 ,$$

and the fractional error in τ is then the fractional error in measuring :

$$\frac{1}{2}(V_\infty^2 - V_0^2) .$$

If the fractional error in measuring velocity is δ, and if the dispersion region in V^2 occupies a fraction x of V_0^2, then ε, the fractional error in τ, is given by :

$$\varepsilon = \frac{2\delta}{x} .$$

Now x may be related to the relaxing specific heat $C_r = C_0 - C_\infty$. We have, for C_r small :

$$x \sim \frac{C_r}{C_\infty} \left\{1 + \frac{C_\infty}{R}\right\}^{-1}$$

Now if C_∞ is the translational and rotational heat capacity, that is, is we are dealing with vibrational relaxation :

$$x = \frac{C_r}{12\,R}$$

for non-linear molecules, and :

$$x = \frac{C_r}{8.75\ R}$$

for linear molecules.

For rough quantitative discussion, we take x as 0.1 $C_r/R = 0.1\ h_r$, where $h_r = C_r/R$. We thus have for the fractional error in relaxation time :

$$\varepsilon \sim \frac{20\delta}{h_r}:$$

that is the fractional error in relaxation is proportional to the fractional error in measuring velocity and inversely proportional to the relaxing specific heat.

It is usually clained (1, 2) that $\delta \sim 10^{-3}$ in conventional ultrasonic work, so, if we require ε to be less than 5%, $h_r \geqslant 0.4$ or $C_r \geqslant 0.8$ cal mole^{-1} deg^{-1}. However, the dispersion curve is not usually defined by only one point. If we take into account the improvement of accuracy brought about by replication, we can say that an effective lower limit to C_r for accurate measurement of relacation time is about 0.4 cal mole^{-1} deg^{-1}. This is in agreement with the fact that the molecules with the lowest vibrational heat capacity for which ultrasonic relaxation times have been reported are methane and ammonia, with C_r of 0.6 and 0.5 cal mole^{-1} deg^{-1} respectively.

If however it were possible to improve the accuracy in velocity measurements by a factor of 5 this would result in a corresponding decrease in the minimum C_r for reliable relaxation time measurement.

In Edinburgh we have been considering the possibility of achieving such an improvement in accuracy, and Mr. Blythe in my department has carried out experimental and theoretical investigations of a high-accuracy interferometer. The simple theory of the interferometer suggests that all one need determine is the frequency of the source and the positions of the reflector in which maximum acoustic impedence is observed. One must also know the temperature at which the measurement is carried out.

Since sound velocity depends on $\sqrt{T}$, an error of 0.02° corresponds to 1 in 30,000 in V at room temperature — so temperature control and determination is hardly a problem. Again, frequency measurement can easily be made to within 1 cycle per second at 100 kc/sec, so again there is no fundamental difficulty.

As far as maxima in acoustic impedence are concerned, the position is much less simple. Not only must the positions of these maxima be measured with the desired accuracy, but one must be assured that they correspond to the propagation of plane waves in the interferometer : or if they do not, one must know the relationship between the positions of the maxima observed with the propagation mode actually taking place and the corresponding plane wavelength. Further, one must be certain that there are no diffraction effects coming into play. It turns out that these factors are more significant than the accuracy of measurement.

Location of the positions of maximum acoustic impedence can be achieved to about 0.5 μ. This means that if the positions of the number of peaks occupying about 1 cm of travel are determined, and if this is the limiting factor, an accuracy of about 1 in 20,000 can be obtained. Measuring the distance to slightly better than an absolute accuracy of 0.5 μ is quite feasible. In our apparatus we use an optical Moiré fringe distance measuring device, accurate to 10^{-5} cm over a travel of 2 cm, developed by Ferranti Ltd. However, this accuracy is of little avail if the apparent wavelength fluctuates from peak to peak because of diffraction effects, and if the plane wave is not excited because of wave guide effects.

We were originally interested in frequencies below 100 kc/sec, and in this range these difficulties are appreciable. They have not received great attention in the literature of ultrasonic investigation of energy transfer (though they have been mentioned by various authors) because absolute measurements of velocity have rarely been made. Usually the apparatus has been calibrated with a gas of known sound velocity. The deviations from the plane wave velocity are not large, so that provided the wavelength in the comparsion gas is not too different from the wavelength in the test gas, trouble from this cause is not apparent. The absolute error in wavelength due to waveguide effects is proportional to the square of the wavelength, and can be allowed for if the apparatus is calibrated with a number non-dispersing gases of different sound wavelengths, and the diffraction effects even at a frequency of 80 kc/sec are not too serious with gases of a molecular weight of 30 or greater, so that an absolute accuracy of a little better than 1 in 2,000 can be obtained with this apparatus. Better results could probably be obtained at higher frequencies — or at lower frequencies if the apparatus were made large enough. This last method is however, obviously unsatisfactory for use with gases which are expensive or difficult to prepare.

To summarize, it appears that improvement by a factor of at least two at a frequency of 100 kc/sec, and perhaps five at higher frequencies can be obtained using very accurate distance measurement apparatus and taking account of wave-guide effects. A fuller account of this work will be published in due course.

Unfortunately, those molecules which have small relaxing heat capacities also tend to have long relaxation times and hence low frequencies of interest. It is in just this region that the extra accuracy is hardest to attain.

4.2 **Ultrasonic absorption.**

Whereas there is only one main method of measuring the velocity of ultrasound, there are a number of methods of measuring absorption, and it is therefore more difficult to provide simple generalizations. We may however discuss the situation under the same headings as before.

4.2.1 *Limitation of operating conditions.*

Measurement of sound absorption requires a source of sound, usually a loud speaker or a quartz crystal, and a receiver, usually a microphone of some sort. It seems therefore that the absorption method is subject to the same temperature limitations as the sound velocity method. Once again it is not impossible that temperatures substantially above those at present in use could be attained : the technical problems would be greater but the accuracy of temperature control and temperature uniformity required would be less.

The frequency range can be wide — conveniently wider than that for ultrasonic velocity measurement. It is usually convenient to use a frequency around 10 kc/sec, but lower frequencies than this have been used in a Kundt's tube. Moreover, absorption due to relaxation processes is appreciably greater than classical absorption and therefore measurable even at frequencies considerably less than that corresponding to the relaxation time. Absorption measurements can also be carried over a range of pressure. This means that the absorption method is more flexible as far as frequency/pressure is concerned than the sound velocity method, a striking example being the recent determination of the relaxation time of nitrogen at 203 °C(5).

4.2.2 *Limitations of accuracy.*

We consider that, as is usually the case, the measurement of absorption is carried out at a frequency appreciably below the relaxation frequency, i.e. $\omega\tau \leqslant 1$. Under these conditions :

$$\tau = \frac{\alpha_{\tau} V}{\pi \omega^2 x}$$

where x has the same meaning, subject to the same limitations, as in § 4.1.2. α_τ is the absorption coefficient due to relaxation processes, the total absorption α, being given by $\alpha = \alpha_\tau + \alpha_{cl}$ is the classical absorption. The fractional error in τ will then be equal to the fractional error in α_τ. If the fractional error in measuring α is ξ, the fractional error in determining α_τ is $\xi(1 + \alpha_{cl}/\alpha_\tau)$. We now have to calculate α_{cl}/α_τ.

At room temperature for small gas molecules α_{cl} is about $10^{-13} f^2 \text{ cm}^{-1}$, or :

$$\alpha_{cl} \sim 10^{-13}\, \omega^2/4\pi^2$$

Again, for $\omega\tau \leqslant 1$, we can show that :

$$\alpha = \frac{\omega^2}{\omega_{max}} \cdot \frac{x}{2\mathrm{V}}$$

where ω_{max} is the frequency of maximum absorption.

We have then, that :

$$\frac{\alpha_{cl}}{\alpha_\tau} \sim \frac{10^{-13}\, \omega_{max}\, \mathrm{V}}{2\pi^2 x}$$

$$\frac{10^{-13}\, \omega_{max}\, \mathrm{V}}{2h_r}$$

If ε, the fractional error in τ, is to be no more than twice ξ, the fractional error in α, $\alpha_{cl}/\alpha_\tau < 1$.

For this to be so :

$$2h_r \geqslant 10^{-13}\, \omega_{max}\, \mathrm{V}\,.$$

Now $\mathrm{V} \sim 2\text{-}4 \times 10^4 \text{ cm sec}^{-1}$, for most gases of interest, so that :

$$h_r > 2\text{-}4 \times 10^{-9}\, \omega_{max}\,.$$

Now for a gas with a relaxation time about 1 μ sec, $\omega_{max} \sim 10^7 \text{ sec}^{-1}$, so $h_r \geqslant 2 \times 10^{-2}$, if ε is to be $\varepsilon \nleqslant 2\xi$. It is difficult to make a generally applicable estimate of ξ, but 5×10^{-2} seems to be in accord with good modern practice. This means that $h_r \sim$ (say) 2×10^{-2} is a lower limit of h_r for measurement of τ to 10%. This is an appreciably less stringent condition than that arrived at for the sound velocity method. It does correspond to a little less than the level possibly attainable in the most accurate sound velocity measurement under consideration. However there is the disadvantage that all dissipative processes add together to produce an overall absorption coefficient, whereas, with sound velocity, if the time constants are sufficiently different it is possible to resolve the processes. This is only possible with absorption if the actual absorption peaks are measured.

5. APPLICATION TO MOLECULES

We restrict this discussion to vibrational relaxation processes. Most rotational relaxation is fairly efficient collisionwise, and the actual numbers for rotational relaxation times are therefore of rather less general interest. Moreover, since only a good order of magnitude theory of vibrational translational relaxation times is available, rather than a numerically precise one, we are not particularly interested in relaxation times as short as the collision period, but rather in relaxation times corresponding to from about 10 to 10^8 collisions. It appears that, in general, complex molecules with a number of fairly low frequency vibrations have short relaxation times, so that a consequence of our general order of magnitude interest in the phenomena is that we are not often interested in molecules containing more than a few atoms. There is therefore at most only a few dozen pure compounds for which vibrational relaxation times are of theoretical interest. Most of these have already been studied. Many of those remaining are diatomic molecules with a relatively low relaxing heat capacity at moderate temperatures and are therefore not readily accessible to ultrasonic investigation. Figure 1 gives a plot of vibrational heat capacity against temperature for a number of molecules, and across it are drawn lines corresponding to the relaxing heat capacity detectable by ultrasonic velocity measurement with 1 in 1,000 accuracy, velocity measurement with 1 in 5,000 accuracy, and an indication of the best attainable by absorption methods.

It will be seen that measurements on most polyatomic molecules are accessible by standard ultrasonic techniques, and that improvement of ultrasonic techniques will only make accessible information about a relatively small number of molecules, chiefly hydrides.

The foregoing applies to single pure compounds. However, one of the most interesting features of the field is the dramatic and specific effect of certain added molecular species on vibrational relaxation times. H_2O for example, is about 1,000 times more efficient in deactivating vibrationally excited CO_2 than is CO_2 itself.

The effect of additives is so far only partially understood. It seems that the most important contribution of increase in accuracy in measurements of ultrasonic velocity might be in the ability to study mixtures with lower concentrations of relaxing molecules than at present possible : this might allow the elucidation of certain ano-

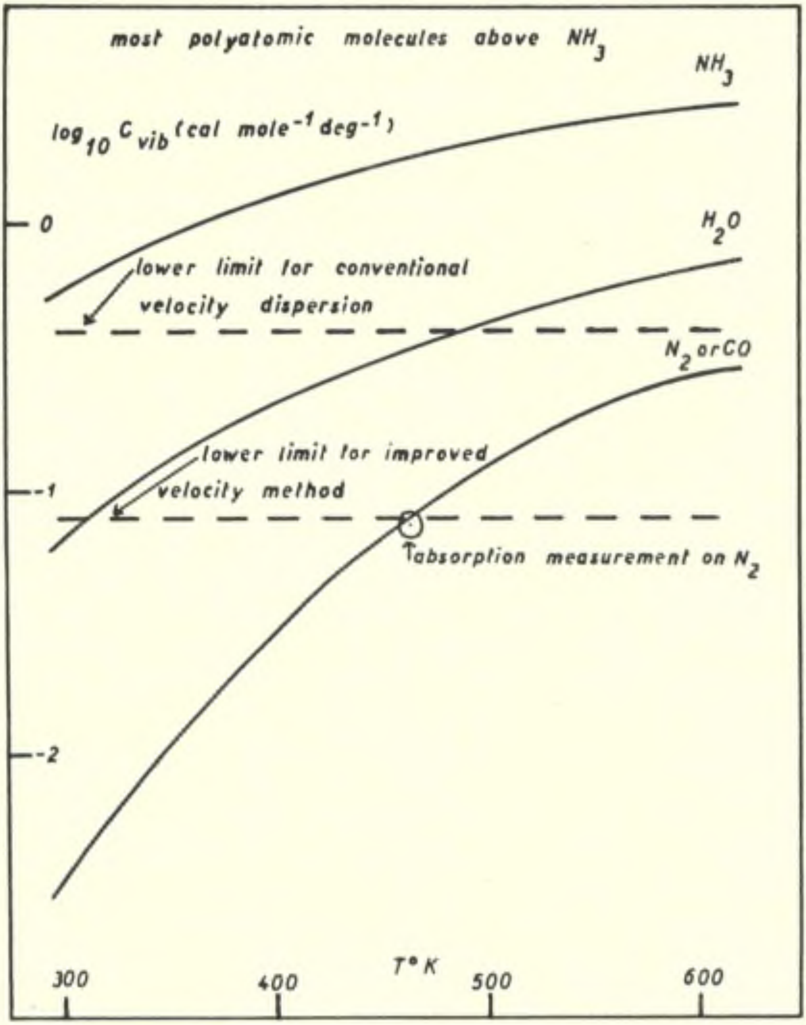

Fig. 1. — Plot of the logarithm of vibrational heat capacity against temperature for NH_3, H_2O, N_2 and CO. Most polyatomic molecules lie above NH_3 on this plot. The lower limits of C_{vib} which can be detected by conventional ultrasonic velocity dispersion and by improving the accuracy by a factor of 5 are shown. The point corresponding to the absorption measurement for nitrogen [5] is also shown.

malous results, such as the apparent superiority of argon to nitrogen as a deactivating species.

ADDENDUM

In view of the relatively small number of molecules amenable to study by the ultrasonic method, it seems important to choose for investigation series of molecules about which something definite can be said theoretically, and to compare experiment with theory in rather a precise way. Surprisingly, considering the long history of the method, there is still room for such investigations. Since my formal paper for this conference was prepared, we have in Edinburgh completed a comparative study of the vibrational relaxation times of some hydrides and deuterides which has given interesting results, and Professor Ubbelohde at Imperial College has examined the relative effects of H_2O and D_2O as vibrational energy transfer catalysts (6).

In changing from a hydride to a deuteride, the form of the vibrations is not in general changed, although the frequencies are. If there is a heavy atom present, the total mass, and hence the average molecular velocity, is little changed, and the intermolecular force field is hardly changed at all. This means that the change in vibrational relaxation time should depend mainly on the change in vibration frequency, and therefore that the relaxation times in deuterides should be shorter than the relaxation time in hydrides. It is possible to show quantitatively, using the Landau-Teller or Herzfeld-Litovitz equations, that this should be so, and this we set out to confirm, as we thought, for the compounds CH_4, CD_4; SiH_4, SiD_4; PH_3, PD_3; and NH_3, ND_3. The results for ammonia differ from the rest, and I have already discussed them at this meeting. For the others, the vibrational relaxation time in the deuterides is about 1.5 times *longer* than the hydrides. This means that energy transfer in the hydrides relative to deuterides is more efficient than one would expect on the simple theory.

It seems to me that the explanation may lie in the greater rotational velocity of hydrides than deuterides, thanks to their lower moments of inertia. In methane, for example, the vibration mode of lowest frequency corresponds to a bond-bending motion, and if the potential depends on nearest-atom interactions such a motion could easily be affected by a rotating molecule nearby, without any relative motion of mass centres taking place. The average peripheral velocity of rotation in methane is several times greater than the average translational velocity, so it is not absurd to consider the effect of rotation independently of translation. If one does this, and writes the probability of a vibrational transition as equal to the number of hard sphere collisions, without specification of relative velocity, times a Landau-Teller type expression in which the peripheral rotational velocity is substituted for the translational velocity and averaged over rotational states, one predicts that the vibrational relaxation time of CH_4 will be shorter than that in CD_4, by a factor roughly in agreement with experiment. These results were obtained by myself and Dr. A.J. Matheson (7).

List of molecules for which translational-vibrational ultrasonic results are known. References in (1), (2) and (3).

N_2, O_2, NO, Cl_2, Br_2, I_2

CO_2, N_2O, CS_2, COS, SO_2, NH_3, ND_3, PH_3, PD_3, BF_3, SiH_4, SiD_4, SF_6

CH_4, CHF_3, CF_4, CH_3Cl, CH_2FCl, $CHClF_2$, $CClF_3$, CH_2Cl_2, $CHCl_2F$, CCl_2F_2, $CHCl_3$, CCl_3F, CCl_4, CH_3Br, $CBrF_3$, $CClBrF_2$, CH_2Br_2, CBr_2F_2, CH_3I,

C_2H_6, C_2H_5F, CH_3CHF_2, C_2F_6, C_2H_5Cl, CH_3CHCl_2, CH_2ClCH_2Cl, CF_2ClCF_2Cl, C_3H_8

C_4H_{10}, C_6H_{12}, C_6H_{14}

C_2H_4, C_2H_3F, CH_2CF_2, C_2F_4, C_2H_3Cl, CHCl:CHCl, $CHCl{:}CCl_2$, C_2H_3Br, C_2H_3I,

C_3H_6 (propene)

C_2H_2

C_4H_6
CH_3OH, CH_3OCH_3, $C_2H_5OC_2H_5$, CH_3CHO,

C_3H_6 (cyclopropane)
C_6H_{12}, C_6H_{10}, C_6H_6, C_2H_4O

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Discussion du rapport de M. Cottrell

M. Ross. — The determination of potential parameters for a particular model of interaction from measurements of the compressibility and the viscosity of gases shows a difference between the systems H_2-H_2 and D_2-D_2. The energy parameter for the H_2-H_2 system is about 6% larger, but the size parameters of the two systems are the same.

M. Cottrell. — The virial coefficients of CH_4 and CD_4 are known to differ only slightly. Moreover, larger changes in intermolecular force function, such as those exhibited in the series CH_3F, CH_3Cl, CH_3Br and CH_3I, do not appear to affect the dependence of energy transfer probability on frequency.

M. Porter. — It may be relevant to the problem of vibrational relaxation in deuterated molecules to mention that the intramolecular conversion of electronic into vibrational energy also shows a greatly reduced efficiency when hydrogen atoms are substituted by deuterium. Wilse - Robinson has explained this phenomenon in terms of tunnelling from one potential energy surface to the other, which will clearly lead to a greater efficiency in the hydrogenated molecule. I confess that it is difficult to see how quantum mechanical tunnelling effects can be relevant to the vibrational relaxation problem but the similarity in behaviour is suggestive.

M. Wigner. — If one knows sufficiently little about a phenomenon, it is always easy to give an explanation. In the present case, it is conceivable that the crossing point between Dr. Porter's two energy surfaces lies within the somewhat larger range of the zero point vibration of H, but well outside the smaller range of the zero point vibrations of D. This would explain that the rate is higher for the hydrogen compound than for the deuterium compound.

M. Linnett. — I would like to make two very small points :

1) In discussing the unexpectedness of Prof. Cottrell's results for CH_4 and CD_4, we must remember why he expected the efficiencies to

be the order opposite to that found. This was that in CD_4 the vibrational quantum is smaller than in CH_4 and so less energy is transferred to translation. Consequently the transfer would be expected to be more efficient for CD_4.

Examples of energy transfer in hydrogen and deuterium compounds in which this translational factor is not involved are therefore hardly relevant to our present discussion.

2) The potential energy functions of interaction of H_2 and H_2, and D_2 and D_2 are different if we consider the energy as a function of « intermolecular » distance. However, they are the same if we write the energy as a function of the positions of the four nuclei. Consequently Prof. Cottrell is correct in his statement that the potential functions are the same.

M. Kuhn. — It has been found experimentally in the case of CCl_4 that the molecules containing the heavy carbon isotope ^{13}C were more volatile than the light molecules containing ^{12}C. It has been shown that this difference is to be expected by a consideration of the Van der Waals attraction forces emanating from the dispersion exchange effect, provided that the comparatively small infrared exchange effect is taken into account besides the usual UV exchange effect.

In the « normal » case, Fig. 1, e.g. realized in the case of the noble gases, the potential energy curves are identical for the light and heavy atomic species; the heats of vaporization Λ'_{ol} and Λ'_{oh}, calculated from the minimum of the potential curve, are identical. Because of the difference in zero point energy E_{ol} and E_{oh} of the vibration of the entire molecule round the position of minimum potential energy in the condensed state, the heat of vaporization Λ_{ol} of light molecules is, in this normal case and in a low temperature range, smaller than that of the heavy molecules Λ_{oh}. Consequently the light molecular species is in the « normal » case more volatile than the heavy species.

The reason for a higher volatility of the heavy molecular species, as observed in the case of CCl_4 mentioned, is due to a difference in the potential energy curves, i.e. in the Van der Waals attraction forces.

The Van der Waals attraction force due to the dispersion effect

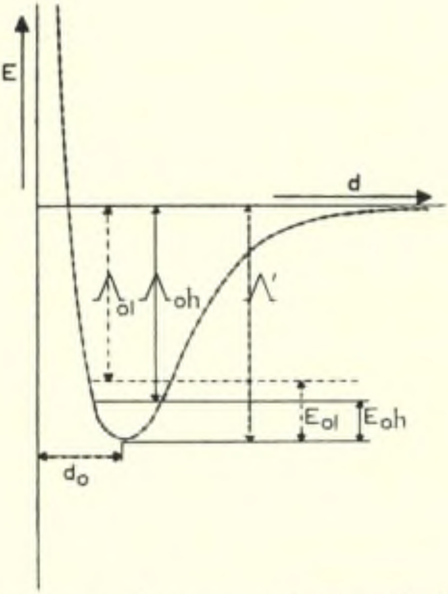

Fig. 1. — In the simplest case the energy as a function of the distance *d* between the centers of gravity of two molecules is the same for light and heavy molecules.

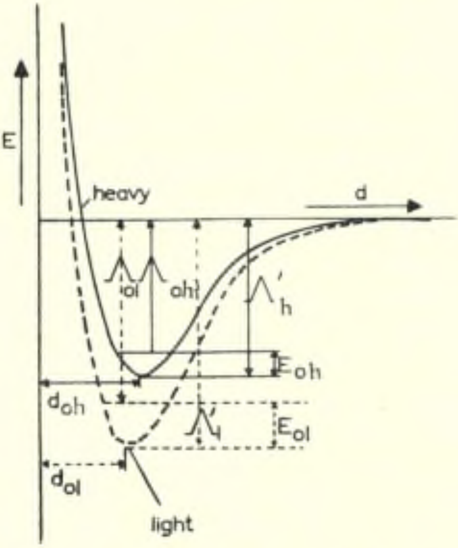

Fig. 2. — Smaller van der Waals attraction energy between heavy than between light isotopic molecular species.

by virtue of all absorption bands of particles 1 and 2 is in the general case given, according to London, by

$$U_{12} = -\frac{3}{2}\frac{h}{d^6}\sum_{i,k} \alpha_{1i}\cdot\alpha_{2k}\frac{\nu_{1i}\,\nu_{2k}}{\nu_{1i}+\nu_{2k}} \tag{1}$$

h being Planck's constant, d the distance between the particles, ν the absorption frequencies and α the corresponding static polarisabilities.

If the ultraviolet absorption frequencies and polarisabilities are identical and designated by ν_{lo} and α_{lo} respectively, while the infrared frequencies and polarisabilities are in a simple case ν_{IR} and α_{IR}, we botain from (1)

$$U_{12} = -\frac{3h}{4}\frac{\alpha_{lo}{}^2}{d^6}\,\nu_{lo}\left(1+2\,\frac{\nu_{IR}\,\alpha_{IR}}{\nu_{lo}\,\alpha_{lo}}\right) \tag{2}$$

The infrared contribution α_{IR} to the static polarisability is identical for the heavy and light species; ν_{IR} however, i.e. the internal infrared vibration frequency e.g. of the carbon atom inside the CCl_4-tetrahedron, will be higher in the case of the light and small in the case of the heavy isotopic species. Therefore the depth of the energy curve and correspondingly the heat of evaporation will be increased in the case of light relative to the heavy molecular species. See Fig. 2.

Taking into account both the differences in the van der Waals energy curve and the zero point energy E_{ol} and E_{oh} of the vibration of the entire molecule round the position of the minimum of the potential curve (as explained in Fig. 1) we obtain the situation indicated in Fig. 2 from which it can be seen that due to the smaller attraction between molecules of the heavy molecular species the heavy molecules may become more volatile than the light molecules. A more quantitative treatment, using the actual polarisability and frequency data has shown that the difference of the Van der Waals attraction produced by the infrared dispersion effect contribution explains qualitatively and approximately in a quantitative way the high volatility of $^{13}CCl_4$ relative to $^{12}CCl_4$ and the analogous differences in related compounds. (See P. Bärtschi and W. Kuhn, Helv. chim. acta **40**, 1084-1103 (1957); english translation by R. Presser : United Kingdom Atomic Energy Authority, Development, and Engineering group series 157 (CA); P. Bärtschi and W. Kuhn, Proceed. Sympos. Isotope Separation Amsterdam 1957, part II, Chapter 5).

M. Karplus. — Why does a change in vibrational frequencies influence the dispersion forces ?

M. Kuhn. — The answer is evident from eq. (2) whose second term contains the infrared absorption frequencies. The analysis of the derivation of this equation shows that when two particles having both the same ultraviolet and an infrared vibration frequency ν_{l0} and ν_{IR}, are approaching each other, a removal of the degeneracy takes place, due to coupling between the resonators. The sum of the frequencies and therefore also the zero state energies ($h\nu/2$) of the resulting non degenerate system is smaller (in a way depending on the original frequencies given in equation (2)) than the sum of the frequencies in the original degenerate system.

M. Shuler. — Professor Cottrell, if I understood him correctly, made the statement that small differences in the intermolecular forces should not have any significant influence on the vibrational-translational transition probabilities such as evidenced, for instance, by CH_4 and CD_4. According to the theoretical treatment of Herzfeld, however, the transition probabilities (and thus the number of effective collisions) are *very* sensitive to the slope of the repulsive potential. It may therefore perhaps be possible to explain Prof. Cottrell's results on the basis of the different force fields of CH_4 and CD_4.

M. Hornig. — I would like to suggest a possible explanation for the failure of CD_4 to relax vibrationally at a faster rate than CH_4. It lies in the fact that when the atoms in CH_4 or CD_4 are displaced the carbon atom moves in a direction opposite to the hydrogens (or deuterium) in order to keep the centre of mass fixed. Hence the displacement of hydrogen with respect to the center of mass is greater than deuterium. In particular, the vibrational mode involved in accoustic relaxation is the bending mode. If the H-C-H angle is displaced by $\Delta\theta$, the displacement in center of mass coordinates is $r_{C\text{-}H}\Delta\theta \times (12/16)\sqrt{2/3}$ while that of deuterium is $r_{C\text{-}D}\Delta\theta \times (12/20)\sqrt{2/3}$, a ratio of 20/16 in favor of hydrogen. If the interaction potential between the colliding molecule and CH_4 is predominantly with the H (or D) atoms, the external force, $\partial V/\partial\theta$, is always greater for CH_4 than CD_4.

M. Cottrell. — The effect is about as large for silanes as for methanes although the silicon atom will move less far than the carbon atom.

M. Widom. — What is the nature of the lowest frequency vibration in methane ?

M. Cottrell. — The lowest vibration frequency is an anti-symmetrical bending.

M. Herzberg. — It seems to me that the striking difference in vibrational transfer between CH_4 and CD_4 may be understood on a semiclassical basis. CH_4 is a nearly spherical molecule, but in a vibrating molecule there is a slight deviation from sphericity. It is this deviation from sphericity that determines the speed of the vibrational transfer. Clearly, the deviation from sphericity for the ν_4 vibration of CD_4 is less than for that of CH_4, and therefore vibrational transfer in CD_4 should be more difficult than in CH_4.

M. Hornig. — I should like to ask Dr. Cottrel whether the dispersion arising from structural relaxation of imperfect gases is taken into account and whether it is of any importance. It must occur in the same general region as the other fast relaxation we have discussed.

M. Cottrell. — In reply to Dr. Herzberg's point concerning vibrational amplitudes, it is correct to say that the change in amplitude with substitution of deuterium for hydrogen will operate to make energy transfer more difficult for the deuterium compound. However, this effect is taken into account in the theory by the appearance of the square of the matrix element for the displacement of the oscillator in the pre-exponential factor, and it does not outweigh the effect of the vibration frequency in the exponential which works in the opposite direction. Taking Dr. Hornig's point about the change from molecule stationary to mass centre stationary into account again moves the theory in the right direction but still not nearly enough. The conventional calculation, with the amplitude included in the matrix element, and taking only translational velocity into account gives a relaxation time for CH_4 longer by a factor of about 5 than for CD_4, whereas what is observed is a factor of 1.5 in the other direction. Thus what we need is a substantial effect, and I do not see anything other than rotation which can provide this.

In reply to Dr. Hornig's point about virial coefficients : use of the statistically measured virial coefficient should be adequate unless the « double molecules » associate and dissociate at a frequency of interest. If they do this, the process should make a contribution to the specific heat, which would show up in the measured velocity.

I should finally say that the remark in my paper about shock tubes only applies to shock experiments in which bulk properties such as density are measured. Where the concentrations of individual species can be measured spectroscopically, the shock tube can reveal more detail, so much so, in fact, that one wonders whether there is much useful left to be done by the ultrasonic method.

M. Kantrowitz. — I should like to call briefly to your attention the impact tube method for measuring rates to the approach of equilibrium. [J. Chem. Phys., **14**, 150, 1946)]. This technique is particularly useful when large gas samples are available for measurement.

M. Ubbelohde. — The impact tube method gives accurate results but suffers from the disadvantage that quite large quantities of gas are needed, making its use awkward for some molecules whose behaviour is particularly interesting.

THE STUDY OF CHEMICAL REACTIONS IN CROSSED MOLECULAR BEAMS

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1. INTRODUCTION

The principal approach to the experimental study of chemical kinetics has remained essentially unchanged for over one hundred years. The rates of change of concentrations of reactants or products in a reaction are measured as a function of concentration, time, and temperature and one or more rate coefficients, defined in an empirical rate equation deduced from these experiments, can be obtained as a function of temperature. The temperature dependence of the rate coefficient and a theory for this dependence (usually a very simple theory) provide an estimate of the activation energy. A mechanism for the reaction needs to be postulated and must be consistent with the observed rates; the mechanism can seldom be proved unique. Although the outline of this approach is simple, many variants have been introduced relying on special techniques; among these are : the use of reactants labeled with radioactive or stable isotopes, the detection of free radicals as intermediates by spectroscopic and resonance methods, the application of many analytical instruments, and the attainment of extreme variations in temperature in reactions in shock waves. The validity of this basic method and the ingenuity and sophistication brought to its application are shown by an impressive literature on rates and mechanisms of reactions (1).

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* Alfred P. Sloan Foundation Fellow.

An alternative approach to investigations in chemical kinetics consists of the determination of molecular rather than microscopic properties of the reacting system. The technique of molecular beams (2) is well suited for such studies and was suggested nearly forty years ago by Fraser (3); only recently, however, has work begun in a number of laboratories. The purpose of this article is to review some experiments on chemical reactions in crossed molecular beams.

II. THEORY

A. The rate coefficient.

The rate of an observed reaction is an average of all possible molecular events leading to reaction, weighted by the probability of occurrence of each event. Let us consider a bimolecular gas phase reaction with reactants A and B, products C and D, and let A(i) denote an isolated molecule of species A in the internal quantum state (i). For the reaction :

$$\mathrm{A}(i) + \mathrm{B}(j) \rightleftharpoons \mathrm{C}(l) + \mathrm{D}\,(n) \tag{1}$$

the rate coefficient in the forward direction, k_f, is :

$$k_f(ln/ij) = \int \cdot\cdot \int \frac{p}{\mu}\, \sigma_{\mathrm{R}}(ln/ij;\, p\Omega) f_{i_{\mathrm{A}}}(p_{\mathrm{A}}) f_{j_{\mathrm{B}}}(p_{\mathrm{B}})\, d\Omega\, dp_{\mathrm{A}}\, dp_{\mathrm{B}}, \tag{2}$$

where p is the relative momentum and μ the reduced mass of the reactants, σ_{R} the differential chemical reaction cross section, Ω the solid angle of scattering, and $f_{i_{\mathrm{A}}}$ the momentum distribution function of A(i). The total chemical reaction cross section for Eq. (1), $\sigma_{\mathrm{R}}(ln/ij;\, p)$ can be written

$$\sigma_{\mathrm{R}}(ln/ij;\, p) = \int_{\Omega} \sigma_{\mathrm{R}}(ln/ij;\, p\Omega)\, d\Omega, \tag{3}$$

or can be related in classical mechanics to the probability of reaction (4) P($ln/ij;\, pb\varepsilon$), a function of the impact parameter b and azimuthal angle ε,

$$\sigma_{\mathrm{R}}(ln/ij;\, p) = \int_{b} \int_{\varepsilon} \mathrm{P}(ln/ij;\, pb\varepsilon)\, b\, db\, d\varepsilon. \tag{4}$$

Although the momentum distribution functions may in principle be time dependent (5), the use of Maxwellian distributions is almost always sufficient (6); in this case the rate coefficient, on transformation to relative coordinates, becomes a weighted average of the total chemical reaction cross section :

$$k_f(ln/ij;\ \mathrm{T}) = (\pi\mu)^{-\frac{1}{2}} \left(\frac{2}{k\mathrm{T}}\right)^{\frac{3}{2}} \int_0^{\infty} \sigma_{\mathrm{R}}(ln/ij;\ \mathrm{E})\,\mathrm{E}e^{-\frac{\mathrm{E}}{k\mathrm{T}}}\,d\mathrm{E}. \qquad (5)$$

The integration in Eq. (5) extends over all possible values of the relative energy $\mathrm{E} = p^2(2\mu)^{-1}$.

The rate coefficient of the reaction, Eq. (1), in the forward direction summed over all possible initial and final states of reactants and products can be written as :

$$k_f(\mathrm{T}) = (\pi\mu)^{-\frac{1}{2}} \left(\frac{2}{k\mathrm{T}}\right)^{\frac{3}{2}} \int_0^{\infty} \sigma_{\mathrm{R}}(\mathrm{E})\mathrm{E}e^{-\frac{\mathrm{E}}{k\mathrm{T}}}\,d\mathrm{E} \qquad (6)$$

$$\sigma_{\mathrm{R}}(\mathrm{E}) = \sum_{ij} \mathrm{X}_{i\mathrm{A}}\,\mathrm{X}_{j\mathrm{B}} \Big\{ \sum_{ln} \sigma_{\mathrm{R}}(ln/ij;\ \mathrm{E}) \Big\}\ , \qquad (7)$$

where Eq. (7) defines the reaction cross section $\sigma_{\mathrm{R}}(\mathrm{E})$. We observe that the fractions of molecules of each species in given quantum states, $\mathrm{X}_{i_{\mathrm{A}}}$, $\mathrm{X}_{j_{\mathrm{B}}}$, may be functions of time if the rate of the reaction is comparable to the rate of relaxation of the internal distributions (7, 8). However the rate coefficient will be a function of temperature if the fractions are at their equilibrium values at all times.

The total chemical reaction cross sections, Eqs. (3), (4), and (7), are of great experimental and theoretical interest. There exists the possibility of their *a priori* calculation from solutions of the Schrödinger equation. The difficulties of this approach for a complete analysis have been insurmountable to date (9-12). In fact, even reliable estimates of potential energy surfaces of reacting systems, a prerequisite for the solution of the scattering problem, are not available.

The cross section can be written easily for the simple model of the collision of two hard spheres which can change from reactants to products if the energy along the line of centers on contact exceeds a given threshold value E*. Let us consider reactants and products in their ground states only; the total chemical reaction cross section for this model is :

$$\begin{aligned} \sigma_{\mathrm{R}}(\mathrm{E}) &= 0 & \mathrm{E} &< \mathrm{E}^* \\ \sigma_{\mathrm{R}}(\mathrm{E}) &= \pi d^2 \left(1 - \frac{\mathrm{E}^*}{\mathrm{E}}\right) & \mathrm{E} &\geqslant \mathrm{E}^*\ , \end{aligned} \qquad (8)$$

where d is the hard sphere diameter. Substitution of Eq. (8) into Eq. (6) yields :

$$k_f(\mathrm{T}) = \pi d^2 \left(\frac{8k\mathrm{T}}{\pi\mu}\right)^{\frac{1}{2}} e^{-\frac{\mathrm{E}^*}{k\mathrm{T}}} \tag{9}$$

the well known expression obtained from the simple collision theory of chemical kinetics.

If the chemical reaction cross section is written :

$$\begin{aligned} \sigma_{\mathrm{R}}(\mathrm{E}) &= \mathrm{O} & \mathrm{E} &< \mathrm{E}^* \\ \sigma_{\mathrm{R}}(\mathrm{E}) &= \alpha(\mathrm{E})\left[1-\frac{\mathrm{E}^*}{\mathrm{E}}\right] & \mathrm{E} &\geqslant \mathrm{E}^*, \end{aligned} \tag{10}$$

so that the function $\alpha(\mathrm{E})$ accounts for the deviation of the cross section from that of the hard sphere model, then the rate coefficient becomes (5) :

$$k_f(\mathrm{T}) = \left(\frac{8k\mathrm{T}}{\pi\mu}\right)^{\frac{1}{2}} \varkappa(\mathrm{T}) e^{-\frac{\mathrm{E}^*}{k\mathrm{T}}} \tag{11}$$

$$\varkappa(\mathrm{T}) \equiv (k\mathrm{T})^{-2} \int_0^\infty \xi\alpha(\mathrm{E}^* + \xi)\, e^{-\frac{\xi}{k\mathrm{T}}}\, d\xi\,.$$

These equations show that deviations in the energy dependence of the total cross section from hard sphere behavior appear in the pre-exponential temperature coefficient of the rate coefficient. Frequently it is difficult enough to measure the rate coefficient over a range of temperature with precision adequate for the estimation of the exponential temperature dependence of the rate coefficient; the analysis of the pre-exponential temperature coefficient for the purpose of obtaining information about the deviation function $\alpha(\mathrm{E})$ has not been possible from rate measurements.

B. Kinematics of collisions.

In the collision of two molecules, the conservation laws of energy and linear and angular momentum are of interest and may, in special cases, be of dominant importance (13-15). Let the inital velocities of two molecules in perpendicularly intersecting beams be $\mathbf{v}_1$ and $\mathbf{v}_2$, Figure 1. The center of mass vector $\mathbf{v}_c$, also called the centroid,

$$(m_1 + m_2)\, \mathbf{v}_c = m_1\mathbf{v}_1 + m_2\mathbf{v}_2 \tag{12}$$

intersects the initial relative velocity vector, $\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2$, at a point determined by the equations :

$$\mathbf{v}_1 = \mathbf{v}_c + \frac{m_2}{m_1 + m_2}\,\mathbf{v} \tag{13}$$

$$\mathbf{v}_2 = \mathbf{v}_c - \frac{m_1}{m_1 + m_2}\,\mathbf{v}\,. \tag{14}$$

The final relative velocity vector $\mathbf{v}'$ may be considered to pivot around the end of $\mathbf{v}_c$ and the final velocities of the products of the collision, $\mathbf{v}_3$ and $\mathbf{v}_4$, are related to $\mathbf{v}_c$ and $\mathbf{v}'$ by equations analogous to Eqs. (13, 14). For the final velocity vector drawn in Figure 1, the molecule with velocity $\mathbf{v}_4$ is scattered into a laboratory angle β, measured from $\mathbf{v}_1$ in the plane of the beams.

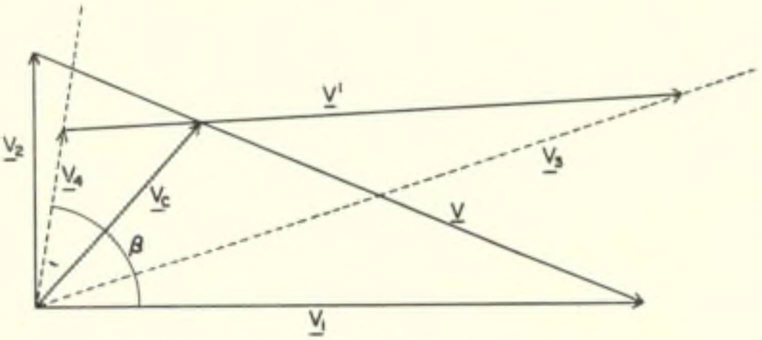

Fig. 1. — Vector diagram of initial and final velocities of a collision.

In an elastic collision the relative speed is an additional invariant of the collision, but in inelastic or reactive collisions the final relative kinetic energy, $E' = \frac{1}{2}\mu'(v')^2$, may differ from its initial value E. The length of the line segment $v'm_3(m_3 + m_4)^{-1}$ represents the speed of particle 4 with respect to the center of mass.

If m_3 is very much smaller than m_4, and E′ cannot exceed E greatly, then the vector $\mathbf{v}_4$ may be restrained to a small cone with $\mathbf{v}_c$ as its axis. In this case the scattered product molecule with velocity $\mathbf{v}_4$ appears primarily at the same laboratory angle as the centroid. If the cone is sufficiently narrow, the intensity of scattered product is enhanced; however, the narrower the cone, the poorer is the experimental angular resolution in the center of mass system and the more difficult the measurement of a differential scattering cross section. The product molecule with speed v_4 may appear at any laboratory angle if $v'm_3(m_3 + m_4)^{-1}$ exceeds v_c in length (14).

The initial angular momentum is a vector sum of the initial orbital angular momentum, $L = \mu vb$, and the rotational angular momenta J_1, J_2 of the reactants. The orbital angular momentum vector must be perpendicular to the relative velocity, but the distributions of rotational angular momenta are uniform in space. If, as is usually the case, $L \gg J_1, J_2$ then the total angular momentum is nearly parallel to L. With the additional restriction $L \gg J_3, J_4$ the final orbital angular momentum is nearly parallel to L and v' nearly perpendicular to L. Thus, an anisotropy in the distribution of scattered product may be expected even if we suppose that the final relative velocity vectors are distributed uniformly about $L(L \gg J_1, J_2)$. This can be seen in Figure 2 which illustrates a vector diagram for some initial **v** and **L**. The final relative velocity vectors are distributed uniformly about **L**, as indicated by the radii of the circle. For a given **v**, all **L** uniformly distributed about **v** are possible so that the distribution of final relative velocity vectors, obtained as shown by the rotation of Figure 2 about **v**, is denser along the **v** axis than near the plane of the orbital momenta (13). Some anisotropy can still be expected on relaxation of the condition $L \gg J_3, J_4$.

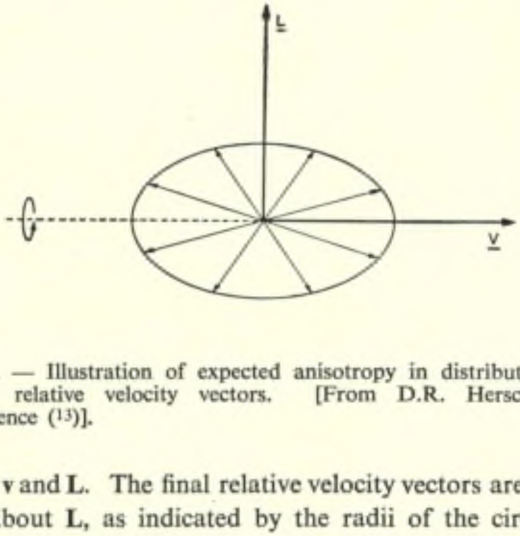

Fig. 2. — Illustration of expected anisotropy in distribution of final relative velocity vectors. [From D.R. Herschbach, reference (13)].

A marked change may occur in the orbital angular momentum during a collision if the ratio of the reduced mass of the reactants to that of the products differs greatly from unity. A compensating change must then occur in the rotational momenta as required by the conservation of total angular momentum. Thus if the reduced mass of the products is much less than that of the reactants, the products may be in highly excited rotational states ($J' \gg L'$) with the orientation of the rotational momentum vectors nearly parallel to the initial angular momentum (13, 16).

C. The scattering cross section.

The evaluation of chemical reaction cross sections from measurements on scattered products requires certain relations which are developed in this section.

Let us consider two beams intersecting at angles ($\gamma\delta$) in a common volume element $d\tau$, Figure 3, and let dn_1 and $dn_2(v_2\gamma\delta)$ be the density of molecules in each beam with speeds v_1 and v_2, respectively. The number of reactive collisions per unit time is equal to the flux of centroids of products, $P(v_1v_2\gamma\delta)dv_1dv_2d\gamma d\delta$ and is related to the reaction cross section by :

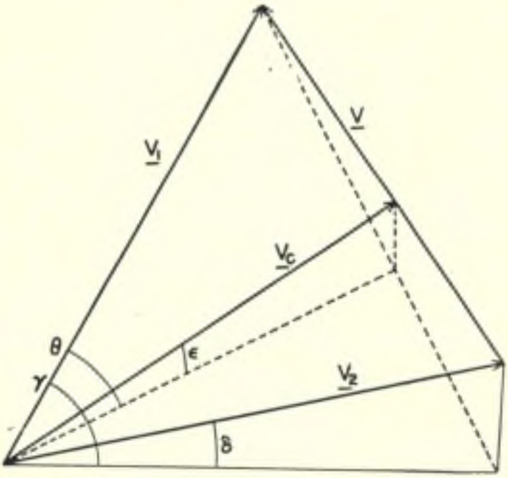

Fig. 3. — Vector diagram of a collision of two molecules with velocities (v_1 v_2), beam intersection angles (γ, δ), and direction angles of centroid (θ, ε).

$$P(v_1v_2\gamma\delta)dv_1dv_2d\gamma d\delta = \sigma_R(v)v\,dn_1(v_1)dn_2(v_2\gamma\delta)d\tau(\gamma\delta). \qquad (15)$$

If the width of beam 1 is l and beam 2 effuses from a point source a distance D from beam 1, then the collision volume element can be written :

$$d\tau(\gamma\delta) = l\mathrm{D}^2 \left[\cos\delta\cos\left(\gamma - \frac{\pi}{2}\right)\right]^{-3} d\gamma d\delta \tag{16}$$

for the range of beam intersection angles $d\gamma d\delta$. The density of molecules 2 in their beam source, at temperature T_2,

$$dn_2(v_2) = 4\pi n_2 \left(\frac{m_2}{2\pi k\mathrm{T}_2}\right)^{\frac{3}{2}} v_2^2\, exp\left[-\frac{m_2\, v_2^2}{2k\mathrm{T}_2}\right] dv_2\,, \tag{17}$$

is related to the density in the beam formed by effusive flow through an orifice of area a_2,

$$dn_2(v_2\gamma\delta) = \frac{a_2}{4\pi\,\mathrm{D}^2}\left[\cos\delta\cos\left(\gamma - \frac{\pi}{2}\right)\right]^2 \mathrm{I}_2(\gamma\delta)dn_2(v_2). \tag{18}$$

The function $\mathrm{I}_2(\gamma\delta)$ is the ratio of the intensity of beam 2 at $(\gamma\delta)$ to that at $\gamma = \frac{\pi}{2}$, $\delta = 0$, the intersection angles of the K beam with the normal to the orifice area a_2.

We now consider some special cases :

1. Collisions of two velocity-selected, perpendicular beams.

If two beams collide at right angles ($\gamma = \frac{\pi}{2}$, $\delta = 0$) in a collision volume τ and the velocity distribution in each beam is proportional to a δ-function,

$$dn_1(v_1) = n_1\delta(v_1 - v_1^0) \tag{19}$$

$$dn_2\,(v_2\gamma\delta) = n'_2\delta(v_2 - v_2^0)\,, \tag{20}$$

where n'_2 is the density in beam 2, then the number of product molecules formed per unit time :

$$\int..\int \mathcal{P}(v_1v_2\gamma\delta)dv_1dv_2d\gamma d\delta$$

is

$$\mathcal{P}(v_1v_2) = \sigma_{\mathrm{R}}\left(\sqrt{v_1^2 + v_2^2}\right)\sqrt{v_1^2 + v_2^2}\; n_1n'_2\tau\,. \tag{21}$$

The superscripts on the speeds are omitted in Eq. (21).

2. Collision of a velocity selected beam with a thermal beam.

The velocity distribution of beam 1 is given by Eq. (19) and that of beam 2 by Eq. (17) so that the number of products molecules produced per unit time can be readily obtained by substitution. For later reference we wish to establish the flux of centroids of products in a differential range of centroid angles ($d\theta$, $d\varepsilon$), Figure 3. The kinematics of a collision provides the transformation relations from the variables ($v_2\gamma\delta$) to ($\theta\gamma\varepsilon$) and we obtain for the flux of centroids at θ, and $\varepsilon = 0$ (16) :

$$\mathcal{P}(v_1\theta\varepsilon q_o)\Delta\theta\Delta\varepsilon = \tag{22}$$

$$\frac{4G}{\sqrt{\pi}} n_2 \frac{N_1}{v_1} q^3{}_o \int_{\gamma=\theta}^{\pi} \sigma_R(v) I_2(\gamma, \delta=0) \sin\theta \sin^2\gamma \sin^{-4}(\gamma-\theta) v$$

$$\exp\left\{-\left[\frac{q_o \sin\theta}{\sin(\gamma-\theta)}\right]^2\right\} d\gamma\Delta\theta\Delta\varepsilon\,,$$

where the relative speed is :

$$v = v_1 \left\{1 + \left[\frac{m_1 \sin\theta}{m_2 \sin(\gamma-\theta)}\right]^2 - \left(\frac{2m_1 \sin\theta \cos\gamma}{m_2 \sin(\gamma-\theta)}\right)\right\}^{\frac{1}{2}} \tag{23}$$

and the symbol q_o denotes the ratio :

$$m_1 v_1 (m_2 v_{2o})^{-1}, \quad v_{2o}^2 = 2kT_2 m_2^{-1}\,.$$

G is an apparatus factor with dimensions of a volume.

3. Collision of thermal beams.

If two thermal beams with distributions of speeds given by Eq. (17) intersect at right angles ($\gamma = \pi/2$, $\delta = 0$) then the number of products formed per unit time, $\mathcal{P}(T_1T_2)$, is :

$$\mathcal{P}(T_1T_2) = \tau\int\ldots\int \sigma_R(v) v\, dn_1(v_1)\, dn_2(v_2, \gamma = \pi/2, \delta = 0)\,. \tag{24}$$

An equation for the flux of centroids at given direction angles ($\theta\varepsilon$), analogous to Eq. (22), can also be derived for this case (15).

D. Elastic scattering.

For the purpose of a comparison of the elastic scattering of reactive and non-reactive systems, to follow below, we cite here some essential results of the theory of elastic scattering of two bodies (17, 18). A typical trajectory, in relative coordinates, is shown in Figure 4 for classical dynamics according to a spherically symmetric potential of interaction representing attraction and repulsion. The impact parameter b and the differential elastic scattering cross section $\sigma(E\chi)$, a function of the scattering angle χ, are related by the equation :

$$\sigma(E\chi) \sin\chi\, d\chi = b\, db\,. \tag{25}$$

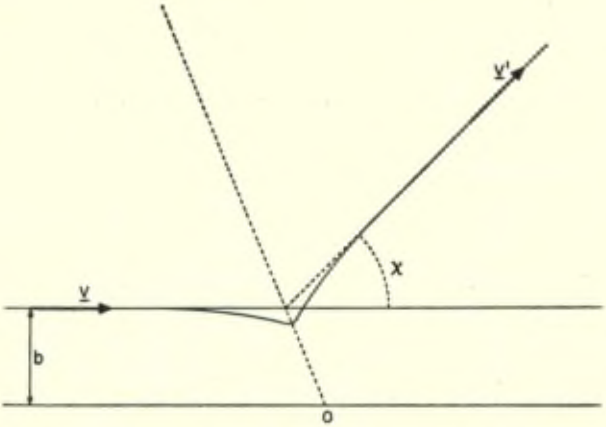

Fig. 4. — Classical trajectory of a particle of reduced mass μ and impact parameter b scattered by a potential of force, centered at 0, through a relative scattering angle χ.

We shall make use of the assumed form of intermolecular potential (exp-six potential) (19) :

$$V\left(\frac{r}{r_m}\right) = \frac{\varepsilon}{1 - 6\alpha^{-1}}\left[\frac{6}{\alpha}\, e^{\alpha\left(1 - \frac{r}{r_m}\right)} - \left(\frac{r_m}{r}\right)^6\right] \tag{26}$$

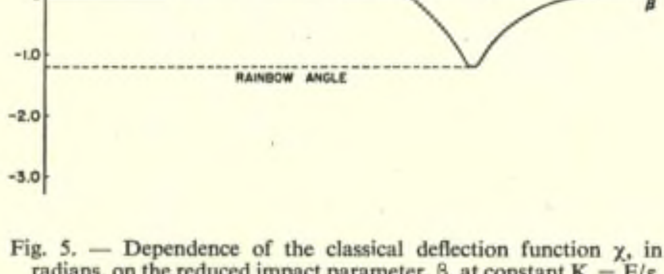

Fig. 5. — Dependence of the classical deflection function χ, in radians, on the reduced impact parameter, β, at constant $K = E/\varepsilon$. If χ is less than the rainbow angle, positive and negative values of the deflection function contribute to an observed χ of given magnitude.

expressed as a function of a reduced distance, where $-\varepsilon$ is the minimum value of the potential, at the distance r_m. The dependence of χ on the reduced impact parameter, $\beta = b/r_m$, at constant $K = E/\varepsilon$ is shown in Figure 5. For an observed scattering angle less than the rainbow angle there are three corresponding values of β and the right hand side of Eq. (25) has to be understood as a summation over all contributing branches of the deflection function. For scattering angles larger than the rainbow angle, χ is a single valued function of β. The reduced distance of closest approach, y, during a collision is calculated from the equation :

$$\left[1 - \frac{V(y)}{E}\right] y^2 = \beta^2 \tag{27}$$

and is a single valued function of β, hence a single valued function of χ, for scattering angles larger than the rainbow angle.

The classical differential scattering cross section is infinite at the rainbow angle, Figure 6, but the quantum mechanical scattering cross section may be expected to, and in fact does, deviate from the

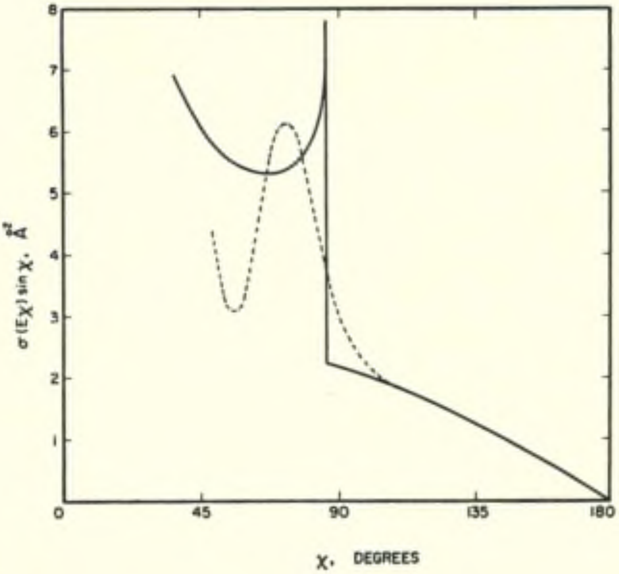

Fig. 6. — Calculated elastic scattering cross section vs. scattering angle for a given potential energy of interaction. Solid line : classical calculation. Broken line : quantum mechanical calculation. [From K.W. Ford and J.A. Wheeler, reference (20)].

classical value near the rainbow angle (20). This holds true for values of the reduced energy and size parameter r_m for which the classical and quantum mechanical cross sections are identical in angular regions removed from the rainbow angle. The predictions for the cross section obtained from a first order W.K.B. approximation of the phase shifts in the quantum theory of scattering (21) are presented in Figure (6) for the same potential used for the calculation of the classical scattering cross section. (20).

From the experimental determination of the position of the rainbow angle the potential parameter ε is easily deduced (22, 23). For illustration, we show in Figure 7 a plot of the function $\sigma(\bar{E}\chi)\sin\chi\ vs\ \chi$ for the system K-Kr, where $\bar{E}$ is the relative energy (see below). The potential parameter ε is 0.18 kcal/mole. The solid line connects the experimental points and the dotted line represents a theoretical calculation of $\sigma(\bar{E}\chi)$ sin χ according to classical mechanics with use of the potential, Eq. (26), $\alpha = 12$, and ε deduced from the experiment, the functions being fitted to the experimental values near $\chi = 40^o$.

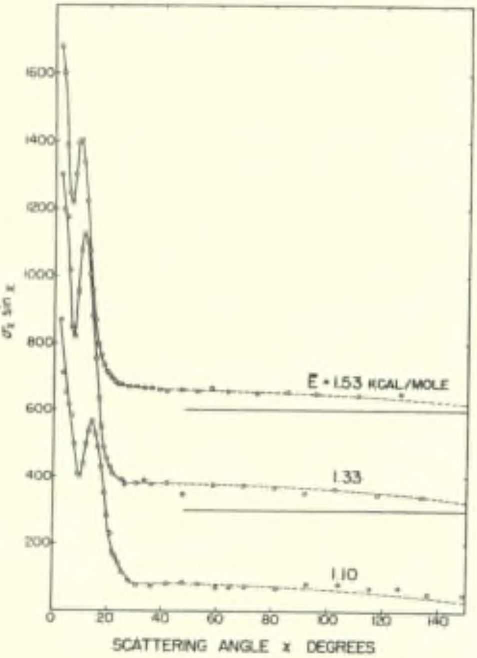

Fig. 7. — Elastic scattering of the system K-Kr. [From references (16) and (22)].

III. CHEMICAL REACTIONS IN CROSSED THERMAL BEAMS

Up to the present only a small number of experiments have been performed on the reactive scattering of crossed molecular beams. Some of these experiments made with thermal beams are described in this section.

A. The reaction of K with HBr.

The first experiment which showed that significant measurements could be made on the product molecules formed in reactive scattering of crossed thermal beams was Taylor and Datz' study of the reaction K + HBr (24). Their experimental results have been reinterpreted by Datz, Herschbach, and Taylor (15).

In the experiment K and HBr effused from thermal ovens at temperatures variable over the ranges 541 °K to 837 °K and 373 °K to 460 °K, respectively. The K beam was well collimated, but the HBr emerged from its oven as a spray which intersected the K beam at right angles. The fluxes of K atoms and KBr molecules were measured by surface ionization detectors moving in the plane of the two beams. The detectors consisted of heated filaments of metals with high work functions. If an atom with a low ionization potential impinges on such a filament it releases an electron to the metal and evaporates as an ion which can be collected at a negatively charged electrode. The efficiency of surface ionization detectors is near unity for the measured species but near zero for normal background gas, and hence they have been used in the majority of molecular beam experiments.

For the present reaction the desired distinction between K and KBr could be made because a tungsten surface ionizes both K and KBr while a platinum surface ionizes K but reflects almost all KBr molecules (25). The product flux could therefore be measured as a function of angle from the K beam by taking the difference of the signals from the two wires. The experiment consisted of measuring the angular distributions of the flux of KBr in the plane of the K beam and the normal to the HBr oven (the laboratory plane) for various ratios of the temperatures in the two beam ovens.

An analysis was made of these measurements to deduce a threshold for the total reaction cross section.

The complete kinematics of the angular distribution of KBr in relative coordinates is complex. However, as discussed in Section II B, a useful approximation is available. The low mass of H compared to KBr and the small amount of energy liberated in the reaction (change in zero point energy of the reaction, $\Delta D_0^o = -4.2$ kcal/mole) result in keeping the KBr very close to the center of mass. Thus the distribution of KBr expected may be represented by the distribution of centroids for the products (KBr + H) of the reaction.

The models chosen for the energy dependence of the reaction cross section about the threshold were assumed to be expressible as a power series :

$$\begin{aligned} \sigma_R(E) &= O & \qquad E &< E^* \\ \sigma_R(E) &= \pi d^2 \sum_n c_n (E^*/E)^n & \qquad E &\geqslant E^*, \end{aligned} \tag{28}$$

where E^* is the threshold energy and the c_n are dimensionless adjustable parameters. Two special cases are : (A)$c_0 = 1$, $c_{n>0} = 0$ and (B)$c_0 = 1$, $c_1 = -1$ and $c_{n>1} = 0$, Eq. (8). In case A, $\sigma_R(E)$ is a step function with respect to relative energy and impact parameter but independent of orientation and internal excitation. Case B involves the additional assumption that only the component of relative velocity along the line of centers at impact is effective. The analysis of the measurements was restricted to beams intersecting at right angles.

Figure 8 shows the measured angular distribution of KBr as well as the distributions of centroids predicted on the basis of case B with various choices of threshold energy E^*. The sharp fall in the measured KBr intensity at small angles may be due only to the difficulty of detecting KBr accurately in the presence of large intensities of elastically scattered K. The experimental maximum in the KBr distribution appears at an angle corresponding to that predicted for E^* in the range 2.5 - 3.0 kcal/mole and this value was suggested by the authors as the activation energy. On the other hand the distribution at large angles is not well fitted by the same theoretical curves. A possible explanation of the discrepancy lies in the neglect of the angular spread of the HBr beam. A reasonable fit to the point could probably be found with $E^* \simeq 0$ and an HBr spread with a width at half height of about 20°.

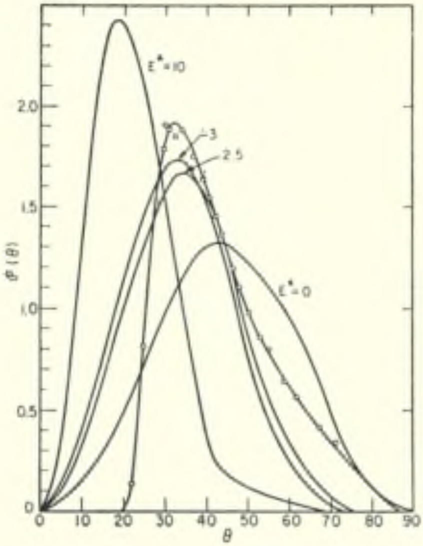

Fig. 8. — Comparison of observed angular distribution of KBr (circles) with calculated distribution of centroids. The energy dependence of the total reaction cross section is taken as that of case B, Eq. (28). The curves are normalized to unit area and E* is a parameter in the calculation. [From Datz, Herschbach, and Taylor, reference (15)].

This experiment shows that in the measurement of the total cross section the necessary averaging over the distributions in the thermal beams may leave a considerable ambiguity in the conclusions which may be drawn about the chemistry of the reaction.

B. The reaction of alkali metals with alkyl halides.

The study of reactive scattering in crossed molecular beams has been extended to systems for which the masses of the products are much more nearly comparable than is the case for the K + HBr reaction. Therefore the products were not restricted to staying close to the center of mass vector. The reactions studied were those of K, Rb, and Cs with a series of alkyl iodides (26). The experimental variables were the temperatures of the two beams, the relative masses of the reactants and the angle of intersection of the beams.

The results may be illustrated by a plot of the measured current to the two detectors *vs* laboratory angle for K + CH_3I, Figure 9. Here the center of the KI distribution appears as a separate maximum centered at 83° from the K beam. An alternative and perhaps more informative representation of the results is a velocity vector diagram,

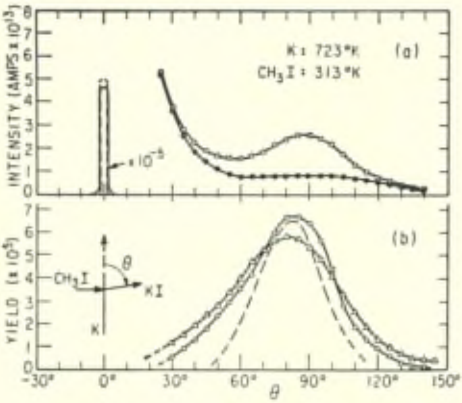

Fig. 9. — Scattering of K + CH_3I. (*a*) Intensity of scattered signal as measured by Pt (solid circles) and W (open circles) surface ionization detectors. Pt measurements are normalized to W measurement in main K beam. Main K beam shown at laboratory angle $\theta = 0°$, is attenuated 7% by CH_3I crossed beam. (*b*) Detected KI distribution for two experiments. [From reference (26)].

Figure 10, which is drawn for K and CH_3I intersecting at right angles (see Section IIB). The circles centered at the end of the center of mass vector represent for different final relative kinetic energies E′ the loci of points which KI molecules may reach in the time the center of mass has travelled the indicated distance. It is interesting to note that for $E' = 1$ and for the K and CH_3I velocities chosen for the diagram the product KI is limited to the range

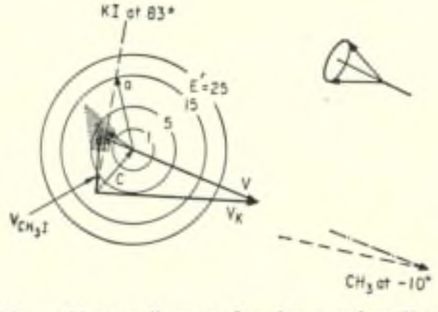

Fig. 10. — Vector diagram for the reaction K + CH_3I.
[From reference (26)].

$40^\circ \lesssim \theta \lesssim 75^\circ$ in the laboratory system for any relative scattering angle. On the other hand for $E' \gtrsim 7$ kcal/mole KI may appear at any laboratory angle.

In scattering experiments like those discussed here, all relative orientations and impact parameters of reactants occur and hence there is cylindrical symmetry of the final relative velocity vectors about the initial relative velocity. However, even when the products of each collision separate in random directions the conservation of angular momentum may require a deviation from spherical symmetry about the tip of the center of mass vector (13). (See discussion in Section IIB.)

The detected distribution of products is also shown on the velocity vector diagram by the hatched areas. Half of the KI recoil vectors end within the cross hatched and 90 per cent within the singly hatched area. To obtain this information it is not sufficient to have only measurements of the scattered product in the laboratory plane such as those shown in Figure 9 because the product may appear at a given laboratory angle, say 83°, with various values of E′. (See the two vectors drawn in Figure 10. Note also that the same absolute value of the scattering angle in the center of mass system can lead to product detection at two laboratory angles. The product molecule KI formed in a collision with final relative velocity vector **a** appears at a laboratory angle of 83° whereas a molecule KI formed in a collision with a relative scattering angle equal in magnitude but opposite in sign appears at a laboratory angle of 240°.) In order to distinguish between the contributions to the scattering at 83° (laboratory angle) from the various E′ the authors made measurements of the scattering out of the laboratory plane. For $E' =$ 2 kcal/mole the angular distribution above and below the plane would be compact, as was actually observed and shown by the hatching. On the other hand an E′ of 15 kcal/mole would have led to observation of KI at larger angles out of the plane of the beams.

The integrated intensity of KI led to an estimate of 10 Å^2 for the total reaction cross section. The activation energy was found to be less than 0.3 kcal/mole from measurements made with incident beams from sources at various temperatures.

Of particular interest is the asymmetry of the flux of KI about the center of mass vector. This result indicated that almost all the detected KI returned in the direction from which the original K had come. The corresponding CH_3 must necessarily have continued in the K direction. The absence of a similar KI intensity on the K beam side of the center of mass vector showed that the collision could not have been " sticky " enough to endure for a significant time compared to the rotational period of the complex ($\sim 10^{-12}$ sec.). The dashed curve in Figure 9*b* was calculated by assuming that all the KI returned at 180° from the original K direction with $E' = 1.6$ kcal/mole.

Similar experiments with Rb and Cs as the alkali metal scattered from various alkyl iodides also showed that the observed alkali iodide had been formed in reactions with negligibly small activation energies, and a major fraction of the energy liberated in the reaction appeared as internal energy of rotation and vibration rather than as translational energy.

IV. CHEMICAL REACTIONS IN CROSSED BEAMS WITH ONE REACTANT BEAM VELOCITY SELECTED

The introduction of velocity selection, even of one reactant beam, has permitted the observation of some interesting features of both reactive and elastic scattering.

A. The reaction of K with HBr.(16)

This reaction has been reinvestigated in a crossed beam experiment in which the K beam was velocity selected. The mechanical velocity selector was a rotating cylinder engraved with helical slots, which transmitted a range of velocities, Δv at v_1, with a width at half height given by $0.084\ v_1$.

1. Angular Distribution of KBr.

The experiment consisted of colliding a velocity selected beam of K, with speed v_1, and flux $N_1 = n_1 v_1$ molec/cm²/sec., with a thermal beam of HBr effusing from a source of density n_2 and temperature T_2. The angular distribution of HBr could be approximated in three ways: A) The beam intersection angles ($\gamma\delta$), Figure 3, were restricted to $\gamma = \pi/2$, $\delta = 0$. The plane defined in this case by the two beams was called the laboratory plane ; B) The HBr beam was fan-shaped with range of beam intersection angles $0 < \gamma < \pi$, $\delta = 0$, and the angular distribution I (γ, $\delta = 0$) was measured in the laboratory plane; C) The HBr beam was cone shaped and assumed to have cylindrical symmetry around the normal ($\gamma = \pi/2$, $\delta = 0$).

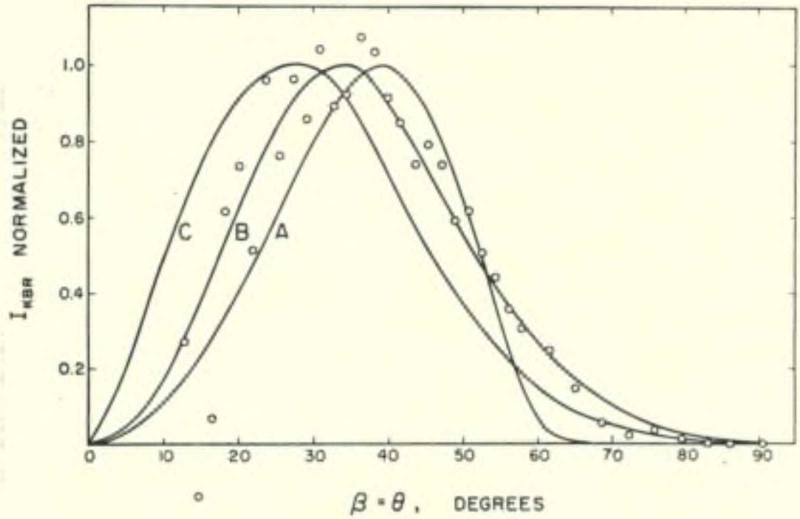

Fig. 11. — Comparison of measured angular distribution of KBr, circles, with several calculated distributions of centroids of products, normalized at the maxima (see text). $\overline{E}$ = 1.99 kcal/mole, q_0 = 1.48.

Figure 11 shows the angular distribution of KBr for given v_1 measured in the laboratory plane as a function of the laboratory scattering angle β from the main K beam. For comparison, angular distributions of centroids of products were calculated for the three approximations cited for the distribution by use of Eq. (22) for case C and corresponding analogous equations for cases A and B. In the calculations the total chemical reaction cross section was taken to be constant. The measured points agree well with the curve for approximation B for the HBr distribution and it may be expected that deviations of measured angular distributions from calculated distributions provide some information on the energy dependence of cross sections. However for this comparison to be meaningful the angular distribution of HBr must be known more precisely than it was in this experiment.

2. Energy dependence of the reaction cross section.

The energy dependence of the reaction cross section σ_R was obtained from measurements of the KBr flux for various K atom speeds. For each of these speeds, the detector was positioned at the laboratory angle corresponding to the centroid direction angle for the maximum flux of centroids and the given angular distribution of HBr. In Figure 12 the plotted points represent the variation of the cross section $\sigma_R(\overline{E})$ with $\overline{E} = 1/2\ \mu\ [\bar{v}_1^2 + \bar{v}_2^2]$, $\bar{v}_2^2 = 8kT_2/\pi m_2$, calculated from the measurements with approximation B for the angular HBr distribution. The curves marked A and C show the variation as calculated by use of approximation A and C for the HBr distribution. The energy dependence of the cross section for the model of hard spheres, Eq. (8), with assumed activation energy $E^* = 0.15$ kcal/mole is given by curve D.

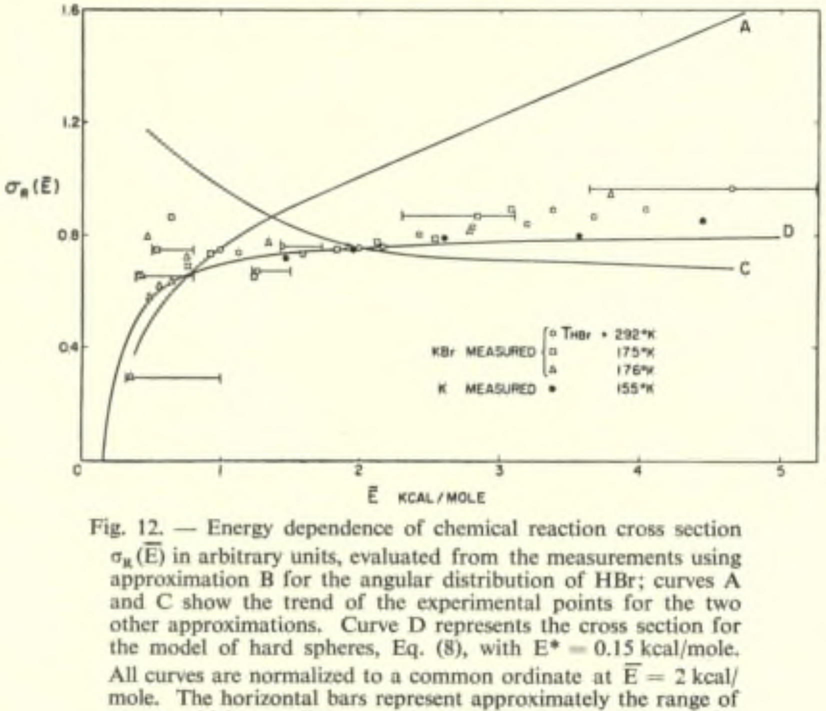

Fig. 12. — Energy dependence of chemical reaction cross section $\sigma_R(\overline{E})$ in arbitrary units, evaluated from the measurements using approximation B for the angular distribution of HBr; curves A and C show the trend of the experimental points for the two other approximations. Curve D represents the cross section for the model of hard spheres, Eq. (8), with $E^* = 0.15$ kcal/mole. All curves are normalized to a common ordinate at $\overline{E} = 2$ kcal/mole. The horizontal bars represent approximately the range of energy which contributes to the reaction at the given E_s for distribution B.

Two observations were made on the analysis of the measurements on the product molecule : first, the threshold of the reaction cross section was less than 0.4 kcal/mole, and, second, the cross section varied but little with energy above this value.

3. Elastic Scattering of K from HBr.(16, 22)

The elastic scattering in reactive systems is of interest because under certain conditions the probability of reaction, Eq. (4), may be deduced from such experiments. The measured differential scattering cross section multiplied by sin χ, $\sigma(E\chi)$ sin χ, is shown in Figure 13 as a function of the relative scattering angle χ for five initial relative energies. As in the K-Kr system, marked rainbow scattering was observed. It was assumed that the elastic scattering of K-HBr could be treated as a two body problem, and if the intermolecular potential could be taken to be of the form Eq. (26), $\alpha = 12$, then the potential parameter ε could be determined from the measurements, $\varepsilon = 0.55$ kcal/mole.

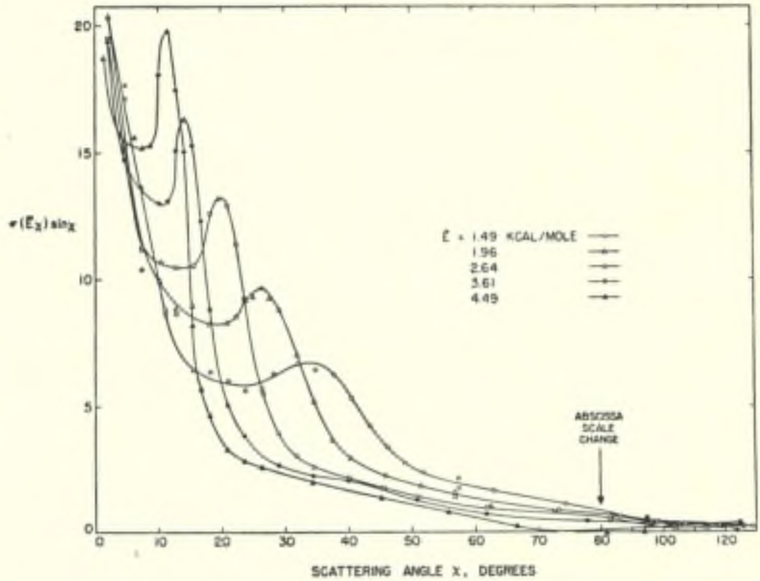

Fig. 13. — Elastic scattering of the system K-HBr : the function $\sigma(E\chi)$ sin χ, in arbitrary units, *vs.* the relative scattering angle χ.

The distinct difference in the elastic scattering behavior of the two systems K-Kr and K-HBr at large scattering angles was ascribed to the occurrence of chemical reaction. A quantitative interpretation of this difference required either measurements of the elastic scattering of a non-reactive system structurally similar to K-HBr or a theoretical calculation of the elastic scattering of K-HBr. An approximation to the latter choice was made by assuming that the theory of scattering for a two-body problem with the potential form, Eq. (26), and ε determined for this system was adequate for the calculation of the hypothetical elastic scattering of K-HBr in the absence of reaction. In this approximation the effects of non-reactive inelastic scattering, the deviations from spherical symmetry of the force of interaction, and the influence of the possibility of reaction on the dynamics of the elastic scattering were all neglected. It is difficult to estimate the magnitude of the possible errors incurred in this approach as little experimental or theoretical information is available on differential inelastic scattering cross sections. Hence for the present an evaluation of the interpretation of the measurements of elastic scattering by means of this theoretical model must be made on the degree of consistency and utility of the results.

For the experimental condition of the intersection of a velocity selected K beam of speed v, with a perpendicular thermal beam of HBr with average speed $v_2 = (8kT_2/\pi m_2)^{1/2}$, the number of scattered K atoms arriving per unit time in a solid angle element at a relative scattering angle is proportional to the non-reactive differential scattering cross section, $\sigma(\overline{E}\chi)$, a function of the relative initial kinetic energy, $\overline{E}$. The calculated flux of K atoms corresponding to the identical experimental conditions but for the hypothetical case of no chemical reaction was taken to be proportional to $\sigma_e(\overline{E}\chi)$ so that the reaction probability P was :

$$P(\overline{E}\chi) = \frac{\sigma_e(\overline{E}\chi) - \sigma(\overline{E}\chi)}{\sigma_e(\overline{E}\chi)}. \tag{29}$$

For scattering angles larger than the rainbow angle the probability of reaction could be expressed also as a function of b, the impact parameter, or the reduced distance of closed approach y, or the potential energy at the reduced distance of closest approach, $V(y)$.

For the assumed model of two-body collisions, the cross section $\sigma_e(\overline{E}\chi)$ could be calculated for the potential function, Eq. (26), and the potential parameter ε (19). There remained the need for the potential parameter r_m, which was not sufficiently well known although it could be estimated from the application of the semiclassical theory to the rainbow scattering region. The calculated cross section therefore had to be fitted to the experimental value at some angle where no reaction occurred. Visual comparison of the elastic scattering of K from Kr and HBr suggested that the probability of reaction began to differ from zero in the vicinity of $\chi = 27^{\circ}$ for the curve for $\overline{E} = 4.49$ kcal/mole. This angle was referred to as a threshold angle. The threshold angles for the remaining curves were then calculated from the requirement that the ratios of the measured functions $\sigma(\overline{E}\chi)$ at the threshold angles agreed with calculated ratios predicted by classical scattering theory. This arbitrary and ad-hoc choice of threshold angles for the five curves could be made to result in identical threshold distances of closest approach. (Compare with the analysis of the system K-CH$_3$Br, below.)

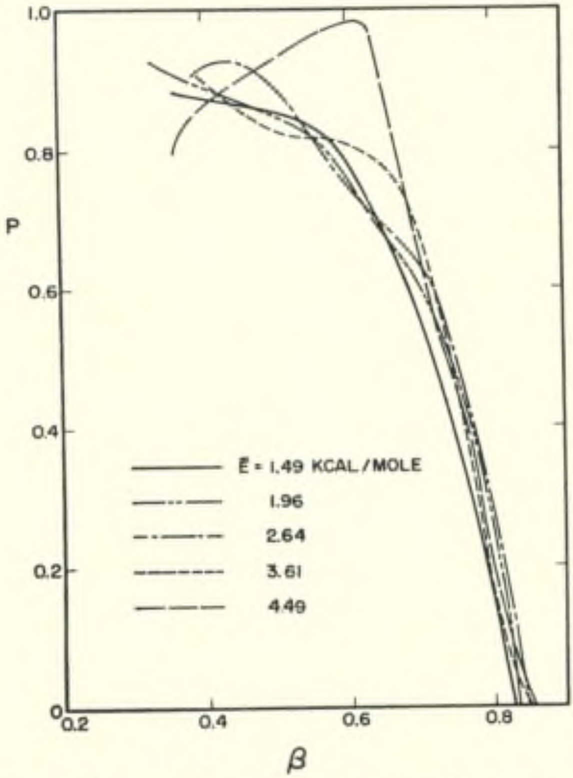

Fig. 14. — The probability of reaction for K + HBr as a function of the reduced impact parameter, β, and initial relative kinetic energy, $\overline{E}$.

The probability of reaction for the system K-HBr is shown in Figure 14 as a function of the reduced impact parameter β and in Figure 15 as a function of the potential energy at the distance of closest approach. The threshold energy for reaction is 0.15 kcal/mole, in agreement with the upper limit of 0.4 kcal/mole obtained from measurements on KBr. The asymptotic value of P is not unity and this was taken as an indication of a steric factor. For the model of hard spheres P is a unit step function of V (y) for a steric factor of unity. The probability of reaction attains its plateau value (~ 0.9) at about $V(y) = 1.2$ kcal/mole, and for this P reaction was said to occur for the range of impact parameters $0 < \beta < 0.6$, or $0 < b < 2.7$ Å for $r_m = 4.5$ Å.

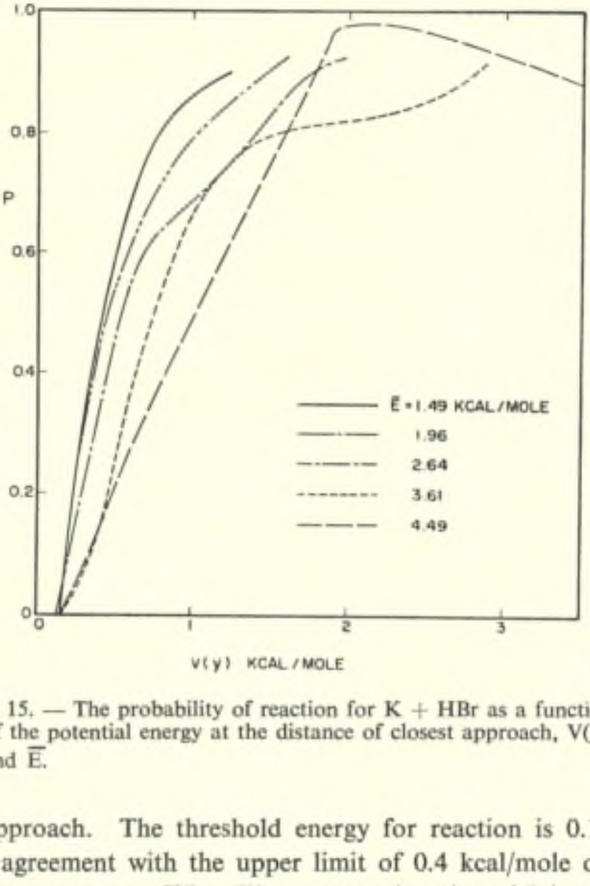

Fig. 15. — The probability of reaction for K + HBr as a function of the potential energy at the distance of closest approach, $V(y)$, and $\overline{E}$.

The reaction of K + HBr is an example of the case discussed in Section IIB; namely a large change in the reduced mass occurs during the reaction, and the product molecule may be expected to be formed in highly excited rotational states. Indirect evidence for this prediction was provided by the observed decrease of the probability of reaction with increasing $\overline{E}$ at constant $V(y)$.

A simple calculation illustrates the point. The angular momentum of HBr was much less than the initial orbital angular momentum and could be neglected. The final orbital angular momentum was much less than the initial value not only because of the decrease in the reduced mass but also because of a likely reduction in impact parameter. The reaction is exothermic, but the change in zero point energy ΔD°_0 is only — 4.2 kcal/mole so that no large change in relative speed could have occurred. To a first approximation, therefore, the rotational angular momentum of KBr could be taken equal to the initial orbital angular momentum. The entries in Table I were calculated according to this scheme for the rigid rotor, harmonic oscillator model for HBr and KBr. Near the threshold of the reaction the energy available to the products for translation and vibra-

Distribution of energy in the products of the reaction K+HBr.

$\overline{E}$, kcal/mole	—	1.49	—	—	4.49	—
Angular momentum of HBr $j=2$, gm cm^2(mole-sec)$^{-1}$	—	0.00155	—	—	0.00155	—
Rotational energy of HBr $j = 2$, kcal (mole)$^{-1}$. . .	—	0.15	—	—	0.15	—
$V(y)$, potential at distance of closest approach, kcal (mole)$^{-1}$	0.15	0.6	1.2	0.15	0.6	1.2
Impact parameter, b, A° . .	3.72	2.92	1.67	3.84	3.53	3.21
$\mu v b$, nearly equal to angular momentum of KBr, gm cm^2 (mole-sec)$^{-1}$	0.068	0.053	0.030	0.121	0.111	0.101
Rotational energy of KBr. .	2.52	1.55	0.51	8.07	6.83	5.65
Rotational quantum number	104	—	—	186	—	—
Sum of final relative kinetic energy and vibrational energy of KBr,kcal(mole)$^{-1}$	3.17	4.14	5.18	0.59	1.83	2.42
Maximum vibrational state of KBr	5	6	8	1	3	4

tion was *much larger* for the case with initial energy $\overline{E} = 1.49$ kcal/mole than for $\overline{E} = 4.49$ kcal/mole. Hence the phase space available and the reaction probability were larger. For smaller impact parameters, or larger $V(y)$, this difference in energy available for translation and vibration became less and the reaction probabilities for the various $\overline{E}$ approached each other.

It was of interest to extrapolate the probability of reaction near the threshold at constant $V(y)$ to $P = 0$, that is an extrapolation to so large a value of $\overline{E}$, or $\mu v b$, or rotational energy of KBr, that reaction was not possible within the requirements of conservation of energy and angular momentum. With the approximations stated above, and the definitions : $\overline{E}_{P=0}$ the empirically extrapolated value of $\overline{E}$ at $P = 0$; $E_{r,\,KBr}$, the rotational energy of KBr, and I the moment of inertia of KBr, the following equations could be written:

$$\left[1 - \frac{V(y)}{\overline{E}_{P=0}}\right] y^2 = \beta^2 \tag{30}$$

$$\overline{E}_{P=0} + 4.2 = E_{r,\,KBr} \text{ kcal/mole} \tag{31}$$

$$E_{r,\,KBr} = \frac{\mu b^2 \overline{E}_{P=0}}{I}. \tag{32}$$

The reduced impact parameter β could be calculated from Eq. (30) when $\overline{E}_{P=0}$ was known, and the impact parameter b itself was then obtained from Eq. (32). Therefore the size parameter of the potential energy, $r_m = b/\beta$, could be evaluated and was found to be $r_m = 4.5$ Å. It must be remembered at this point that the shape of the curve of probability of reaction *vs* $V(y)$ depended on the ad-hoc choice of threshold angles and therefore some changes in the discussion above may be necessitated by more precise measurements.

The total chemical reaction cross section could be calculated from measurements on elastic scattering by use of Eq. (29) and :

$$\sigma_R(\overline{E}) = 2\pi r_m^2 \int_0^{\beta_{max}} P(\overline{E}\beta)\beta d\beta \tag{33}$$

where β_{max} is the reduced impact parameter at $P = 0$. The absolute value of $\sigma_R(\overline{E})$ was 34 Å^2 at $\overline{E} = 2.6$ kcal/mole. The variation of $\sigma_R(\overline{E})$ with $\overline{E}$ is shown in Figure 12 as closed circles where the values calculated from Eq. (33) were normalized to those obtained from measurements on KBr.

B. The reaction of K with CH_3 Br (27)

1. Measurements on KBr.

The ratio of the masses of the products, CH_3 and KBr, and the difference in zero point energy, estimated to be $\Delta D_0^o = -24$ kcal/mole, indicate that the product molecule KBr was not confined to a narrow cone around its centroid but could appear over a large range of laboratory angles, in some cases at all angles. A search for KBr in the laboratory plane in the quadrant containing the centroid showed that the product flux at the detector was below the limit of detection. The evidence for the absence of KBr was provided by the identical signals received by the W and Pt detectors, Figure 16, the signals being normalized at the main K beam.

2. Measurements on K.

Measurements on the non-reactive scattering of potassium are shown in Figure 16 as plots of the differential scattering cross section, multiplied by sin χ, $\sigma(\overline{E}\chi)$ sin χ, and its dependence on the relative scattering angle for four relative energies $\overline{E}$. At small scattering angles each curve displays a maximum, characteristic of the rainbow phenomenon predicted for two body collisions. The maximum, however, is much less pronounced than in the systems K-Kr and K-HBr. For the analytic form of intermolecular potential, Eq. (26), $\alpha = 15$, the potential parameter ε could be calculated from the positions chosen for the rainbow angle (horizontal arrows) and was found to be $\varepsilon = 0.32$ kcal/mole for K-CH_3Br.

Threshold angles are discernable for three curves (vertical arrows). The threshold angle for the curve of lowest energy was taken to correspond to a distance of closest approach equal to the average of those distances for the other three energies. The procedure followed in the analysis of the elastic scattering in the system K-HBr was applied for the calculation of the function $\sigma_e(\overline{E}\chi)$ sin χ for the hypothetical case of no reaction. The same assumptions were necessary, namely the elastic scattering of K-CH_3Br can be treated as a two-body problem and its dynamics are unaffected by the possibility of reaction. The curves labelled I represent the calculated functions $\sigma_e(\overline{E}\chi)$ sin χ fitted to the measured functions at the threshold angles.

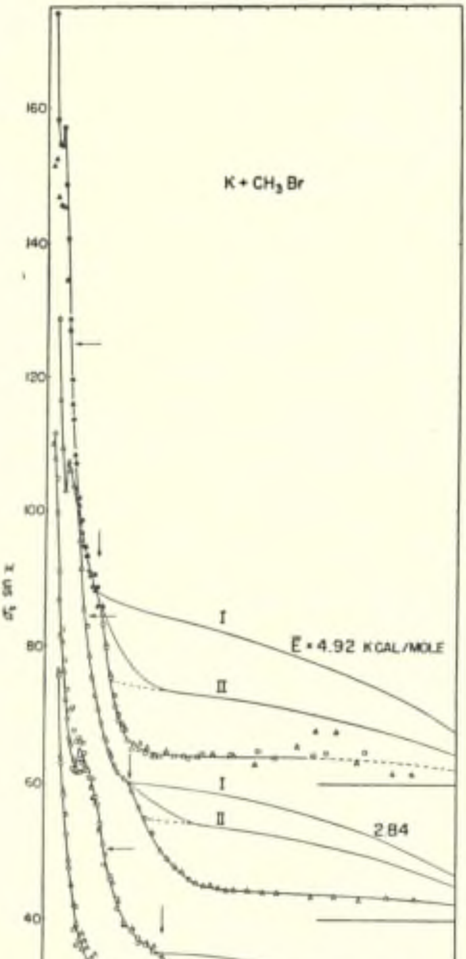

Fig. 16. — Non-reactive scattering of the system K-CH$_3$Br; the measured cross section, $\sigma(E\chi)\sin\chi$, for K scattered by CH$_3$Br. Triangles denote measurements with a tungsten filament as a surface ionization detector; circles, platinum filament, normalized at main K beam. Horizontal arrows mark chosen rainbow angles and vertical arrows mark threshold angles.

The ratios of the values of $\sigma(\bar{E}\chi)\sin\chi$ at the threshold angles, however, did not agree with the ratios calculated from the theoretical model. In order to demonstrate the influence of the choice of the theoretical elastic scattering curves on the probability of reaction a second set of theoretical curves, labelled II, is shown in Figure 16. The functions of this set obeyed the theoretical ratios for $\chi > 55°$, but were simply drawn in for smaller χ to connect with the measured functions at the threshold angle. The calculated curves for methods I and II were identical for the lower two energies.

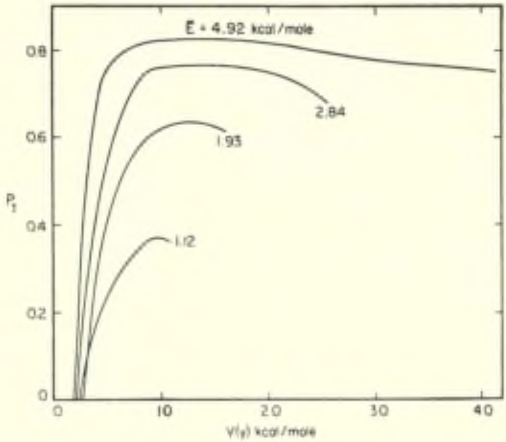

Fig. 17. — Probability of reaction *vs.* potential energy at distance of closest approach evaluated with use of theoretical curves I.

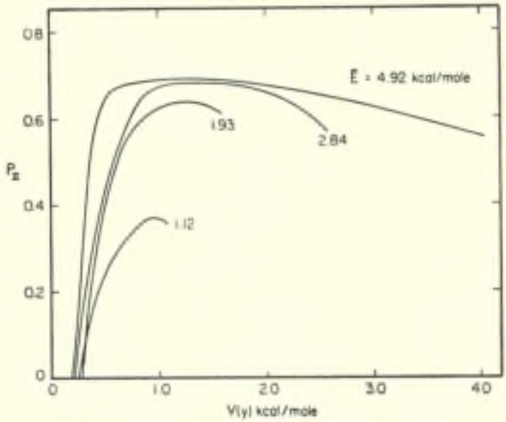

Fig. 18. — Probability of reaction *vs.* potential energy at distance of closest approach evaluated with use of theoretical curves II.

Figures 17 and 18 show plots of the probability of reaction, Eq. (29), as evaluated from the sets of theoretical curves I and II. There is not very much difference between P_I and P_{II} so the probability of reaction appears to be relatively insensitive to the method of calculating $\sigma_e(\bar{E}\chi) \sin \chi$. The features of the curves of P *vs* V (*y*) are the nearly constant threshold of reaction, 0.24 kcal/mole, independent of $\bar{E}$, the rise to a maximum less than unity, and the variation of the probability of reaction with $\bar{E}$.

In comparing the systems K-HBr and K-CH_3Br, it was noted that the threshold energies of reaction were nearly the same, and in both systems reaction could occur over a large range of impact parameters. The variation of the probability of reaction with initial energy at constant V(*y*), however, is distinctly different in the two systems. This is to be expected as no large change in reduced mass occurs in the system K-CH_3Br during reaction. It is possible that the increase of P with $\bar{E}$ at constant V(*y*) is due to the penetration of a barrier.

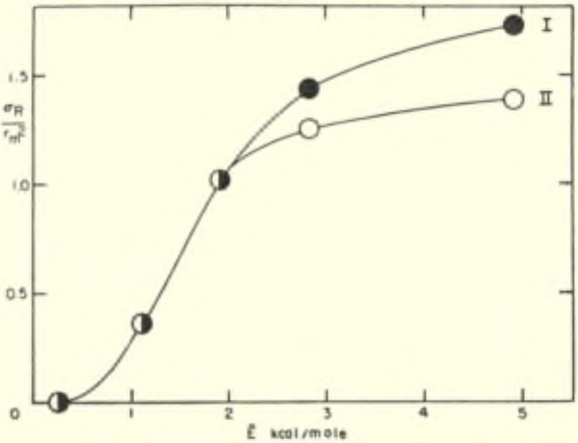

Fig. 19. — Reduced total chemical reaction cross section *vs.* $\bar{E}$, evaluated by methods I and II.

The variation of the total chemical reaction cross section with initial relative kinetic energy calculated from P_I and P_{II} and Eq. (33) is shown in Figure 19. If the potential parameter r_m for K-CH_3Br was taken to be same as for K-HBr then the absolute value of the total reaction cross section was estimated to be 21Å^2 at $\overline{E} = 1.93$ kcal/mole.

V. COMMENTS

Of interest among the results of molecular beam studies of reactive scattering are : the measurements of differential chemical reaction cross sections, which can lead to information about the distribution of energy in the products; the large size of the absolute total chemical reaction cross sections; the large range of impact parameters leading to reaction; the importance of the restrictions imposed by the kinematics of the reactions; and the possibility of deducing a probability of reaction. The study of problems in chemical kinetics by molecular beam techniques appears promising; new experimental techniques can be expected to enlarge greatly the number of reactions which can be examined.

There is no shortage of suggestions for improvements and extensions of the experiments as well as suggestions for the study of other systems. We mention only two points : the activation energies of most reactions of interest are too large to allow the study of these reactions in thermal beams and techniques are required for the production of neutral beams with energies in the range 10-100 kcal/mole. Velocity selection of beams, although useful, is not likely to be sufficient, but should be supplemented by quantum state selection provided that the consequent loss in intensity is not prohibitive.

ACKNOWLEDGMENT

The work of many people has been summarized in this paper; in this laboratory important contributions have been made by Dr. R.W. Roberts, Dr. D. Beck, Dr. M. Ackerman and Miss A.L. Moursund. We thank Professor Herschbach for some helpful comments on the manuscript.

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Discussion du rapport de M. J. Ross

M. Voevodsky. — How did you choose the J value for the hydrogen halide ?

M. Ross. — The oven temperature of the hydrogen halide source is known and the most probable value of the rotational quantum number J is chosen.

M. Polanyi. — Are the calculations on the influence of the requirement of conservation of angular momentum valid near zero impact parameter, or for head-on collisions ?

M. Ross. — These calculations are restricted to the region near the threshold of the reaction or large impact parameter. The assumption made concerning the complete conversion of the initial orbital momentum to rotational momentum of KBr does not hold for small impact parameters.

M. Karplus. — Let us consider a classical collision reaction

$$K + HBr \rightarrow H + KBr$$

and make the approximation that Br is infinitely heavy and that HBr is in the rotational ground state. Because the hydrogen is so much lighter than the potassium, the hydrogen cannot accept the angular momentum of the incident K atom. Hence the KBr will be rotationally excited. The rotational excitation energy will then not be available to the outgoing hydrogen atom.

Notation : m_K, m_H — masses of K, H, $m_H \ll m_K$
v_K, v_H — velocities of K, H, $v_H \gg v_K$
b_K, b_H — impact parameters of K, H, $b_K \sim b_H$
r_K, r_H : K-Br and H-Br bond lengths
J_K : angular momentum of KBr
ΔE : heat of reaction

Angular momentum conservation :

$$(1)\quad m_K v_K b_K = m_H v_H b_H + J_K$$

Energy conservation :

$$(2)\quad \Delta E + 1/2\, m_K v_K^2 = 1/2\, m_H v_H^2 + 1/2 \frac{J_K^2}{m_K r_K^2}$$

Solve (1) for J_K and insert into (2). Collect terms with m_K and m_H :

$$(3)\quad \Delta E + 1/2\, m_K v_K^2 \left(1 - \frac{b_K^2}{r_K^2} \right)$$

$$= 1/2\, m_H v_K^2 \left(1 - \frac{2 v_K}{v_H} \frac{b_K b_H}{r_K^2} + \frac{m_H}{m_K} \frac{b_H^2}{r_K^2} \right)$$

Since the coefficient on the right hand side is close to one, we see that the kinetic energy available to the H atom decreases drastically as the impact parameter b_K increases. We see that the KBr internal energy $J_K^2/2m_K r_K^2$ has used up all the available energy $1/2\, m_K v_K^2 + \Delta E$.

M. Kantrowitz. — What are the possibilities of extending this type of measurement to other reactions ?

M. Ross. — The choice of reactions studied was limited by the detector used. The measurement on reactions in general requires the use of a detector of wider applicability such as a mass spectrometer.

M. Kantrowitz. — The use of high intensity molecular beams might be considered to extend the range of applicability of these techniques.

ELECTRON-MOLECULE AND PHOTON-MOLECULE COLLISIONS

by **J. D. MORRISON** *

I. INTRODUCTION

When a beam of electrons, or other elementary particles is passed through a gas, energy may be absorbed from the beam, and some of the gas molecules may be raised to an excited state, this being usually observable by the subsequent emission of radiation. If the incident energy is great enough, ionization of the molecules may occur, which may be readily detected by electrical means. The first experiments on the behaviour of molecules under electron impact were carried out in apparatus of very simple type, but through the work of Franck, Hertz, Lenard, Lozier and their successors, the theory was developed on which are based most of the modern ideas of molecular energy states. At certain critical energies, discontinuities occur in the amount or kind of excitation or ionization produced, and these were related to the existence of excited states at these energies. This early work on critical potentials has been adequately summarized by Brode (1933) (1).

By the combination of a mass analyser with the ionization apparatus, the scope of the experiments is greatly extended. It is found that in addition to the processes giving rise to a stable positive molecule-ion and an electron, there may be other processes where the initial ionization reaction is followed by fragmentation. The fragments, if charged, can then be detected and identified by measurement of their masses. With an apparatus of this type, the exper-

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imental data consist of sets of curves relating the ion current produced at each mass number, to the energy of the electron beam used to produce the ionization, the gas pressure and electron current being held constant. The curve for each mass number possesses a more or less distinct threshold, and this gives the minimum energy required for the process leading to that particular ion. Threshold energy values taken from these curves have been often employed in conjunction with each other, or with other energy quantities, to calculate ionization potentials and the energies of dissociation of chemical bonds. In principle the method seemed excellent, but in practice the results were frequently inconsistent amongst themselves and with values obtained by other methods. The unreliability of the results is due to difficulties both in experimental technique, and in interpretation. In the present report, the discussion will be confined mainly to those collision processes which can be studied in this way. It will emerge that this is not such a serious limitation as it might at first seem.

In the transfer of energy from an electron or photon to a molecule, it is possible to distinguish the primary process of energy absorption, which is very rapid, and the secondary processes, which take place in consequence of this energy absorption at some later time. The primary process can not be observed, and it is necessary to deduce its mechanism from the various secondary processes which can be observed. To keep the problem as simple as possible, the conditions of experiment will be restricted so that only the unimolecular reactions of the excited molecule can occur.

It proves possible to gain some insight into the primary process, and this in turn permits a more satisfactory interpretation of the experimental data. By making certain mathematical assumptions, subsequently justified by experiment, it is possible to predict the probability of ionization processes, and to show that overlapping processes can clearly be distinguished, provided that their separation in energy is greater than that of the half-width of the electron energy spread. Different classes of process can have differing threshold laws, which are however related together in a simple manner. It is demonstated qualitatively that the observed data on ionization efficiencies can be interpreted directly in terms of relative electronic transition probabilities.

The detailed shape of the ionization efficiency curves conveys a great deal more information than just the thresholds, and it is possible by a study of this shape to build up a picture of the potential functions for the various electronic states of the molecule-ions, and to interpret complex dissociation phenomena. All of the methods in use before concentrated on the measurement of thresholds, and particularly in the case of fragment ions, the results lacked any real significance.

The interpretative problem is now solved, but the lack of resolution obtainable with practicable electron beams limits the value of the method. Beams of photons have the advantage that much narrower spreads in energy can be achieved; also the interpretation of the experimental results in terms of electronic transition probabilities would be simplified. On the other hand, the available range of energies is limited, and the intensities which can be attained are very much less than for electrons. In spite of this, photon beams have been employed successfully in a mass spectrometer to record ionization efficiencies. Their use confirms immediately the theory developed for the case of electron impact. The much narrower energy spread permits in some cases the clear resolution of vibrational levels within excited states of the ions, providing useful clues to the identification of the orbitals which have been ionized. Dissociation limits can be recorded in the curves for both parent and fragment ions. Varying types of threshold law can be observed, and the processes thereby identified. A given ionization efficiency curve may contain contributions from several types of process.

Using the methods which have been developed, electronic states of molecule-ions can be measured at energies as high as 350 e.v., a region almost inaccessible to other methods of study. These data are of considerable value in connection with current theories of molecular orbitals. The possibility of being able to measure electronic transition probabilities directly is interesting. There are indications of the presence of some electronic states which would not be expected on the basis of theory. Where kinetic energy is liberated in a dissociation reaction its total amount may be inferred from the detailed shape of the curves. More recently, successful electron velocity analysers have been built, and used in a mass spectrometer. With these, the energy spread attainable is of the same order as that for photons, while there is no limitation on the energy range.

Until very recently, it would have appeared that the limits of resolution in energy had almost been reached. A mathematical study of the methods made in the last few months now holds out the possibility that in the near future it may be possible to achieve considerably higher resolutions.

In the present state of the subject, the study of collision reactions is able to contribute greatly to the knowledge of the upper states of molecules. Its results are also of particular relevance to many problems of a very practical nature at the present time. A knowledge of the energies required to break the various chemical bonds in molecules is a prerequisite to any attempt to predict the course of chemical reactions. The burning of flames and high temperature combustion in general require for their understanding a knowledge of the excited states of the molecules involved. The way in which molecules in the mass spectrometer break up under bombardment by electrons and photons is very closely related to the way in which they behave when undergoing radiation damage. Whereas in the latter case the primary reactions are confused by complicated secondary and tertiary reactions, in the former the primary step of breakdown can be isolated and studied. Finally, there is the possibility that ion chemistry may well prove in the future to have valuable industrial applications.

2. EXPERIMENTAL METHODS

In this particular field of study, the experimental methods are of great importance, and the production of accurate and reproducible ionization efficiency data presents many problems. In spite of the many advances which have been made in experimental techniques most workers in the field would agree with the comment made recently by Collin (2) : " It can be seen that the reproducibility of the measurements is far from good, although they represent the mean of ten or fifteen measurements. Also it must be admitted that not all breaks occur each time a curve is taken... ". At various times since the earliest experiments on the ionization of gases by electron impact, different workers have recorded unusual structure in their curves, which could not be related to any known energy state. The most recent example (1961) of this is the case of Ar^+, where it might be expected that no possible error should arise (3).

Even when a gas is studied on the one instrument, the relative slopes of various parts of a given curve, and the position of the breaks, may change over a period of hours. If this is so, it can hardly be expected that the results of different instruments will agree more closely.

Clearly the experiments involve a great number of variables, many of which are even now not fully understood. It is necessary, therefore, to specify the conditions of any given experiment with great care.

2.1 **Ionization efficiency.**

The absolute ionization efficiency is defined as the number of ions produced by one electron or photon on passing through 1 cm of gas at 1 mm Hg pressure and 0° C, and it is a function of the energy of the ionizing particle. The pressure, path length etc. can be measured fairly accurately in simple apparatus, such as that of Lozier (4). When a mass analyser is employed, it is almost impossible to estimate the volume of the ionizing beam effective in ionization as seen by the collecting system. In the latter work therefore, only relative ionization efficiencies are quoted.

2.2 **Requirements of apparatus.**

The first requirement for ionization efficiency studies is a collimated beam of electrons, or photons, which must be as nearly monoenergetic as possible, and the energy of which can be varied in a continuous manner. The second is a collision chamber, where this beam is allowed to pass through the vapour to be studied. The molecules of the gas should be in their lowest neutral energy state. The beam, after crossing the collision chamber, has to be monitored. Finally, means have to be provided for removing and analysing any products of collisions. When the products are charged, this can be done very simply by applying a potential gradient across the collision zone.

The pressure of sample in the ionizing region is maintained sufficiently low that the mean free path of the gas molecules is very much greater than the dimensions of the collision chamber. The probability of an excited molecule striking any of the others is then small. A typical pressure is 10^{-6} mm Hg. The current density of the ionizing particles is never greater than 10^{15}-10^{16} per cm^2 per sec., usually much less than this, and the probability of the one particle striking two molecules, or the one molecule being struck by two particles, in succession is low. Under these conditions, the number of electrons or photons absorbed or scattered by collision is a very small fraction of the total beam, and the relative ionization efficiency for any given ionic species is given by the ratio of the ion current to the electron or the photon current.

2.3 **Sources of ionizing particles used in collision studies.**

2.3.1 *Electrons.*

With one exception, all ionization efficiency work until 1953 and most since then has been carried out using electrons as the ionizing particles. It is a very simple matter to produce a well collimated beam of electrons, and the energy of this can be controlled very easily over a very large range of energies.

Unfortunately, the electrons emitted by the simplest electron source, an incandescent filament of tungsten or tantalum at 2000-2500 °K, are not monoenergetic, but possess a spread in energies which is described by a quasi-Maxwellian distribution for this temperature (5). A beam of nominally 10 volt electrons contains 80% of the electrons with energies between 10.0 and 10.5 e.v., and the other 20% with energies ranging up to 12 e.v. or more. This energy spread has been a major cause of the difficulties in interpreting ionization efficiency data, because it has the effect of smearing out thresholds and other structural details in the curves. Numerous attempts have been made to reduce it. Two ways are possible. The first is to use a low-temperature source or to make use of some other emitter which has naturally a narrow spread, while the second is to start with the beam from a hot filament, and to use some kind of energy filter.

The first approach is disappointing, in that the possible sources are either of very low efficiency, or are very easily poisoned. Numerous attempts have been made to construct electron velocity selectors, of magnetic (6) and electrostatic (7) types, and to combine them with the ion source of a mass spectrometer (8). In most cases the currents obtainable have been very small, and the results have not fulfilled expectations. It becomes very clear, from both approaches, that even if a reasonably monoenergetic beam can be obtained, it is very difficult to prevent it acquiring a spread during its subsequent passage through the electron gun and collision chamber.

Over the last few years, a method which was first suggested by Fox and his associates has found extensive application. This is the retarding potential difference (R.P.D.) method (9). With this, it is claimed that effective energy spreads of as low as 0.06 e.v. half-width can be achieved. There seems little doubt that in skilled hands this is so, but there have been some cases where it would appear that the resulting data have been distorted by instrumental effects. Figure 1 shows the gun system employed. The main source of trouble is the retarding electrode 1, which is very sensitive to surface contamination. The modified gun of Cloutier and Schiff, in which the retarding electrode is placed behind the filament, may be more satisfactory (10).

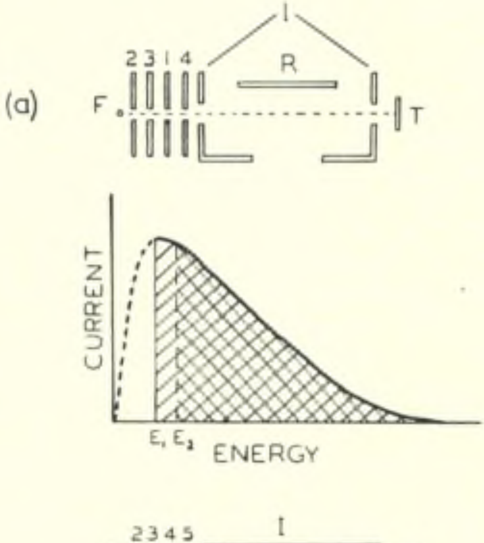

Fig. 1. — Diagram of electrode arrangement used in R.P.D. method by (*a*) Fox (9), (*b*) Cloutier and Schiff (10). F = filament; 1 = retarding electrode; 2 to 5 = accelerating electrodes; I = ion chamber; R = repeller. The effective energy spread is that in the band between E_1 and E_2.

The first successful application of an electron selector to a mass spectrometer was made by Clarke (11), although the reduction in energy spread achieved was not very great. Recent work by Kerwin and Marmet (12) has resolved many of the difficulties associated with the design of a practical electron selector. They have shown that the failure of earlier designs was due to space-charge effects caused by scattered electrons reflected at polished metal surfaces. By the use of deflector plates constructed of 98% transparent tungsten mesh, a trapping system for the stray electrons, and special techniques to reduce the reflectivity of the walls of the ionization chamber, they have shown that energy spreads of 0.05 e.v. or less may be readily achieved. This type of selector was combined with a mass spectrometer by Marmet and the author (13), the source used being shown in Figure 2. Because of the very low electron energies (0.5-2 e.v.) used in the selector, especial care has to be taken to reduce stray magnetic fields in the source region to a very low value. An ionizing beam of 3×10^{-8} A can be obtained with an energy spread which is believed to be as low as 0.03 e.v.

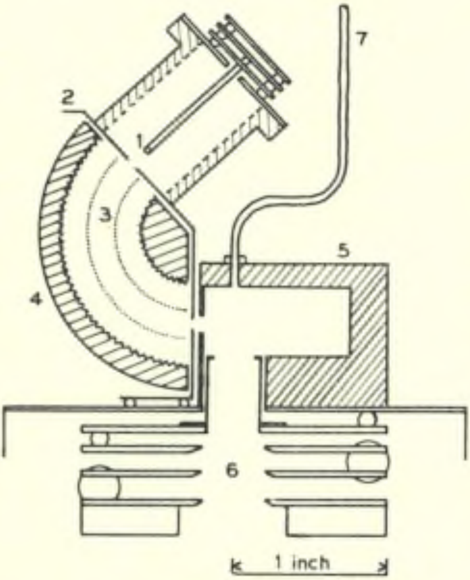

Fig. 2. — Ion source using electron velocity selector. 1 = filament; 2 = slit plate; 3 = deflecting grids; 4 = electron trapping electrode; 5 = ion chamber; 6 = ion gun; 7 = gas inlet.

2.3.2 *Photons.*

There is as yet no way of producing a beam of monoenergetic photons, and then continuously varying their energy. The only solution is to use a light source producing U.V. radiation over a wide range of frequencies, and to use a monochromator to select a narrow band of this.

It was shown first by Terenin and Popov (14) in 1932 that a beam of photons in the near U.V. could be used to produce ionization in TlI and a mass spectrometer was used to analyse the products. Apart from this pioneer study, no further work was done until 1953 when Watanabe and his associates (15) demonstrated that beams of photons with low energy spreads and continuously variable energy could be produced in a vacuum monochromator, and employed to measure total ionization efficiencies for some organic substances. These experiments were carried out with gas pressures much higher than normal in ionization work (up to 1 cm Hg). Lossing and Tanaka (16) showed that a resonance lamp could produce enough intensity to be used in a mass spectrometer ion source.

The combination of a monochromator and a mass spectrometer is not simple, for a number of reasons. At photon energies greater than 7 e.v. the monochromator has to be evacuated. At energies from 7 to 12 e.v., windows of LiF can be used to isolate the light source, grating chamber, and ion source. At higher energies the entire system must be windowless. The Seya-Namioka monochromator (17) is almost the only type suitable, because in it the position of the entrance and exit slits, and of the grating, are fixed, while the direction in which the selected beam emerges is constant.

Such a combination has been made, by Hurzeler, Inghram and Morrison (18), by Weissler, Samson, Ogawa and Cook (19), and later by others (20). The light source used for the first work was a capillary discharge in a mixture of hydrogen and deuterium (21). This requires a pressure of 8 mm Hg in the lamp, and at currents of 300 μA enables a beam of 10^8-10^9 photons per second and an energy spread of 0.04 e.v. to be sent through the ionization chamber. This light source is far from ideal, in that the radiation used is the many-line spectrum of H_2. There are several regions of energy where the intensity is low, and also under some circumstances errors may arise due to its use, as will be referred to later.

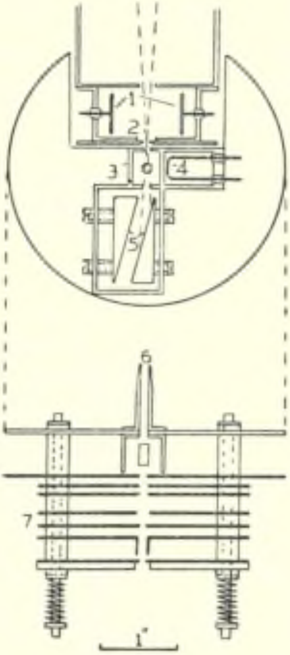

Fig. 3. — Photoionization source (18). 1 = trapping electrodes for secondary electrons; 2 = exit slit of U.V. monochromator; 3 = ion chamber; 4 = auxiliary filament; 5 = photoelectric detecting plates; 6 = gas inlet; 7 = ion gun.

The rare gas continua (22), which cover the ranges Kr 7.5-9.4, Ar 8.8-12.0, Ne 12.0-18.0 and He 13.5-21.0 e.v. would be much more satisfactory from this point of view. The first three require pressures of approximately 200 mm Hg, and can be excited readily by a microwave source, but have been considered too unsteady to be usable for the present purpose. There are conflicting reports regarding the correct pressure to develop the He continuum, but here there is the added difficulty that there must be continuous pumping through the entrance and exit slits of the monochromator, in order to obtain a pressure gradient from millimetres Hg in the lamp to 10^{-4} mm in the grating chamber, thence to 10^{-6} mm in the ionization chamber of the mass spectrometer.

The alternative to the use of continua is to make use of various spark sources, such as the Lyman discharge (23), or the sliding spark (24). These produce line spectra which extend as far as 24 e.v. or more, and have the drawback that the ionization efficiency can be sampled only at a series of points which may be 0.5 or more e.v. apart. Nevertheless, these have been used by Weissler (19), and later by others (20), with a mass spectrometer to study several gases.

Attempts have been made to design light sources using magnetic concentration of the discharge, but the results have not been very successful, and there is still a great need for intense sources of radiation for the energy region below 1500 A. Table 1 lists the types of electron and photon sources used, with their main characteristics.

TABLE 1. — Electron and photon sources.

Source	Energy spread (half-width) e.v.	Beam intensity (particles/sec)	Comments
Electron :			
Tungsten ribbon emitter	0.3 -0.5	10^{13}-10^{14}	Very stable.
BaO-SrO emitter	0.15 -0.3	10^{13}-10^{15}	Easily poisoned.
Photoelectric surfaces . .	0.2	Low	Easily poisoned.
Field emitter	3-5	10^{12}	Very difficult to use.
R.P.D. method	0.05 -0.10	Effectively 10^{12}	Sensitive to condition of retarding electrode.
Electron selector	0.03 -0.10	10^{11}-10^{12}	Very stable.
Photon :			
Monochromator with H_2/D_2 capillary discharge	0.001-0.04	10^{8}-10^{9}	Many-line spectrum.
Inert gas RF discharge.	0.001-0.04	10^{8}-10^{9}	Continuum; requires high pressure in lamp; unstable output.
Spark sources	0.001-0.04	10^{9}-10^{10}	Line spectrum; produces severe electrical noise.

2.4 Ionization chambers.

The requirements of a good collision chamber are as follows' It should be possible to maintain the gas to be studied in it at a steady pressure and constant temperature. Only the reactions which are to be examined shall take place there. It must be possible to measure the intensity of the ionizing beam, and withdraw the collision products for analysis without disturbing the conditions in the chamber. Finally, collision products formed elsewhere must not be able to diffuse into the chamber.

Some of these are conflicting requirements. The drawing-out field should be at least 10 v/cm for efficient extraction of the ions, while to avoid perturbing the electron energy it should be as small as possible. To measure the beam, a trapping electrode has to be maintained at a potential appreciably above that of the ion chamber. Ions may then be formed in this region with high probability, and diffuse back into the chamber. The electron beam may suffer defocussing in the collision chamber, to a different extent at different energies. The ions may then be formed at different places in the chamber, and their analysis may be affected.

Developments in design have been to the overcoming of these many defects. The use of a magnetic field prevents defocussing of the electrons, but can not be used with an electron velocity analyser, for obvious reasons. Pulse techniques have been used very successfully to obtain a field-free region for collisions, and at the same time to get more efficient ion-drawout conditions (25). In these, voltages are applied alternately to the electron accelerating electrodes, and the ion repellers, at some frequency in the range 50-200 kc/s. This reduces the spread in electron energies due to the repeller cross-field.

Photons have the great advantage that they are not affected by the ion draw-out field, and the source can then be designed as part of an efficient ion gun. Greater care has to be exercised even than for electrons, to suppress the formation of photo-electrons or secondary electrons, since these could in some circumstances be accelerated and cause collision reactions. If the walls of the collision chamber are made of metal, it must be cleaned frequently by abrasion to give reproducible results. More satisfactory materials for the walls have been found to be " electron velvet " or pure graphite.

It is very difficult to avoid discrimination against ions which are formed with initial kinetic energy. Ions formed at rest in the ion chamber diffuse out of the ionizing region with a random velocity the same as that of the neutral gas at source temperature, i.e. $kT \sim 0.02$ e.v. Some ions may be formed with kinetic energies as high as 5 e.v., and hence travel rapidly out of the ionizing region to the walls. The photon impact sources should be better for their study, in that the higher the ion draw-out field, the less the effect of any initial velocity.

2.5 Measurement of electron and photon beams.

The quantity which is required is the ratio of the ion current to the current of ionizing particles, for each setting of the energy. This requires either that the ionizing beam shall be constant, or that it should be measured continually. For electrons, emission regulators have often been employed. These have the disadvantage that the filament temperature may change over the range of an ionization efficiency curve. It is not very difficult to design an ion chamber which has an electron current versus energy characteristic which is almost a constant.

When electron selectors are used, the beam currents are so low that it is necessary to use electrometer amplifiers to measure them. With most mass spectrometers, this amplifier is at a potential well above ground. The recording device must then either be operated at this potential, or a servo mechanism used to drive a slave potentiometer at ground potential.

For the monitoring of photon beams, two methods have been employed. The first of these makes use of the direct photoelectric effect of the beam on a metal surface, as in Figure 3. The photoelectric yield of such a surface increases smoothly with the energy, and requires to be calibrated. Once calibrated, it appears to be very stable. The photo-currents obtained are of the order of 10^{-12} A, and an electrometer amplifier is necessary for their measurement. In this case the photo-current varies over wide limits as a function of the energy, and has to be measured simultaneously with the ion current at each energy setting.

A simpler method of recording the photon intensity is by the use of a photomultiplier coated with Na salicylate. The quantum yield of Na salicylate has been found by Watanabe (26) to be constant over the range from 2200 to 800 Å The output currents from the photomultiplier are at ground potential and are sufficiently great that a cathode follower stage can drive a pen recorder directly. Care has to be taken in the preparation of the salicylate film, and it is claimed that its sensitivity decreases after prolonged exposure to high vacuum.

2.6 **Mass analysers.**

Almost all of the types of mass analyser have at some time been used to examine the products of electron and photon impact, each possessing some special advantage. The problems are not quite the same as for ordinary analytical work. The ion sources are usually very inefficient, and the need is for high sensitivity, with resolution in mass being a secondary consideration. Most work has been done with magnetic analysers, of either sector or 180° types. The 180° types are less well suited to this work, because the source is completely immersed in the main magnetic field. This gives excellent collimation of the electron beam, but limits the space available for elaborate electrode structures. It also precludes the use of the magnetic or electrostatic electron energy filters. The 90° or 60° instruments are very much better in this regard. There is plenty of space in the neighbourhood of the ion source, and it is a relatively simple matter to reduce the stray magnetic field in this region to as low as 0.01 gauss (27). A typical instrument, used by the author for this work, is a single-focussing 12″-radius 60°-sector type, used with slit widths to give a mass resolution of 1 in 300. Differential pumping is employed between the source and analyser regions.

The cycloidal mass spectrometer should in theory give no discrimination against ions with initial kinetic energy, but it does not appear to have been used in their study. The high luminosity instruments devised by Kerwin (28) should be of value where sensitivity is a limitation. It is probable that an increasing amount of work will be done in the future using time of flight or radiofrequency mass spectrometers. Their freedom from a magnetic field, and ability to make use of an extended source should outweigh their low resolving powers. One such instrument (the Paul type) has been used recently in a photoionization study of argon and nitrogen.

2.7 **Measurement of ion beams and data presentation.**

The last few years have seen the almost exclusive adoption of electron multipliers for the measurement of ion intensities. The sensitivity of a simple collector and electrometer amplifier is limited by resistor noise to 10^{-15} to 10^{-16} A for a 1 second response of the measuring device. A 16-stage multiplier will give 0.1 v pulses across a $10^6\ \Omega$ resistor for each ion striking the first stage, while the pulses produced by random electrons in the multiplier are usually not more than one-fifth of this. The random count due to stray ions can be reduced to the order of 10^{-21} A. Under these conditions the statistics of ion counting set the lower limit to the accuracy with which curves can be measured. Usually other sources of variation are much more serious. The pulses produced by the multiplier can be amplified by a pulse amplifier, pulse height discriminator, and counted. It is possible to make use of this arrangement to distinguish between ions which would otherwise be indistinguishable, e.g. N_2^{++} and N^+. The pulse-height distribution for the former species has a maximum at approximately twice that of the latter, so that the pulse-height discriminator can be set to filter out most of the N^+ ions.

It has been found by the author that allowing the last stage of the multiplier to charge a condenser connected to an electrometer amplifier gives a very simple yet accurate way of recording currents in the range 10^{-19} to 10^{-14} A. A switch across the condenser is allowed to open at time $t = 0$, and is closed again after a time determined by a simple clock circuit.

To produce an ionization efficiency curve, using electrons, the ion to be studied is brought to focus on the collector, and the ionizing energy is then raised in equal steps, while the ion and electron currents are recorded. When the energy spread is narrow, and to obtain greater accuracy, it is necessary to sample the curve at a very large number of points. This can be very tedious. Use can be made of computing amplifiers and other simple circuitry to carry out the measurements automatically. An integrating circuit supplied with pulses of equal size produces an accurate staircase voltage, which can be applied to the ion chamber. These pulses can be derived from the timing circuit which gates the ion-current integrator. A curve produced in this way is shown in Figure 4. The use of integrating circuits in this manner suggests a method for making use of a badly fluctuating electron or photon source in ionization studies. If the electron or photo-current is allowed to charge an integrator until its output operates a Schmitt trigger circuit, a time interval is obtained which can be used to gate the integrator recording the ion current.

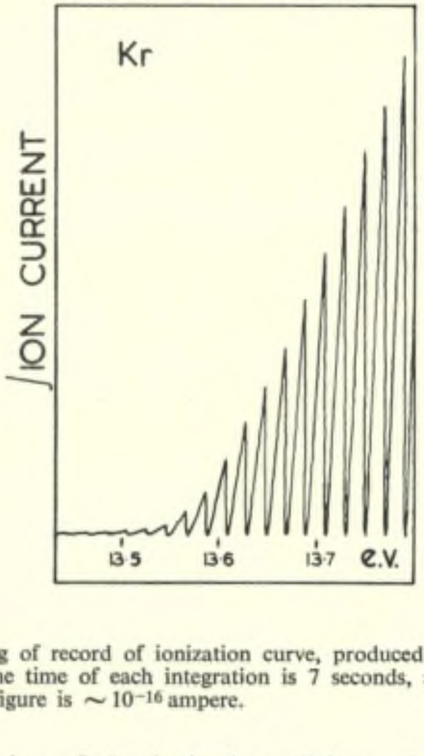

Fig. 4. — Tracing of record of ionization curve, produced using ion current integration. The time of each integration is 7 seconds, and the maximum current in the figure is $\sim 10^{-16}$ ampere.

The presentation of the ionization efficiency data for electron impact calls for a very high degree of linearity and signal-handling capacity in the apparatus. These requirements can be reduced, with no loss in accuracy, if the first differential of the ionization efficiency is recorded directly.

2.8 **Other measurements.**

2.8.1 *Kinetic energies of ions.*

Direct measurements may be made of the kinetic energy of dissociation possessed by fragment ions. This can be done roughly by study of ion peak shapes (29), also by making use of the pulse technique described earlier. For an ion with only thermal energy a plot of ion current versus frequency is constant above approximately 50 kc/s, and falls off below this. When kinetic energy is present the current does not become constant until higher frequencies.

The most accurate measurements of kinetic energies are made by retardation experiments using a special collector (30), or by making use of an ion velocity analyser (31). With these methods, accuracies of ± 0,05 e.v. or better may be achieved.

2.8.2 *Lifetimes of metastable states.*

In many cases when polyatomic molecules undergo electron or photon impact, the molecular ion is formed in a state which after a short time breaks up into charged and neutral fragments. These fragments may then undergo similar breakup. The lifetimes of these states are of very great interest in the theory of unimolecular decomposition. Such " metastable " processes can be clearly distinguished in the mass spectrum, and identified. Estimates can be made of the mean lifetimes of these states, by the effect of either the ion accelerating voltage, or the ion drawing-out field, on the " metastable " peak height (32).

2.8.3 *Other methods of measurement of excitation.*

When excitation is produced by an electron beam it can be detected by the subsequent emission of radiation, by the emission of secondary electrons when the excited molecules reach a metal electrode, or by the measurement of the slow electrons resulting from the inelastic collision. With the exception of resonance processes, the first of these is difficult to measure because of sensitivity limitations (33), while the second is restricted to metastable states (34).

The trapped electron method devised by Schulz (35) is of particular interest, in that it is one of the few methods which involves the direct detection of the electrons which have lost energy in a collision. It has the disadvantage that it is restricted to the very slow electrons arising in such collisions, and hence will give a true picture of excitation probability as a function of energy only in the neighbourhood of the threshold.

2.9 Sources of error in measurements.

2.9.1 *Calibration of the energy scale.*

When electrons are used as ionizing particles, the nominal voltage applied to the beam may be in error by as much as 1-2 e.v. Also, the form of the electron energy distribution may change over the energy range studied. Contact potentials of variable magnitude exist between the filament, and the ion source. If the electron current density is too high, space charge may cause a shift both in the average energy and in the energy distribution (36). The ion drawing-out field has the same effect.

The best solution so far, and it is not very satisfactory, is to use the ionization curves for the rare gases, where the energy states are known accurately, to calibrate the energy scale. This calibration has to be carried out as close as possible in time to any measurement. It has been suggested (37) that the R.P.D. method in principle should give an absolute energy scale, although experimentally this is open to question. Calibration of the energy scale for negative ions is even less satisfactory (38).

For photon impact, the situation is quite different. Once a grating monochromator has been adjusted, its energy scale remains fixed. The frequencies of the resonance lines of the elements permit a very accurate calibration of the scale. The band of wavelengths passed with a given slit width is constant, which means that the energy spread increases with energy. This effect is quite predictable, and can be allowed for.

The use of a source which is a line spectrum, instead of a true continuum, can produce spurious structure if the resolving power of the monochromator is low. This effect, and also the effect of any irregularities in the wavelength drive for the grating, will be systematic, and will always appear at the same points on the energy scale.

2.9.2 *Secondary reactions in the ion chamber.*

A careful study of ionization efficiency curves using an electron selector (39), has revealed an unexpected source of error. When the energy spread used is narrow, it is possible to detect details of structure in the IE curves which before were completely obscure.

The lack of reproducibility in this structure makes it hard to have much confidence in any detailed interpretation. The first experiments indicated that when an electron beam is flowing in the ion chamber at energies much below that necessary to produce free ions, conditions may be set up which affect the subsequent production of ions. If the ionizing energy is switched at time $t = 0$ from different values below the threshold of ionization to a given value above it, the ion current varies in the manner shown in Figure 5. In all cases,

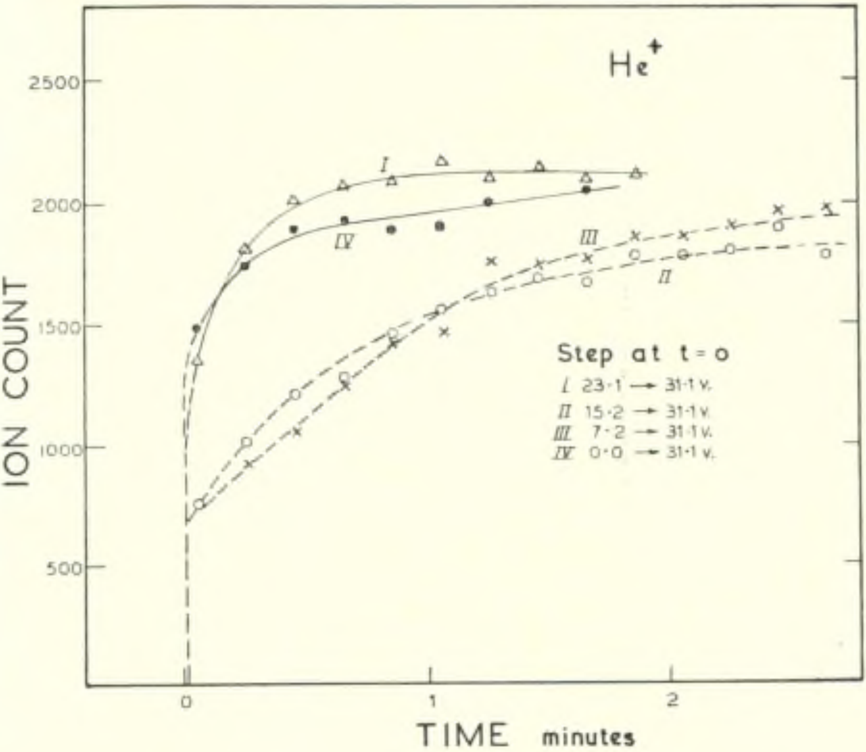

Fig. 5. — Curves showing behaviour of ion current when a step is applied to the ionizing electron energy at $t = 0$. The initial energy for $t < 0$ is in each case less than the ionization threshold energy, and the final energy is the same in all cases.

the current at time $t > 5$ mins is the same. Phenomena of this type are observed for all the gases studied. A second group of experiments were carried out with mixed gases, at pressures well below those at which molecule-molecule collisions should be probable. It was possible to obtain breaks in the IE curves which indicated that interactions between the molecules were taking place (Fig. 6). At this stage it was realized that, when a gas is introduced to a vacuum system, some of it is absorbed on the walls even at very low pressures If there is a monolayer of gas on the surface of the ion chamber, and the pressure in the chamber is 10^{-5} mm Hg, then there are 10^4 to 10^5 times as many molecules on the walls as there are in the space between the walls. If ions are being formed on the walls, the observed phenomena might be accounted for. That ions might be formed

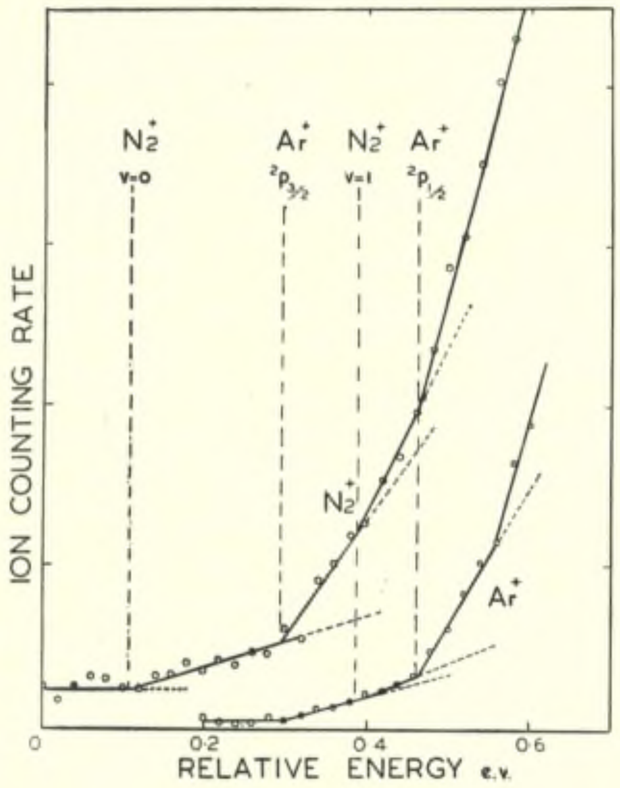

Fig. 6. — Ionization efficiency curves for N_2^+ and Ar^+, when the gas pressure in the ion chamber is reduced to 10^{-4} mm Hg after having been maintained at 10^{-2} mm Hg. The known energy states are shown by vertical broken lines, and the changes in gradient appear in both curves, indicating that interaction of some kind is occurring.

on the walls in large numbers, has been demonstrated very clearly by Moore (40). These effects are most noticeable at very low ion drawing-out potentials. If the latter is increased, the energy spread becomes slightly worse, but the secondary phenomena become much less important.

3. INTERPRETATION OF THE DATA

In general appearance, with very few exceptions, all ionization efficiency curves produced by electron impact show very little detail for what are in fact complex processes. They are characterized by a more or less well defined threshold, the curves then rise over a range of from 10 to 100 e.v. to a broad maximum, after which they fall slowly to zero over some thousands of e.v. The first interest in these curves was concerned with the measurement of the threshold energies. The thresholds were never sharp, due in part at least to the energy spread of the ionizing beams used, and numerous empirical methods were employed to determine the co-called appearance potentials. As a result, the values obtained prior to 1950 show many discrepancies, both between the results of the different methods, and with spectroscopic values. This situation has been remedied only by gaining some insight into the mechanism of the primary process of energy transfer between the ionizing particle and the molecule.

3.1 Mechanism of energy transfer.

3.1.1 *Momentum transfer.*

An electron or photon is defined as having collided with an atom, if any change can be detected in its direction of motion and/or velocity from the values before the interaction. From the classical point of view, the simplest type of interaction will be that of transfer of translational energy. The maximum fraction of the initial energy of a colliding electron which can be transferred in this way to an atom at rest is 0.002 for the hydrogen atom, and it is proportionately less for any heavier atom. For low electron energies, this gain in translational energy is therefore not significant; for photons, it is negligible.

3.1.2 *Transfer of electronic excitation.*

The gas molecules are assumed to be at rest before collision in their lowest electronic state. At the temperature of the source, the large majority of the molecules are in their lowest vibrational state.

For atoms the following possibilities must be considered :

(*a*) Electron capture to produce a negative ion;

(*b*) Excitation of a neutral state, by promotion of one or more electrons to orbitals of higher energy. This will normally return to its lowest state by radiation of a photon. If this state is above the lowest ionization potential autoionization may occur;

(*c*) Ionization, by the loss of one electron, and possibly the excitation of others. Subsequent autoionization of one or more of these is possible;

(*d*) Multiple ionization, by the loss of several electrons, and possibly the excitation of others.

For molecules, there are the following additional ways in which energy may be transferred :

(*a*) Electron capture to produce a negative ion, with dissociation to fragments, one negatively charged;

(*b*) Excitation of a neutral state,

  i. in stable region by increase in electronic vibrational or rotational energy. This may return to the lowest state by emission of radiation, or undergo pre-dissociation. If the state is at an energy greater than the lowest ionization potential, autoionization, or autoionization and fragmentation may occur. Radiationless transition to an unstable state is possible, followed by dissociation;

  ii. in unstable region, followed by dissociation to neutral fragments, or to a positive and negative ion pair;

(*c*) Ionization of molecule by loss of one electron, and possible excitation of others as (*b*) i. This stage may be

  i. stable, but possibly undergo radiationless transition to an unstable state with dissociation;

  ii. unstable, undergoing dissociation to one positively charged and one or more neutral fragments;

(*a*) Multiple ionization in either i. a stable state, or ii. an unstable state dissociating to give two or more fragments, one or more being positively charged.

The transfer of rotational energy is not significant.

3.1.3 *Franck-Condon considerations.*

Vibronic excitation of molecules by electron or photon impact is described very satisfactorily in terms of the Franck-Condon principle. The absorption of energy from the incoming electron or photon takes place in a time of the order of 10^{-16} sec or less, and can be manifested only in a redistribution of the orbital electron density. In each electronic state, the motion of the atomic nuclei is determined by the potential field of these electrons. A rapid

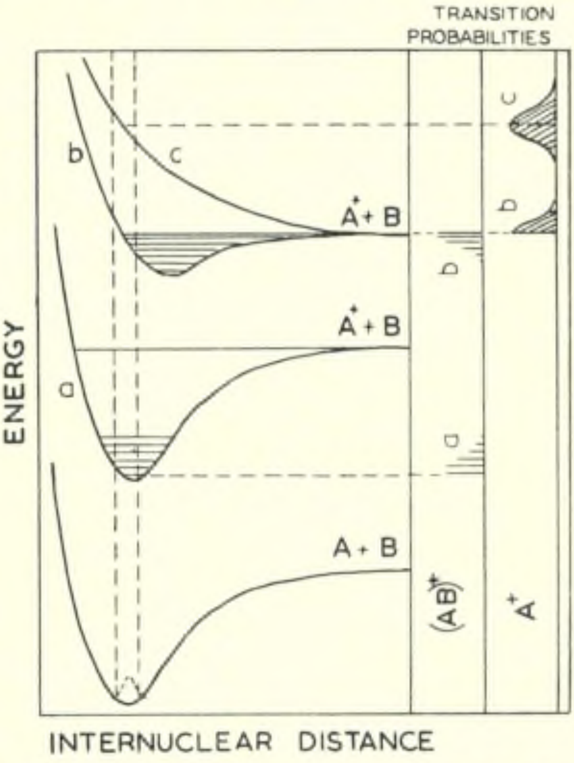

Fig. 7.— Potential energy diagram for a hypothetical diatomic molecule AB. The Franck Condon region is indicated by vertical broken lines. The probabilities of ionizing transitions to states of types (*a*), (*b*) and (*c*) are indicated at the right hand side of the figure, for the parent ion $(AB)^+$ and the fragment A^+.

change in electronic distribution will have little immediate effect on the nuclei, because of their much greater mass. The accompanying change in vibrational excitation will then depend only on the character of the nuclear motions in the two electronic configurations.

The probability of transition between vibrational levels v'' and v' of electronic states e'' and e' can be written as

$$P = [\int \psi_{e''v''}(r)\, G_{e''e'}(r)\, \psi_{e'v'}(r)\, dr]^2, \tag{1}$$

where $G_{e''e'}$ is the matrix element of the perturbing function between states e'' and e'. The Franck-Condon principle is equivalent to stating that if $G_{e''e'}$ is a very slowly varying function of interatomic distance, a reasonable approximation is obtained by taking it outside the integral sign.

For diatomic molecules, the application of the Franck-Condon principle to the potential energy diagram for the various electronic states gives a very convenient qualitative picture of their behaviour under photon and electron impact. This is shown in Figure 7. By making use of various approximations to the potential function, the distribution of the amplitudes of the vibrational overlap integrals for transitions to various ionized states can be calculated (41). It remains to give the quantity $G_{e''e'}$ experimental significance.

3.1.4 *Probability of a single process as a function of energy.*

Before any attempt can be made to disentangle the ionization efficiency curves found in practice, it is necessary to consider the probability of a single process, involving the absorption by an atom of a given amount of energy E_c, from a particle with energy E. For $E < E_c$ it will obviously be zero. For $E > E_c$ the probability need not necessarily be zero, provided that there is some way in which the excess energy $(E - E_c)$ can be removed from the system.

Various attempts have been made to calculate the dependence of the transition probability on the energy of the incident particle, making use of the Born approximation. Massey and his colleagues (42) have suggested that the probability of excitation processes will be different depending on whether angular momentum is transferred from the bombarding particle during impact or not. Considerations such as this may well be important in determining the overall shape of the probability curves over a range of hundreds of e.v., but the assumptions on which the calculations rest have usually been considered by the authors not to be valid in the immediate neighbourhood of threshold (43). The intervals at which their probability curves are calculated preclude any very accurate comparison with experimental data.

The most fruitful approach has arisen from a suggestion made by Wigner (44) in 1948. Discussing two-particle collision reactions generally, he proposed that the probability of a given reaction near threshold would depend solely on the ability of the collision complex to dissociate. This in turn would depend on the long range interaction of the dissociating particles, and not on the nature of the transition.

Wannier (45) extended this idea specifically to the case of direct ionization by electron impact, where the dissociating particles separate in a Coulomb field. He postulated that the way in which the excess energy was carried off after the reaction determines the threshold law. He attempted to take into account the interaction between the charged particles in the retreat zone, and predicted that single ionization by electron impact should follow a threshold law which was proportional to the 1.127th power of the excess energy.

Conservation of momentum requires that almost all of the excess energy will be carried off by the electrons. With two electrons leaving the collision complex (single ionization by electron impact) the total energy of the electrons is determined, and one degree of freedom remains. If interaction between the electrons is neglected (46), the probability of ionization P(E) is a linear function of $(E-E_e)$. With three electrons (double ionization) there are two degrees of freedom, hence $P(E) \propto (E-E_e)^2$ and so on.

Extension of this simple hypothesis to single ionization by photon impact and excitation by electron impact, would predict a step function dependence on the excess energy.

Geltman (47) made detailed calculations using a modified Born-Oppenheimer approximation and predicted the same threshold laws as those of Wannier for *n*-fold ionization by electron and photon impact. His calculations for excitation reactions suggested that P(E) for the case of electron impact should be proportional to $E(E-E_e)^{x/2}$, where x is 1 for atoms and heteronuclear molecules, and 3 and 1 for homonuclear molecules according to whether they have even or odd symmetry. The present author has suggested (48) that Wannier's simple hypothesis may be of even more general applicability, and that the threshold law is determined solely by the number of electrons leaving the collision complex simultaneously. The force field operating may be of secondary importance. A freedom factor n is defined which for any excitation or ionization process is equal to the number of electrons leaving the collision complex. The probability of energy transfer over threshold is related to the freedom factor by the nth integral

$$P(E) \propto \int \underset{\cdots}{n} \int_{0}^{E} \delta\,(E - E_c) \cdot dE^n \,, \qquad (2)$$

For $n > 1$ this equals $(E\text{-}E_c)^{n-1}/(n - 1)\,!$ when $E > E_c$. $\delta(E\text{-}E_c)$ is a δ-function centred on E_c.

The simple energy-space argument of Wannier would seem to require that the excess energy in the collision complex should be exchanged between the electrons which are subsequently going to carry it away. The breakdown of the threshold law which always occurs at higher energies would seem in these terms to be due to the breakdown of this exchange mechanism. One very interesting class of ionization reactions is that where the primary step is that of excitation, and where this is followed at some later time by autoionization. The primary process occurs in 10^{-16} sec, and the ejection of the autoionized electron at some time later than this in the range 10^{-16} to 10^{-12} sec. If the autoionization is very rapid, it will be indistinguishable from direct simultaneous ionization, and will have that threshold law. If it is relatively slow, $\sim 10^{-12}$ sec, then very little exchange indeed can occur between the two ejected electrons, and the threshold law will be that for excitation. It would appear that, at intermediate lifetimes, the threshold law should be intermediate between the two cases, that is, for photons it should be a sharp rise at threshold, followed by a slow decay to zero at higher energies. The rate of this decay will be inversely proportional to the lifetime of the excited state. For electron impact it should be the integral of this.

3.1.5 *Other factors affecting sharpness at threshold.*

The foregoing discussion is based on the assumption that the energy required for a transition between the ground state and some excited level of the atom or molecule is a sharply defined quantity E_c.

This is not strictly correct, in that there will be an unsharpness in defining all the values E_e given by the uncertainty relation. The half-width of this uncertainty distribution in the energy range 10-30 e.v. is of the order of 0.001 e.v.

The random velocities of the gas molecules in the ion source will introduce a distribution due to the Doppler effect, which for electron impact and source temperatures of 500 °K will have a half-width of up to 0.02 e.v.

The energy spread of the ionizing beam of photons or electrons will introduce yet a third distribution of half-width from 0.5 e.v. down to 0.03 e.v. The effect of these various spreads is given by their convolution integrals with the various probability functions P(E).

Until very recently, the first two were insignificant in comparison with the third, and the observed ionization probability could be written as :

$$i(\mathrm{V})_{obs} = \mathrm{P(E)} * m(\overline{\mathrm{U}}), \tag{3}$$

where $m(\overline{\mathrm{U}})$ is the energy distribution $m(\mathrm{U})$ reversed on the energy scale.

At source temperatures of 500 °K, not all the gas molecules will be in the lowest vibrational level of the ground state. If the vibrational spacing is very close, < 0.03 e.v., the individual processes will not be resolved, and an apparent one-sided distribution will be superposed on the other factors determining the curve shape. This has been discussed by Watanabe in the interpretation of photoionization efficiency results (49).

3.1.6 *Experimental evidence regarding threshold laws.*

To determine the form of the ionization and excitation probability curves near threshold, it is necessary to make use of spectroscopic evidence regarding the presence of electronic states. The first experiments were carried out using the monatomic gases, since the energy levels are known accurately (51), and in the case of the rare gases, are well spaced. The curves for the production of singly-charged helium by electron and photon impact are shown in Figure 8. In this case there is known to be only one state possible, at energies up to 59 e.v. In the latest experiments using electrons, it can be stated with confidence that the ionization probability is

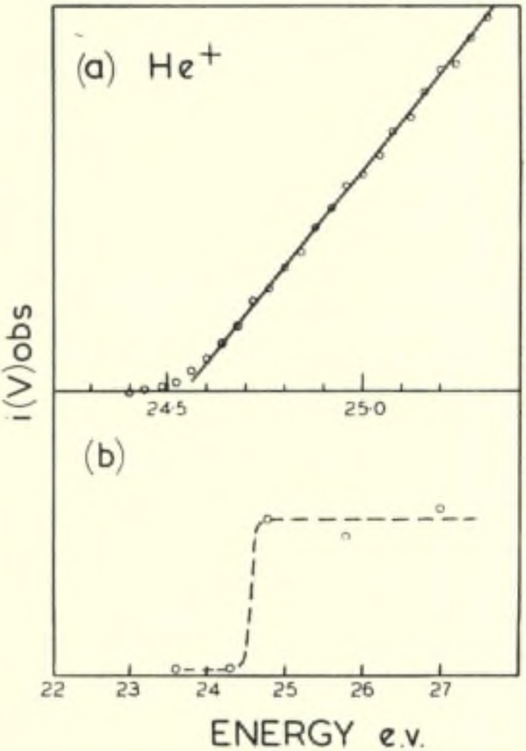

Fig. 8. — Ionization efficiency curves for He^+ measured with (*a*) electron impact, (*b*) photon impact (19).

accurately linear over a range of from within less than 0.05 e.v. of threshold, to at least 5 e.v. above it. The photon impact data are less satisfactory, but are not inconsistent with a step-function threshold law.

The curves for single ionization in the other rare gases are much easier to measure, but are complicated by the fact that there are two states close together in energy, and also there is a series of neutral excited states of the atoms lying between these. The data for neon and argon are shown in Figure 9. In the electron impact case, it would seem that linear increases are associated with both the $^2P_{3/2}$ and $^2P_{1/2}$ states of the ion. The photon impact data are not recorded at sufficiently close intervals to resolve these, but again appear to be step functions of the energy.

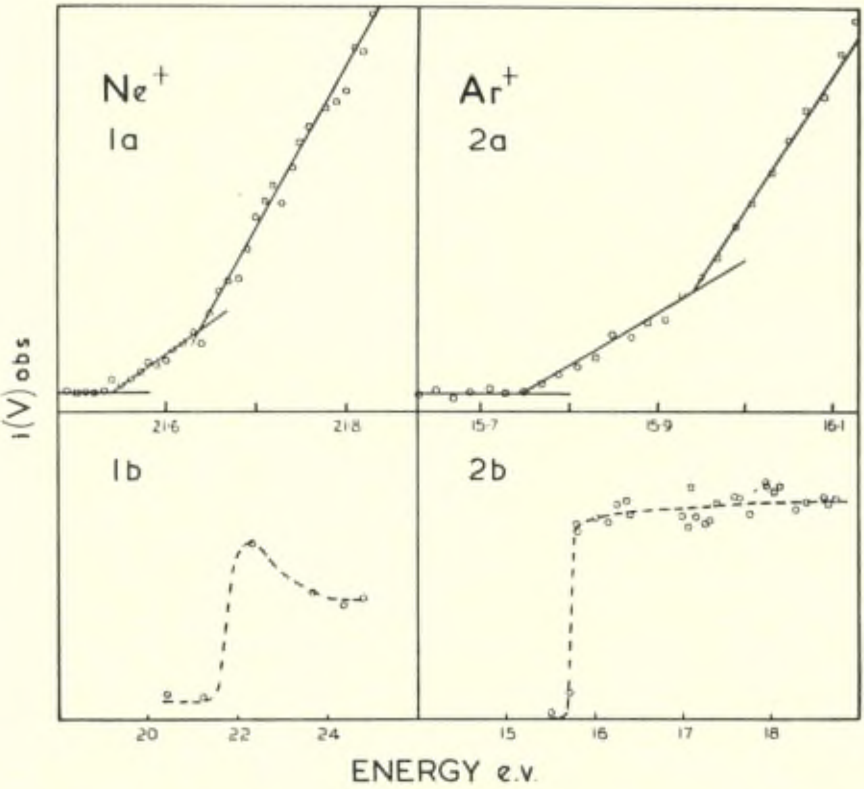

Fig. 9. — Ionization efficiency curves for Ne^+ and Ar^+ measured by (*a*) electron impact (39), (*b*) photon impact (19, 52).

Processes of multiple ionization have been observed only for electron impact. It was first suggested by Clarke (11) that his data for Xe^{2+} obtained with an electron selector might follow a square threshold law. The ideal test case is that of He^{2+}, and the curve obtained by Fox (53) using the R.P.D. method, is convincing evidence of a square law. Dibeler, Krauss and Reese (54), and also Dorman, Morrison and Nicholson (55) measured the efficiency curves for processes of up to 6-fold ionization in Na, Ne, Ar, Kr, Ze and Hg and claimed that their data are more consistent with *n*th power

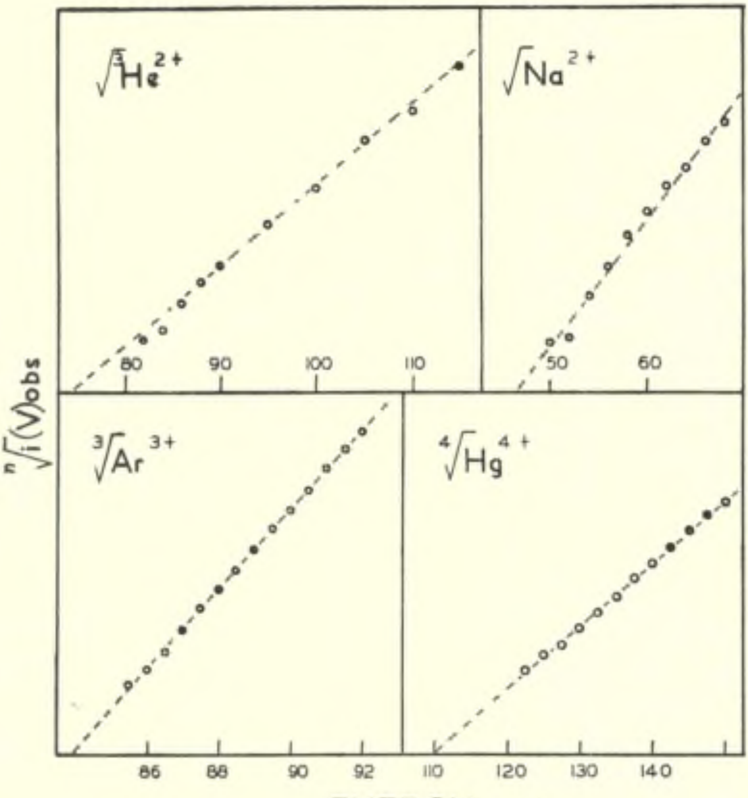

Fig. 10. — Ionization efficiency curves for doubly-charged He (53) and Na (54), triply-charged Ar and quadruply-charged Hg (55), measured using electron impact.

threshold laws. On the other hand, Fox (53) and Blais and Mann (56) claimed that their data on the other doubly-charged rare gases and Au respectively could be interpreted in terms of a series of linear segments. The balance of evidence is believed by the present author to favour the *n*th power law for *n*-fold ionization by electron impact, since it is notoriously easy to fit a square law curve by linear segments, especially when experimental scatter is present. Theory would predict a linear law for double ionization by photon impact, but this has so far not been observed.

The evidence for processes of excitation is slightly less direct. Excitation processes can be studied in the mass spectrometer, provided they lead to an ionized product by some secondary mechanism. Such processes are ion-pair formation, and autoionization. Figure 11 shows the data for two such ions arising from

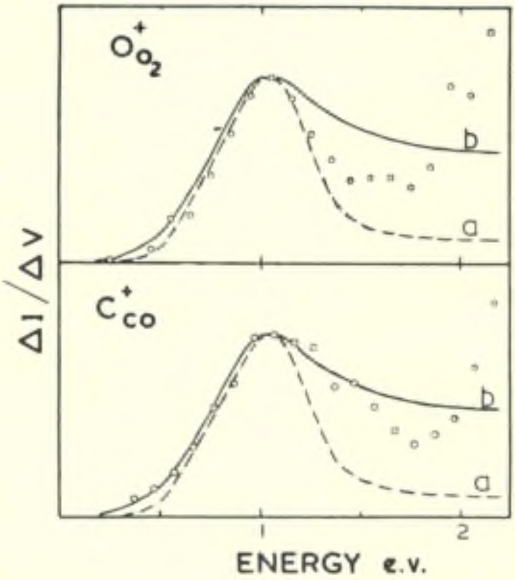

Fig. 11. — First differential ionization efficiency curves for C^+ from CO, and O^+ from O_2, measured with electron impact (57). The broken lines are the curves calculated from the electron energy spread assuming that the level is sharp and that the threshold law is a step; the solid lines the curves assuming the square root law. The Franck-Condon factors can only raise the experimental points above these lines, never lower them.

an ion-pair process. When allowance is made for a certain amount of broadening due to the Franck-Condon factor, the data are consistent with a step function for electrons and a δ-function for photons, and rule out the $(E-E_c)^{1/2}$ or $(E-E_c)^{3/2}$ laws suggested by Geltman.

A large number of ionization efficiency curves for singly-charged molecular ions exhibit features which can not be explained in terms of a sum of direct ionization processes. These features can be accounted for perfectly, if it is assumed that autoionization is occurring with a threshold law which is a step for electron impact, and a δ-function for photon impact. These processes will be superposed on the normal curves for direct singly ionization. This is illustrated in Figure 12, showing the photon impact data for HI^+

and CH_3I^+, and also in Figure 24 showing the electron impact data for Xe^+. Excited states of the neutral molecule are shown in the upper part of the figure.

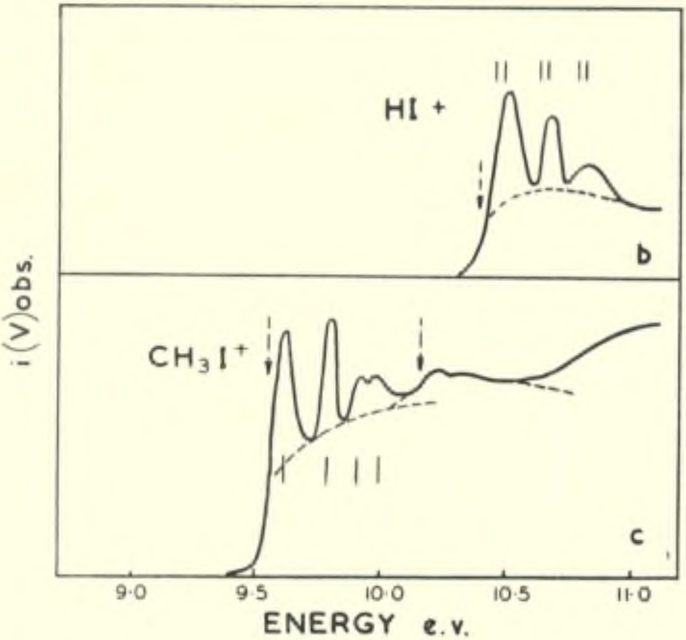

Fig. 12. — Photoionization efficiency curves for the parent ions from HI and CH_3I (57). Ionized states are indicated by arrows, neutral states by lines superposed on the figures. The positions of the peaks agree with those of these neutral states to within 0.02 e.v.

The trapped electron experiments of Schulz (58) give results for excitation processes which are much more like resonance peaks. It could be however that the results of this method are not directly comparable to the other electron impact data, but should be closer to their first differentials. The results of experiments on the production of a given spectroscopic emission line stimulated by electron impact do not appear to agree with the step-function law (59).

Several ionization efficiency curves have been published for the metals, using the R.P.D. method, which show apparently a set of peaks superposed on a linear increase, and it has been claimed that these peaks are due to autoionization processes, although the agreement with the spectroscopic levels seemed forced (56, 60). One such case is of particular interest. If the data of Blais and Mann for Ag^+ are replotted as a first differential curve, Figure 13, it

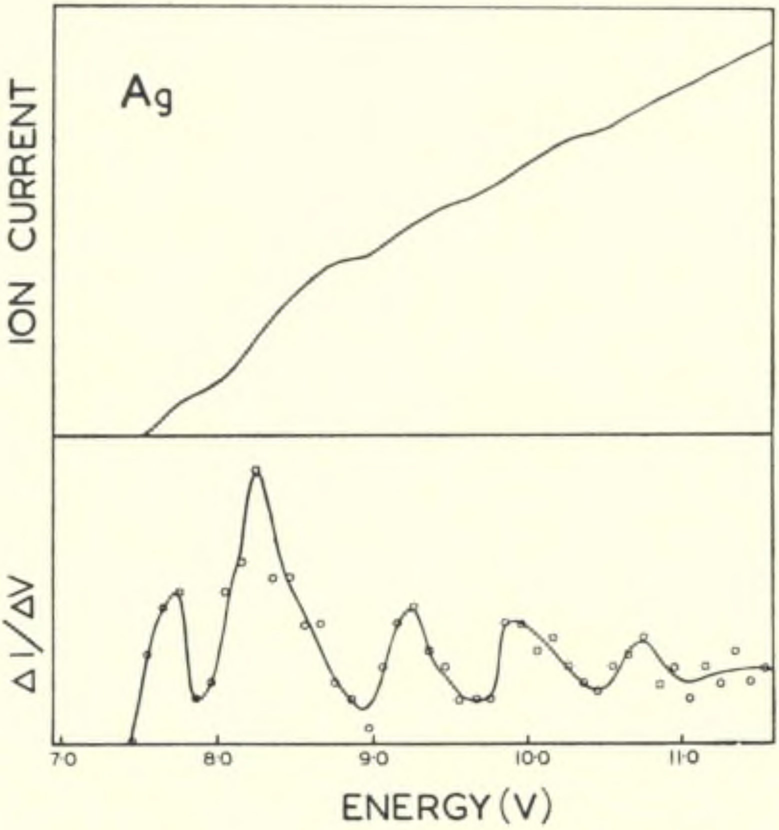

Fig. 13. — Ionization efficiency curve for Ag^+, measured with electron impact by Blais and Mann (56). In the lower part of the figure is plotted the first differential curve.

appears as a series of peaks, each of which has a steeply rising front edge, and a more gradual fall on the high energy side. The maxima of these peaks fit the known levels much better. Further, such asymmetric first differential peaks would be predicted by the theory for an autoionization process induced by electron impact, where the lifetime was very short. The step due to the direct ionization must be of small amplitude in comparison with the peaks.

Processes of electron capture have been studied by several workers (61), and, as might be expected, are found to consist of a sharp peak at E_c. Figure 14 shows two such processes. The peak for O^- is broadened by the Franck-Condon factor.

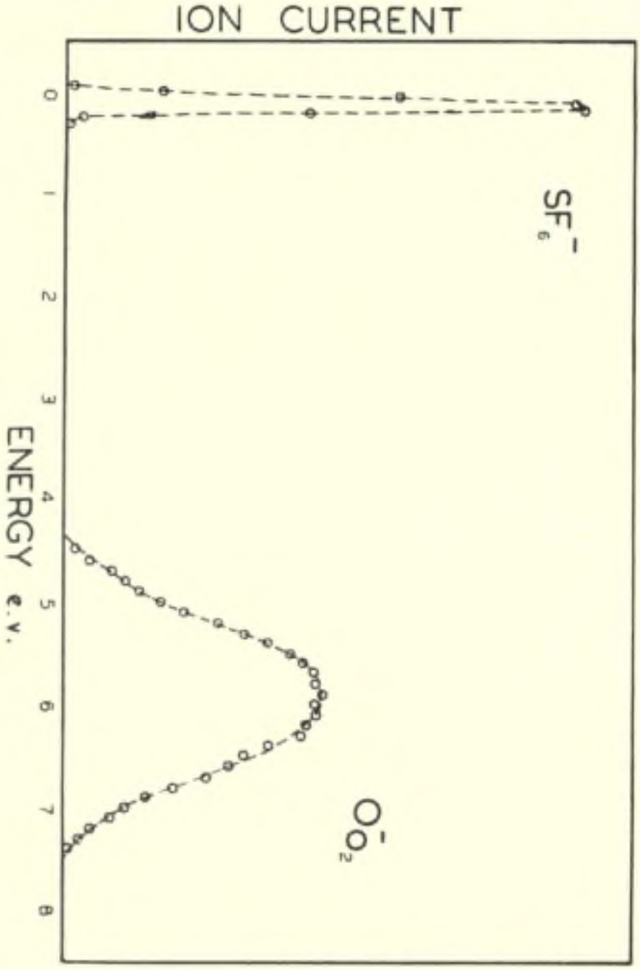

Fig. 14. — Ionization efficiency curves for electron capture processes leading to formation of SF_6^- and O^- (74). The peak for O^- is broadened presumably because of the Franck-Condon factor.

Taken overall, the experimental evidence regarding threshold ionization and excitation probabilities is accounted for very satisfactorily in terms of the freedom factor, while the results of more elaborate calculations appear in some cases at least to be directly contrary to fact.

3.1.7 *Structural factors affecting ionization probabilities.*

While the threshold law is apparently not dependent on the nature of the transition, its breakdown at higher energies does depend on various structural factors peculiar to the atom or molecule concerned. For a transition to a discrete upper state with defined energy, it is convenient to regard the ionization probability as the product of two independent functions of the ionizing energy, one dependent only on the freedom factor as defined above, the other on a structural factor. The latter is a function of a number of molecular properties, amongst these being the lifetime of the collision complex. It is very difficult to obtain much experimental evidence regarding it, because all ionization efficiency curves at higher energies are composed of many overlapping processes. It does appear to have the general form of an exponential decrease :

$$\mathrm{S(E)} = \exp - \left(\frac{\mathrm{E} - \mathrm{E}_c}{\mathrm{E}_c}\right)^2 q \,, \tag{4}$$

where q is proportional to the total number of electrons in the molecule being ionized. It is possible then to write the ionization probability as a function of the energy E, namely,

$$p(\mathrm{E}) = \mathrm{K} \cdot \mathrm{P(E)} \cdot \mathrm{S(E)} \,. \tag{5}$$

If it is assumed that no interaction occurs between different processes, the ionization efficiency for the production of a given ionic species will be given by the sum of the separate ionization probabilities for all the possible states of the ion, and can be written as

$$\mathrm{I(E)} = \sum_i \mathrm{K}_i \, \mathrm{P}_i \, \mathrm{(E)} \tag{6}$$

3.1.8 *Relative electronic transition probabilities.*

Where all the processes have the same freedom factor, the K_i of Eq. (6) give a set of measures of the relative electronic transition probabilities for each of the levels of the ion, which are closely related to the quantities P of Eq. (1).

When transitions with differing freedom factors are compared, it is necessary to take into account the form of the various $p(\mathrm{E})$. If it is accepted that the form of the ionization probability curve for a process with freedom factor n is a function of the excess energy given by Eq. (2), then the nth derivative reduces to a δ-function at E_c. When an energy spread is present in the ionizing beam, the nth derivative reduces to the reversed energy distribution centred about E_c, and the area under this distribution is a measure of the transition probability. The maximum value of the distribution is proportional to its area. This calculation of the transition probability is an approximation because of the structural factor, but because the latter is so slowly varying a function of the energy, in comparison with the part due to the freedom factor, it is a fairly good one.

Transitions to upper states which are continuous may be considered as transitions to a large number of discrete states very closely spaced in energy, without very great error.

The units in which the K values are measured depend on the freedom factor for each process, being relative transition probability per unit energy to the nth power. This is at first sight rather strange, but is directly comparable with the calculation of oscillator strengths for bound-bound and bound-free transitions in spectroscopy, although so far in the latter case only processes of freedom factor zero and unity have been considered.

3.2 Identification of class of processes.

By making use of the results of the previous section on the form of ionization probability curves for single processes, and taking into account the Franck-Condon considerations, it is now possible to make a very complete interpretation of more complex ionization efficiency curves.

Firstly, the shapes of the various features in the curves enables the classes of processes occuring to be identified. The first differential curve for electron impact, or the direct curve for photon impact, for the production of a singly-charged ion should consist of a series of steps, at each of the levels of the ion, if only direct single ionization is occurring. If peaks occur in the curve, these must be due either to autoionization, or to the production of that ion in an ion-pair process. Another possibility, which would however be very difficult to observe because of the Franck-Condon factor, is where a singly-charged ion could be formed by the dissociation of a doubly-charged ion. In this case, the probability for its production should be that of a double ionization process.

The application of this principle to the available data shows that autoionization is quite common in atoms, and is especially so for molecules containing electrons occupying π-orbitals (62). Surprisingly, autoionization does not appear to be very important in multiple ionization processes, at least in the vicinity of the first threshold. It might have been expected that cascade ionization, which is known to occur to some extent in xenon (63), would be a more probable process than the ejection of four or five electrons simultaneously, but this is not so.

3.3 Experimental determination of transition probabilities.

For processes of direct single ionization, the electronic transition probabilities can be measured very easily in practice, by taking for electron impact the second differential, and for photon impact

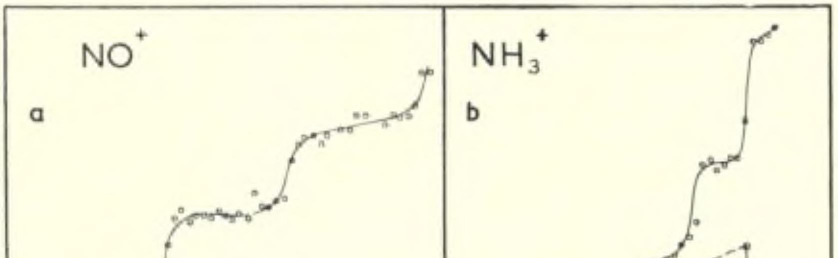

Fig. 15. — Photoionization efficiency curves for (*a*) NO^{+}(64), (*b*) NH$_3^{+}$(65), (*c*) *n*-propanol(18) and electron impact curve for H$_2^{+}$(66) (*d*). The electronic transition probabilities (see text) are superposed on each curve in idealized form except for *n*-propanol, where the individual vibrational levels are not distinguished.

the first differential of the ionization efficiency curve. In favourable cases the individual vibronic transition probabilities can be obtained, as is shown in the data of Figure 15. Even where the vibrational structure can not be resolved, the second differential curve gives the envelope of the transition probabilities.

For processes of multiple ionization, it is not usually practicable to calculate the *n*th differential curves, because of experimental scatter. The transition probability K for the least energetic process of each kind can be found by fitting the data with a curve of form

$$i(\mathrm{V}) = \mathrm{K}(\mathrm{V} - \mathrm{E}_c)^k / k\ ! \,, \qquad (7)$$

where k is the appropriate degree of ionization.

For processes of excitation, the heights of the peaks in the first differential curve for electron impact, or the direct curve for photon impact give the required probabilities. The heights of the peaks in the trapped electron data of Schulz can be used similarly. A very similar approach to this problem has been adopted by Lorquet (67), but in this case an attempt is made to fit the ionization probability curves by an empirical expression over a greatly extended range.

Transition probabilities have been measured in this way for a series of processes in the rare gases, and several molecules. The results obtained on different mass spectrometers, and by different workers agree fairly well (68).

TABLE 2.

Charge on ion	Relative electronic transition probability (K)			
	Krypton		Xenon	
	Kiser	D. & M.	Kiser	D. & M.
1^+	2.0	2.0	2.0	2.0
2^+	0.04	0.03	0.06	0.09
3^+		5×10^{-6}	1.5×10^{-4}	2×10^{-4}
4^+	6×10^{-9}	1×10^{-10}	1×10^{-7}	3×10^{-8}
5^+		2×10^{-13}	5×10^{-11}	2×10^{-11}

These transition probabilities have been used by Chupka (79) in studies of the kinetics of unimolecular dissociation processes.

An attempt has been made by Fox (69), to place some of the mass spectrometric data on ionization cross sections near threshold on a more nearly absolute basis, by comparison with total ionization experiments.

3.4 Shapes of upper state potential energy curves.

The form of the electronic transition probability curves derived from ionization efficiency data as described in the preceding section, can be used to make deductions regarding the shape of the upper state potential energy curves, when the Franck-Condon considerations are taken into account. The profiles of the vibronic transition probabilities of Figure 15 show very clearly that the lowest ionized state of NO has very nearly the same internuclear spacing as the ground state, while in NH_3 and *n*-propyl alcohol the configurations are considerably different. Such information may give useful clues regarding the particular orbital ionized in each state. Where the electron ionized is non-bonding, little change in configuration may occur; where it is bonding, larger changes are probable. In the case of NH_3 it is believed that although the electron ionized is non-bonding, the configuration changes to the planar form in the ion (70).

The transition probability curves shown in Figure 16 for ions from propylamine and acetaldehyde, show clearly that in the first case both ions arise from the same state, while in the second case the lowest state of the parent ion is completely stable, and the second state dissociates completely. Deductions of this kind have been made by many workers (71), but complications arise in the case of the more complex molecules, which will be discussed in a later section.

It is also possible to make use of arguments based only on energy values to demonstrate the form of the upper state potential energy curves. In this way it has been shown that the potential energy curve for doubly-charged diatomic molecule-ions are very probably of the unusual form shown in Figure 17, where the stable state of the ion is 3-5 e.v. above its dissociation limit (62). This finding is supported by a recent theoretical calculation (72).

For many complex molecules, the form of the potential energy hypersurface for the parent ion must be such that rearrangement of the chemical bonds occurs. Extensive studies of this type of process have been made by Meyerson (73).

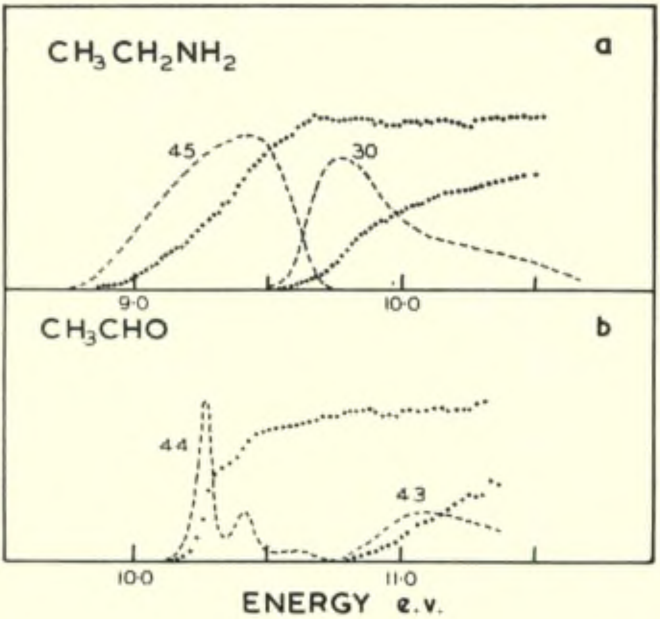

Fig. 16. — Photoionization efficiencies (points) and electronic transition probabilities (broken lines) for parent and fragment ions from ethylamine and acetaldehyde ([18]).

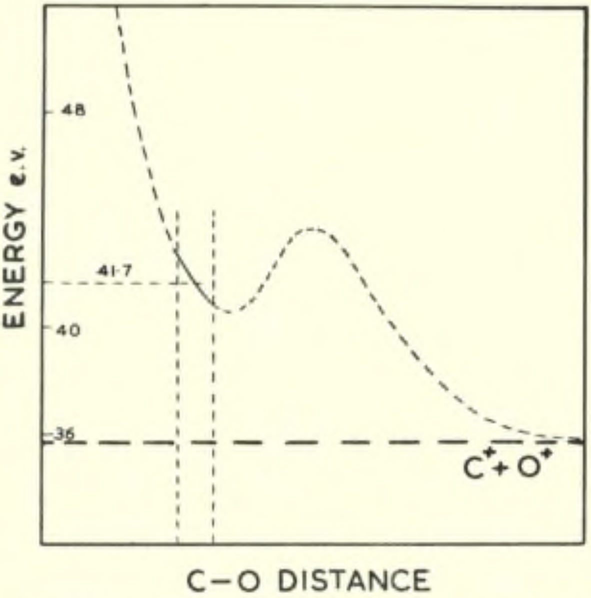

Fig. 17. — Potential energy curve for doubly-charged diatomic molecular ions, deduced on energetic grounds. The Franck-Condon region is indicated by vertical broken lines.

3.5 **Determination of energy quantities.**

The fact that different classes of process obey different threshold laws makes it necessary to take this into account in the determination of energy thresholds. Many of the errors in the past have occurred through a lack of realization of this. It is customary to define two energy quantities for transitions to each electronic state of a molecule. The " adiabatic " ionization potential is the energy for the transition $v_0' - v''_0$, while the " vertical " ionization potential is the energy required for the most probable transition from $e''v_0''$ to state e'. When the vibrational levels in the upper state are close, the vertical value is given closely by the energy distance between the ground state and the maximum of the profile of the upper state vibrational transition probabilities. In the case of NO^+, the most probable transition probability is 0.1 e.v. different from this value.

A set of vertical ionization potentials can be measured for simple molecules in this way (74), even where some of the transitions are to wholly repulsive states. It is also possible, from the envelope of the vibrational transition probabilities, to determine whether an adiabatic value can be measured at all or not. For example, in cases (*a*) and (*d*) of Figure 15, the lowest peak almost certainly corresponds to the adiabatic transition. In cases (*b*) and (*c*) Figure 15 and (*a*) Figure 16, the adiabatic value is not being observed.

With increase in resolving power, it is becoming possible to measure vibrational spacings. In measurements of the lowest ionized state, it is not necessary to use a mass analyzer, and an extensive compilation of values obtained in this way has been made by Watanabe (75). This type of measurement is not restricted to stable molecules, and radicals such as methyl, ethyl and propyl etc. have been studied in a mass spectrometer with both electron and photon impact (76). The ionization energies are of interest, when compared with the results of theoretical calculations (77).

3.6 **Dissociation of molecular ions.**

A molecule, after ionization by electron or photon impact, may undergo dissociation to charged and neutral fragments. The primary process of ionization takes place in $\sim 10^{-16}$ sec, but the subsequent unimolecular dissociation, involving the motions of relatively heavy particles, requires a considerably longer time. If this time is so long that it becomes commensurate with the time spent by the ions in travelling through the mass analyser, etc., obviously the proportions of ions detected as excited parent, and as fragments will not be independent of it (78).

For a mass spectrometer and ion source of the type described in section 2.6 it can be calculated (79, 80) that a newly formed ion of mass 84 spends from 1 to 5 μ sec in the chamber, depending on the point of formation. If the parent ion dissociates in this time, the fragment ion will be detected normally. The ion then spends 1 μ sec in the ion gun, and fragments which form here are spread over the whole mass range and effectively lost. The ion then spends 5 μ sec in a field free region, 3 μ sec in the magnetic field, and another 5 μ sec in a field free region before being collected. Fragments formed in the first region are detected as so-called metastable ions, those in the second are lost, and those in the third are recorded as if they were parent ions (Fig. 18).

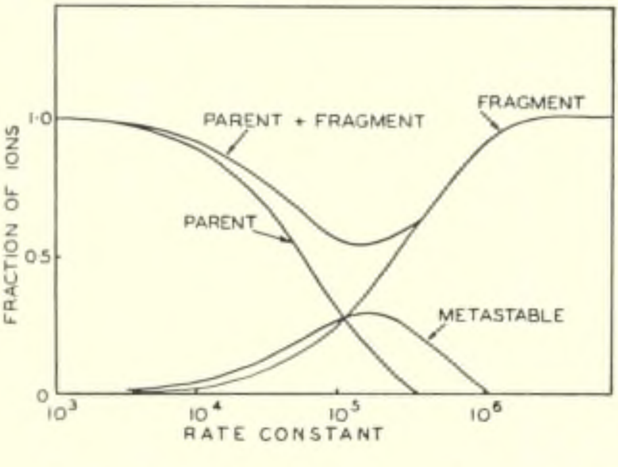

Fig. 18. — Fraction of ions which will be observed as parent, metastable or fragment, as a function of rate constant for unimolecular decomposition, according to calculation of Chupka (79).

In the case of diatomic molecules, the times required for the dissociation are short ~ 10^{-12} sec, and Franck-Condon considerations and the threshold law alone determine the ionization efficiency curves (81). Figure 19 shows a typical fragment *i*(V) curve of this

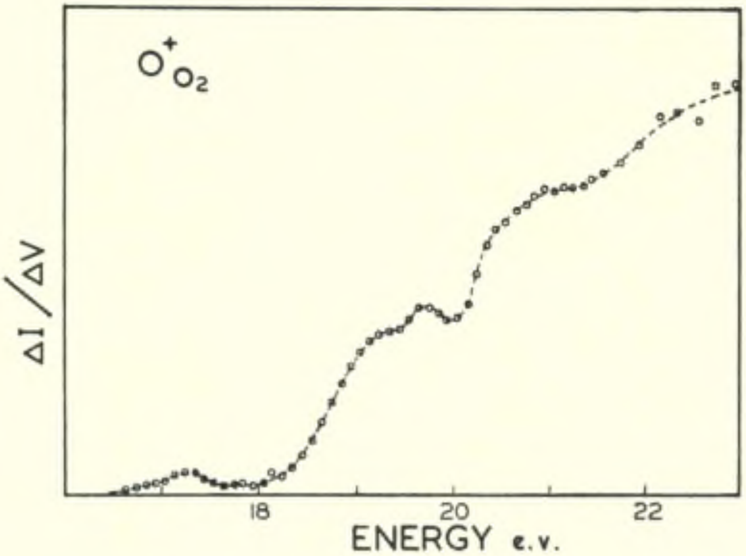

Fig. 19. — First differential ionization efficiency curve for O^+ fragment from O_2. The structure in the curve indicates that the ion is being formed from at least five states of the molecule-ion.

type. Such curves can be interpreted directly to calculate dissociation energies, electron affinities and other energy quantities. Atomic fragment ions are often observed possessing large amounts of kinetic energy, which must be taken into account in these calculations. Stevenson (82), and Schaeffer (83) have calculated the relative abundance ratios for H^+/H_2^+, D^+/D_2^+ and predicted the isotope effect on the mass spectrum for a number of simple molecules, with some degree of success.

In the case of polyatomic molecules, particularly the saturated hydrocarbons, the production of numerous " metastable " ions shows that the dissociation times may be much longer, up to 10^{-5} sec or more. Further, while the ionization efficiency curves for the parent and fragment ions from simple molecules show ample evidence for the presence of well defined energy states up to at least

25 e.v., the more complex molecules show very little evidence for states above the lowest. The electronic transition probability curves, measured as above, show a broad maximum, extending in some cases for as much as 4-6 e.v. While it might be expected that vibrational levels should not be resolved, some indication should be found of electronic states. Also, the fragment ions do not appear to carry off any significant amount of kinetic energy (84).

The dissociation reactions occuring after impact can be regarded as unimolecular reactions in the zero pressure limit. As such, they differ slightly from those treated by Slater (85), Hinshelwood (86), Rice and Ramsperger (87) and Kassel (88). The first suggested that an energized molecule would decompose when the vibrations of the various excited normal modes are in phase to produce a critical extension of a given bond. Transfer of energy between normal modes need not occur. The second theory assumed that a molecule can be represented by a system of coupled oscillators, and that energy is exchanged between these oscillators many times during the life of a molecule. In gas reactions, elastic collisions with neighbouring molecules are sufficiently frequent to ensure this randomization. Dissociation will occur when a critical amount of energy accumulates in one bond.

Both theories lead to an expression for the rate constant of the dissociation which is of the form

$$k = \nu\,[(\mathrm{E} - \mathrm{E}_o)/\mathrm{E}]^{n-1}\ \mathrm{sec}^{-1} \qquad (8)$$

ν, the frequency factor, may be calculated from vibrational data, or treated as a free parameter, E is the excitation energy, E_o the threshold energy for the dissociation and n is the number of internal degrees of freedom.

Rosenstock, Wallenstein, Wahrhaftig and Eyring (89) postulated that a molecule of even only moderate complexity could possess so many energy states, and that the potential hypersurfaces for these would intersect each other at so many points, that radiationless transitions could occur very frequently. The energy of a molecule excited initially in one state, could very rapidly be randomly distributed over all possible states. Given this mechanism of energy randomization the theory of Kassel could be extended to the zero pressure case, and an attempt could be made to calculate the mass spectra of such molecules, and their dependence on temperature.

The publication of this theory stimulated many experiments designed to check its validity. The fact that fragment ions in such processes possessed very little kinetic energy favoured the idea that the energy was distributed in various internal modes. Friedman, Long and Wolfsberg (90) raised the objection that in large molecules, a considerable amount of excess energy should be needed over the minimum required for dissociation, in order to obtain rates of reaction fast enough that the fragment ions could be observed in the mass spectrometer at all. Since the dissociation energies calculated using appearance potential data on polyatomic fragments agreed with results from thermal data, the statistical theory could not hold in the neighbourhood of threshold. This is not a serious objection, as Wallenstein and Krauss (91) point out, since the agreement between experiment quoted is not conspicuously good.

Chupka (79) showed that the electronic transition probability curves for each ion, obtained in the manner of section 3.4, could be used to give an experimental verification of the relationship between the rate constant as calculated from the theory, and the

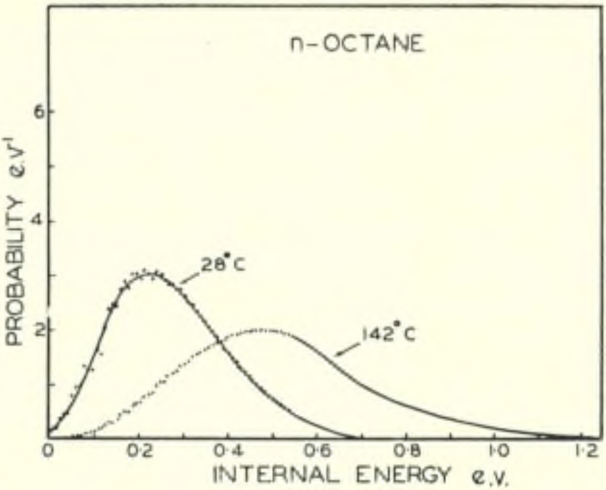

Fig. 20. — Probability distribution for internal energy in *n*-octane at 28 °C and 142 °C, calculated by Steiner, Giese and Inghram (80).

excess energy ($E-E_0$), if they were plotted as fractions of the total ionization transition probability. He accepted that large amounts of excess energy were not found, but suggested that for primary decompositions, the thermal energy, Figure 20, already present in the molecule might mask the effect. The curves obtained, Figure 21, showed a marked qualitative resemblance to those of Figure 18, and should make it possible to test the theory quantitatively. Unfortunately, the adiabatic ionization potential of the molecule can not be measured, nor is it possible to estimate the energy of formation of the fragments with any great accuracy. In the data of Figure 21 there is a serious discrepancy between the observed and calculated energy scales. This has been found also in later studies (92). To obtain a satisfactory correlation between the curves, it is necessary to assume that the number of oscillators *n* is appreciably less than that required by the theory, by as much as 5-fold.

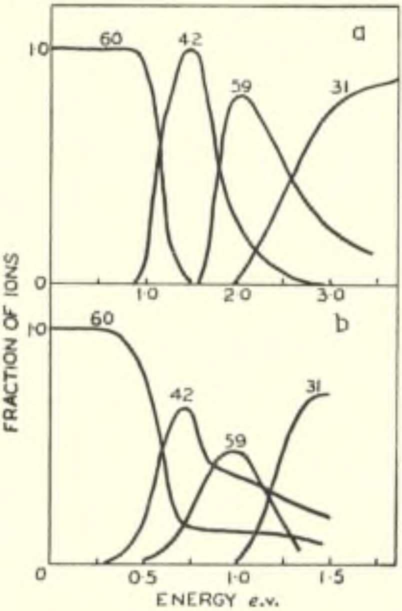

Fig. 21. — Fraction of ions appearing as parent and fragments for *n*-propanol as function of energy above dissociation limit (*a*) according to calculations of Friedman, Long and Wolfsberg (78), (*b*) using normalized transition probability plot of Chupka (79). A serious discrepancy occurs between the two energy scales.

A very complete and careful study has been made of the alkanes using photon impact, by Steiner, Giese and Inghram (80). The results were interpreted in a manner similar to Chupka. The agreement of the results with the statistical theory is again qualitatively good, but calls for a very much reduced number of degrees of internal freedom. The effects of temperature and dwell-time in the ion source were studied in this work, and these also required a smaller number of degrees of freedom, unfortunately not the same as that required to account for the observed curve shapes. These authors suggested that a modified form of Slater's original theory might give a better representation of their data. Various attempts have been made to modify the rate equations of the original statistical theory to make this fit the observed data, by Vestal and Rosenstock (93), Rosenstock (94), Wallenstein and Krauss (91) and others (95).

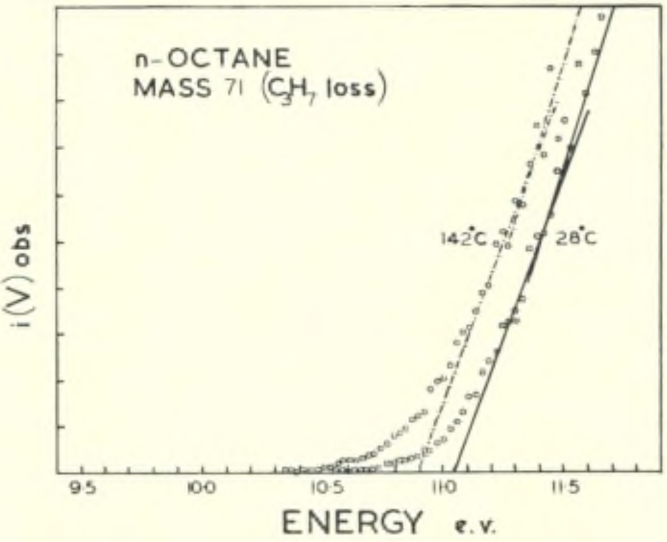

Fig. 22. — Effect of ion source temperature on photoionization efficiency curve for mass 71 fragment from *n*-octane (80).

Is is becoming evident that the initial postulate of unlimited radiationless transitions in a practical continuum of states is not valid in all cases. Particularly where π-electron systems are involved, the levels are spaced at approximately 1 e.v. (96), and it seems that even in the paraffins the levels will tend to cluster together in bands.

The principal merit of the statistical theory was its simplicity, and it would appear that in its simple form it is inadequate for the quantitative prediction of dissociation probabilities near threshold, for molecules containing up to 20 atoms. It remains to be seen whether the theory will still be of value for more complex systems, whether it can be modified successfully, or whether an entirely different approach is necessary.

RECENT DEVELOPMENTS

It has always been believed that higher resolution of details in ionization efficiency curves could be achieved only by the use of a more monoenergetic source of ionizing particles. Almost all of the improvements in technique described have been towards the construction of better energy filters, where a narrower and narrower slice is taken out of some initial distribution, and used to produce the ionization. A limit is set to this process, because it is already becoming evident that the narrower the energy spread achieved in this way, the less the current, and therefore the poorer the signal-to-noise ratio in the resulting ionization efficiency curve.

Numerous attempts have been made in the past to remove the effect of energy spread from the data by analytical methods, but all have failed. One reason was because of the scatter in the experimental observations which make up any given curve, the other was the fact that the exact form of the energy distribution was not known, nor could it even, for electrons, be assumed to remain exactly of the same form at all values of the energy. A study made over the last few months on the optimum use of ionization data, has produced some rather surprising conclusions (97).

The problem is as follows. As stated above, in the ideal case the ionization efficiency $i(\mathrm{V})$ is the result of the convolution of the probability of ionization by an electron of energy E, with the reversed energy distribution of the ionizing beam, i.e. :

$$i(\mathrm{V}) \propto \mathrm{I}(\mathrm{E}) * m(\overline{\mathrm{U}}) . \tag{9}$$

The result of experiment is a set of samples of $i(\mathrm{V})$ at equally spaced intervals in V, and it is desired to find the corresponding $\mathrm{I(E)}$. If there is no random scatter in the values of $i(\mathrm{V})$ and the energy spread $m(\mathrm{U})$ is also known accurately sampled at similar intervals in U, i.e., $\Delta\mathrm{U} = \Delta\mathrm{V}$, it is possible to determine $\mathrm{I(E)}$ uniquely at a similar set of intervals in E, provided certain not very restrictive boundary conditions are met.

This deconvolution operation can be carried out in several ways, the most elegant being by the use of Fourier transforms. One can write :

$$\mathrm{T}\{\mathrm{I(E)}\} = \frac{\mathrm{T}\{i\mathrm{V})\}}{\mathrm{T}\{m\ \overline{\mathrm{U}})\}}\ ;\quad \mathrm{I(E)} = \mathrm{T}\{\mathrm{T}\{\mathrm{I(E)}\}\} \tag{10}$$

In any actual case, $m(\mathrm{U})$ is not known with certainty. It is however usually possible to make a very good guess at its form. If noise-free data $i(\mathrm{V})$ are deconvoluted in terms of this guess at $m(\mathrm{U})$, denoted by $\widetilde{m}_1(\mathrm{U})$, the result is obtained :

$$\frac{\mathrm{T}\{i(\mathrm{V})\}}{\mathrm{T}\{\widetilde{m}_1(\overline{\mathrm{U}})\}} = \mathrm{T}\{\mathrm{I(E)}\} \times \frac{\mathrm{T}\{m(\overline{\mathrm{U}})\}}{\mathrm{T}\{\widetilde{m}_1(\overline{\mathrm{U}})\}} = \mathrm{T}\{\mathrm{I(E)}\} \times \mathrm{T}^{\prime} m_1(\overline{\mathrm{U}})\},$$

where :

$$m_1(\overline{\mathrm{U}})^{*}\ \widetilde{m_1}(\overline{\mathrm{U}}) = m(\overline{\mathrm{U}}) \tag{11}$$

$$\mathrm{T}\{\mathrm{T}\{\mathrm{I(E)}\} \times \mathrm{T}\{m_1(\overline{\mathrm{U}})\}\} = \mathrm{I(E)} * m_1(\bar{\mathrm{U}}) = i_1(\mathrm{V}) \tag{12}$$

This states that deconvoluting $i(\mathrm{V})$ in terms of a guess at $m(\mathrm{U})$, namely $\widetilde{m}_1(\mathrm{U})$, will give a new $i_1(\mathrm{V})$ which has apparently been measured with a narrower energy spread $m_1(\mathrm{U})$. Error in choosing $\widetilde{m}_1(\mathrm{U})$ is not serious, and the better $\widetilde{m}_1(\mathrm{U})$ approximates to $m(\mathrm{U})$ the narrower the effective spread which can be achieved. In practice, random scatter in the experimental curves could still make the application of this deconvolution operation valueless.

An actual experimental ionization efficiency curve can be written in the form :

$$i(\mathrm{V})_{obs} \propto n(\mathrm{V}) + \mathrm{I(E)} * m(\overline{\mathrm{U}})\,, \tag{13}$$

where $n(V)$ represents the random scatter. $n(V)$ can however be decomposed into the sum of two parts $n_1(V)$ and $n_2(V)$. The first of these is incompatible with $I(E) * m(\overline{U})$, and the second is compatible. By "incompatible" it is meant that no possible real function $I(E)$ when convoluted with $m(\overline{U})$, could produce the observed fluctuating curve $n_1(V)$. The criterion for incompatibility is that $n_1(V) * m(\overline{U}) = 0$, and this can be applied very readily to the Fourier transform of $i(V)_{obs}$.

Making use of this criterion, it is possible to obtain an $i(V)_{calc}$ from which all incompatible scatter has been removed. In all cases a most striking improvement in the appearance of the data is achieved. This $i(V)_{calc}$ can now be deconvoluted in the manner described above. The relationship between signal-to-noise ratio in the data and attainable resolution then emerges very clearly. When noise is present, it affects both the amplitudes and phases of the vectors composing $T\{i(V)_{obs}\}$. This effect is most serious in the terms farthest from the origin, which are most necessary to

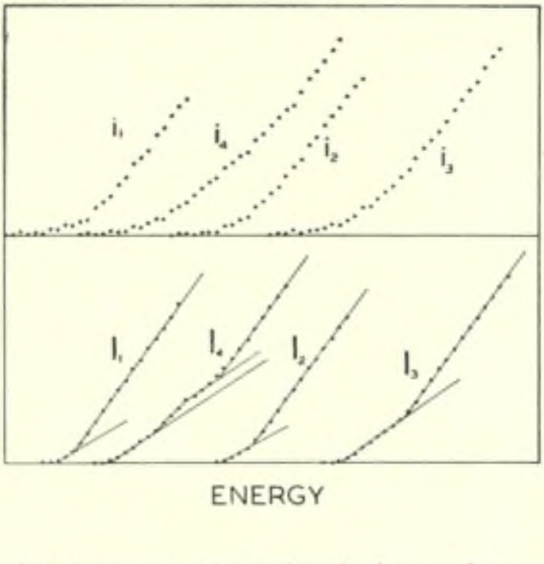

Fig. 23. — i_1, i_2, i_3, i_4 represent curves made up by the sum of two equal processes spaced at 1/4 ×, 1/2 ×, 1 × and 2 × the half width of an energy distribution, respectively, with in the case of i_4 a step half way between these. Random scatter is added to the data. The results of carrying out the noise removal and deconvolution operations on these are shown in curves I_1, I_2, I_3 and I_4.

obtain high resolution in the result. It is possible to show that as the scatter in the original data is less, so the solution which can be obtained shows sharper and sharper resolution, with a limit set by the interval of sampling of the data.

Yet other criteria may be applied to reduce the effect of the random noise even more.

A test made of these methods on artificial examples, showed that improvements in signal-to-noise ratio of the order of twenty times could be achieved, and that some measure of reduction of the energy spread could be achieved even in most unlikely cases. Figure 23 shows one such example. The application of the method to experimental data is simple. The second differential of the ionization efficiency data for He, measured by electron impact,

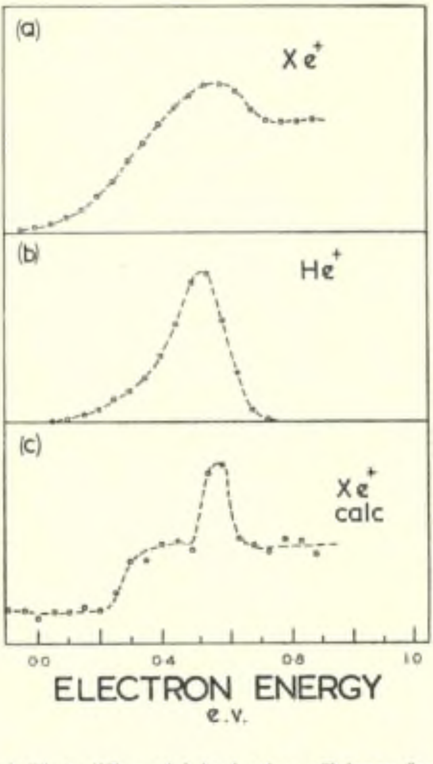

Fig. 24. — (*a*) First differential ionization efficiency for Xe.
(*b*) Second differential ionization efficiency for He.
(*c*) Result of noise removal and deconvolution operations.

gives an estimate of the reversed energy spread of the ionizing beam, and the processes of noise removal and deconvolution are carried out using this. Figure 24 shows the result for Xe^+. There is manifestly a sharpening up of the structure, and the threshold law for direct single ionization to the $^2P_{3}/_{2}$ state is clearly distinguished from that due to autoionization to the 6*d* level of the atom.

It would appear that the resolution in energy which can be achieved by this technique is limited mainly by the smallness of the intervals at which the data can be sampled, the random noise in the data, and the accuracy with which the electron energy spread can be estimated. The actual total energy spread of the ionizing beam is much less important (in theory it should not matter at all). So far, improvements in energy spread of four to five-fold have been achieved. The present results show very clearly that the best use has not been made of such information already present in ionization data.

The study also shows that the key to higher resolution in energy is to increase the amplitude of the Fourier transform of the energy distribution at the values farthest from the origin. The conventional way of doing this, by using a velocity selector, is not a good way, because it at the same time increases the scatter in the same region of the transform. An unconventional approach, suggested by this study, is to introduce a number of kinks in the initial energy distribution, without altering its total width. Such a beam would possess very high information content in the sense that random scatter could be much less able to degrade the $i(V)_{obs}$ curves produced with it, and it should be capable of giving very high resolving powers.

Additional comment after the meeting

Dr. Herzberg has drawn my attention to some recent theoretical calculations, by U. Fano (*Phys. Rev.* **124,** 1866, 1961), of the cross-section for auto-ionization processes. When account is taken of the effects of configuration interaction, a behaviour of the cross-section at treshold is predicted which is exactly that observed for the case of Xenon.

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Discussion du rapport de M. J.D. Morrison

M. Herzberg. — I am puzzled by the asymmetric contour of the preionized absorption lines of xenon. Most of the atomic lines that are broadened by preionization (auto-ionization) are broadened symmetrically as far as I know. Are you really sure that these lines are asymmetrically broadened, and if so, does Professor Wigner perhaps know of a theoretical explanation why the lines should be asymmetrically broadened ? Normally, it is assumed that the width of the lines is determined by the uncertainty relation, that is, the shorter the life time of the excited state, the greater is the width, and this symmetrical broadening must surely be there in addition to any asymmetrical broadening that may also exist. (Additional remark : Since the meeting I have learned of the paper by Fano, *Phys. Rev.* **124**, 1866 (1961), in which a detailed explanation of the asymmetric line shapes is given.)

M. Morrison. — The shape of the photoionization efficiency curve for Xe^+ is in excellent agreement with the latest data obtained by Huffmann (personal communication) on the UV absorption cross-section for Xe in this energy range. The asymmetry of the *nd* series of autoionizing levels is most marked, while the *ns* levels are quite sharp.

On the other hand, the shape near threshold of the cross-section curve for some excitation reactions induced by electron impact, *e.g.* some of those measured by Schulz, can be interpreted very simply by assuming that a transient negative ion is formed. As the excess energy is greater, so the lifetime of this transient state becomes less, and the cross-section will change from that for an electron capture process to that for a direct excitation.

M. Wigner. — I would like to make a few remarks on the threshold laws which play such an important role in Dr. Morrison's discourse.

There are two groups of threshold laws. The first group relates to reactions in which two particles collide and two particles are formed.

Such a reaction is, for instance, the excitation of an atom or a molecule by electron impact, or the photo-ionization :

$$\mathrm{Xe} + e \rightarrow \mathrm{Xe}^* + e$$

$$\mathrm{Xe} + h\nu \rightarrow \mathrm{Xe}^+ + e$$

There are other processes in which three particles result from the collision of two :

$$\mathrm{Xe} + e \rightarrow \mathrm{Xe}^+ + 2e$$

or :

$$\mathrm{H}_2 + e \rightarrow 2\mathrm{H} + e$$

Evidently, there are even more complicated processes and Dr. Morrison has mentioned some of them.

In the simplest case, that is when two particles result from the collision of two particles, the threshold law can be derived rather easily. Furthermore, the derivation is almost as rigorous as the derivation of the regularities connected with the conservation of angular momentum. Actually, only three cases have to be distinguished if we do not pay attention to the angular momentum of the final state and if we disregard the various scattering processes such as depolarization in which no energy exchange takes place. If at least one of the products of the reaction is uncharged, the threshold law is $\sigma \approx (\mathrm{E} - \mathrm{E}_0)^{1/2}$ where σ is the cross section for the process, E the total energy in the center of mass coordinate system and E_0 the threshold energy, i.e., the minimum E at which the reaction becomes possible. If both reaction products are charged, the cross section sets in with a finite value if the charges are opposite; it sets in infinitely slowly (that is, infinitely many energy derivatives of σ are zero) if the electric charges of the reaction products have the same sign. I believe that there is also good experimental evidence for all three laws. The first one, the $(\mathrm{E} - \mathrm{E}_0)^{1/2}$ law, has been demonstrated most precisely in nuclear collisions, by means of the principle of detailed balance. It follows from the threshold law and the principle of detailed balance that the *reaction cross section* of very slow neutrons is *inversely* proportional to the square root of the neutron energy and this is the famous and well confirmed $1/v$ law. Figure 8*b* of Dr. Morrison's paper gives a beautiful example for the sudden onset of a finite cross section in a reaction from which two particles with opposite charges, He^+ and an electron, emerge. The " freedom factor " for reactions in which two like charges are formed contains the so-called Gamow factor exp ($c\mathrm{E}^{-1/2}$) but these play no very important role in chemical physics.

The mere existence of a threshold law, no matter how securely established, is of no very great value unless the limit of its validity is known. This limit is given by the energy interval in which Dr. Morrison's « structural factor » shows an appreciable variation. Unfortunately, little can be said about this factor on the basis of general principles in the case of atomic or chemical processes, but Dr. Morrison has already given a general picture. Perhaps I can make a negative statement at this point : there is no reason to expect the threshold law to be valid at the energy of the next threshold, unless this leads to products with different angular momenta or parities. From this point of view, figure 15*a* of Dr. Morrison's paper is somewhat surprising : the consecutive thresholds observed differ only in the vibrational quanta of the NO^+ molecule. Hence, one would expect anomalies in the cross section already *below* every new threshold. There seems to be little indication of such anomalies.

The theoretical treatment of collisions from which three or more particles emerge is much less secure and must be based, apparently, on much more intricate considerations. Also, many cases have to be distinguished because one has to specify the charges of three, rather than of only two, particles. Experimental evidence, and some very elementary arguments, surely seem to support the laws suggested by Dr. Morrison. In particular Wannier's $(\mathrm{E} - \mathrm{E}_o)^{1.127}$ law seems to be incompatible with the evidence of his Figure 8*a*. This indicates an $\mathrm{E}\text{-}\mathrm{E}_o$ law and the increased exponent would give sufficient curvature to the line to bend it above the straight line by about 0.2 cm both at 24.6 eV and at 25.3 eV. There are other experiments which also support the $\mathrm{E}\text{-}\mathrm{E}_o$ law. This is surprising because Wannier's calculation is very reasonable even thoug it is not absolutely convincing.

The possible complexity of the threshold laws for reactions leading to three or more products is very beautifully illustrated on page 422 of Dr. Morrison's article, and I would like to draw attention to the point he makes. If the ionization by electron impact can be described as a two-stage process, the first stage of which is the excitation to a state which then decomposes by auto-ionization, the threshold law will be the $(\mathrm{E} - \mathrm{E}_o)^{1/2}$ law. E is the energy necessary to reach the excited state. This picture implies, as explained by Dr. Morrison, that the lifetime of the excited state is very much longer than the time of the collision between electron and atom. If the lifetime of the excited state is not very much longer than the time of this collision, the picture becomes valid only approximately. There will be, then, some reaction even for $E < E_0$ and the $(E\text{-}E_0)^{1/2}$ curve will be washed out, particularly at $E < E_0$. There will be a lower threshold, at the E at which the ionization becomes energetically possible, but this is of no interest now. At any rate, the threshold behavior $(E\text{-}E_0)^{1/2}$ will become increasingly inaccurate as one considers auto-ionizations with shorter and shorter lifetimes of the auto-ionizing state. A. Pais has considered such situations in some detail when investigating the « woolly cusps » of the cross section *vs.* energy curve.

Summarizing, I would say that the threshold law for reactions resulting in the formation of only two particles is very well established theoretically. Experimental results which are in conflict with them ought to be carefully scrutinized. Conversely, such results would be very interesting and significant if fully verified. However, the threshold law, as its name indicates, applies in principle only to the immediate neighborhood of the threshold. It is difficult to tell, in general, how far it extends. As a rule, the more simple a system is, the wider is the range of validity of the threshold law. In the case of reactions resulting in three or more particles, the threshold laws are less securely established theoretically, and it would not be so surprising if they were not valid.

Communicated after the meeting :

The May 1st issue of the *Physical Review Letters*, which reached Princeton simultaneously with the report of this discussion, contained an article by R.H. McFarland (*Phys. Rev. Letters*, **10**, 397 (1963)) on the excitation efficiency, by electron impact, of two of the levels of He, the 4^1D and the 5^1D levels. The diagram showing these efficiencies is reproduced herewith, together with the legend of the Figure; they show that the square root law is valid in this case near the threshold. Since one of the reaction partners, the He atom, is uncharged, this is the expected threshold law. As Professor Morrison remarked, the threshold law is valid only over a limited region, in one case apparently 0.1 eV and in the other case about 0.2 eV. Nevertheless, these are appreciable magnitudes if expressed in units meaningful for chemical reactions, namely 2.5. and 5.0 kcal.

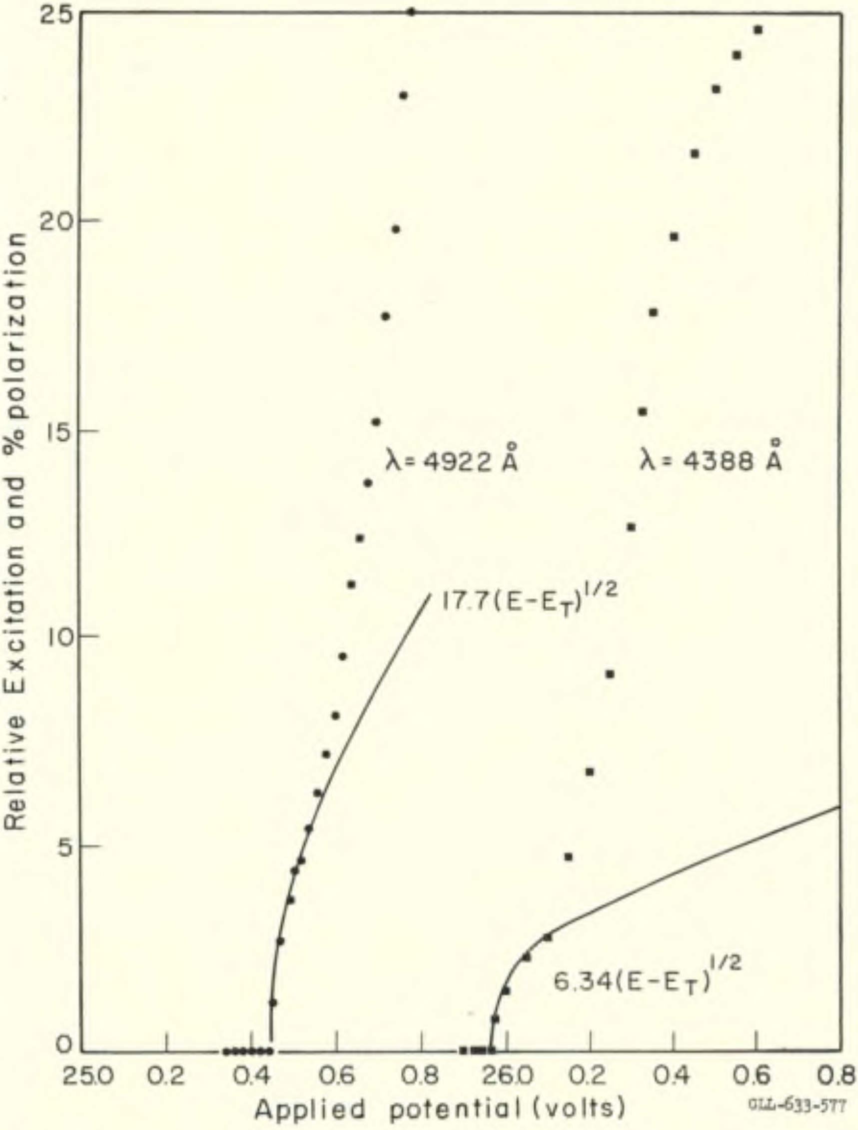

Fig. 2. — The relative excitation efficiency versus applied electron acceleration potential for two diffuse singlet transitions. Below the energy necessary to excite the next higher state, the measured excitation efficiency points shown conform to an expected square root dependency as indicated by the calculated solid line curves.

M. Morrison. — Professor Wigner has pointed out that theoretically it would be expected that the force field in which the electron separates from the other particle formed by dissociation of the collision complex, would affect the cross-section for the process above its threshold in a marked fashion. Experimentally it would seem that if this is the case, it is so only over a very small energy range $< 0.05 - 0.1$ eV. immediately above the threshold, and that above this there is little effect. Is it possible that at higher excess energies a polarization effect could make the force field at close distances always more nearly $1/r^2$ than $1/r^4$?

M. Karplus. — I should like to illustrate Professor Wigner's description of threshold behavior in two-particle reactions with two brief calculations. The first applies to the energy interval immediately above threshold. For collisions between massive particles, however, this interval may be so small that no measurements can be carried out in it. I therefore present a second discussion that applies to a somewhat higher energy interval.

1. The quantum mechanical calculation applies when an outgoing particle is light and cannot carry away any appreciable angular momentum.

If the final particles have no long range interactions, then the cross-section is proportional to the phase space available at the given energy E above the threshold E_o, $\sigma(E) \sim \int p'^2\, dp'\ \delta(E'-E)$. For atomic excitation by an electron, $e^- + A \rightarrow A^* + e^-$, we have :

$$E - E_o = \frac{p^2}{2m_e}$$

Hence :

$$\sigma(E) \sim \int p'\, dE'\ \delta(E' - E) \sim (E - E_o)^{1/2} \qquad \text{(I)}$$

If there is a long range interaction between the final particles as in the photo-ionization process

$$h\nu + A \rightarrow A^+ + e^-,$$

then the density of states has to be computed more carefully. For Coulomb forces, one obtains

$$\sigma(E) \sim \theta(E - E_o) \quad \text{(step function)}$$

because the density of states does not drop to zero at threshold.

As Professor Wigner has pointed out, this result is connected to the behavior of the inverse reaction cross section by detailed balancing as follows :

Suppose our process is $\Delta E + A + B \rightarrow C + D$. At equilibrium the rate of reaction is

(density of A + B states) × (relative flux of AB) × (cross-sections)

$$\sim v_{AB} \times v_{AB} \times \sigma_{AB \rightarrow CD}.$$

The rate of the reversed process is

$$\sim v_{CD} \times v_{CD} \times \sigma_{CD \rightarrow AB}$$

by the same argument. Hence we have

$$\sigma_{AB \rightarrow CD} = \frac{v_{CD}{}^2}{v_{AB}{}^2} \sigma_{CD \rightarrow AB} \approx (E-E_0)\, \sigma_{CD \rightarrow AB} \qquad \text{(II)}$$

since $v_{AB}{}^2$ is large and slowly varying near threshold and

$$v_{CD}{}^2 = 2m_{CD}\,(E-E_0).$$

We therefore conclude from I that

$$\sigma_{CD \rightarrow AB} \sim (E-E_0)^{-1/2} \sim 1/v_{CD}$$

2. Classical calculations apply when the outgoing particles are so heavy that many angular momentum states are important even at the lowest *measurable* energies above threshold.

We again use detailed balance.

Now in the classical limit

$$\sigma_{CD \rightarrow AB} \sim \pi R^2$$

(a constant), where R is the radius of interaction (which is assumed large compared to the wavelength of the particles). Hence the energy dependence of the endothermic cross-section is

$$\sigma_{AB \rightarrow CD}(E) \sim E - E_0 \qquad \text{(III)}$$

If there is a long range interaction between the outgoing particles, then there will be a deviation from this law as in the quantum-mechanical case.

The transition energy between the two regimes is determined by $pR \sim \hbar$, where p is the outgoing relative momentum and R the interaction radius. This relation becomes $30\,R\sqrt{m\,(E - E_0)} \sim 1$ when R is expressed in angstrom units, m (the reduced mass) in AMU, and the energy in electron volts. Clearly electronic process will be in regime (I) and ionic or atomic processes in regime (III) if the energy resolution is tenths of a volt.

M. Inghram. — I think it should be pointed out that there is no general agreement among the experimentalists on the validity of the step function for reactions in which an electron leaves a neutral species. In fact, all experimentalists have interpreted their data as consistent with a $(E\text{-}E_0)^{1/2}$ law. I would note specifically results on the production of metastable states of hydrogen as done by Lichten, the production of He_2^+ in which the initial step is the production of an excited state of He, and the photodetachment of an electron from 0^- as studied by Branscomb and Smith. The new and contradictory results of Morrison are thus most interesting. They will, undoubtedly, stimulate further work.

M. Voevodsky. — Does a statistical redistribution of the excess energy of an excited ion take place before dissociation ?

Does the nature of the elementary act of dissociation depend on the locus of primary excitation, on the initial configuration of the particle at this moment and, generally speaking, on the mechanism and the possible paths of energy transfer ?

M. Inghram. — I wish to reply to Professor Voevodsky's question concerning mass spectrometer studies of the kinetics of dissociation of excited molecules.

The studies most commonly made in mass spectrometers are studies of the kinetics of dissociation of excited molecular ions. One may ask the question : do the same relations apply to the kinetics of dissociation of an ion that apply to a molecule ? There is general agreement, and if anyone here disagrees I would like to know about it, that if one is working with the ground state of an ion, and if the parameters used in the equations are the frequencies and energy parameters of the ground state of that ion, then the kinetic equations should apply equally well to ions and molecules. While there is such agreement on theory there is no experimental verification of this assumption; it certainly needs to be checked experimentally.

In regard to initial excitation of the molecule ion, several methods have been used : electron impact, ion impact, and more recently, photon impact. The discussion of Morrison on threshold laws is quite pertinent to these cases. Electron impact thus leads to a range of excitation which is zero at maximum energy and increases linearly toward lower excitations. Photon impact excites all states up to the maximum equally, and ion impact, in the ideal case, leads only to a specific but unfortunately not continuously variable energy state. The three methods are related, since the third is the second derivative of the first, and the first derivative of the second.

Historically, electron impact was the first technique to be applied to kinetic problems, and it clearly indicated shortcomings of the HKRR theory as modified by Wallenstein, Wahrhaftig, Rosenstock and Eyring and others. More recently, in Chicago, Chupka and Steiner, Giese and Inghram have applied the photoionization technique to the problem. The latter authors in the paper, referred to by Voevodsky and Morrison, in *J. Chem. Phys.* **34**, 189 (1961), have concluded in essence that the theory of Wallenstein et al.. is fundamentally incorrect, i.e., that a statistical theory cannot quantitatively account for the results. We prefer the Slater approach, but, unfortunately, he specializes on the second page of his paper so that it does not apply to the zero pressure case. I should point out that a number of people do not agree with the conclusion of the Steiner et al. paper and that they are extensively modifying the theory and are getting considerably better agreement. I will, however, remain on the limb, believing that though the theory certainly qualitatively predicts the proper behavior it will never agree quantitatively with the experimental results.

The arguments for the above statement are too long and involved to be given here, and for details one must refer to the *J. Chem. Phys.* paper referred to earlier. Several points, however, can be made.

1. It is not equivalent to put energy into a molecule thermally and by photon, i.e., the temperature shift in dissociation threshold is not that which a simple statistical theory would predict.

2. Temperature shifts for different modes of decay of a single molecule are not equivalent.

3. Competition of different dissociation processes at higher energies indicates that the detailed « shape » of the molecule at the time of excitation is the determining factor.

All these results are consistent with the concept of energy flow and, in my mind, not of randomization.

Several other types of experiments are possible. Professor Giese of the University of Chicago has detected reactions of the type

$$C_2H_5I^+ + C_2H_5I \rightarrow C_4H_{10}I_2^+ \rightarrow C_2H_5I^+ + C_2H_5I$$

In this case when the initial $C_2H_5I^+$ has an energy less than 1 volt, the $C_4H_{10}I_2^+$ has a « half life » of more than 10^{-5} sec. He suggests that one could make a compound state of known energy content and study kinetics of decay of such molecules.

Finally, I would point out that in all impact studies made to date a great deal of information is being thrown away by not also studying simultaneously the electrons given off in the ionizing collision. Using photon impact such studies can be made and experiments along this line can be expected to yield more detailed data on unimolecular decay.

M. Slater. — As I have shown in « Theory of Unimolecular Reactions », any theory based on a molecule as a system of $\mathbf{n}$ classical harmonic oscillators, and giving an Arrhenius form $\mathbf{k} = \mathbf{A}\ \exp(-\mathbf{E}_o/\mathbf{T})$ of first order rate constant, must necessarily have an average specific rate of the form :

$$\mathbf{k_E} = \mathbf{A}\,\frac{(\mathbf{E} - \mathbf{E}_o)^{n-1}}{\mathbf{E}}$$

for the decomposition of molecules of energy **E**. Similarly an Arrhenius form of rate for any molecular model of harmonic quantum oscillators implies a $\mathbf{k_E}$ of Kassel's quantum form, although it also implies (with a limitation mentioned in my book) that the oscillators are degenerate (as in Kassel's form). What is needed is a more general quantum form of $\mathbf{k_E}$, since the classical form is fairly certainly an inadequate approximation. It is not certain, however, that $\mathbf{k_E}$ is always a relevant quantity for reactions of specifically excited molecules, since the initial « state » of the molecule after excitation may be specially favourable (or unfavourable) to early dissociation, and $\mathbf{k_E}$ may therefore be too broad an average. The parameter «**n**» on the other hand is the number of « oscillators » or degrees of freedom which are effectively related to the reaction coordinate. Even if we allow moderately free internal energy transfer, **n** may often be less than the total number of internal degrees of freedom; this would be expected if, for example, the reaction coordinate were a bond between heavy atoms, and the molecule also contained considerable hydrogen.

M. Rice. — When a molecule absorbs a photon in the visible or ultra-violet, it is generally excited to a higher electronic state. At the same time, as is seen from the operation of the Franck-Condon principle, it may be expected that vibrational energy will also be excited. If this vibrational energy is sufficient, the molecule may be capable of dissociation in the new electronic state by the same mechanism that unimolecular reactions ordinarily take place, namely, by eventual accumulation of sufficient energy in the bond which breacks. This is undoubtedly the mechanism of photodecomposition of many complex molecules (see Rice, *Proc. Nat. Acad. Sci.*, **15**, 459 (1929)). At sufficiently high pressures deactivation by collision may take place, as with azoethane (see Cerfontain and Kutschke, *Can. J. Chem.* **36**, 344 (1958)).

A similar mechanism for the decomposition of fragments formed in the mass spectrograph may also be expected. An ion formed by electron bombardment will be likely to have acquired at the same time enough vibrational energy to enable it to decompose. Calculations on processes in the mass spectrometer, on essentially this basis, using the quantitative formulation of unimolecular reaction rate theory of Marcus and Rice, have been made recently (e.g., Wolfsberg, *J. Chem. Phys.*, **36**, 1072 (1962)). The calculations are similar to those on excited molecules made by Rabinovitch and coworkers.

M. Osberghaus. — Information on energy transfer from low energy electrons to molecules has been gained from mass spcetroscopy mainly. Some recent measurements (H. Ehrhardt and U. Erbse (1963), *Z. Physik*, **172**, 210) of the inelastic scattering of electrons in the energy range from 30 to 200 eV by n-Heptane have bearing on the validity of the assumption made by the statistical theory of mass spectra and the role played by states of the neutral molecule with an excitation energy far above the ionization level. For n-Heptane the findings are : The distribution function of the energy transferred covers a wide range, of the order of 100 eV for 200 V-electrons. Only a small part of this energy shows up as kinetic energy of the electrons ejected from the molecule. The probability of transferring energy below or slightly above the ionization limit is small. On the other hand it is known experimentally that in the case of saturated hydrocarbons the cross sections for causing neutral decays (the excited molecule producing only neutral fragments) and ionic decays (one of the fragments is ionized) are about equal. It follows that not only ionic decays but neutral decays also happen via states that are to a large extent far above the ionization limit.

M. Morrison. — I should like to refer to some recent work by the Liège school which has been communicated to me by Professor D'Or.

This work is concerned with two aspects of energy transfer in gases, namely (1) energy transfer from an electron or photon to an atom or molecule, and (2) internal transfer of energy within a molecule.

Lorquet has attempted to interprete the mass spectra of some polyatomic molecules, by assuming that they possess well-defined

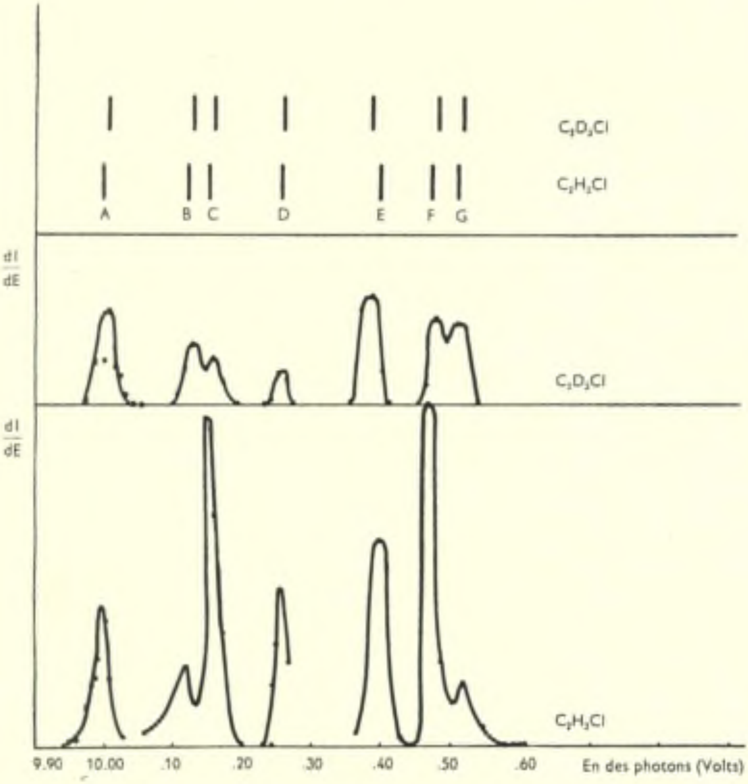

Fig. 1.

Fig. 2.

and non-interacting electronic states, and in terms of the population of the different vibronic levels of the ion after transition has taken place. For some relatively simple systems at least, this approach is reasonably successful.

An experimental study of the rate of decomposition of some polyatomic « metastable » ions by Momigny has suggested that some of these can decompose by two mechanisms each of which has a specific rate constant. These mechanisms are distinguished by possessing different energy thresholds. The rate constants appear to decrease with increase in electron energy. This has been interpreted by assuming that « metastable » transitions are due mainly to predissociation phenomena in the ionized molecule.

Both of these studies therefore show that many molecule-ions possess a series of well-defined electronic states, in contradiction to one of the basic assumption of the quasi-equilibrium theory of mass spectra.

A photoionization study of C_2H_3Cl and C_2D_3Cl by Momigny has shown a wealth of structure (see figures 1 and 2) to be present in the ionization curves, and this has been interpreted in terms of electronic and vibrational levels of the ions.

An attempt has been made by Lorquet to calculate by quantum mechanical methods the way in which electronic excitation may diffuse along a polymer chain, iso-polybutadiene, causing cis-trans isomerization. The results are in qualitative agreement with experiment.

A study of cis-trans isomers of cyclane derivatives by Natalis, shows that in each case, the cis-isomer, with the higher internal energy, is the less stable in the ionized state. The difference in threshold energies for the main fragment ions is of the same order of magnitude as the difference in the internal energy.

The stability difference between the ions given by the two isomeric forms of a given molecule seems therefore to be due to the release of potential energy when the ring of the ionized molecule is broken, and its conversion into vibrational energy.

ON THE MECHANISM OF VIBRATIONAL ENERGY RELAXATION

by Prof. **V.N. KONDRATIEV**

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The conversion and exchange of vibrational energy in molecular collisions are of great importance for the relaxation processes in gases. Yet this problem is far from being completely elucidated. Some results of theoretical investigations in this field were reported here in the papers presented by Wigner, Rice and Prigogine. Among earlier investigations in this field I would mention, first of all, the paper by Laidler and Shuler.(6) I shall discuss here certain experimental results, mainly in order to formulate questions that have received yet no appropriate answer.

It is known from experiment and theory (i) that *one* vibrational quantum may undergo relatively ready conversion into translational energy, especially so at high temperature : $AB^*(v = 1) + M = AB$ $(v = 0) + M$. The conversion of a vibrational quantum into another: $AB^*(v = 1) + CD\,(v = 0) = AB\,(v = 0) + CD^*(v = 1)$ occurs easily too, as well as conversion into the energy of spin-orbital coupling, as far as it follows from processes (ii) of the type $Hg'(^3P_1) + N_2(v = 0) = Hg'(^3P_0) + N_2{}^*(v = 1)$. All these processes may be considered as transitions from one potential energy surface to another in a region of intersection or close approach.

However, the processes taking place in the conversion of larger amounts of vibrational energy into translational, vibrational, or electronic energy are not sufficently studied. One of the possible obvious approaches to the understanding of the nature of these processes would be their comparison with well studied processes of energy conversion in a single molecule. Such would be, for example,

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(i) See (5), §. 21.

(ii) The asterisk denotes vibrational, and the prime electronic excitation.

the pre-dissociation of a molecule, which might be taken as a model for the conversion of vibrational into translational energy (via the electronic state) occuring by collision of a vibrationally excited molecule AB^* with a particle M. The latter process may be interpreted as a decomposition of the $(AB \cdot M)^*$ complex (which is similar to the pre-dissociating molecule) into fast AB and M particles.

Another process occuring in a single molecule is the spontaneous transition of an energized molecule (AB^*) to an active state ($AB^{\neq}$) during a unimolecular decomposition. The vibrational energy distributed among many degrees of freedom is then concentrated at the bonds being broken, which results in unimolecular decomposition : $AB^* \rightarrow AB^{\neq} \rightarrow A + B$. By analogy with the process $AB^* \rightarrow AB^{\neq}$ the exchange of vibrational energy in the collision of two molecules, $AB^* + CD = AB + CD^*$, may be considered as redistribution of vibrational energy in the complex $(AB \cdot CD)^*$ similar to the transition complex $AB^{\neq}$.

The energy of electronic excitation may also take part in the conversion of vibrational energy in the molecular complex. An analogue of this process occuring in a single molecule would be internal predissociation (3), i.e. spontaneous transition of the molecule from one stable electronic state to another, also stable. Sharp energy resonance is one of the obvious requiremements for such transitions.

The interconversion of vibrational and electronic energy in molecular collisions is most obvious in the quenching of atomic fluorescence. The quenching of fluorescence by two and multi-atomic molecules is often interpreted as conversion of electronic into vibrational energy.(7) This should apparently be considered as an experimental fact. Indeed, while, for example, quenching of the sodium D-fluorescence by hydrogen might be interpreted as a chemical process : $Na' + H_2 = NaH + H$ (—7.7 kcal/mole), the quenching of D-fluorescence by nitrogen (8) occuring with a still greater cross-section cannot be interpreted otherwise than by conversion of electronic into vibrational energy : $Na' + N_2 = Na + N_2^*$. (i)

(i) Suggestions have sometimes been made concerning the great importance of resonance between the electronic and vibrational energies in the fluorescence quenching. However, it must be said that resonance seems to play a secondary role here. A convincing argument against these suggestions would be the experiments on the quenching of the resonance fluorescence of thallium by hydrogen. Notwithstanding a sharp resonance

$$\mathrm{Tl}' \, (7s\,{}^2S_{1/2} - 6p\,{}^2P_{1/2}) - H_2^*(v = 8) = -0.034 \text{ ev}$$

there is practically no quenching (10).

The transfer of electronic energy in collisions between atoms and molecules occurs rather readily. This may be seen, for example, from sensitized fluorecence. Consequently, it would seem justified to connect certain cases of dissociation in collisions between electronically excited atoms and molecules with the transfer of electronic excitation. For example,

$$Xe' + H_2\,(^1\Sigma_g^+) = Xe\,(^1S) + H_2\,(^3\Sigma_u^+) \rightarrow 2H.$$

The conversion of vibrational energy in a molecular complex seems to proceed as the transition of the system from one potential surface to another. The rate of this process will naturally depend on the interaction forces between the particles in the complex, on the initial energies of the particles, and on the lifetime of the complex.

Chemical interaction, in particular that observed in exchange reactions, is one of the types of strongest interaction in collisions. Indeed, the ready conversion and exchange of vibrational energy is characteristic of these reactions. Some of the many available examples are :

$H_2 + J_2 = 2HJ + 2.2$ kcal/mole, $E = 40$ kcal/mole,
$OH + H_2 = H_2O + H + 14.8$ kcal/mole, $E = 10$ kcal/mole,
$H + O_3 = HO + O_2 + 76.7$ kcal/mole, $E = 5$ kcal/mole.

Chemical interaction undoubtedly plays an important role also in physical processes of exchange and conversion of energy. This was first suggested by Frank and Eucken (2) for the interconversion of vibrational quanta and translational energies of colliding molecules. It may be assumed that, to the same or even to a greater extent, the above is true for processes connected with conversion of large portions of internal energy in molecular collisions. Unfortunately experimental data that could have been used for substantiating this suggestion are scarce and not very reliable. Evidence was obtained recently in mass spectrometric investigations, made by Phillips and Schiff (9), that vibrationally excited N_2 molecules formed in the process $N + NO = N_2 + O + 75$ kcal/mole are capable of splitting ozone molecules. The rate constant of the process $N_2^* + O_3 = N_2 + O_2 + O$ was found to be 5.4×10^{-13} cm^3 molecule^{-1}sec^{-1}, which is by only a factor of one thousand lower than the kinetic collision rate. The rather high rate of this process may be due to chemical interaction between N_2^* and O_3 and to the consequent easy conversion of the

N_2^* vibrational energy in the intermediate $(N_2 \cdot O_3)^*$ complex formed in the reaction :

$$N_2^* + O_3 = (N_2 \cdot O_3)^* = N_2 + O_2 + O$$

It will be of interest to note that vibrationally excited O_2 molecules formed in the process $O + O_3 = 2\,O_2 + 93$ kcal/mole are not capable of splitting ozone (1), as does the N_2^* molecule. The absence or the negligibly low probability of the process $O_2^* + O_3 = O_2 + O_2 + O$ seems to be accounted for by weak interaction between O_2 and O_3 (non-existence of O_5 contrary to N_2O_3).

However, this chemical criterion for the rate of conversion of vibrational energy in molecular collisions does not seem to be decisive in every case. For instance, the ready conversion of the electronic excitation energy of sodium atoms into vibrational energy of nitrogen molecules (and also of CO, CO_2, etc) would scarcely be due to chemical interaction between particles in the $(Na \cdot N_2)$ complex. There is also no reason for suggesting the importance of chemical interaction between particles in the $(NaCl \cdot N_2)^*$ complex, apparently involved in the mechanism of chemiluminescence quenching in the highly rarefied flame of $Na + Cl_2$ (or $HgCl_2$).(4)

Thus, even if the mechanism of conversion and exchange of vibrational energy might be considered as essentially elucidated, the quantitative aspect of the problem, in particular the rates of the processes and the factors determining these rates, remains almost completely unsettled.

Among the problems that should be subjected to further explicit theoretical and experimental investigations I would mention the following :

1. What are the factors accounting for the formation of a molecular complex and its stability ?

2. Should a distinction be made between addition and exchange reactions when the chemical interaction is of importance in the complex formation ?

3. What is the correct quantitative measure for chemical interaction (Q, E, or other) ?

4. What are the possibilities opened by approximate calculation of complexes at various degrees of excitation ?

5. What is the rate of energy distribution in a complex ?

6. What is the rate of energy distribution among products of decomposition of the complex ?

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Discussion de la communication de M. Kondratiev

M. Norrish. — I am happy that Professor Kondratiev has presented a contribution which is so closely concerned with the matter I have raised in my paper. I would like to refer to two points which he has emphasized. First, in relation to the deactivation of excited mercury and sodium atoms, I do not feel that we can regard the deactivation of sodium atoms, which involves an energy switch of 2.09 eV., as being one which can be accounted for by near resonance in the vibrations of the deactivating species. The data which I have presented in my paper show the enormous difference between saturated and corresponding unsaturated hydrocarbons. This in itself points to the formation of a complex between sodium and the deactivating molecule. The general idea has been put before us by Dr. Linnett. His postulation of a complex involving electron transfer may well account for the facts. As to the ultimate fate of the energy which is released, it would appear as translational, rotational and vibrational energy in the products. The amounts involved in particular degrees of freedom cannot at present be predicted. The contrast of mercury with sodium which I have endeavoured to make in my contribution is quite marked. The small change from Hg 6^3P_1 to Hg 6^3P_0, which is the order of 0.218 eV., is a magnitude which can readily be taken up by vibrational modes as has been pointed out by Zemansky. If I have misrepresented Professor Kondratiev, I hope he will forgive me.

I am not able to agree with Professor Kondratiev's contribution in relation to the decomposition of ozone. I would briefly like to recapitulate the facts. They may be described as follows.

In the red part of the spectrum, ozone is photolyzed to give 0^3P atoms; in the ultraviolet, the photolysis results in O^1D atoms. As far as I understand it, this point is not contested by my Russian friends. The secondary reactions which can follow these primary processes are

$$O^3P + O_3 = O_2 + O_2 \qquad + 93 \text{ Kcal.} \qquad (1)$$

$$O^1D + O_3 = O_2 + O_2 \qquad + 138 \text{ Kcal.} \qquad (2)$$

The energy appears at least in part in vibration in the oxygen molecule and so one may write O_2^*. In the ultraviolet, this O_2^* is sufficiently energised to propagate further reactions :

$$O_2^* + O_3 = O_2 + O_2 + O^1D \qquad - \ 69 \text{ Kcal.} \qquad (3)$$

The reaction

$$O_3 = O_2 + O^1D \qquad - \ 69 \text{ Kcal.} \qquad (4)$$

requires 69 Kcal. and if the output of reaction (2) can be made available, the chain can be propagated. The evidence is that this is so, since, the output of reaction (2) appears in vibration with up to 17 quanta in the ground state and then rapidly fades; molecules with more than 17 quanta are not seen because they react. The correspondence between 17 quanta and the energetics of reaction (4) is striking.

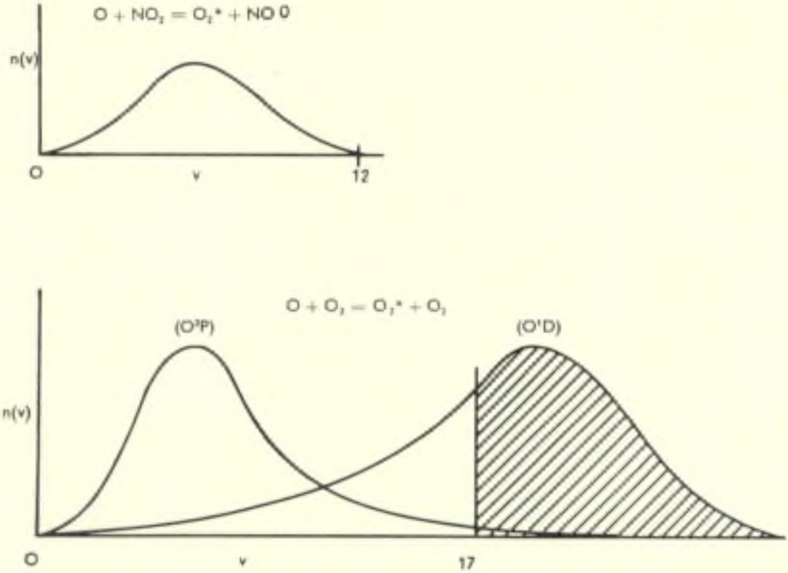
We may ask ourselves why reaction (1) is not a propagating reaction since 93 Kcal., which is in excess of that required, are liberated. In this connection let us first direct our attention to the analogy

$$NO_2 + h\nu = NO + O \qquad - \ 73 \text{ Kcal.} \qquad (5)$$

$$O + NO_2 = NO + O_2 \qquad + \ 46 \text{ Kcal.} \qquad (6)$$

Here we find a distribution in the vibrational levels of O_2 extending over the whole range of the energy evolution. We may therefore assume the same to be true for ozone but in the case of reactions (5) and (6), there will be a distribution in the vibrational levels up to the maximum of the energy of the exothermic reactions. Thus for O^3P there will be a potential distribution from zero to 93 Kcal.; for O^1D, a distribution from zero to 138 Kcal. The appropriate curves are shown in the accompanying figure. I would therefore submit that this idea gives a complete picture of the reaction and *if* argument is to be drawn by analogy, *my* analogy with the reaction of NO_2 in favour of vibrating O_2 molecules being the effect ivechain carrier is a closer one than suggested by Professor Semenov in favour of electronically excited O_2 by analogy with Hg 6^3P_1. In conclusion, I would still ask him by what evidence in view of the facts he would prefer electronic rather than vibrational excitation of O_2 in the O_3 decomposition.

It cannot be denied that the ${}^3\Sigma_u^- \ O_2$ molecule is excited to the order of 70 Kcal. and thus on energetic grounds it is possible to consider it as a chain carrier. Even if the energy of the electronically



Schematic representation of the vibrational distribution in molecular oxygen [$n(v)$] resulting from the spreading over the whole of the exothermicity of the reaction. — (shaded area represents zone of reaction.)

excited O_2 can be internally converted to vibrational energy in the ground state, it is not easy to see how the sharp division between relaxation and reaction occurs at $v = 17$. Professor Semenov's argument on the basis of chain length does appear to carry serious weight from the view-point of the mechanism of chain propagation. In particular, I would emphasize that the shortness of the O_3 chains can be described in terms of the strong reverse reaction

$$O + O_2 + M = O_3 + M \tag{7}$$

which must be fully considered in any discussion relating to the probability of chain propagation.

In answer to Professor Kondratiev's communication, I have presented the evidence for the molecular chain carrier in the decomposition of osone as highly vibrationally excited molecules. There are, as I have explained, analogous systems with which this can be compared. However, the argument is by no means based solely on analogy; in fact the observed cut off at $v = 17$ corresponding to the energy required for the fission of O_3 has been emphasised. The *direct* evidence supports vibrational rather than electronic excitation in the oxygen molecule.

M. Kondratiev. — Prof. Norrish believes that the absence of the chain reaction

$$O(^3P) + O_3 = O_2^* + O_2, \quad O_2^* + O_3 = O_2 + O_2 + O$$

is due to the fact that the energy of O_2^* is insufficient for the second of these processes to occur. However, this is scarcely the case, since a similar reaction

$$N + NO = N_2^* + O$$

liberating by 18 Kcal/mole less energy than reaction

$$O(^3P) + O_3 = O_2 + O_2$$

yields N_2^* molecules that seem to be capable of splitting ozone

$$N_2^* + O_3 = N_2 + O_2 + O$$

Isn't it evidence in favour of readier energy exchange in the $N_2 \cdot O_3$ complex, compared with $O_2 \cdot O_3$?

M. Norrish. — Professor Kondratiev's consideration of the reaction

$$N + NO = N_2^* + O$$

and subsequent reactions with ozone lead me to make a few remarks. Dr. Thrush and Dr. Clyne in my laboratory, have measured the rate of the above reaction and have shown it to be very fast. They conclude that the spin conservation rules will hold. Arguing on energetic grounds, the N_2 will be formed in the ground state so that the oxygen atoms will be in the ^3P state. The reaction of O^3P with ozone is known to be fast from the flash photolysis experiments so that at least one half of the ozone decomposed could be accounted for in this way. It must be pointed out that Professor Kondratiev has only considered vibrationally excited oxygen formed by the reaction of O^3P with ozone. We have shown, in fact, that we are concerned with O^1D in chain propagation which is capable of giving rise to vibrationally excited oxygen potentially to the limit of dissociation. I would specifically refer to the diagram which I have appended to my previous remarks. If vibrationally excited nitrogen in its ground state can give rise to the fission of ozone, which Professor Kondratiev attributes to a relatively strong intermediate of N_2 and O_3, from the viewpoint of the overall reaction, this would seem to be analogous to the decomposition by vibrationally excited oxygen. In the last analysis relating to the reaction

$$N + NO = N_2^* + O$$

resort must be made to experiment and personally I do not feel sure that the last words have been said. I hope I have shown that the experimental observations are in favour of vibrationally excited oxygen as the molecular chain carrier in the decomposition of ozone.

M. Voevodsky. — The discussion between Prof. Norrish and Prof. Semenov on the ozone decomposition mechanism results from different approaches to experimental data obtained by Norrish on the distribution of excited oxygen over different vibrational energy levels. The suggestions of Prof. Semenov, discussed in detail in his paper, are based on Prof. Laidler's theoretical calculation. Prof. Norrish has communicated some new experimental results that can be regarded, however, only as an indirect proof of his standpoint.

I would say that from a general point of view Semenov's hypothesis postulating electronically excited molecules as chain carriers seems to be more plausible. It must be emphasized, however, that at present there is no direct evidence that would make it possible to prove or discard either scheme proposed.

M. Widom. — Would Professor Kondratiev give us more detail about the case he mentioned in his paper of the failure of H_2 to de-excite Tl in spite of sharp resonance ? What states of the Tl atom are involved ?

M. Kondratiev. — In mentioning the quenching of thallium fluorescence I meant the work of Prilezhayeva, where it was shown that hydrogen will not quench the resonance fluorescence of thallium even at pressures as high as $P_{H_2} = 1$ *atm*, in spite of the sharp energy resonance (the difference in the vibrational energy of the H_2 molecule occupying the $v = 8$ level and the electron excitation energy of a thallium atom is only 0.034 eV). I believe that this fact may be considered as a convincing argument against the concept of the importance of energy resonance in fluorescence quenching.

M. Gaydon. — Prof. Norrish has expressed doubt about the conversion of electronic into vibrational energy when excited Na is quenched by N_2. Experimental evidence for this type of conversion is provided by recent work of Dr. I. Hurle at Cornell; he finds that when shock-heated nitrogen is expanded through a nozzle to low pressure and temperature the reversal temperature remains high (2300 °K) because it follows the frozen vibrational temperature of N_2. I am, however, in agreement with Prof. Norrish in realizing the importance of chemical affinity on the probability of interconversion of energy; the radiationless transition will depend on the crossing of potential energy surfaces and this is more likely to occur if there is strong interaction between the colliding species. The proportion of energy converted from the electronic form into vibration and into translation will depend on the crossing point of the potential energy surfaces. At high temperature the potential surfaces will be modified by the addition of rotational energy, and exact resonance of a particular vibrational energy level with the electronic energy level will not be required.

M. Osberghaus. — There are recent measurements on the quenching of sodium fluorescence by N_2 and He [W. Demtröder (1962), *Z. Physik* 166, 42]. The measurements are made by observing the decrease in lifetime of the excited state. This method avoids some of the difficulties connected with line shapes that arise with the older method for weakly quenching gases. Whereas the quenching cross section for N_2 agrees very well with the earlier measurements — especially with the value given by Prof. Norrish — a cross section for He is found which is surprisingly large ($\pi R^2 = 0{,}34 \cdot 10^{-16}\,\mathrm{cm}^2$). It has about the value measured by Prof. Norrish for CH_4.

M. Karplus. — Where does the energy go?

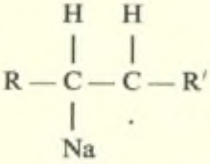
M. Linnett. — If, for small intermolecular distances, the potential energy surfaces for the initial and final states come near one another, transfer will be facilitated. This may result also in a transfer to vibrational energy if, at the configuration of close approach, the bond length of the molecule for minimum energy is different for the two states, the reason being then analogous to that embodied in the Franck-Condon Principle.

It seems to me that the interaction of sodium or thallium with H_2 will not be expected to involve the electron transfer forces that may come into play for sodium and N_2; (see Laidler and earlier discussion).

This difference may be due to the fact that in N_2 there is a multiple bond. This would fit in with the data presented by Professor Norrish.

M. Ross. — I would like to inquire if the quenching of electronically excited sodium requires an activation energy; in other words, are the repulsive forces of the system of importance?

M. de Boer. — Referring to the intermediate formation of a « complex », I want to draw the attention to the enormous difference in quenching efficiency between olefins and paraffins, as found by Prof. Norrish. It might be possible for a sodium atom, or an excited sodium atom to form a metastable (endothermic) addition product with an olefine, such that — temporarily — a radical is formed of a constitution



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ R & - & C & - & C & - & R' \\ & & | & & \cdot & & \\ & & Na & & & & \end{array}$$

such as is given by Br atoms who indeed form such metastable components.

Also might be envisaged that Na (excited) gives a similar compound with N_2 molecules. Such a metastable compound might offer an explanation for the still unexplained « promotion » effect of sodium in the ammonia catalysis reaction.

M. Norrish. — The striking difference between the quenching of the sodium fluorescence by saturated and unsaturated hydrocarbons has been stressed in my earlier comment on Professor Kondratiev's communication. In this case resonance with vibrational levels does not appear to be a suitable explanation and the formation of a complex is clearly favoured. This is to be compared with the case of Hg 6^3P_1 to Hg 6^3P_0 where the energy difference is of a magnitude corresponding to a few vibrational quanta. In terms of the energy involved, the quenching of excited thallium atoms by hydrogen is comparable with that of the sodium fluorescence quenching previously considered. It is, therefore, not surprising that the quenching is small even under the conditions of near resonance. Assuming that a particular electronic excitation energy of an atom were less than the dissociation energy of a given diatomic molecule, a vibrational level could always be found in the region of near resonance. If energy matching were the sole condition for quenching, any diatomic molecule satisfying the above condition should deactivate any excited atom efficiently, particularly where near resonance corresponded to a high vibrational level where the energy difference between levels would be small and the probability of obtaining close matching high.

M. Ross. — Does not the concept of a collision complex imply an effective coupling of at leat some of the vibrational degrees of freedom with the relative translational motion of the colliding particles?

M. Oosterhoff. — I feel more and more confused about the meaning of the word « complex ». Prof. Porter, talking about iodine atom recombination, used the word — I think — to indicate a classical chemical complex between the iodine atom and a third body, stabilized by collision with another « third » body. Prof. Wigner pointed out that a hollow in the potential curve for two approaching particles would result in an acceleration which would make such a hollow unfavourable for complex formation.

In Prof. Mayer's remark on the lifetime of a complex formed in a radical recombination reaction, was pointed out the importance of the many degrees of freedom in which the energy could escape for some time, which would make the lifetime sufficiently long.

There were many other remarks about complexes which, interesting and illuminating as they were, still did not give an unequivocal meaning to this word. I would be very happy if somebody could give a practical definition which we could use in the future.

M. Voevodsky. — In what concerns the problem of complex formation in different cases of energy transfer and in different chemical elementary acts it would perhaps be useful to define the notion of the complex lifetime in the following sense. If a pair (or a greater number) of particles hold together (due to any possible kind of forces) for a time (θ) that is greater than the time needed for an elementary process (τ) then one may say that a complex has been formed. If the reverse is true, we may say that a collision took place. Thus, depending upon the process investigated the same species formed in a collision may be regardered as a complex (for processes for which $\tau > \theta$) or es a collision ($\tau < \theta$).

M. Ross. — Measurements of the differential chemical reaction cross section of the reaction of alkyl halides and alkali metals (Hershbach and co-workers) show a strong asymmetry in the angular dependance in the cross section. The occurrence of such an asymmetry requires that the collision time is short compared to the time of rotation of the collison complex.

M. Linnett. — When no electron transfer occurs the forces involved are of the dispersion kind. If there is electron transfer, as has been suggested in the Na/N_2 collision, then the forces are of the kind encountered in chemistry and one is more tempted in such an event to speak of a complex.

M. Karplus. — What is a « complex » in the sense in which we use this word when we discuss the electronic de-excitation

$$Na' + N_2 \rightarrow Na + N_2.$$

It seems to me that a « complex » is an atomic configuration in which all the interatomic distances are small and which exists for several periods of some characteristic frequency of interacting molecules. In one case, the frequency to be considered is the vibration frequency of N_2. The fact that N_2 becomes vibrationally excited can be interpreted in terms of a quasi-stationary ($Na'N_2$) in which the N-N potential is substantially disturbed. As the Na recedes, the N_2 system will be left in a superposition of vibrational states.

REMARKS ON SCATTERING THEORY

by **I. PRIGOGINE**

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I. INTRODUCTION

The beautiful report presented by Prof. Wigner has emphasized the fundamental importance of scattering processes. This encourages me to summarize some recent results obtained by our group.(1) I want to stress immediately the fact that the examples I shall indicate have nothing to do with chemical reactions proper. They can only be considered as typifying the kind of difficulties which will have to be overcome by any theory of chemical reactions starting from first principles.

An interesting application of the methods I shall outline, to the dissociation of homonuclear diatomic molecules, has been published by J. Light.(2) We shall however not discuss it here.

We shall first outline the general method we have developed and then consider three characteristic examples, involving transfer of energy from translational degrees of freedom to other translational degrees of freedom or from translation to radiation.

II. GENERAL METHOD

As an introduction to the general N-body problem let us consider briefly the scattering theory in classical mechanics.(1, 3, 4)

Our starting point is the Liouville equation for the density function in phase space $\rho(\mathbf{x}, \mathbf{v}, t)$

$$\frac{\partial \rho}{\partial t} = [\mathrm{H}, \rho] . \qquad (2.1.)$$

This equation may also be written

$$i\frac{\partial \rho}{\partial t} = \mathrm{L}\rho\,. \tag{2.2}$$

L, called the Liouville operator, is a hermitian operator in phase space.

To a decomposition of the Hamiltonian (λ is a coupling constant measuring to " strength " of V)

$$\mathrm{H} = \mathrm{H}_o + \lambda \mathrm{V}\,, \tag{2.3}$$

corresponds a similar decomposition of L into

$$\mathrm{L} = \mathrm{L}_o + \lambda\delta\mathrm{L}\,. \tag{2.4}$$

In the scattering problem (*)

$$\mathrm{H}_o = \frac{v^2}{2}, \qquad \mathrm{V} = \mathrm{V}(\mathbf{x}) \tag{2.5}$$

and therefore

$$\mathrm{L}_o = i\mathbf{v}\cdot\frac{\partial}{\partial \mathbf{x}}, \qquad \delta\mathrm{L} = i\frac{\partial \mathrm{V}}{\partial \mathbf{x}}\cdot\frac{\partial}{\partial \mathbf{v}}\,. \tag{2.6}$$

We now expand ρ in the eigenfunctions of the unperturbed Liouville operator L_o (these eigenfunctions are plane waves)

$$\rho = \left(\frac{2\,\pi}{\mathrm{L}}\right)^3 \sum_{\mathbf{k}} \rho_{\mathbf{k}}(\mathbf{v}, t)\, e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{v}t)} \tag{2.7}$$

and substitute back into (2.2). We then obtain the set of equations

$$\frac{\partial \rho_{\mathbf{k}}}{\partial t} = \lambda\left(\frac{2\,\pi}{\mathrm{L}}\right)^3 \sum_{\mathbf{l}} e^{i\mathbf{k}\cdot\mathbf{v}t}\ \mathrm{V}_{\mathbf{l}}\, i\mathbf{l}\cdot\frac{\partial}{\partial \mathbf{v}}\, e^{-i(\mathbf{k}-\mathbf{l})\cdot\mathbf{v}t}\, \rho_{\mathbf{k}-\mathbf{l}} \tag{2.8}$$

In a scattering problem we are essentially interested in the time change of $\rho_o(\mathbf{v}, t)$ which describes the velocity distribution of the particles in the beam.

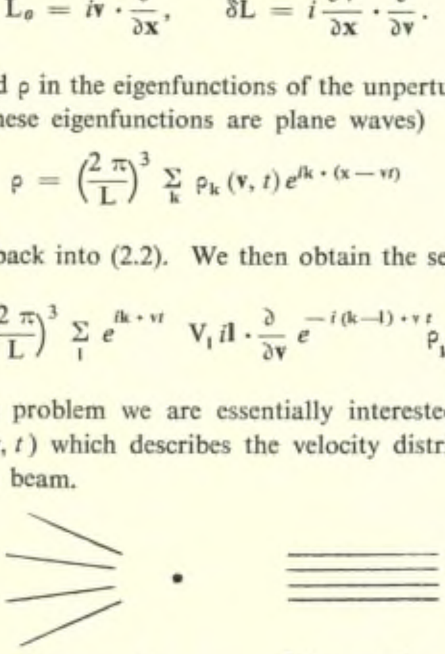

Fig. 2.1.

(*) We shall generally take the mass of the particles equal to one.

For times long with respect to the duration of the collision the following equations can be shown to hold :

$$\rho_0(t) = \rho_0(0) + \frac{t}{L^3} \int d\mathbf{x} \frac{\partial V}{\partial \mathbf{x}} \cdot \frac{\partial}{\partial \mathbf{v}} f(\mathbf{x}, \mathbf{v}) . \tag{2.9}$$

Here the second term corresponds to the effect of the scattering; $f(\mathbf{x}, \mathbf{v})$ is the time independent solution of the Liouville equation with the boundary condition that the incident flow is given by $\rho_0 (\mathbf{v}, t = 0)$. It satisfies the integral equation

$$f(\mathbf{x}, \mathbf{v}) = \rho_0(\mathbf{v}, t = 0) + \lambda \int d\mathbf{x}' \, G(\mathbf{x} - \mathbf{x}'; \mathbf{v}) \frac{\partial V}{\partial \mathbf{x}'} \cdot \frac{\partial}{\partial \mathbf{v}} f(\mathbf{x}', \mathbf{v}). \tag{2.10}$$

Here the function $G(\mathbf{x} - \mathbf{x}'; \mathbf{v})$ may be called the " free-particle propagator " by analogy with the terminology of quantum theory. The equation (2.10) plays here the same role as the Schwinger-Lippman equation in the quantum theory of scattering (see the report by Wigner at this conference).

Let us now go to the general N-body problem (in classical mechanics). Instead of (2.5) we take the sum of binary interactions

$$V = \sum_{j > n} V_{jn} \tag{2.11}$$

and (2.8) now becomes (*)

$$\frac{\partial \rho_{\{k\}}}{\partial t} = \lambda \left(\frac{2\pi}{L}\right)^3 \sum_{j > n} \sum_{\mathbf{l}} e^{i(\mathbf{k}_j \cdot \mathbf{v}_j + \mathbf{k}_n \cdot \mathbf{v}_n) t} \, V_{\mathbf{l}} \, i\mathbf{l} \cdot \left(\frac{\partial}{\partial \mathbf{v}_j} - \frac{\partial}{\partial \mathbf{v}_n}\right)$$

$$e^{-i[(\mathbf{k}_j - \mathbf{l}) \cdot \mathbf{v}_j + (\mathbf{k}_n + \mathbf{l}) \cdot \mathbf{v}_n] t} \, \rho_{\mathbf{k}_j - \mathbf{l}, \mathbf{k}_n + \mathbf{l}, \{k'\}} . \tag{2.12}$$

As indicated by (2.12) we have two " selection " rules for the change of $\rho_{\{k\}}$ through interactions :

a) only two wave vectors **k** are changed through an elementary interaction (this is a direct consequence of the assumption of the binary forces);

b) the sum of the wave vectors is conserved.

(*) $\{ \mathbf{k} \}$ means a whole set of wave vectors.

The set of equations (2.12) express the occurrence of " transitions " between the Fourier coefficients $\rho_{\{k\}}$. Now these Fourier coefficients have a simple meaning: we have seen that $\rho_{\{0\}}$ is the velocity distribution, similarly the Fourier coefficients $\rho_{k,-k}$ (two non vanishing wave vectors) are the Fourier transform of the binary correlation function and so on.

We may therefore say that (2.12) describes the transitions from one kind of correlations to another, or in other words a " *dynamics of correlation* ".

The Fourier coefficient ρ_0 plays a special role in the sense that it carries no information whatsoever about space inhomogeneities or correlations.

We shall use a diagram technique which stresses the difference between ρ_0 and the other Fourier coefficients. We shall draw a line for a " state " corresponding to a *non-vanishing* wave vector. For example $\rho_{k,-k}$ will be represented by two lines. On the other hand each interaction will be represented by a vertex.

Taking account of the two selection rules we have mentioned, we obtain the following six basic diagrams which describe the " elementary processes " of our dynamics of correlations (all diagrams have to be read from right to left).

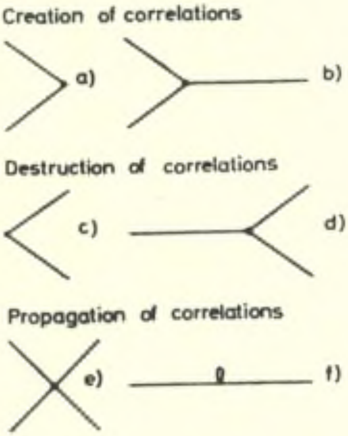

Fig. 2.2.

For example in diagram (*c*) two particles j and n corresponding to vanishing values of the wave vector interact and form a binary correlation ($\mathbf{k}_j + \mathbf{k}_n = 0$, see Fig. 2.3).

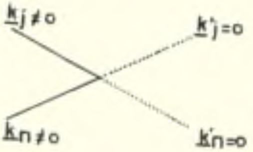

Fig. 2.3.

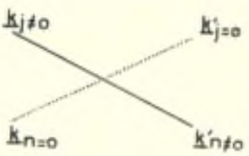

Fig. 2.4.

In diagram (*f*) we have what may be called an " exchange of correlation " between particles j and n. This process is represented in greater detail in Figure 2.4. One may perhaps say that in this diagram representation any homogeneous situation plays somewhat the role of the ground state or the vacuum in quantum field theory while inhomogeneities or correlations appear in a fashion similar to elementary excitations.

The iteration solution of equation (2.12) is built up by diagrams involving an arbitrary number of elementary processes of Figure 2.2. A specially important role is played by connected diagrams relating ρ_o to ρ_o (see Fig. 2.5 for an example).

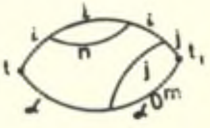

Fig. 2.5.

Such diagrams relate the velocity distribution at time t_1 to the velocity distribution at time t.

The method we have summarized leads to the derivation of a general " master equation " for the evolution of the velocity distribution, valid to all powers of the coupling constant or the concentration. This equation is of the form (1, 5)

$$\frac{\partial \rho_o(t)}{\partial t} = \int_o^t \mathrm{G}\,(t - t_1)\, \rho_o(t_1)\, dt_1 \,. \tag{2.13}$$

Here G $(t - t_1)$ is a collision operator corresponding to a general diagonal fragment of the form represented in Fig. 2.5. This collision operator includes both multiple scattering and effects related to the finite duration of the collision (" non-markoffian " effects) which can in general not be neglected.

We want to stress that all this theory can be developped both in classical or in quantum mechanical terms.(1, 6) In fact our second example will refer to a quantum mechanical situation. There is then a very interesting relation with S-matrix theory which is described in detail in a forthcoming paper by Résibois.(7)

II. TRANSPORT EQUATION OF A PLASMA

As the first example I want to consider the transport equation of a plasma as first derived by Balescu.(8, 9) In a weakly coupled gas (the coupling constant λ is small) the only diagonal fragment one has to consider is that of Figure 3.1.

Fig. 3.1.

It gives a cross-section proportional to λ^2 and represents the Born approximation. The corresponding transport equation is the usual Fokker-Planck equation. To obtain the Boltzmann equation valid for strong short range forces in a dilute gas we have to sum over all successive two particle Born approximations (see Fig. 3.2).

Fig. 3.2.

However neither the Fokker-Planck nor the Boltzmann equation gives an adequate description of the plasma because there remains a divergence in the cross section due to the long range character of the Coulomb forces. The situation is similar to that of the well known virial expansion in classical equilibrium statistical mechanics.

No expansion restricted to a finite number of terms can lead to the Debye-Hückel limiting law. The way out of this difficulty has been indicated by Mayer (10) who has shown that the correct result is obtained as the result of a *complete* summation of a specially simple class of clusters.

The situation is similar here. Indeed Balescu has shown that the long distance divergence is eliminated through the summation of the diagonal fragments represented in Figure 3.3.

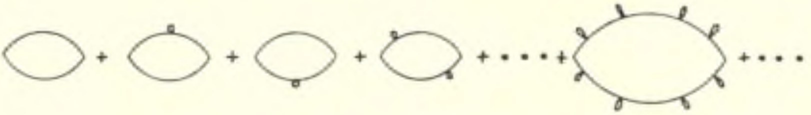

Fig. 3.3.

Physically these diagrams represent a *binary correlation built up and propagated through the cooperation of an arbitrary number of particles.* We have here a collision mechanism of a truly remarkable type. Indeed we have to consider simultaneously collisions involving 2, 3 ... particles. It is only through the cooperation of all these collision processes that the long range divergence is eliminated and that a finite cross-section is obtained.

III. THREE BODY COLLISIONS

It is of course of great interest to study three body collision problems. While the general solution of this problem appears still very remote, Résibois (11) was able to solve it for hard spheres in the limit of low energies.

Contributions to a three body collision are represented on Figure 4.1.

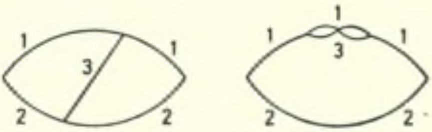

Fig. 4.1.

However such diagrams which represent "Born approximations" diverge for strong interactions ($\lambda \to \infty$). We need thus at least some partial summation of the type necessary to go from a Fokker-Planck to a Boltzmann equation. This Résibois (11) has achieved by using as a new "expansion parameter" the number of so called "binary kernels", each binary kernel describing exactly a two body collision between intermediate states. In other words each kernel corresponds already to the summation of a Born series. For example in Figure 4.2 we have three such Born summations, one between particles 1 and 2, the second between particles 1 and 3, and finally between 1 and 2 again.

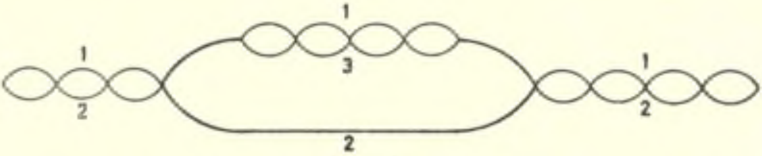

Fig. 4.2.

This method is very similar to the binary expansion method introduced by Yang and Lee in equilibrium statistical mechanics.(12)

The characteristic parameter of the problem is

$$a\widetilde{k} \quad \text{or} \quad \frac{a}{\lambda} \tag{4.1}$$

where $\widetilde{k}$ is the average momentum of the particles and λ the corresponding de Broglie wave length; a is the scattering length. At sufficiently low temperature

$$a\widetilde{k} \ll 1 \quad \text{or} \quad \frac{a}{\lambda} \ll 1\,; \tag{4.2}$$

the binary expansion then converges rapidly.

The results are the following: the binary transition probability is of the form

$$P_2 \sim \frac{a^2 \widetilde{k}}{\Omega}, \tag{4.3}$$

where Ω is the volume; the corresponding three body transition probability is

$$P_3 \sim \frac{a^3}{\Omega^2 \widetilde{k}}. \tag{4.4}$$

As could be expected the ratio

$$\frac{P_3}{P_2} \sim \frac{a}{\Omega \widetilde{k}^2} \tag{4.5}$$

decreases where temperature increases. This is a direct consequence of the incertitude principle. To achieve a three body collision we need an intermediate state formed by two particles say 12 whose life time is of the order :

$$\Delta\tau \sim \frac{1}{\Delta E} \sim \frac{1}{\widetilde{k}^2} \tag{4.6}$$

and decreases with temperature.

V. RADIATION DAMPING IN SYSTEMS OF CHARGED PARTICLES

As the third example I would like to consider briefly the transfer of energy from translation to radiation in the presence of an external magnetic field.

It should be emphasized that the method we summarized in § 2 remains valid for problems involving both particles and fields.(13) Indeed it is well known that a field may be considered as a collection of harmonic oscillators. Therefore the problems of evolution of systems of particles and fields are similar to those of systems of particles and harmonic oscillators. In other words the evolution of a field to statistical equilibrium is expressed by equations which remind sharply those of an anharmonic solid. Only here the " anharmonicity " is due to the very presence of matter (see for more details (14)), because in the absence of matter there is no transfer of energy between the different degrees of freedom of the field.

In comparison with the previous paragraphs the characteristic feature is the appearance of new diagonal fragments in which both particles and field oscillators take part (see Fig. 5.1 and 5.2). The dotted line represents a *field* inhomogeneity or correlation.

Fig. 5.1.

Fig. 5.2.

Both in the initial and the final states we have an arbitrary energy distribution over the degrees of freedom of the oscillators but no average fields. But during the collision there is now a field acting. By taking account of such diagrams we obtain an evolution equation both for particles and the field oscillators which incorporate features such as radiation damping and Compton effect (see Mangeney (14)). A specially striking case where a statistical treatment is useful is precisely the problem of radiation damping in the presence of an external field. Let us consider a single particle of mass m in a magnetic field. The radiation damping is given in the non-relativistic approximation by

$$\frac{e^2}{mc^3}\,\omega_L^2\,kT \tag{5.1}$$

where ω_L is the Larmor frequency

$$\omega_L = \frac{eH_0}{mc}. \tag{5.2}$$

Now it is clear that the radiation damping in a system of particles must be sensitive to the correlation between particles. In the limit of a uniform electrical current the radiation damping must even vanish identically (see for an excellent discussion Ivanenko and Sokolov (15)).

Recently Mrs. F. Henin has developed a general formula including the effect of correlation on radiation damping which contains the previous known situations as special cases(16). For the radiation emitted by groups of particles in cyclotrons, Henin's formula reduces to an expression derived by Kapitza and Vainshtein(17) but it permits to treat many other situations like the effect of plasma correlations on radiation damping. For example, in an equilibrium non-relativistic plasma there appears besides (5.1) a " mutual " radiation damping term of order

$$\frac{e^2}{mc^3}\,\omega_L^2\,kT\left[\frac{kT}{mc^2}\,\frac{\omega_p^2}{\omega_p^2+\frac{kT}{mc^2}\,\omega_L^2}\right], \tag{5.3}$$

where ω_p is the plasma frequency.

VI. CONCLUSIONS

As the conclusion to this report I would like to stress the fact that the problem of scattering and of energy transfer requires in many cases the cooperation of a large number of degrees of freedom. This is specially true in problems involving charged particles or fields. A striking example is an important investigation carried out recently by Balescu on unstable plasmas.(18) He has shown that the collision operator is a functional of the velocity distribution changing its form when we go from a stable to an unstable plasma. How far are we here from the classical Boltzmann equation in which the only statistical element is the distribution function while the collision cross-section is an " individual " property given once for all !

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Discussion de la communication de M. Prigogine

M. Wigner. — It is difficult to comment on a wealth of new ideas and suggestions as we just heard Prof. Prigogine to present. I am doing it only in order to initiate the discussion. As I understand it, Prof. Prigogine starts from the observation that the Liouville equation is linear, and he proposes, therefore, to apply to it the methods of solution which have been developed in the past years in quantum field theory. This then raises the question, which I would like him to answer, whether similar ideas could be applied to the quantum mechanical density matrix, the equation for which is also linear. In this connection I am wondering also whether Prof. Prigogine could compare the use of the methods which he discusses, that is the use of the Feynman diagrams, for wave functions and for essentially quadratic quantities, such as the Liouville's function or the density matrix. I know that in many cases, such as the derivation of the conservation laws, working with the density matrix is rather awkward.

M. Prigogine. — The method summarized in my paper can be applied both to classical and to quantum mechanical systems.

As well known the role of the classical density in phase space $\rho\,(\mathbf{x}, \mathbf{p}, t)$ is played in quantum mechanics by the statistical operator ρ which satisfies the so-called von Neumann equation

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}\,[\mathrm{H}\,\rho - \rho\,\mathrm{H}]. \tag{1}$$

At first this equation looks very different from the Liouville equation (formula 2.2 of my paper). However we can easily put (1) into a form in which the analogy becomes obvious. Let us indeed introduce the usual interaction representation. We then obtain instead of (1)

$$\frac{\partial \rho_{int}}{\partial t} = \frac{\lambda}{i\hbar}\,(\mathrm{V}_{int}\,\rho_{int} - \rho_{int}\,\mathrm{V}_{int}). \tag{2}$$

We now study the matrix element $<\mathbf{p}\,|\,\rho_{int}\,|\,\mathbf{p}'>$ of ρ in momentum representation. However in the place of $\mathbf{p}$ and $\mathbf{p}'$ we now introduce variables $\mathbf{P}$ and $\mathbf{k}$ defined by :

$$\begin{aligned} \mathbf{p} &= \mathbf{P} + \hbar\,\mathbf{k} \\ \mathbf{p}' &= \mathbf{P} - \hbar\,\mathbf{k}. \end{aligned} \tag{3}$$

We also introduce the notation

$$\begin{aligned} \langle \mathbf{p} |\, \rho_{int} \,| \mathbf{p}' \rangle &= \langle \mathbf{P} + \hbar\,\mathbf{k} |\, \rho_{int} \,| \mathbf{P} - \hbar\,\mathbf{k} \rangle \\ &= \rho_{\mathbf{k}}(\mathbf{P}). \end{aligned} \tag{4}$$

After a few elementary calculations we may then show that $\rho_{\mathbf{k}}(\mathbf{P})$ satisfies the equation

$$\begin{aligned} \frac{\partial \rho_{\mathbf{k}}(\mathbf{P})}{\partial t} &= \lambda \left(\frac{2\,\pi}{\mathrm{L}}\right)^3 \sum_{j>n} \sum_{\mathbf{l}} e^{i(\mathbf{k}_j \cdot \mathbf{P}_j + \mathbf{k}_n \cdot \mathbf{P}_n)t} \\ & \mathrm{V}_{\mathbf{l}} \frac{1}{i\hbar} \left[e^{\frac{\hbar}{2}\mathbf{l} \cdot \left(\frac{\partial}{\partial \mathbf{P}_n} - \frac{\partial}{\partial \mathbf{P}_j}\right)} - e^{-\frac{\hbar}{2}\mathbf{l} \cdot \left(\frac{\partial}{\partial \mathbf{P}_n} - \frac{\partial}{\partial \mathbf{P}_j}\right)} \right] \\ & e^{-i[(\mathbf{k}_j - \mathbf{l}) \cdot \mathbf{P}_j + (\mathbf{k}_n + \mathbf{l}) \cdot \mathbf{P}_n]t} \quad \rho_{\mathbf{k}_j - \mathbf{l},\, \mathbf{k}_n + \mathbf{l},\, \{\mathbf{k}'\}}(\mathbf{P}) \end{aligned} \tag{5}$$

The analogy with the classical equation (2.12) of my paper is striking. The only difference is that the differential operator

$$\mathbf{l} \cdot \frac{\partial}{\partial \mathbf{p}} \tag{6}$$

which appears in the classical equation is now replaced by the *displacement operator*

$$\frac{1}{\hbar} \left[e^{\frac{\hbar}{2}\mathbf{l} \cdot \frac{\partial}{\partial \mathbf{p}}} - e^{-\frac{\hbar}{2}\mathbf{l} \cdot \frac{\partial}{\partial \mathbf{p}}} \right] \tag{7}$$

The appearance of the displacement operator (7) expresses the well known feature that in quantum mechanics a finite momentum change occurs in a single step.

Similarly in the second quantization formulation we write :

$$n = \mathrm{N} + \nu \qquad n' = \mathrm{N} - \nu \tag{8}$$
$$\langle n |\, \rho \,| n' \rangle = \rho_{\nu}(\mathrm{N})$$

and we obtain :

$$i \frac{\partial \rho_{\nu}(\mathrm{N}, t)}{\partial t} = \frac{\lambda}{2\mathrm{L}^3} \sum_{klpr} v(klpr)\, \delta^{kr} (\mathbf{k} + \mathbf{l} - \mathbf{p} - \mathbf{r})\, e^{i(\varepsilon_k + \varepsilon_l - \varepsilon_p - \varepsilon_r)t}$$

$$\Big\{ [(\mathrm{N}_k + \nu_k)(\mathrm{N}_l + \nu_l)(1 + \theta \mathrm{N}_p + \theta \nu_p)(1 + \theta \mathrm{N}_r + \theta \nu_r)]^{1/2}$$

$$\overset{-}{\eta}_k \overset{-}{\eta}_l \overset{+}{\eta}_p \overset{+}{\eta}_r - [(1 + \theta \mathrm{N}_k - \theta \nu_k)(1 + \theta \mathrm{N}_l - \theta \nu_l)(\mathrm{N}_p - \nu_p)$$

$$(\mathrm{N}_r - \nu_r)]^{1/2} \overset{+}{\eta}_k \overset{+}{\eta}_l \overset{-}{\eta}_p \overset{-}{\eta}_r \Big\} \rho_{\nu_k - \frac{1}{2}, \nu_l - \frac{1}{2}, \nu_p + \frac{1}{2}, \nu_r + \frac{1}{2}, \{\nu'\}}(\mathrm{N}, t). \qquad (9)$$

The operators act on functions of numbers N_k and are defined by

$$\overset{\pm}{\eta}_k f(\mathrm{N}_k) = f(\mathrm{N}_k \pm 1/2). \qquad (10)$$

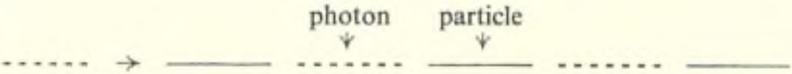
The essential point is that by eliminating finally the commutator which appears in (1), we have given to the quantum mechanical equation a form very similar to that valid in classical mechanics. Interesting applications of this formalism have already been published, specially by Résibois [*Physica*, **27**, 541 (1961)] (see also a forthcoming paper by Résibois in *Physica*) and Fujita [*Physica*, **28**, 567 (1962)] who have also discussed the relation of this method with the work of Van Hove [see L. Van Hove, *Physica*, **23**, 441 (1957)]. I would like to make also the two following brief remarks :

(*a*) we use a diagram representation; however our diagrams always refer to *correlations* and *not* as the Feynman diagrams to the changes in occupation numbers;

(*b*) there is no difficulty associated with the conservation laws. The invariance of the Hamiltonian with respect to translation gives rise to a law of conservation of " wave vectors " equivalent to momentum conservation. Energy conservation appears also naturally as a " resonance " property valid for long times. But we do not want to go more into details about these questions which have been treated elsewhere (see I. Prigogine, Non Equilibrium Statistical Mechanics, Wiley-Interscience, New York and London, 1962).

M. Kantrowitz. — Can your method explain the increase of the scattering cross section of photons near the plasma frequency ?

M. Prigogine. — I believe that it can. Calculations in this direction are presently made by Mangeney (Institut d'Astrophysique, Paris). The main point is to replace the oscillator line (see fig. 5.1 and 5.2 of my paper) by a " collective line " involving multiple scattering of the photon by many electrons



This is similar to the replacement of the particle line by the Balescu line in the plasma problem

(see fig. 3.3 of my paper).

M. Mayer. — There are several distinct cases that are described as the N-body problem. In neutral gases one can usually describe everything in terms of a succession, two-body, three-body, etc. effects, and the series converge rapidly. Plasma, that is gases with charged atoms, have a 1/R potential that diverges, and even the two-body term diverges. It is interesting that Prof. Prigogine's group have shown that the same technique of reordering the summation method permits one to get a convergent result for time change problems as for equilibrium.

In liquids the gas sum, two-body, three-body, etc. does not converge in the equilibrium case. My impression is that the technique of Prof. Prigogine's school will also not converge in this case, and that another method must be used.

M. Prigogine. — Non equilibrium statistical mechanics is always a more difficult subject than equilibrium statistical mechanics. It would therefore be paradoxal if a dynamic theory of liquids could be developed while an equilibrium theory is still lacking.

The basic problem is the complicated mechanical structure of the many-body collision operators. Some hope lies in the further development of the binary kernel method due to Résibois mentioned in par. 4 of my paper.

M. Morrison. — An important feature of the matrix equation described by Prof. Prigogine is its non-markoffian character. It stresses therefore the importance of the time element in chemical reactions which is specially striking in the experimental results I have described in my report.

M. Herzfeld. — The non-markoffian character of Prof. Prigogine's equation means that for many processes a description in terms of the usual gas kinetics cross sections may be insufficient. This seems a very interesting conclusion.

M. Prigogine. — In answer to the two remarks by Prof. Morrison and Prof. Herzfeld, I would like to come back briefly to the special meaning of non-markoffian processes.

As has been emphasized already long time ago by Bogolioubov (1947), the approach to equilibrium involves at least two time scales :

(1) the duration of the collision, of order

$$t_{coll} = \frac{a}{v}, \tag{1}$$

where a is the range of the potential and v the velocity of the molecules;

(2) the relaxation time or time between two collisions

$$t_{rel} = \frac{1}{\mathrm{Ca}^2\, v}. \tag{2}$$

Now the important fact is that the ratio of (1) to (2)

$$\frac{t_{coll}}{t_{rel}} = a^3\mathrm{C} \tag{3}$$

is precisely the characteristic parameter which measures the deviation from ideal gas behavior in the equation of state. Therefore no theory which wants to describe the approach to equilibrium in dense systems can do so without taking account of the finite duration of the interaction and that means precisely a non-markoffian description.

A very simple model of a non-markoffian process has recently been published by Haubold [K. Haubold, *Physica*, **28**, 834 (1962); see also L. Van Hove, Fundamental Problems in Statistical Mechanics, North-Holland Publ. Comp., Amsterdam 1962, and L. Van Hove and E. Verboven, *Physica*, **27**, 418 (1961)]. The main characteristics is the feature that the approach to equilibrium is no more monotonous.

The statement that the evolution equation for the velocity distribution (or in the quantum case the populations of the various levels) is non-markoffian is an unavoidable consequence of classical or quantum mechanics.

In the chemical case it is tempting to consider similar evolution equations. For example the non-markoffian generalization of the simple rate equation

$$\frac{dn_A}{dt} = -\alpha n_A \tag{4}$$

would be

$$\frac{dn_A}{dt} = \int_0^t K(t - t_1)\, n_A(t_1)\, dt_1. \tag{5}$$

Equation (5) reduces to (4) if the population $n_A(t)$ varies slowly over the duration of the process. However an exact formulation of this idea starting from first principles is still lacking.

M. Shuler. — The rate equations written and used by chemists are markoffian rate equations. In view of the non-markoffian nature of a large number of transport processes, the question arises as to the validity of the markoffian rate equation commonly used to describe chemical rate processes. To answer my own question I would say that while from a fundamental approach the equations may very well be non-markoffian in form, from an operational and practical (i.e. correlation with experimental results) point of view, the markoffian formulation should give valid results for most of gas-phase kinetics.

M. Hornig. — But that is what this conference is about. If the total concentrations are specified in kinetic equations and reaction is taking place before the various relaxation processes are complete, they most certainly do have a memory of when they were formed. The rate constants then depend on the extent to which the molecules are relaxed.

M. Porter. — Is it not true that any rate equation can be made markoffian provided the species in the concentration terms $[n_i]$ are sufficiently microscopically defined ?

If this is correct the usual kineticist's procedure of describing a reaction in terms of the minimum number of steps which can be represented by time-independent rate constants seems to be the most satisfactory way of avoiding non-markoffian relationships.

M. Shuler. — It is certainly correct that many non-markoffian processes can be transformed to markoffian processes by the introduction of additional variables. In chemical reactions, these additional variables would supplement the gross concentration variables through specification of the population distribution in the quantum level system. Thus, use of the proper distribution function in place of the gross concentration may well transform a non-markoffian to a markoffian rate equation. An even more refined treatment could be formulated by the introduction of correlation functions.

M. Résibois. — It is clear that if one goes back from the master equation to the Liouville equation the description becomes again markoffian because the Liouville equation

$$i \frac{\partial \rho}{\partial t} = L\rho$$

relates the change of ρ to its value at the same time. However such a description would be in general without any practical interest.

M. Widom. — The condition that the time of duration of a collision be small compared to the time between collisions, mentioned by Prof. Prigogine, is just the condition that triple and higher order collisions be negligible compared to binary collisions.

M. Kuhn. — The existence of memory effects from one collision to the next rises the question whether the actual state of a given molecule at a given time can be described unambiguously in the usual terms. If memory effects have to be reckoned with in the case of many or all the molecules present we meet the difficulty of defining the concentration of the initial product and for this reason the difficulty of stating a reaction velocity in terms of the concentration of the initial products.

M. Linnett. — A real situation in which an incomplete knowledge of the energy distribution, and of the consequences of changes in that distribution, affects our ability to transfer a velocity constant from one situation to another is the following : we have studied the mechanism of chemical reactions such as the oxidation of carbon monoxide at temperatures around 600 °C in the past to obtain the velocity constants of the component reactions. However, it is clear that we cannot transfer these velocity constants without questions to a carbon monoxide flame (making, of course, the ordinary Arrhenius adjustment) because the molecules and radicals in flames may have abnormal distributions among vibrational levels since the reaction time may be comparable to or shorter than the vibrational relaxation time.

M. Prigogine. — It is clear that the practical importance of non-markoffian equations for chemical kinetics is still an open question. It should however be emphasized that the mere introduction of intermediate states cannot *in general* eliminate the non-markoffian character. Indeed any collision process and more generally every process leading to a change in population has a finite lifetime, and non-markoffian behaviour is unavoidable if the changes in populations become sufficiently rapid.

The main point is to understand that a collision process is not just an arbitrary classical or quantum mechanical process but involves at least two " inverse processes ", one of the " creation " of correlations, the other of " destruction " of correlations (see par. 2 of my paper). While each elementary process of the type represented in figure 2.2 of my paper, is instantaneous, the total collision process is not, and cannot be made so by a simple refinement in the specification of the populations.

I would therefore go as far as to state that the usual markoffian description of chemical reactions is simply a consequence of the origin of this science which naturally enough originated in the study of slow reactions.

Discussion générale

M. Ubbelohde. — Studies of reaction kinetics have been enriched by much more detailed understanding of activated states of molecules, and of rate processes whereby such states are supplied and are vacated.

The powerful techniques of thermodynamics invite attempts to derive at least general information about rate processes from more or less sophisticated theories of microscopic reversibility and detailed balancing. Discussions show, however, that there are limits to the cogency of such general arguments, which may prove to be incomplete in cases that are of particular interest experimentally. Although its applicability should always be considered, thermodynamics cannot be regarded as setting limits to effective investigations, either theoretical or experimental.

Improved experimental access to higher temperatures has been made possible by modern techniques. Inevitably, in many cases excited states are arrived at in various ways that are not fully reversible.

Discussions show that mechanisms of energy exchange for rotational, vibrational and electronic energy in terms of molecular quantum mechanics have acquired fresh urgency, and are stimulating much research at the present time. A variety of higly suggestive mechanisms of energy exchange are being examined for their practical relevance, as well as in relation to indeterminancy concepts as applied to intermediate states during collisions, at which the repulsion energy is maximized. Conditions favouring transfer depend on quantum rules applied to the energy and position of atoms in the collision complex, and also on possibilities for smudging or broadening these rules so as to permit a wider range of conditions for effective energy exchange. At the present time, it seems fair to say that the leading factors have all been identified, but that their relative importance in specific cases may still require elucidation. In the same context, average lifetimes of excited states as ended by various processes have acquired renewed significance, as a result of improved methods of characterization in various researches.

In this group of discussions, our researches are greatly hampered by the very uneven state of our information about attractive and repulsive force fields. For attraction, and for primary electrostatic repulsion, we do know enough about most simple systems to make reasonable calculations for a collision process. For polyatomic systems with several atoms dispersion attractive forces begin to introduce problems of anisotropy, but normally at least the directions of maximum and minimum attraction can be spotted. But repulsive forces due to electron cloud overlap for non-bonded atoms involve some big question marks which are particularly awkward for energy transfer calculations. Even if one assumes repulsions given by an overlap of Thomas Fermi electron clouds around a pair of nuclei, the nature of the composition rules for repulsions between dissimilar atoms does not appear to emerge in any simple way from the repulsion potential between a pair of similar atoms. And the possibility of repulsive force fields with non-spherical distribution around any nucleus, due to influence of neighbours, may likewise be important in collisions with a vibrator.

a) Dissociation et recombinaison des molécules biatomiques.

M. Hornig. — The chairman has asked me to collect some of the questions and problems relating to Professor Rice's discussion of the dissociation of diatomic molecules and the recombination of atoms in the presence of a third body. Some of the main problems which we are discussing are certainly these :

1° If the rate of dissociation is written in the form

$$k = \mathrm{C}Ze^{-\mathrm{D/RT}}$$

where Z is the collision frequency between X_2 and M and D is the dissociation energy of X_2, the measured values of C are always much greater than unity, being of the order of 100 or more when M is a rare gas atom. All of the approaches discussed give explanations of this observations so in a sense it is no mystery. The question is wheter one of these explanations is predominantly important.

2° The constant C has been found to decrease with increasing temperature. If it is represented in the form

$$\mathrm{C} \sim \mathrm{T}^{-n},$$

then $n \simeq 1.5 - 2.0$ in all of the dissociation reactions thus far studied, namely H_2, I_2, Br_2, O_2 and N_2. Consequently the explanation cannot depend strongly on the chemical nature of the molecule.

If $k_d/k_a = K$, a point which was much discussed earlier, recombination rates should have the same temperature dependence. It is indeed found experimentally that recombination rates decline as the temperature increases and can be represented in at least two different ways

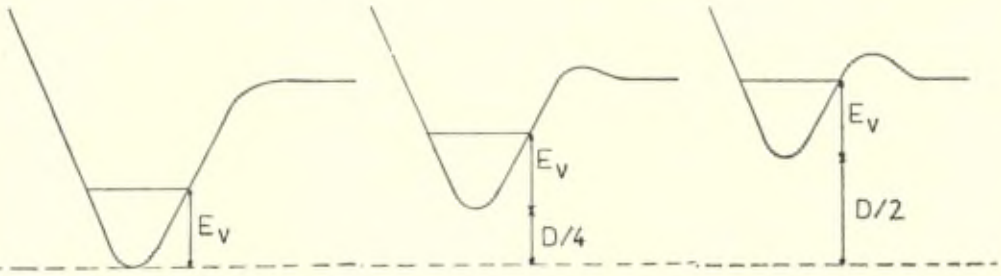
$$k_a = BT^{-n} \text{ or } B'e^{E/RT}.$$

Such an inverse temperature dependence can be derived from a variety of sources, such as the decrease in collision cross section with increasing velocity which occurs for attractive force fields, or the effect of other degrees of freedom. The second form of the equation follows very naturally from the « complex mechanism », although the values of E required seem to be too large to be reasonable, at least when the third body is a rare gas.

3° There is a great difference in the effectiveness of various third bodies and their effect on the temperature coefficient. One wonders to what relative extent this depends on the formation of complexes, the size of the third bodies or the presence of internal degrees of freedom.

4° A question with which I am particularly concerned is the role of rotation in the dissociation or recombination mechanism.

If we consider the position of a particular vibrational level as the rotational energy is increased, the successive effective potential energy curves and positions of the level are something like this :



Because of the 2J + 1 rotational degeneracy the high rotational levels are very probable. For a fixed J (or E_r) the molecule must climb the vibrational ladder to dissociate, in the fashion discussed by Montroll and Shuler, Nikitin and others. However, it is well established that J may change very rapidly in collisions and Δ J per collision may be large. Therefore a molecule in a given vibrational level may move rapidly back and forth among the potential curves corresponding to different E_R. Therefore, if the sum of vibrational plus rotational energy is about equal to the dissociation energy, a further increment in either the vibrational or the rotational energy leads to dissociation. Of course there is an effect of the rotational barrier since it must be surmounted, but for realistic situations it rarely exceeds a few kilocalories in magnitude.

An exact calculation of this problem has not been carried out but a rough answer can be obtained easily. If one ignores two factors, (a) the « rotational barrier », which is probably small, and (b) the depletion in the population of upper vibrational levels, then one need only ask what fraction of the molecules have a combined vibrational plus rotational energy in the vicinity of the dissociation energy. For a classical harmonic oscillator and a rigid diatomic rotator, the fraction with total energies within ΔE of dissociation would be

$$\frac{\Delta E}{kT}\left(\frac{D}{kT}\right)e^{-D/kT}$$

If these energetic molecules, which are close to dissociation, exchange a fraction f of the relative kinetic energy on collision, the fraction which acquires an energy greater than D, and therefore dissociates, can be obtained straightforwardly. The resulting rate constant is, to a good approximation,

$$k = Z\,\frac{f(2-f)}{(1-f)^2}\;\frac{D}{kT}\;e^{-D/kT}$$

when f is in the range between 0 and 0.5. For $f = 0.25$, $D = 4$ Kcal./mole, $RT = 3$ Kcal./mole, this provides a factor of 12, somewhat smaller than actually observed. It also shows one of the sources of the inverse temperature dependence. The factor is considerably increased if the harmonic oscillator is replaced by a Morse oscillator or any other model which increases the density of levels near dissociation.

Of course this must be corrected for the effects previously mentioned, and particularly for the non equilibrium population of vibrational states. With regard to this point one should note that if, because of the rotational contribution, the average molecule dissociates from vibrational levels far below the dissociation limit. the depopulation is distributed over many vibrational levels so that the deviation of the population is not nearly as great as found by Montroll and Shuler. Furthermore, the spacing of the vibration levels near the dissociation limit is much greater with high rotational energies than in the non-rotating case, since they may be levels which are seated deep in the potential well of the non-rotating molecule.

M. Semenov. — We had noted already in 1934 that there is no explanation for the extreme values of the preexponential factor for the dissociation constant of biatomic molecules, calculated from the equilibrium constant and the recombination rate constant. A theoretical explanation given recently by Nikitin may not prove adequate for quantitive treatment. It would be very interesting to discuss this problem thoroughly.

M. Mayer. — I would like to describe a « Poor man's theory » for the reaction

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \rightarrow \mathrm{AB} + \mathrm{M} \qquad \mathrm{I}$$

and its reverse. What I have to say is not new, but I wish to emphasize that the most simple approach does succeed in giving the order of magnitude of the rate of the reactions in equation I.

In the first place may I point out that in the discussion of the rate of I and its reverse there are several problems which are quite distinct, but sometimes confused. Whatever A and B are, there are supposed, in principle at least, to be four realms depending on the different pressures. At low pressures of A, B and M (and in the absence of the product AB), the forward reaction of I is proportional to the product of the three pressures,

$$d\mathrm{C_{AB}}/dt = k_{\mathrm{R}}{}^{(3)}\,\mathrm{C_A C_B C_M}, \qquad (1)$$

and the reverse reaction (in the absence of A and B), would be bimolecular

$$d\mathrm{C_A}/dt = k_{\mathrm{L}}{}^{(3)}\,\mathrm{C_{AB} C_M}. \qquad (2)$$

At sufficiently high pressures of M, however, the forward reaction becomes bimolecular,

$$d\mathrm{C_{AB}}/dt = k_{\mathrm{R}}{}^{(2)}\,\mathrm{C_A C_B} \qquad (1')$$

and the reverse is unimolecular,

$$dC_A/dt = k_L^{(2)} C_{AB}. \tag{2'}$$

Now it need hardly be necessary to point out that it is not experimentally easy to obtain conditions under which all four constants, $k_R^{(3)}$, $k_L^{(3)}$, $k_R^{(2)}$, $k_L^{(2)}$ can be measured. Indeed, although I must defer to my colleagues more experienced in this field, I believe that in no case is more than *one* of the four accurately measured, and only part of the transition $k_R^{(3)}$ to $k_R^{(2)}$ or $k_L^{(2)}$ to $k_L^{(3)}$ observed experimentally, and never ever both the « right » and the « left » constants, except when both are measured at small deviations from equilibrium.

The question has been raised whether the ratios $k_R^{(3)}/k_L^{(3)}$ and $k_R^{(2)}/k_L^{(2)}$ are equal to the equilibrium constant, K, which of course they must be at compositions close to equilibrium. Another question concerns the *shape* of the transition between the two realms (1) to (1′) or (2) to (2′), rather than the numerical values of the constants.

A third question, and it is this to which I address myself concerns the computation of the actual *values* of the constants. Now it should be emphasized that it is extremely unlikely that accuracies greater than one order of magnitude can be expected from any purely *a priori* calculation. What I wish to point out is that accuracies to within nearly one order of magnitude appear to be obtained by the most naive and trivial calculation, and that this method should probably be more, rather than less, valid for complicated than for simple cases.

The calculation follows the simplest transition state method. One simply says that in any single three-body collision, such as that implied by the process I going to the right, one of the three pairs A-B, A-M, or B-M approach first, and the third body approaches later. The total rate is then the sum of three rates, namely those in which the three different pairs approach first, and since we are expecting only order of magnitude agreement, it suffices to set it equal to the fastest of the three. For reasons which will appear later I expect that if M is a rare gas, and especially if A and B are radicals rather than atoms, the fastest rate will be that in which A and B approach first. We may therefore write reaction I in two steps :

$$A + B \rightarrow AB^* \tag*{I'}$$

$$AB^* + M \rightarrow AB + M, \tag*{I''}$$

where, by definition AB^* stands for a molecule whose minimum energy is that of the separated species $A + B$, but which has the energy distribution above that minimum of the Maxwell Boltzmann distribution of the two atoms at the temperature of the reaction.

The essential for the idea is then to write I′ at equilibrium, and for reaction I″ a two-body rate without activation energy and with some normal cross section to be guessed at from the sizes of the molecules, AB and M.

The computation of the equilibrium concentration of AB^* in the presence of the given pressures, P_A, P_B of A and B is simply estimated, since the equilibrium constant K for the reaction $A + B \rightarrow AB$ is known, and AB^* differs from AB only in having the dissociation excess energy above the zero energy.

The calculation leads to different results depending on the number of degrees of freedom in the molecule AB, and on whether the excess energy, the energy E of the A to B bond, is large or small compared to the temperature, RT, and to the energy of separation of quantum states in these degrees of freedom. In the simple case that E is large a factor $(E/RT)^{1/2}$ appears in the rate constant for every internal degree of freedom minus one. (There is a denominator, which for a very large number of degrees of freedom reduces the factor greatly). Put in over-simplified terms this factor multiplies the rate that one might compute for a « three body collision » using reasonable diameters and « ranges » of collision.

The interpretation is simple in classical terms. When A and B are spacially close their potential energy is low, and, in a given trajectory, which has (necessarily) a fixed total energy, their kinetic energy is high. This results in an enhanced momentum, and therefore an enhanced phase space depending on the number of degrees of freedom involved. Of course in the case of many degrees of freedom the extra energy can also « flow » into extended vibrational coordinates as well as into momenta. The Liouville principle of extension in phase assures us that, in the absence of deactivation by collision with M (or other A's and B's) this phase space will actually be filled according to the Boltzmann relation, for all energies above that of A plus B. There now remains, for an exact calculation, only the problem of computing the correct average cross section for deactivating collisions by M (which of course should be corrected for, or allow for, returns by activation from the higher bound states). This would give us an accurate $k_R^{(3)}$ in the limit $P_M \to \infty$, but this is exactly the definition of $k_R^{(2)}$, since higher pressure values correspond to the gradual transition towards $k_R^{(2)}$. A rough estimate that the deactivation cross section is about equal to the so-called geometrical cross section, provided the masses and nearly equal, should give an order of magnitude estimate. Several remarks should be added. Firstly, of course, in some cases the A-M pair may be the long-lived one, or the B-M, or both, and this will particularly tend to be the case if M is a molecule of several degrees of freedom and A and B are atoms. If the A-M (or B-M) bond is strong enough to form stable states (and it is only in this case that one would expect these sequences to take precedence over that of I′ and I″) one must consider

$$A + M \to AM^*, \tag{II'}$$

$$AM^* + M \to AM + M, \tag{II''}$$

$$AM + B \to AB + M, \tag{III}$$

$$AM^* + B \to AB + M, \tag{III'}$$

etc...

A second remark concerns the « sticky collisions », and the transition to the realm where $k_R^{(2)}$ of reaction (1′) occurs. The realm in which the rate constant is given by (1′) is that in which the pressure is so high that reaction I″ is very much more rapid than I′, so that $k_R^{(2)}$ is the rate constant of reaction I′, namely in the absence of AB^* we have,

$$dC_{AB}^*/dt = k_R^{(2)}\, C_A C_B, \tag{3}$$

with the same rate constant as that in eq. (I′). Since this is a reaction without activation energy, and, by definition, with no deactivation, one may express $k_R^{(2)}$ in terms of the average relative velocity and a reasonable cross section.

Since, on the other hand, we have proposed that one may relatively estimate the equilibrium contant.

$$[C_{AB}^*/C_A C_B]_{eq.} = K_{AB}^*, \tag{4}$$

the constants for the invese reaction to I′, namely in the absence of M and A and B,

$$dC_A/dt = \tau^{-1} C_{AB}^*, \tag{5}$$

must be (almost) related to $k_R^{(2)}$ by

$$\tau^{-1} K_{AB}^* = k_R^{(2)}. \tag{6}$$

Now τ is the average life of the excited AB^* molecule, in other words it is the average duration of the collision between A and B.

If the bond energy E is large compared to RT this time τ is larger than the average collision time as calculated by the time necessary to cross, at thermal velocity, the width of potential well, and larger by some powers of E/RT. This can be, and often is, several orders of magnitude.

Thirdly I would like to emphasize that the discussion has not been an *a priori* discussion. We assume that the bond energies and the nature of potential curves and frequencies of all degrees of freedom are known. The point only is that one throws the unknown problem into the evaluation of cross sections under conditions in which these cross sections can be assumed to be, in order of magnitude, geometric.

Mr Slater. — Concerning the pair of reactions $AB + M \rightleftharpoons A + B + M$, it is worth noting that if AB has a potential approximately of the Morse type with *n* discrete levels in all, then the classical vibration frequency in a state near the dissociation limit is about $1/n$ th of the ground frequency, and so may be some 30 times smaller. This smaller frequency is relevent in considering « life-times » of A.B.M. complexes for either reaction.

M. Voevodsky. — One must always remember that for different third bodies the rate constant of the process $A + A + M \rightarrow A_2 + M$ may change by a factor of 200. Since under equilibrium conditions the forward and the reverse reaction rates are equal, that means that the dissociation process must also involve some sort of chemical interaction between A_2 and M since its rate constant must also depend on the chemical nature of M.

It must be noted, however, that the assumption of a complex $A_2...M$ cannot be regarded as an explanation of the abnormally high dissociation rate constant. A possible way to give such an explanation is to take into account the thermal stability of the loose complex $A_2...M$. As the temperature rises its formation becomes more and more difficult and that would lead to a small change in the energy of activation for the dissociation process. If the rate of a process, for which $E = f(T)$, is plotted in Arhenius coordinates the energy of activation thus obtained may differ from the real value. Since the value of the rate constant is real, this would lead to a « compensation » effect — the preexponential factor may become 10 — 100 times greater than its real value. A thorough investigation of the rates in a broad region of temperatures is needed to solve this problem unambigously.

M. Rice. — The fact that the reaction rate $AB + M \rightarrow A + B + M$ exceeds the apparent collision rate offers no essential difficulty. It occurs in large part because the density of energy levels near the dissociation limit, which are the levels which contribute directly to the reaction, is much greater than the density of levels near the minimum of the potential-energy curve. This appears as the factor g_0 in Eq. (2.18) of my report, and as the factor $k\mathrm{T}/\delta\varepsilon_{v0}$ in Eq. (2.21). As noted following Eq. (2.21), Steiner had earlier made a calculation based on the average time of a collision $A + B$ in their mutual potential-energy field, which I have shown to give a result closely equivalent to Eq. (2.21), since the time of a vibration near the dissociation energy (kT below) is equal to $h/\delta\varepsilon_{v0}$. The factors n and $(r_m/r_0)^2$ which appear in Eqs. (2.18) and (2.21), and which may be as large as 5, can also contribute to the large reaction rate.

The high reaction rate cannot be explained by a factor of the type $(\varepsilon_D/k\mathrm{T})^s$, where ε_D is dissociation energy and s is related to the number of degrees of freedom of AB. Even if rotational energy were freely distributable into the bond joining A and B, the probability of its being so redistributed would contain the factor $(\varepsilon_D/k\mathrm{T})^s$ in the denominator; this is quite analogous to the probability for the unimolecular decomposition of an activated molecule. The factor $(\varepsilon_D/k\mathrm{T})^s$ is proportional to the number of configurations possible for a molecule with ε_D. This occurs in the numerator when calculating the number of molecules with energy ε_D (or in a small range), but the probability of reaching the particular configuration necessary for dissociation is inversely proportional to the number of molecules in the range. I believe that the proper way to take care of rotational energy is by multiplication by the factor $(r_m/r_0)^2$ [see Eq. (2.18) of my report and the discussion and reference following this equation.].

I should also like to add a remark about the ratio of the rate constants called $k_R^{(3)}/k_L^{(3)}$ by Mayer. He has stated that this ratio must be equal to the equilibrium constant at compositions close to equilibrium. This, of course, is true, but I should like to point out that I have shown [*J. Phys. Chem.*, **65**, 1972 (1961)] that the measured values of $k_R^{(3)}$ and $k_L^{(3)}$ will be the same, regardless of whether the reaction is near equilibrium or not. In other words, the approach to equilibrium is determined by the measured (nonequilibrium) values of the rate constants, as determined far from equilibrium.

M. Porter. — Thirty years ago a great deal of theoretical effort was devoted to the interpretation of experimentally determined rates of « unimolecular » reactions. Subsequent work has shown that practically every one of those reactions proceeded by complex mechanisms and chains to which the calculations could not have any relevance (although agreement was frequently quite good). This should be a warning to us to ask whether third-order reactions really involve three body collisions or more specifically whether energy transfer is really important in such reactions. Let me give an example which I think everybody will agree involves two distinct processes and undoubtedly goes by the complex mechanism. We (Porter, Szabo and Townsend, *Proc. Roy. Soc.* **A 270**, 493 (1962) have recently studied the recombination of iodine atoms in the presence of nitric oxide as third body. In the complex mechanism involving equilibration of the complex

$$I + M\,(+\,M) \rightleftharpoons IM\,(+\,M) \qquad K$$

$$IM + I \rightarrow I_2 + M \qquad k_3$$

IM is now INO which might be expected to have considerable stability by analogy with ClNO and BrNO, although it does not exist in detectable amounts at equilibrium. The reaction, at low pressure of NO, is accurately third order and the rate constant is 20,000 times faster than that in helium and twenty times faster than the fastest reaction of this type previously investigated.

At higher NO pressures, however, the rate decreases with increasing NO concentration a startling observation at first but one which can be predicted from the above mechanism since when all the iodine atoms are complexed the rate of reaction 3 is zero. Furthermore at high NO pressures a new absorption spectrum appears which is undoubtely that of INO. A detailed analysis of these observations makes it possible to derive not only the overall third order rate constant k_3K but the separate values of k_3 and K. The former is approximately one tenth of the collision number and the latter has the value 0.3 mm^{-1} at 333 °K. The heat of formation of INO from I and NO is not yet known but the equilibrium constant suggests a value of about 10 Kcal/mole.

Here, then, is a case where I think everybody will agree that the complex mechanism is not only valid but essential to interpret the experimental observations. But NOI is not a stable molecule in the ordinary sense and its binding energy is not so much greater than that of other complexes which we have measured to give it a special place in our theory. To chose a few of the values of Porter and Smith we have

$INO \sim 10$ Kcal
$I — I_2$ 5 Kcal
I — Mesitylene 4.1 Kcal
I — Toluene 2.7 Kcal
I — Benzene 1.7 Kcal
I — Argon 1.3 Kcal
I — Helium 0.4 Kcal

These values depend on assumptions about the temperature dependence of k_3 and pre-exponential factors in K and are probably minimum values. They also depend, of course, on the validity of the complex mechanism and the question which we have to answer is at what point does this mechanism cease to be valid. We agree that it is valid for NO as a third body. The efficiency of I_2 is very high and spectra of complexes between iodine atoms and the aromatic hydrocarbons and other molecules have recently been observed during flash photolysis experiments in solution though not in the gas phase (Gover and Porter, *Proc. Roy. Soc.*, **A 262** 476 (1961)). If one uses the values of the heat of formation given above and calculates the equilibrium constant K by statistical mechanics and the value of k_3 by collision theory one gets good agreement with experimental values of the rate constant all the way down to helium. (Porter & Smith, *Proc. Roy. Soc.* **A 261** 28 (1961). For the present therefore the complex mechanism is satisfactory for all third bodies and we have no indication of where to stop applying it. It seems quite possible to me that these forces of interaction — which are much greater than the van der Waals dispersion forces in most cases, and which Smith and I attributed to charge — transfer type complex formation, may be quite general between atoms (or free radicals) and saturated species even when the latter is an inert gas atom.

M. Widom. — Did not Bunker's calculations show that the complex mechanism is unable to account for the recombination rate when helium is the third body ?

M. Porter. — Bunker used van der Waals interactions derived from PV data assuming I is the same as Xe. I am using energies derived directly from the temperature coefficients of recombination data. As you see these are of quite different magnitude.

M. Ubbelohde. — How does Prof. Porter calculate the rate constant for the reaction IM + I ?

M. Porter. — The rate constant k_3 is calculated using classical collision theory, the collision diameter of I being assumed equal to that of Xe and the collision diameter of IM being equal to that of I (since collision must occur with the I part of IM). This may introduce small errors but these are small compared with other uncertainties inherent in all theories such as the unknown statistical factor which may be anything between 1 and 1/16 or more reasonably, as Prof. Rice says, between 1 and 1/5. Of course when the complex becomes very strongly bound, as in INO, there may be a small activation energy and a consequently reduced efficiency of reaction 3 but on the basis of our direct measurements of this factor in the case of INO it is probably not very important with the other third bodies.

M. Semenov. — The explanation given by Prof. Porter for the high values of K on the basis of the loose complexes that he has found experimentally, seems to me quite plausible. In the case of inert gases, however, such an explanation is much more questionable, the K being however large enough.

M. Norrish. — I would like to ask Prof. Hornig if he takes the contribution of the bound state of a complex into account in his explanation of recombination reactions. In the case of the I — He complex, it is unlikely that its lifetime would be greater than 10^{-14} — 10^{-13} seconds.

M. Hornig. — The discussion has been concerned with the mechanism of atom recombination reactions and Prof. Porter has made a strong case for the « complex mechanism ». The question, though, is whether there is really a clear choice to be made. All of the mechanisms which have been discussed for atom recombination, namely

$$X + X + M \rightarrow X_2 + M$$

$$XM + X \rightarrow X_2 + M$$

$$X_2^* + M \rightarrow X_2 + M$$

proceed in the final stage through the formation of the configuration $^{X}_{X}M$, and all are included in the theory of Keck. The question is only whether those $^{X}_{X}M$ configurations in which an XM is in a bound state are the preponderant ones, or whether the unbound states contribute as well. If only bound states are important, Prof. Porter is quite correct. When the X-M binding energy is great, as in the case of I-I_2 or I-NO this state of affairs seems likely, but when the binding energy is small, as with He or A, it appears probable that both bound and unbound states contribute. Bunker and Davidson, for example, calculated that with rare gases the concentration of XM in contact but not bound is about the same as that of bound XM. Hence although the binding enregies quoted by Prof. Porter are probably correct for the strongly bound complexes, these for the He and H may be too large because too much of the reaction is ascribed to complexes.

In any case the binding energies quoted for the rare gases are several times larger than expected for dispersion forces. It may be that the forces between an atom and a rare gas are stronger because of the role played by low lying charge transfer states, for example, but I know of no calculation of the magnitude of such an effect. It seems unlikely in the case of He that such states are important. I should like to stress again that the calculation of Keck is not opposed to the « complex theory », since when an attractive potential between X and M is used the Keck approach automatically includes the effect of complexes.

M. Rice. — As noted in my report, Atack and I measured the stability of the van der Waals complex I_2-benzene and its heat of dissociation. It may be noted that the entropy necessary to obtain the observed stability was such that one needs to assume that the I_2 rotates freely in the complex and can sit anywhere on the benzene molecule. It is found that a good account of the reaction $2I \rightarrow I_2$ in the presence of benzene can be obtained by assuming that the I-benzene complex has very similar properties to the I_2-benzene complex. Since I has only half as many electrons as I_2 this fits in with Porter's contention that something other than dispersion forces are involved in I-benzene. It also implies that the entropy is similar to that of the I_2-benzene complex and that I, like I_2 can sit anywhere on the benzene. In this respect it is different from the *charge-transfer* I_2-benzene complex, whose dissociation constant in carbon tetrachloride has been measured by Benesi and Hildebrand. Judging from their results, the heat of dissociation of the charge-transfer complex is very similar to that of the van der Waals complex observed in the gas phase by Atack and myself, but the charge-transfer complex is much less stable, indicating a lower entropy due to specific orientation with respect to the benzene.

I have made an attempt to calculate the force between an I atom and an Ar atom, assuming it to be the same as the dipersion force between I_2 and Ar and assuming no specificity in mutual orientation. It seesms to me that this gives ample allowance for special forces between I and Ar. This indicated that the complex and collisions rates for $I + I \rightarrow I_2$ in Ar would be comparable. Surely the relative importance of the complex rate should be much less for the reaction in He or Ne, and in these cases, at any rate, I think we can assume a pure collision mechanism.

M. Voevodsky. — In connection with the suggestion that in an I-C_6H_6 complex the iodine atom may have the possibility to move between different carbon atoms, I would like to point out that in a H-C_6H_6 complex, such movements has been studied fairly well by ESR methods : the H atom is localised on one carbon atom.

M. Wigner. — There are four short remarks which I would like to make.

The first of these is that I agree with everything that Dr. Hornig has said. The second is that I really do not see how molecules could be formed without the sum of the kinetic and potential energies of the atoms forming the molecule dropping below zero. That this can be brought about by a third atom from a rather large distance is perhaps not so surprising because the kinetic energy of the atoms which will form the molecule is very large, because they were accelerated toward each other by the attractive potential between them. As a result, a very small change of their relative momenta will give a change in their kinetic energy which is of the order of kT. Only this amount of energy change is necessary since the excess of the total energy of the atoms over the dissociation energy is only of this order of magnitude. Hence, the « third body » has a very large effective cross section.

Lastly, I would like to add a point to Dr. Hornig's discussion. Surely, as Prof. Porter has pointed out, many association reactions

$A + B \rightarrow AB$ proceed mostly via an intermediate compound AM. However, this presupposes the formation of the AM compound, and this itself requires a three-body reaction. If M is a complex molecule, the formation of the AM compound will be faster than the direct reaction $A + B + M \rightarrow AB + M$. However, if M is a noble gas, the reaction $A + M + M \rightarrow AM + M$ may be slower than the direct $A + B + M \rightarrow AB + M$ reaction. There may be more M than B atoms present and this favors the $A + M + M$ reaction. However, the rate constant of this reaction can be excepted to be smaller than that of the direct reaction because the attraction between A and M is weak and the reason for the effectiveness of the third body, given before, does not apply.

Finally, the intermediate mechanism is not even conceivable if there are no atoms present except those which form the compound. Surely, if $I + I + He \rightarrow I_2 + He$ is possible, $I + I + I \rightarrow I_2 + I$ is also possible so that I atoms will associate also in the absence of any other gas. In this case, however, the reaction leading to the intermediate compound is the same as the direct reaction. Hence the existence of the direct reaction must be considered to be established.

M. Light. — There are two points which I would like to mention. First, the evidence presented earlier on the reaction $A + BCD \rightarrow AB^* + CD$ indicated that much of the energy released is found in the newly formed bond. This seems to indicate that there is no complex formed. If a complex with a lifetime much longer than the period of vibration were formed, approximate equipartition of energy between the product molecules would be expected.

Second, a change in the potential energy surface of a diatomic molecule, similar to that mentioned by Prof. Hornig, is caused by an adiabatic interaction of the diatom with a third body. Even though the action variable of the diatom remains constant during such an interaction, a vibrationally excited bound state may be forced into the continuum, presumably with dissociation of the molecule. It is easy to show for weak interactions that such a mechanism leads to a faster rate of dissociation than vibrational transitions do. With strong forces all powers of the interaction potential may be taken into account. The process is analogous to that proposed by J.R. Hiskes for the dissociation of molecular ions.

M. Porter (communication ultérieure). — Of course recombination without complex formation is possible and Professor Wigner has chosen a nice example in the case of three iodine atoms. In practice however the concentration of M is so high that the complex mechanism is probably nearly always predominant. If one sets out the full kinetic scheme of all these possible reactions it appears that the complex mechanism will provide the main recombination route provided that ΔE (complex formation) is greater than kT. (Porter. *Discussion Faraday Soc.* **33**, 198, 1962).

M. Kantrowitz. — I would like to exhibit some recent results of the work of J.C. Keck which is a development of a technique originally proposed by Wigner[1]. Wigner found an upper bound for the equilibrium recombination rate in three body collisions by calculating the rate at which representative points cross a critical surface in phase space on which the relative energy of the recombining pair of atoms is zero. This calculation gives only an upper bound since some of the points will immediately recross the surface returning to the free state. Keck[2] has proposed that a least upper bound can be found by using surfaces described by parameters and varying the parameters to minimize the crossing rate. He has explored a number of simple surfaces and finds that for $kT/D \leqslant 1$ the surface which yields the lowest rate is one for which the relative energy of the recombining pair is equal to the height of the rotational barrier. This surface is shown schematically in Figure 1 where it is designated S_B. It has

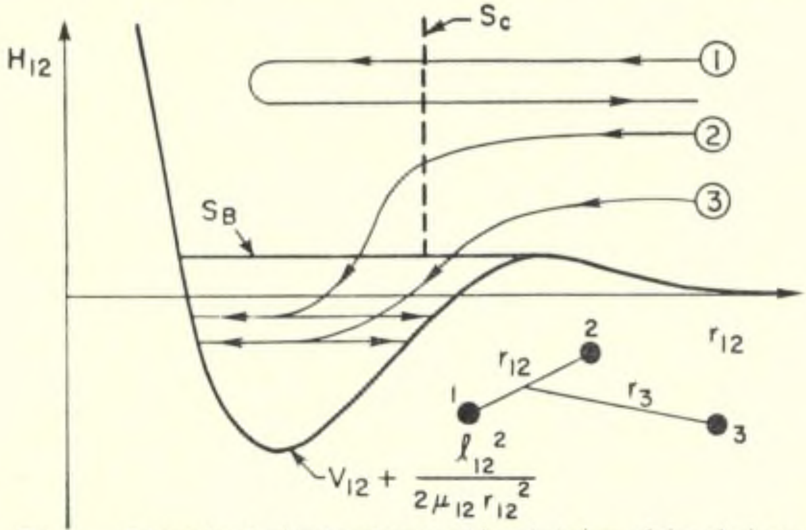


Fig. 1. — Schematic of critical surfaces used in calculations of three body recombination rates : Projection of Collision Trajectoires on H_{12}, r_{12} plane for large r_3.

the property of completely separating the free and bound states of the diatom so that passage through it is a necessary condition for reaction. Also shown in Figure 1 is the surface S_e which is commonly used in collision theory calculations. As illustrated by trajectory 3, passage through S_e is not a necessary condition for reaction unless S_e is located well beyond the range of the force. In this case, however, a large number of trajectories of type 1, which do not lead to reaction, are included. The subjective judgment involved in choosing the best location for S_e is major weakness of all collision theories in which a correct treatment of the mechanics is not included.

A comparison of some of the results obtained by Keck with experiments on the room temperature recombination rate of iodine atoms in the presence of the inert gases is shown in Figure 2. The solid curve is the theoretical upper bound calculated for an assumed three body potential which is the sum of the two body potentials for the

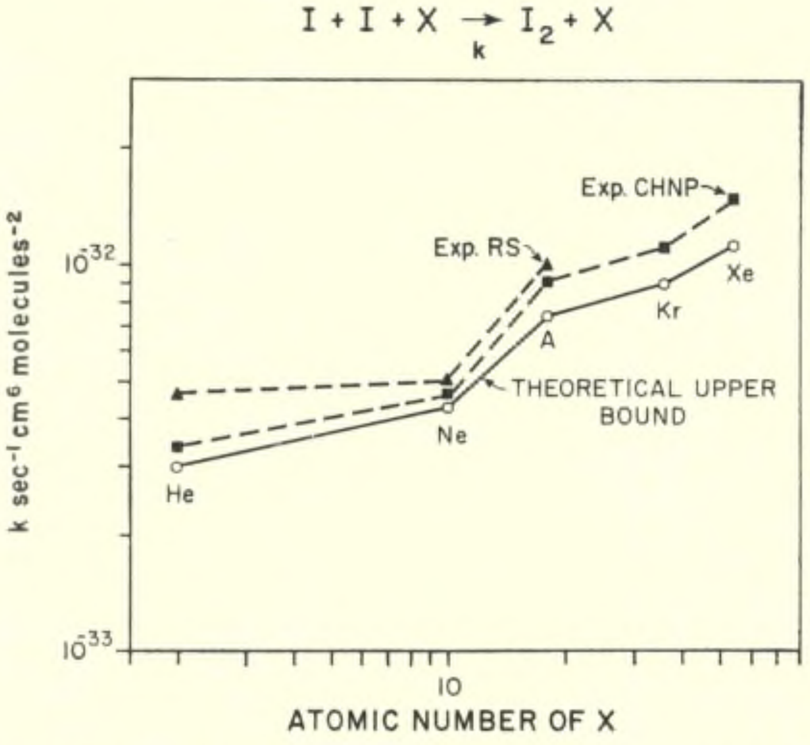


Fig. 2. — Comparison of experimental results on the recombination rate of iodine in the presence of inert gases.

various pairs. The experiments are those of Russell and Simons[3] (curve RS) and Christy, Harrison, Norrish and Porter[4] (curve CHNP). The fact that the upper bound is slightly below the experiments is not regarded as significant in view of the uncertainty in the potential used. An important difference between Keck's theory and collision theories is that it predicts a rate independent of third body mass so that the variation shown in Figure 2 is due entirely to differences in the range of the forces involved.

The most important question which arises in connection with Keck's theory is how much it overestimates the rate because of recrossing. Keck[5] has investigated this effect by numerically integrating

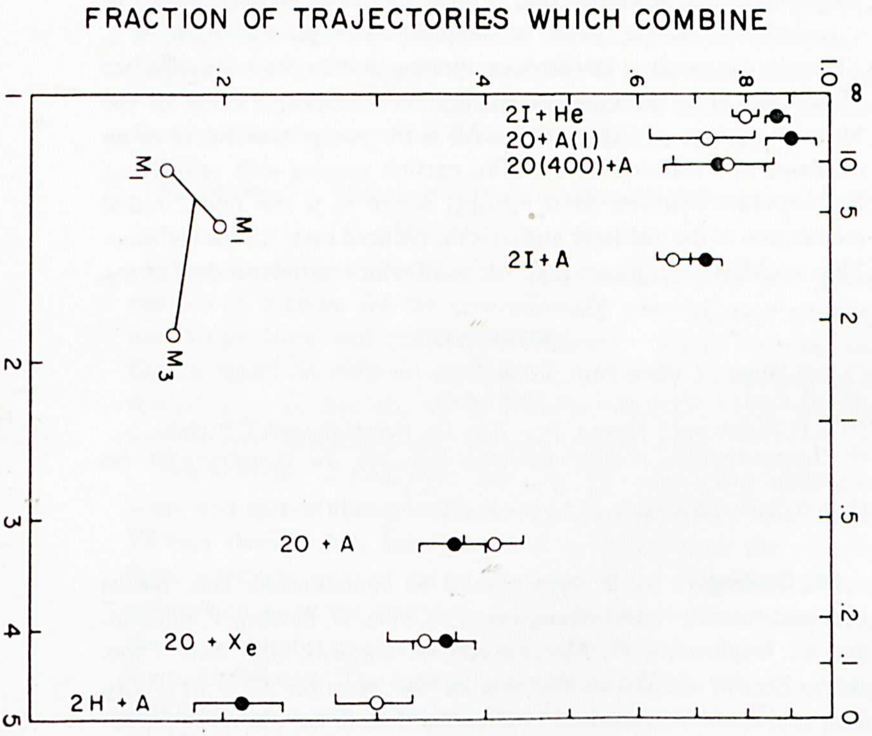


Fig. 3. — Fraction of systems crossing the critical surface S_B in Fig. 1 which resulted in reactions obtained by numerically integrating the equations of motion for a random sample. The open and closed points correspond respectively to kT/D equal .01 and 0.1. The vertical bars give the *rms* deviation due to differences in mass or size, calculations were carried out using the potential for 2O + A but with the atomic mass of A equal to one (point 2O + A (1)) and the atomic mass of O equal to 400 (points 2O (400) + A).

the equations of motion for randomly chosen three particle systems crossing the surface S_B in Figure 1. Some results are shown in Figure 3 where the fraction of systems is plotted as a function of the parameter $1 + (\omega\tau)^2$ where ω is the vibrational frequency of a Morse oscillator at an energy kT below the dissociation limit and τ is the collision time. It can be seen that a surprisingly large fraction of the systems followed resulted in reaction. This is an important advantage of the technique of sampling in the middle of the reaction zone over the more usual one of sampling outside the reaction zone which typically produces an extremely small number of reactions. It is interesting to note that as the mass of the third body, m_3, goes to zero, $\omega\tau$ also goes to zero and the recombination probability goes to unity. Since the reference rate is independent of m_3, this results in a recombination rate which is independent of m_3 for $m_3/m_1 \ll 1$. Although this result at first seems surprising, it is a simple consequence of the fact that the classical reaction rate is proportional to the Maxwell average of $(\Delta E)v_3$ where ΔE is the energy transferred to an oscillator in a collision with a third particle moving with velocity v_3. For impulsive collision $\Delta E \propto p_o(\mu_3 v_3)$ where p_o is the initial radial momentum of the oscillator and μ_3 is the reduced mass for the collision. Thus $<(\Delta E)v_3> \propto p_o <\mu_3 v_3{}^2> \propto p_o k\mathrm{T}$ which is independent of m_3.

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M. Goldfinger. — It seems useful to communicate here results obtained recently in our laboratory (G. Chiltz, R. Eckling, P. Goldfinger, G. Huybrechts, G. Martens and G. Simoens, *Bull. Soc. Chim. Belg.*, **71**, 747 (1962) on the rate of the reaction $Cl + Cl + Cl_2$. This rate could be measured by showing that, in the phosgene photosynthesis, the atom-atom chain breaking step, negligible at room temperature, becomes comparable to the atom-radical step in the temperature range of 500 to 600 °K. The values obtained here are 5 to 8 × 10^9 l^2 mole^{-2} sec^{-1}, with a slightly decreasing trend with increasing temperature; this value is somewhat smaller than the value for the $Br + Br + Br_2$ reaction interpolated at the same temperatures.

It is possible to correlate our value with that given by H. Hiraoka and R. Hardwick, *J. Chem. Phys.*, **36**, 1715 (1962), using the equation given by the latter authors. It is however also possible to represent the results by an almost straight line log k *vs*, 1/T. I would like to ask if in the case of the Br or I-atoms the existing data permit one to decide if a straight line representation as often used is adequate. In the case of our results on Cl-atoms it is not yet possible to make such a decision.

M. Hornig. — It has been asked whether recombination rates follow the linear law

$$\log k_A = A + \frac{E}{R\,T}$$

over a wide temperature range. I should like to mention that Burns in my laboratory has studied the recombination of Br atoms by flash photolysis at temperatures up to 900 °K. His results were that the expression is not linear but flattens very much at higher temperatures, the rate changing very little between 500 °K and 900 °K.

M. Shuler. — I want to adress myself to the dissociation reaction

$$AB + M \rightarrow A + B + M$$

There have been presented to this conference by now several theories to account for the experimentally observed rate constants, and temperature and pressure dependence. These theories, even though based on different assumptions as to the mechanism of the dissociation, all had the virtue that the calculated rate constants were in good agreement with the experimental ones.

This situation is quite reminiscent of the status some 15 or more years ago of the theory of flame velocities in steady state flames. Various theories had been proposed to account for the observed flame velocities, most of the theories were based on entirely different assumption as to the rate determining process, and each particular theory would give good agreement for the particular flame for which it was formulated. The answer, of course, is that the process of flame propagation is a very complicated one, that a correct theory, as pointed out by Hirschfelder and Curtiss, must include all the relevant processes (i.e. heat conduction, chemical reactions, material diffusion, etc...) properly coupled, and that the success of the partial theories were due to the fact that in certain specific flames, certain specific processes were rate determining and thus could be uncoupled from the other processes to a good approximation. I believe that the same situation pertains to the present theories of dissociation. There is, I believe, a « correct » and all-inclusive theory, and many of the theories presented here emphasize specific aspects of the complete theory while neglecting others. Such a « complete » theory for dissociation reactions can certainly be developed in principle even though, at the present time, there is not as yet sufficiently detailed knowledge of various of the parameters to carry out detailed rate calculations. Such a theory must follow the fundamental outline put forth by E.P.Wigner about 25 years ago and followed up recently by J.C. Keck.

Sketched briefly, it will involve the construction of the potential surface representing the interaction $AB + M \rightarrow A + B + M$ which must include all the appropriate anharmonicities, rotational contributions, « complex formation » (i.e. potential minima), etc. The reaction is then studied by investigating the dynamics of representative mass points on the potential surfaces taking due account of phase relationschips, multiple crossings of the energy surfaces, etc... Such a program, to be sure, seems unreasonably ambitious, but the availability of high speed electronic computers brings it much closer to reality. Recent work along these lines by Keck, by Wall, Hiller and Mazur, and by Polanyi (as reported at this conference) seems very promising.

If and when such a formal theory has been developed which takes proper account of all the relevant interactions, the phenomenological theories discussed here should readily be recognizable as convenient approximations whose range of validity will depend strongly on the « chemistry » of the reactants A, B and M and on the strength and form of their interaction.

M. Porter. — Even this approach would not be the best in some cases e.g. the $NO\text{-}I_2$ case, since it would give only a single number, the overall rate constant, whereas more detailed information than this is available experimentally and must therefore be interpreted theoretically. If one disregards mechanism what use are such calculations anyway ? We shall have to rely on experimental data to obtain the data for practical purposes in the foreseeable future. Finally how will you calculate the force fields which are clearly one of the most important factors in any treatment of these reactions ?

M. Shuler. — I quite agree with Professor Porter that it will be necessary to have detailed information on force fields and that we do not have very accurate data on these for many reactions of interest.

Some of these data can be obtained from molecular beam scattering experiments of the type now carried out in a number of laboratories. Another approach to obtaining such data on force fields is through quantum mechanical calculations. Such calculations must however be based on experimentally determined parameters.

M. Kantrowitz. — We may be approaching the point now where theoretical treatment such as Keck's are capable of providing some information on force fields by working backward from measured reaction rates. It is possible that such a procedure would be useful in allowing extrapolation of reaction rate information to temperature ranges other than those where measurements exist and might provide some estimates for measuring reaction rates where measurements do not exist.

M. Cottrell. — Dr. Linnett has asked for examples of energy transfer which involve highly specific interactions. This seems to be so for ammonia where the lowest frequency, about 1000 cm^{-1} is large enough for one to expect de-excitation to require many collisions. We have confirmed Lambert and Salter's[1] observation that the ultrasonic velocity in NH_3 does not disperse up to a frequency pressure ratio of 10Mc sec^{-1} atm^{-1}, indicating that the number of collisions required for vibrational energy transfer, $Z^1{}_{10}$, is less than 15. On the other hand, we have shown[2] that phosphine, PH_3, with a similar vibration frequency, has $Z^1{}_{10} = 900$. The anomalously large energy transfer probability in NH_3 may be caused by an impulsive dipole-dipole interaction occuring when inversion takes place during a collision. The inversion frequency in NH_3 is such that at least one inversion takes place per encounter. On the other hand, the probability of an inversion occuring during an encounter in PH_3 is only 10^{-4}, and the number of collisions required for deactivation is normal. This suggestion appears to be confirmed by the isotope effect, $Z^1{}_{10}$ for ND_3 being about 90, and the inversion frequency for ND_3 being 10 time less than in NH_3. $Z^1{}_{10}$ for PD_3 is about 1200, only slightly greater than that for PH_3.

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M. Duchesne. — I wonder if you have considered the case of arsine in the deactivating process, as this would help to confirm your hypothesis concerned with the part played by the tunnel effect ?

M. Cottrell. — Yes. We are studying arsine at present but we do not have the answer yet.

Mr Ubbelohde. — Can we clarify somewhat the problem of « sticky collisions » ?

M. Shuler. — Could we have a definition of a collision when hard spheres are not involved ?

M. Hornig. — In thinking of a sticky collision perhaps the simplest example is that of an electron and a molecule. The work of G.J. Schulz has shown that even low velocity electrons are very efficient in exciting vibration in N_2, although N_2 relaxes very slowly under ordinary circumstances. The interaction cannot be thought of as an ordinary impulsive collision since the mass ratio is so great. Presumably the reason it is so efficient is that a stable or possibly a transitory N_2^- ion is formed, in which the equilibrium N-N distance is different from that in N_2. This is closely related, of course, to the effects Dr. Linnett has described.

M. Cottrell. — I am not sure that it is necessary to have a definite negative ion state for electrons to cause energy transfer to vibration. We have done a calculation which suggest that sufficient energy could be transferred by polarization of the electron distribution of the molecule by the approach of an electron.

It is possible, however, that this may simply be another way of talking about the same effect.

b) Champs de forces.

M. Linnett. — I wish to draw to your attention four cases in which there are problems concerning the force fields to be used to describe collision processes :

1° For consideration of the combination of two atoms the potential energy curve of the corresponding diatomic molecule is required.

In most cases the form of the lower part and the depth of the minimum only are known accurately. The form of the curve near the limit is usually not known at all accurately except in a few cases such as H_2.

2° Professor Polanyi has told us of his very interesting calculations for the collision process $H + Cl_2 \rightarrow HCl + Cl$ and of the agreement between the theoretical and experimental values for the percentage of the energy that appears as vibrational energy of the HCl. One would like to know (*a*) how sensitive this result is to the form of the field assumed, and (*b*) how the percentage would be affected by changes in the force field and what effects would cause an increase and what a decrease. I think that the result may be rather insensitive to the exact shape of the P.E. « surface » but decided more by its general form.

3° In the collision AB + C the efficiency of transfer of energy from translation to vibration of AB will, on the other hand, depend very critically on the magnitude of the cross-terms in the potential energy expression between r_{AB} and r_{BC}. The size and causes of such cross-interactions are therefore of the greatest importance.

4° In the collision of an atom with a molecule, it is important to know when the forces are simply « dispersion » forces and when other forces, which might be described as chemical, come into play. This will depend on the energy needed to modify the electronic systems of the separate parts. We know that aromatic molecules lose and gain electrons quite readily. Consequently the interaction of an iodine atom with an aromatic molecule is likely to involve attractive forces greater than van der Waals dispersion forces. With an atom like Xenon and molecules like CO, this is also likely to be true, chemical compounds of Xenon and carbonyls are known. On the other hand, with He, Ne and A, for which the ionization potentials are quite a bit larger, the forces are likely to be the simple dispersion ones only.

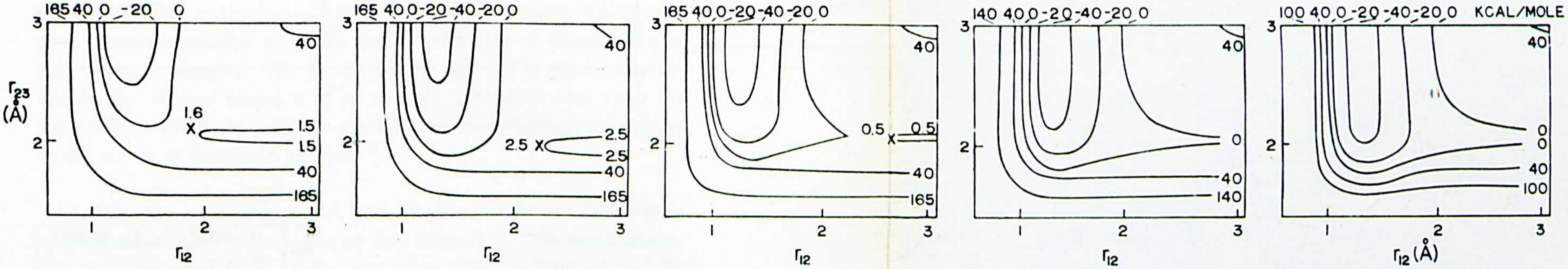
M. Porter. — I think we may encounter rather special forces of interaction between atoms (or free radicals) and saturated molecules. One way of illustrating why this may be so is to consider the molecular orbital theory of interaction between two radicals, two saturated molecules or a radical and a molecule. In each case the highest orbitals of each of the two partners result in two orbitals in the complex, one bonding and one antibonding. In the case of two radicals the two electrons fill the bonding orbital and we get a normal covalent chemical bond; in the case of two saturated molecules we get full bonding and antibonding orbitals and no net bonding. Finally in the interaction of a radical and a molecule we get two bonding and one antibonding electron and net bonding. Of course, if the energies of the original orbitals are very different the interaction will be small but might be expected to contribute significantly to the attraction potential in most cases.

M. Polanyi. — Dr. Linnett has noted the importance in energy transfer calculations of the inclusion of « cross-terms » as well as nearest neighbour interactions. It may be worth pointing out that in the type of calculation that I was discussing for A + BC collisions (sometimes there is no reaction, simply energy transfer) this important term is, as he would wish, always present.

Finally, Dr. Linnett asked whether it is part of our intention to explore the effect of varying the shape of the hyper-surface $V(r_{12}, r_{23}, r_{13})$ accross which our reaction takes place. We have in fact begun to do this. Similar work is going on in several laboratories, I believe (Wall, Hiller and Mazur at the University of Illinois, Blais and Bunker at the University of California).

The first figure shows five potential energy surfaces for linear reaction, $H + Cl_2 \rightarrow HCl + Cl$. They were plotted according to Sato's method, with various overlap integrals (the one at the far left required a modified form of Sato's equation). The most important feature of the surface that is changing is the repulsion between the products (high at the left, negligible at the right). The following figure is really a family of calculations of the type that I described earlier (circles indicate translational energy, triangles vibrational energy; filled-in points for $D + Cl_2$). The $S = O.O$ column repeats the earlier results, for comparison. It can be seen that vibrational energy is least for the repulsive surface at the left, greatest for the attractive. This is precisely what M.G. Evans and M. Polanyi predicted (*Trans. Farad. Soc.* **35** 178 (1939)), though without a computer they could not carry out the calculation for free planar movement across the hypersurface $V(r_{12}, r_{23}, r_{13})$.

The calculations reported here were performed by Mr. Charles Young and Mr. Peter Richardson.



$S_{23} = -0.4$
$S_{12} = S_{13} = 0.15$

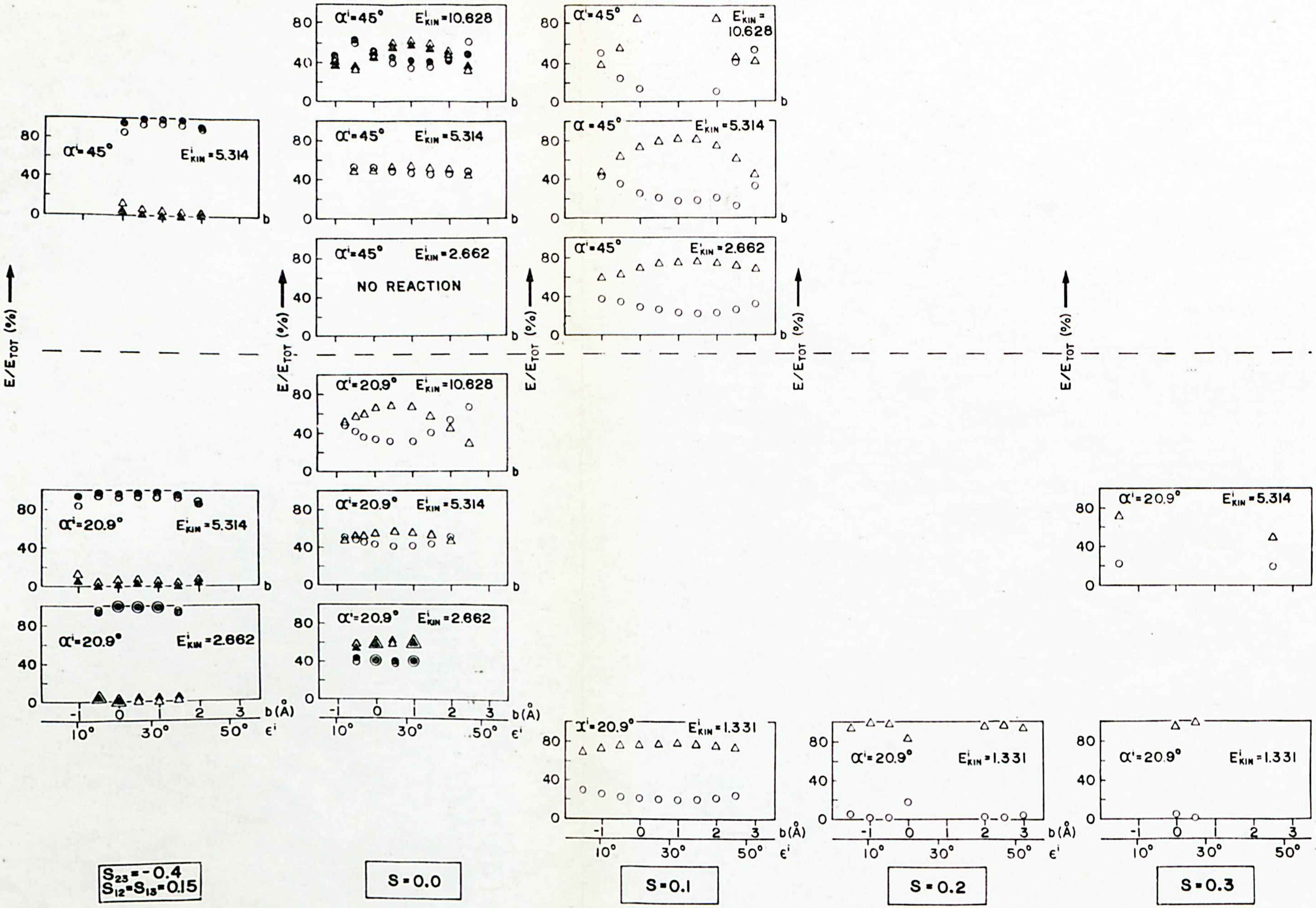
S = 0.0

S = 0.1

S = 0.2

S = 0.3

Fig. 1



α' = 45°
E'KIN = 10.628
E'KIN = 5.314
E'KIN = 2.662
NO REACTION
α' = 20.9°
E'KIN = 1.331
E/ETOT (%)
80
40
0
b
b(Å)
-1
0
1
2
3
10°
30°
50°
ε'
S23 = -0.4
S12 = S13 = 0.15
S = 0.0
S = 0.1
S = 0.2
S = 0.3

Fig. 2

M. Slater. — Although we have considerable knowledge of anharmonic potentials for diatomics, it is difficult to see what form of anharmonic cross-terms should be assumed to connect different « bond »-coordinates in polyatomic molecules.

M. Herzberg. — The potential energy function of several diatomic molecules is rather well known experimentally right up to the dissociation limit for a number of diatomic molecules. By that I mean that all the vibrational levels up to the last one below the limit are known. Unfortunately, this cannot be said for any polyatomic molecule.

M. Morrison. — In any collision process, the intermediate step can be regarded as the formation of a collision complex, which contains a certain amount of excess energy. The rate of dissociation of this collision complex will be dependent upon this excess energy. Would Dr. Wigner expect it to be strongly dependent also upon the force field in which the collision products are dissociating particularly in the region of threshold energies ?

M. Wigner. — I assume that Dr. Morrison refers to the case in which the potential is attractive so that there is no activation mountain and the usual form of the transition state method cannot be applied. As far as I know in this case the question has not been studied in detail and perhaps I am wrong in trying to comment on it. There seems to be no obvious reason for a great difference in the dissociation rate of two systems which differ only in the long-range behaviour of the potential characteristic of the bond to be ruptured. This applies certainly if the potentials drop as fast as $1/r^6$ and probably as soon as they drop faster than $1/r^2$. I believe this follows also from a calculation by means of the extended transition state method if one assumes that there is a distance beyond which the atom to be liberated from its bond is solely under the influence of the long range potential and does not influence any more the internal motion of the residual molecule. By extended transition state method I mean the type of calculation which was used for giving an upper limit to the rate of association reactions.

M. Pauling. — The interaction of an excited mercury atom (Hg^* $6s6p$ $^3P_2$) with a molecule of carbon monoxide must be discussed differently from the interaction with an atom of a noble gas, because of the possibility of forming a chemical bond in the first case and not in the second case. The carbon monoxide molecule may be assigned the structure $:\mathrm{C}\equiv\mathrm{O}:$. With the excited mercury atom it may form a complex $\uparrow \overset{\uparrow}{\mathit{Hg}} - \mathrm{C}\equiv\mathrm{O}:$, using the sigma electron pair of carbon for the bond, which involves a $6s6p$ hybrid bond orbital of the mercury atom, which has an unpaired electron in the other sp hybrid orbital and another one in a $p\pi$ orbital. The electroneutrality rule suggests another structure, $\uparrow \mathrm{Hg} - \overset{\uparrow}{\mathrm{C}} = \ddot{\mathrm{O}}:$, in which the p electron is on the carbon atom; and, of course, the $p\pi$ electron may be involved in the formation of a one-electron bond.

The transition to $^3P_0$ of the mercury atom might correspond to changing the one-electron bond to an anti-bond. The potential energy function in its dependence on the mercury-carbon distance and the carbon-oxygen distance would then be shifted in such a way that the Franck-Condon principle would favor a change in the vibrational quantum number of the carbon monoxide molecule, as is observed.

M. Ubbelohde. — van der Waals-London attraction potentials for a diatomic molecule with only a single electron bond, or with a free valency would be quite different (normally stronger) than for molecules with saturated valencies, since the excitation and ionization energies are quite different.

M. Ross. — In connection with the application of the transition state theory to bimolecular reactions, it is important to point out that the energy dependence of the reaction cross section enters only in the pre-exponential temperature coefficient. Hence a full calculation of the transmission coefficient is required.

M. Voevodsky. — In investigating force fields acting during a collision the experimental methods used should involve characteristic times as close as possible to the collision time. Recently developed radiospectroscopic methods applicable within the range of 10^{-6} to 10^{-10} sec. may prove very effective in such investigations.

c) Réversibilité microscopique.

M. Slater. — Detailed balancing of transitions, or microscopic reversibility, is established for quantum probabilities, but is not always directly valid in classical mechanics, where (compare Tolman's « Principles of Statistical Mechanics ») we may have instead to build up cycles of « corresponding collisions » processes. Detailed balancing is a mechanical phenomenon which maintains pre-existing equilibrium, and so would appear in a different light in non-equilibrium processes, for example in the progress of a unimolecular reaction. Nevertheless statistical ideas closely connected with balance are commonly used in these situations; for example, it is usually assumed that in a lower-pressure or quasi-unimolecular decomposition the rate of activation to a specified high-energy state is such as would balance the rate of deactivation from this state *if* the equilibrium number of high-energy molecules were present (and they are not present at lower pressures). The real assumption being made here is, in fact, that the lower-energy states have effectively their normal population despite the drain from high energies, so that activations occur for this reason at an « equilibrium » rate. In the broader picture of rate theory, I am conscious that I should pay more attention to detailed reverse reaction processes — for example to details of association configurations as the reverse of unimolecular dissociation; considerations of this kind we have seen to be very useful for simpler reactions.

M. Ross. — I would like to make some comments on the terms « microscopic reversibility » and « detailed balance ». Consider an elementary bimolecular reaction, $A + B \rightleftharpoons C + D$. Microscopic reversibility refers to an equivalence of the transition probability of the forward and reverse direction of the reaction, that is

$$\frac{|p|}{\mu}\,\sigma_{AB}(|p|, \Omega)\, d\Omega dp_A\, dp_B = \frac{|p'|}{\mu'}\,\sigma_{CD}(|p'|, \Omega')\, d\Omega'\, dp_C\, dp_D\,,$$

where $|p|$ is the magnitude of the relative momentum, μ the reduced mass (with similar definitions of the primed quantities for products), σ_{AB} the reaction cross section for the forward direction, and Ω a solid angle.

The reaction rate coefficient for the forward direction is

$$k_f = \int \ldots \int \frac{|p|}{\mu}\,\sigma_{AB}(|p|, \Omega)\, f_A f_B\, d\Omega dp_A\, dp_B,$$

where f_A is the momentum distribution function (with the neglect of internal degrees of freedom). At *Chemical equilibrium* f_A is f_A^o, the equilibrium Maxwellian distribution function, and the corresponding rate coefficients are related to the equilibrium constant

$$\frac{k_f^o}{k_r^o} = K.$$

This equation is a statement of detailed balance. As long as the chemical rate is slow compared with other possible relaxation processes then the distribution functions will still be adequately represented by their equilibrium values and the relation of the rate coefficients to the equilibrium constant remains valid.

The second law of thermodynamics can be satisfied without the requirement of detailed balance.

M. Shuler. — The remarks I am about to make are certainly not very fundamental; they relate instead to a practical, experimental criterion on the possible presence of cyclic processes. It can readily be shown (see e.g. J.Z. Hearon, *Bull. Math. Biophys.* **15**, 121 (1953); K.E. Shuler, *Phys. Fluids* **2**, 442 (1959)) that if detailed balancing obtains in transitions between properly defined quantum mechanical states (or chemical species), then the transition probability matrix which enters into the rate equation for the rate of transfer between all the various states (or species) can always be symmetrized. From this it follows that there can be no truly periodic solution (damped or undamped) to the rate equation since all the eigenvalues of the solution will be real (or zero). Cyclic processes without detailed balancing between the participating states (or species), i.e.

$$\begin{tikzcd}
 & A \arrow[dr] & & & & A \arrow[dl, shift left] \arrow[dr, shift left] & \\
C \arrow[ur] & & B \arrow[ll] & \text{rather than} & C \arrow[ur, shift left] \arrow[rr, shift left] & & B \arrow[ul, shift left] \arrow[ll, shift left]
\end{tikzcd}$$

can, however, give rise to periodic (i.e. oscillatory) solutions of the rate equations.

By a very fundamental approach it is possible to connect the principle of microscopic reversibility (which is used here interchangeably with « detailed balancing ») with that of the time reversal invariance and thus establish it on a firm a priori theoretical basis. From an a posteriori, experimental point of view one can argue (more weakly, to be sure) that the principle of detailed balancing at equilibrium is validated by the non-existence, at least as far as I know, of multistate (species) rate processes which have *true* periodic solutions.

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