ELEMENTARY REACTIONS IN THE GAS PHASE INVOLVING EXCITED ELECTRONIC STATES

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Received November 4, 1950

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[1] Atomic Energy Commission Post-Doctoral Fellow, 1949–50; Applied Physics Laboratory Research Fellow, 1950–51.

[2] The work described in this paper was supported in part by the Bureau of Ordnance, U. S. Navy, under Contract NOrd-7386.

I. INTRODUCTION

There are now known a large number of elementary reactions which involve atoms or molecules in excited electronic states. In some of these the electronically excited species are reactants, in some they are products, and in some there is a transfer of electronic energy from one molecule to another, so that both a reactant and a product are excited.

Reactions in which electronically excited reactants play a part are of particular importance in photochemistry and radiation chemistry, while those in which a product is excited are important in connection with flames. The primary processes by which electronically excited atoms and molecules are produced in photochemical and radiochemical systems, such as absorption of radiation or inelastic collisions of high-energy particles, are of a physical nature and will not be discussed in detail in this review. The production of electronically excited species in flames, on the other hand, is quite often due to specific chemical reactions. In some flames, such as the cool flames studied by Polanyi and others (8, 11, 168, 169, 170, 173, 174), the observed luminescence is due entirely to chemically produced, electronically excited atoms or molecules. In hot flames some of the radiation is of the black-body type, i.e., thermal radiation, but superimposed on this is usually some radiation emitted by excited species produced in specific chemiluminescent reactions. The manner of production of these excited species is a matter of great interest, and will be discussed in some detail.

The number of reactions which may occur after a molecule has become electronically excited is quite considerable. There are, in fact, at least nine important and common types of processes which the excited species might undergo; these are listed, with some pertinent examples, in Section II. When one adds to this list the types of reactions involving products in excited states, there is found to be a large number of processes which must be studied. It is of the greatest importance to arrive at an understanding of the factors influencing the rates of such reactions in order that it will be possible to predict which of these processes may occur in a given reaction system. This review is concerned mainly with this problem. After a survey, with examples, of some of the more important reaction types, the processes will be considered from the theoretical standpoint, in terms of potential-energy surfaces and the theory of absolute reaction rates. The available data will then be discussed in some detail with reference to this theoretical background. It is thought that in this complicated field more progress will come from interpreting in this way the experimental data than from attempting to make elaborate calculations, the results of which are only of doubtful accuracy.

II. REACTION TYPES

In photochemical reactions, the excited species is produced by the absorption of radiation of the appropriate wave length by an atom or molecule in the ground state. This type of process can be written in general as

$$A \xrightarrow{h\nu} A^* \tag{1}$$

where the superscript asterisk, as in all the reactions to follow, indicates the electronically excited species. A well-known example of this excitation process is

$$\mathrm{Hg}(6^1S_0) \xrightarrow[\text{(2537 Å.)}]{h\nu} \mathrm{Hg}(6^3P_1) \tag{2}$$

In radiochemical reactions the electronically excited species are produced by inelastic collisions between fast particles (such as α-particles or electrons) or high-energy photons (x-rays, γ-rays) and the atoms and molecules in the reaction system; the energy given up by the high-energy radiation or particles on collision is passed on to the collision partners as electronic excitation or ionization energy. For the case of excitation by α-particles, for instance, this process may be formulated as:

$$A \overset{\alpha}{\rightsquigarrow} A^* \tag{3}$$

An example is the reaction

$$\mathrm{H}_2 \overset{\alpha}{\rightsquigarrow} \mathrm{H}_2^* \rightarrow 2\mathrm{H} \tag{4}$$

postulated by Eyring, Hirschfelder, and Taylor (35) in connection with the para–ortho hydrogen conversion initiated by α-particles. Another type of excitation process of importance in radiochemical systems is that of electron capture by ions, the electrons being produced in the process of ionization accompanying the passage of the incident particles through the reaction system. This process can be written as:

$$A_2^+ + e \rightarrow A^* + A \tag{5}$$

An example is the reaction

$$\mathrm{H}_2^+ + e \rightarrow \mathrm{H}(1^2S) + \mathrm{H}^*(2^2S \text{ or } 2^2P) \tag{6}$$

recently discussed by Magee and Burton (126).

In addition to these physical methods of producing electronically excited species, there are various types of chemical reactions which result in the formation of excited species; these are of particular interest in connection with the study of flames. For example, two atoms or molecules may associate to give an electronically excited molecule, which may then return to the ground state by emission of the characteristic association continuum:

$$A + B \rightarrow AB^* \rightarrow AB + h\nu \tag{7}$$

An example of this type of reaction is (48, 49)

$$O + NO \rightarrow NO_2^* \rightarrow NO_2 + h\nu \tag{8}$$

The association may also take place as a three-body reaction, in which case the third body may stabilize the excited molecule.

$$A + B + C \rightarrow AB^* + C \tag{9}$$

This type of process is exemplified by the reaction (50, 63):

$$O(^3P) + CO(^1\Sigma^+) + M \rightarrow CO_2^*(^3\Pi) + M \tag{10}$$

Another type of association reaction is

$$A + B + C \rightarrow AB + C^* \tag{11}$$

Such a process is involved in the reaction between hydrogen atoms and sodium (127, 137):

$$H(^2S) + H(^2S) + Na(^2S) \rightarrow H_2(^1\Sigma_g^+) + Na^*(^2P) \tag{12}$$

Other processes giving rise to electronically excited products are exchange reactions such as:

$$AB + CD \rightarrow AC^* + BD \tag{13}$$

Reactions of this type have been postulated to account for some of the excited species in hydrocarbon flames (50, 53); examples are

$$CH + O_2 \rightarrow CO + OH^* \tag{14}$$

and

$$C_2 + OH \rightarrow CO + CH^* \tag{15}$$

Another type of reaction is exemplified by

$$Na + NaCl \rightarrow Na^* + NaCl \tag{16}$$

where the *reactant* NaCl is in a vibrationally excited state. This reaction is believed to account for a good part of the electronically excited sodium in the cool flame of sodium and chlorine (125, 173).

Elementary reactions involving excited species as reactants are met with in photochemical and radiochemical systems. The most important types of reactions (other than radiation) that may be undergone by an electronically excited atom or molecule are as follows:

(1) *Spontaneous dissociation:*

$$AB^* \rightarrow A + B \tag{17}$$

Predissociations are of this type, as are the following dissociations of electronically excited olefins (111, 112):

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \tag{18}$$

$$C_3H_6^* \rightarrow C_3H_5 + H \tag{19}$$

(2) *Spontaneous isomerization,* which may be represented as:

$$AB^* \rightarrow BA \tag{20}$$

Several *cis-trans* isomerizations can be induced to proceed by initial electronic excitation, and are therefore of this type (see page 205).

The above two reactions are unimolecular; in addition there are the following bimolecular processes:

(3) *Physical quenching,* in which the electronic energy is removed from the molecule without the occurrence of any reaction:

$$A^* + B \rightarrow A + B \tag{21}$$

An example is the quenching of electronically excited sodium by hydrogen molecules.

$$Na^*(^2P) + H_2(^1\Sigma_g^+) \rightarrow Na(^2S) + H_2(^1\Sigma_g^+) \tag{22}$$

(4) *Transfer of electronic energy to the colliding molecule:*

$$A^* + B \rightarrow A + B^* \tag{23}$$

This type of process (sensitized fluorescence) was first observed by Cario and Franck (17), who found that excited mercury atoms could excite thallium atoms to various excited states.

$$Hg^*(^3P_1) + Tl(^2P_{1/2}) \rightarrow Hg(^1S_0) + Tl^* \tag{24}$$

(5) *Quenching accompanied by dissociation of the colliding molecule, the resulting fragments remaining free:*

$$A^* + BC \rightarrow A + B + C \tag{25}$$

Such a process occurs in the quenching of mercury radiation by hydrogen (167, 214).

$$Hg^*(^3P_1) + H_2 \rightarrow Hg(^1S_0) + 2H \tag{26}$$

(6) *Chemical quenching with dissociation, one of the products of the dissociation becoming associated with the quenched molecule:*

$$A^* + BC \rightarrow AB + C \tag{27}$$

An example is the quenching of excited cadmium by hydrogen, in which case the cadmium hydride is formed (117).

$$Cd^*(^3P_1) + H_2 \rightarrow CdH(^2\Sigma^+) + H \tag{28}$$

(7) *Quenching with dissociation of the quenched species:*

$$AB^* + C \rightarrow A + B + C \tag{29}$$

Induced predissociations are examples of this; also, the following reaction has been postulated as occurring in the hydrogen–oxygen flame (50, 80):

$$OH^*(^2\Sigma^+) + H_2(^1\Sigma_g^+) \rightarrow O(^3P) + H(^2S) + H_2(^1\Sigma_g^+) \tag{30}$$

(8) *Quenching with isomerization of the quenched species:*

$$AB^* + C \rightarrow BA + C \qquad (31)$$

Such a process has been shown to occur when an electronically excited molecule of 1-butene collides with a normal molecule (67, 112).

$$1\text{-}C_4H_8^* + 1\text{-}C_4H_8 \rightarrow 2\text{-}C_4H_8 + 1\text{-}C_4H_8 \qquad (32)$$

(9) *Association between the excited molecule and the colliding molecule:*

$$A^* + B + M \rightarrow AB + M \qquad (33)$$

An example is the reaction between excited oxygen atoms and carbon monoxide in its ground state, with the formation of carbon dioxide in its normal state.

$$O^*(^1D) + CO(^1\Sigma^+) + M \rightarrow CO_2(^1\Sigma_g^+) + M \qquad (34)$$

In view of the large number of reactions that might be expected to occur in any one reaction system, it is clearly of importance to study the factors influencing the rates of reactions of this type. Accordingly, the general principles involved in the construction of potential-energy surfaces for these reactions will now be discussed, and the rate equations will be formulated. The experimental data will then be considered in the light of this theoretical background.

III. Reaction Mechanisms and Reaction Kinetics

A. POTENTIAL-ENERGY SURFACES

To obtain an insight into the mechanisms of elementary reactions involving excited electronic states, it is advantageous to approach the problem by using the theory of absolute reaction rates (32). In particular, potential-energy surfaces relevant to the system under consideration are of great value in elucidating the detailed mechanisms of elementary reactions. The principles and methods of constructing these potential-energy surfaces have been discussed in detail elsewhere (62); nothing essentially new has been added to this general topic since then, and the discussion here will thus deal mainly with the construction and application of potential-energy surfaces in systems involving excited electronic states.

A large number of elementary reactions are three-center reactions, involving the breaking of a single chemical bond and the making of a new bond; such reactions may be represented by the equation

$$A + B\text{—}C \rightarrow A\text{—}B + C \qquad (35)$$

in which the B—C bond is broken and the A—B bond is formed. In the equation, A, B, and C may be atoms or radicals. The present discussion will deal mainly with these three-center reactions.

When no electronically excited species are involved, a process may be represented by the movement of a mass-point over the lowest potential-energy surface of the system. A familiar example is the reaction

$$H + H_2 \rightarrow H_2 + H \qquad (36)$$

the rate of which is measured by following the rate of conversion of para-hydrogen to ortho-hydrogen (40, 59). This reaction was treated theoretically (36), using the London equation (118, 119) to evaluate the potential energy of the H–H–H complex. It is easy to show that for this system, involving only *s* electrons, the most stable configuration corresponds to a linear arrangement of the atoms, so that in carrying out the calculations it is a sufficiently good approximation to consider only linear structures.[3]

For a linear complex the configuration is represented by two interatomic distances r_1 and r_2. Three coördinates are therefore required for a plot of energy against configuration, and contour diagrams such as that shown in figure 1 have been commonly used for purposes of representation. A different type of diagram will be used here, as it is more convenient for reactions involving excited electronic states (102, 103); in this method the relevant potential-energy curves are constructed on two faces of a cube, and the behavior in the interior of the cube is shown by means of suitable sections. Figure 2 shows such a diagram for the H–H–H complex. The connecting surface contains two valleys which rise slightly as they approach one another; the col, where the two valleys meet, represents the configuration of highest potential energy, and therefore corresponds to the activated complex for the system.

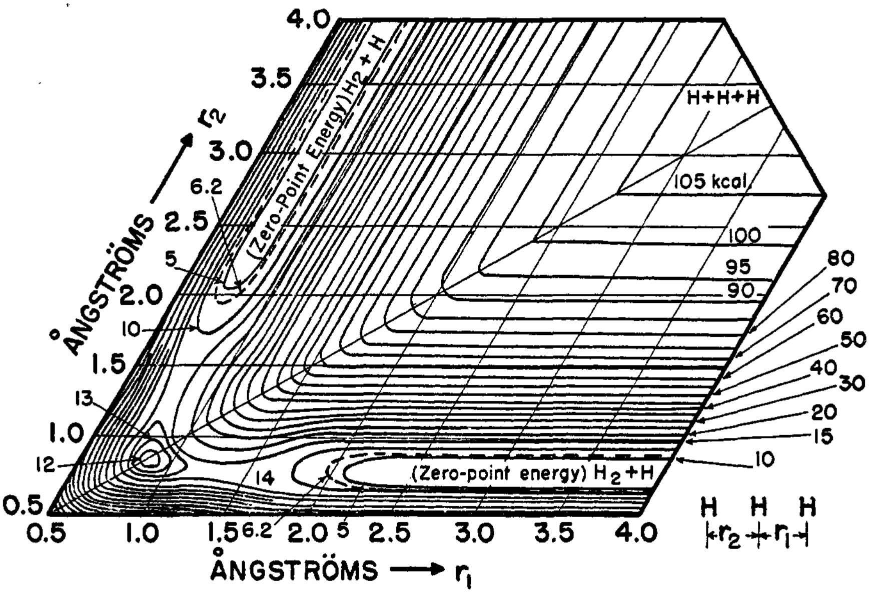

FIG. 1. Potential-energy surface for the system of three hydrogen atoms, based on 14 per cent coulombic energy (after Eyring, Gershinowitz, and Sun (33)).

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[3] When the formation of the activated complex involves *p*, *d*, etc. electrons, the state of lowest potential energy is no longer linear and the London equation is no longer strictly valid. The error in using linear structures for purposes of calculations is, however, probably not too large.

1. *The correlation rules*

When electronically excited reactant or product species are involved, it is necessary to construct potential-energy surfaces for various electronically excited states of the complex and to correlate these with the electronic states of the reactants and products. The first step in this correlation procedure is the determination of the number and spectroscopic designation of the complexes corresponding to the various states and surfaces. This is done by means of the vector model and the Wigner–Witmer correlation rules, and is thus an extension of the method used for diatomic molecules and described in detail by Herzberg (80). There is a great need for the extension of such methods to nonlinear polyatomic complexes, little progress having been made in this direction as yet. The spectroscopic designation specifies the multiplicity $2S + 1$ (where S is the resultant spin quantum number), the space-quantized orbital angular momentum Λ (the states being designated Σ, Π, Δ, etc. according as $\Lambda = 0, 1, 2$, etc.), the + and − character (for Σ states), and the g and u character (for linear molecules symmetrical in the nuclear charges).

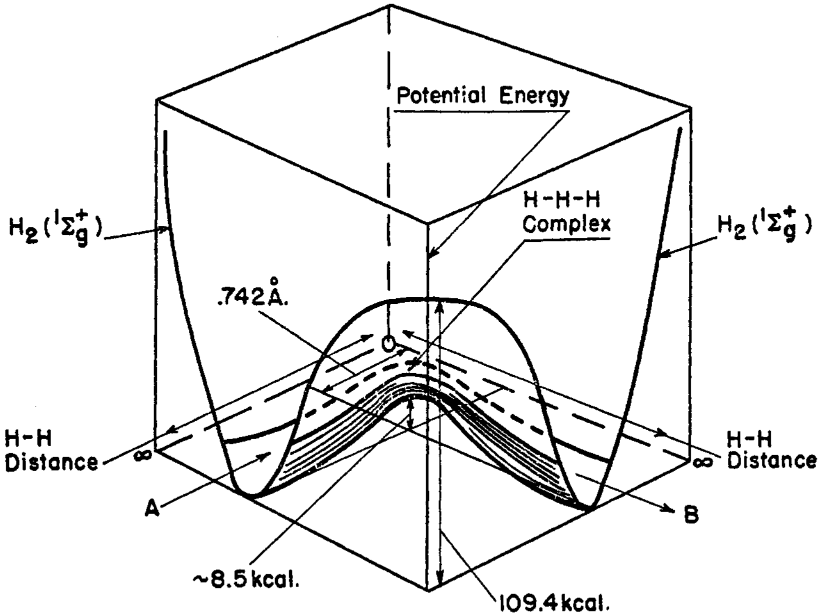

FIG. 2. Potential-energy surface for the system H-H-H. The vertical coördinate represents the potential energy; the horizontal coördinates are H-H distances. The path of the reaction is A → B and the col where the two valleys meet represents the configuration of the activated complex $(H\text{-}H\text{-}H)^{\ddagger}$. Only the ground electronic state ($^1\Sigma_g^+$) is shown.

If atoms or molecules with spins S_1 and S_2 interact to give a complex, the resultant permitted spins are

$$S = S_1 + S_2,\ S_1 + S_2 - 1,\ S_1 + S_2 - 2 \cdots,\ |S_1 - S_2| \tag{37}$$

and the multiplicities of the resulting states are $2S + 1$. The permissible multiplicities are therefore readily found; some common correlations obtained in this manner are given in table 1. As an atom and a molecule or two molecules interact to form a linear complex, the resultant electric field produces a space quantization of the orbital angular momenta in the direction of the internuclear axis. If two atoms with orbital angular momentum quantum numbers L_1 and L_2 are brought together, the resulting components of orbital angular momentum about the line joining the nuclei will be M_{L_1} and M_{L_2}, where

$$M_{L_1} = L_1, L_1 - 1, L_1 - 2, \cdots - L_1 \tag{38}$$

$$M_{L_2} = L_2, L_2 - 1, L_2 - 2, \cdots - L_2 \tag{39}$$

and the quantum number Λ of the molecule thus formed is given by

$$\Lambda = | M_{L_1} + M_{L_2} | \tag{40}$$

TABLE 1

Resultant multiplicities of linear complexes relative to those of the constituent atoms or molecules

MOLECULE A	MOLECULE B	COMPLEX
Singlet	Singlet	Singlet
Singlet	Doublet	Doublet
Singlet	Triplet	Triplet
Doublet	Doublet	Singlet, triplet
Doublet	Triplet	Doublet, quartet
Triplet	Triplet	Singlet, triplet, quintet

only positive values being permitted.[4] This procedure can be extended to the formation of a linear complex from a molecule and an atom, in which case the resulting space-quantized orbital angular momentum would be

$$\Lambda = | M_\Lambda + M_L | \tag{41}$$

and to the formation of a linear complex from two linear molecules where

$$\Lambda = | M_{\Lambda_1} + M_{\Lambda_2} | \tag{42}$$

Some examples of the states resulting in complex formation by an atom and a molecule are given in table 2. In arriving at the states by the use of these tables it may be noted that every possible Λ value may be combined with every possible

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[4] In the case of the approach of an atom to a molecule with the formation of a linear complex, the permitted components of angular momentum of the molecule along the internuclear axis are only $M_\Lambda = \Lambda$ and $M_\Lambda = -\Lambda$; this is to be contrasted with the $2L + 1$ components for the atomic case (equations 38 and 39). We are very much indebted to Dr. G. Herzberg for calling our attention to this point. For nonlinear intermediate complexes, which cannot be characterized by a component of angular momentum about an internuclear axis, additional states may be possible.

multiplicity. The following are some examples of designations arrived at in the above manner:

$$\mathrm{Na}(^2S) + \mathrm{H}_2(^1\Sigma_g^+) \rightarrow \mathrm{NaH}_2(^2\Sigma^+) \qquad (43)$$

$$\mathrm{Na}(^2S) + \mathrm{H}_2(^3\Sigma_u^+) \rightarrow \mathrm{NaH}_2(^4\Sigma^+, {}^2\Sigma^+) \qquad (44)$$

$$\mathrm{Na}^*(^2P) + \mathrm{H}_2(^1\Sigma_g^+) \rightarrow \mathrm{NaH}_2(^2\Sigma^+, {}^2\Pi) \qquad (45)$$

$$\mathrm{Hg}(^3P) + \mathrm{H}_2(^3\Sigma_u^+) \rightarrow \mathrm{HgH}_2(^5\Sigma^+, {}^3\Sigma^+, {}^1\Sigma^+, {}^5\Pi, {}^3\Pi, {}^1\Pi) \qquad (46)$$

The use of these methods in the construction of surfaces will now be discussed with reference to specific examples.

TABLE 2

Electronic states of linear complexes formed from an atom and a molecule

(Atomic correlation rules are given in reference 80)

MOLECULE	ATOM	COMPLEX
Σ	S	Σ
Σ	P	Σ, Π
Σ	D	Σ, Π, Δ
Π	S	Π
Π	P	Σ(2), Π, Δ
Π	D	Σ(2), Π(2), Δ, Φ
Δ	S	Δ
Δ	P	Π, Δ, Φ
Δ	D	Σ(2), Π, Δ, Φ, Γ

2. *Surfaces for the* Na–H–H *system*

One of the most instructive examples of a reaction in which a study of the potential surfaces is of great value in understanding the reaction mechanism is the physical quenching of excited (^2P) sodium by a hydrogen molecule (102),

$$\mathrm{Na}^*(^2P) + \mathrm{H}_2(^1\Sigma_g^+) \rightarrow \mathrm{Na}(^2S) + \mathrm{H}_2(^1\Sigma_g^+) \qquad (47)$$

a reaction that is discussed again from the experimental point of view in Section V. This reaction takes place *via* a complex Na–H–H and it will be assumed for ease of calculation, the error probably not being too large, that the most stable configuration is the linear one (127). The potential-energy surface for this complex may be represented in a three-dimensional diagram in which the coördinates are potential energy, sodium–hydrogen distance, and hydrogen–hydrogen distance. The two profiles of the surfaces which correspond to infinite separation of sodium and hydrogen and of hydrogen and hydrogen are shown on two sides of the cube in figure 3. The lowest curve on the right-hand face is for the system $\mathrm{Na}(^2S) + \mathrm{H}_2(^1\Sigma_g^+)$, and represents the variation of energy with H–H distance in hydrogen; it therefore corresponds to the curve on the right-hand face in figure 2. The curve *NB* in figure 3 corresponds to $\mathrm{Na}(^2P) + \mathrm{H}_2(^1\Sigma_g^+)$, and is therefore similar in form to curve *MA* but is raised by 48.3 cal., which is the energy of the transition Na(^2S) → Na(^2P). The upper curve, passing through H, corresponds to the ionic state Na^+-H^--H, which dissociates to $Na^+(^1S)$ + $H^-(^1S)$ + H(^2S). This dissociated state has an energy higher than that at M, i.e., for Na(^2S) + H(^2S) + H(^2S), by the amount I(Na) − E(H), where I(Na) is the ionization potential for sodium and E(H) is the electron affinity of the hydrogen atom; I(Na) − E(H) has the value 101.5 kcal. To construct the curve for H^--H($^2\Sigma^+$) use has been made of the theoretical calculations of Eyring, Hirschfelder, and Taylor (34).

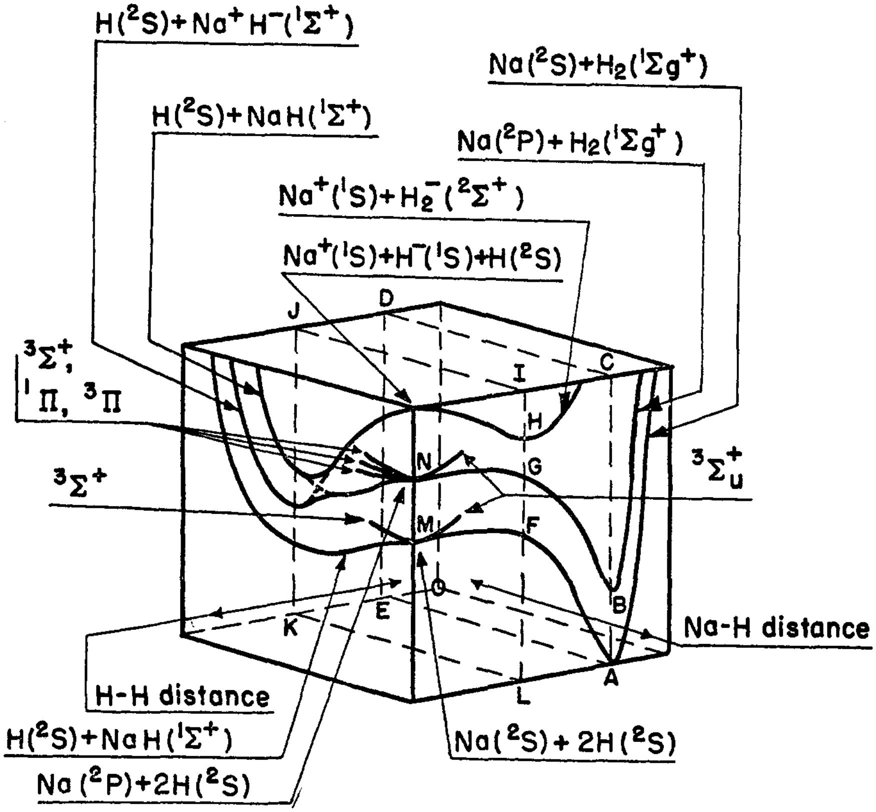

FIG. 3. Potential-energy surfaces for the linear system Na-H-H. The curves on the left-hand and right-hand faces are for Na-H and H-H, respectively. AB = MN = 48.3 kcal. (after Laidler (102)).

The curves on the left-hand face of the diagram correspond to interaction between sodium and hydrogen, with the second hydrogen atom an infinite distance away. A normal (^2S) sodium atom interacts with a hydrogen (^2S) atom to give an attractive $^1\Sigma^+$ state and a repulsive $^3\Sigma^+$ state, of which the former can be constructed from the spectroscopic data; these curves are shown, the latter only incompletely, in figure 3. Excited (^2P) sodium interacts with hydrogen to give a $^1\Sigma^+$ curve, but this is intersected by the ionic curve corresponding to

Na^+-$H^-(^1\Sigma^+)$ + $H(^2S)$. This curve can be constructed by making use of crystal data.

It is now necessary to consider how these potential-energy curves are connected by surfaces in the interior of the cube. This is done by determining the designation of the surfaces, using the vector model. Thus, the surface which passes through the potential-energy curve *MA* corresponds to the complex formed by interaction between a ^2S sodium atom with a hydrogen molecule ($^1\Sigma_g^+$). According to the vector model this interaction gives rise to only one state, its designation being $^2\Sigma^+$. Similarly, the only surface passing through the lowest curve on the left-hand face, arising from interaction between $H(^2S)$ and $NaH(^1\Sigma^+)$, is of designation $^2\Sigma^+$. It is evident that these states are identical, and that the lowest curves on the two faces are connected by a single surface, $^2\Sigma^+$.

The other surfaces are specified in a similar manner. Thus the interaction of a ^2S sodium atom with a $^3\Sigma_u^+$ hydrogen molecule gives two states, $^4\Sigma^+$ and $^2\Sigma^+$; similarly, $H(^2S)$ + $NaH(^3\Sigma^+)$ gives $^4\Sigma^+$ and $^2\Sigma^+$. The two repulsive curves in figure 3, passing through the point *M*, are therefore connected by two surfaces, $^4\Sigma^+$ and $^2\Sigma^+$.

There are several surfaces involving excited sodium, but of these only the lowest is of interest from the point of view of the quenching. This corresponds to a $^2\Sigma^+$ state, and connects the curves for $Na(^2P)$ + $H_2(^1\Sigma_g^+)$ and $NaH(^1\Sigma^+)$ + $H(^2S)$. Similarly, the ionic curves shown in the figure are connected by a single $^2\Sigma^+$ state.

It is now necessary to consider the shapes of these surfaces. The lowest surface, the $^2\Sigma^+$, corresponds to the surface upon which the H + H_2 reaction occurs, and is of the same general form; its energy is given by (118)

$$E = Q - [(1/2)\{(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2\}]^{1/2} \tag{48}$$

where Q is the sum of the coulombic energies and α, β, and γ are the exchange energies between the constituent atoms of the complex. The surface has been constructed (102) using the semiempirical method, the potential-energy curves being obtained from spectroscopic data. The proportion of coulombic energy was taken as 12 per cent for the H—H bond and 22 per cent for the Na—H bond; this latter figure is the average of 12 per cent for H—H and 32 per cent for Na—Na, these being the most satisfactory figures for bonds involving electrons having principal quantum numbers of 1 and 3, respectively (4, 183).

It has been seen that two surfaces, $^2\Sigma^+$ and $^4\Sigma^+$, connect the two repulsive curves passing through *M*. By the method of bond eigenfunctions (188) the energy of the $^2\Sigma^+$ is found to be, to the approximation of neglecting double-exchange integrals,

$$E = Q + [1/2\{(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2\}]^{1/2} \tag{49}$$

while that of the $^4\Sigma^+$ state is

$$E = Q - \alpha - \beta - \gamma \tag{50}$$

As the exchange integrals α, β, and γ are of negative sign, these surfaces represent highly repulsive states, and in fact play no part in the quenching reaction.

The lowest surface passing through the point N has been seen to correspond to a $^2\Sigma^+$ state. The contour diagram for this surface can be constructed in an approximate manner by using equation 48. When this is done, it is found that the surface is at all points well above the lowest surface. Since the quenching involves transition from this surface to the lowest surface, and proceeds readily, it is evident that a third surface must intersect both surfaces and allow a transition between them. This surface is the one corresponding to the ionic state. The reaction therefore proceeds *via* a transition first from the upper to the polar surface, and then from the polar to the lower surface, and can be represented as

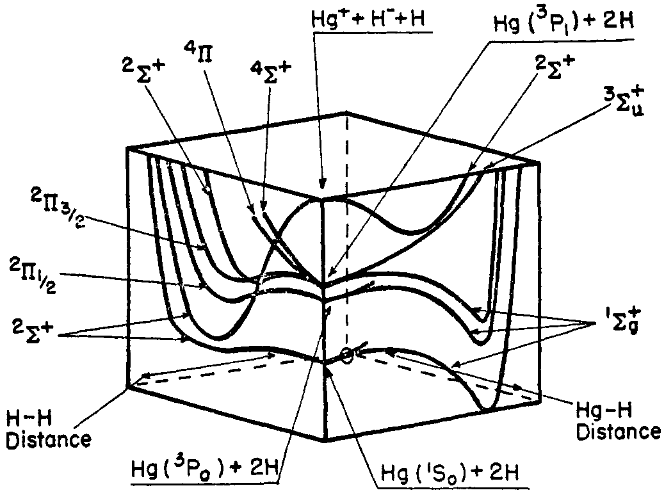

FIG. 4. Potential-energy surfaces for the linear system Hg–H–H. The curves arising from the $3P_2$ state of mercury are omitted for simplicity and some of the repulsive curves are continued for only a short distance (after Laidler (103)).

$$Na^*(^2P) + H_2(^1\Sigma_g^+) \rightarrow NaH_2^*(^2\Sigma^+) \rightarrow Na^+H_2^-(^2\Sigma^+)$$
$$\rightarrow NaH_2(^2\Sigma^+) \rightarrow Na(^2S) + H_2(^1\Sigma_g^+) \quad (51)$$

The question of the transitions between the surfaces is considered later.

3. *Surfaces for the* Hg–H–H *system*

When an excited mercury atom (^3P) reacts with a hydrogen molecule, hydrogen atoms are formed, the overall process being

$$Hg(^3P) + H_2(^1\Sigma_g^+) \rightarrow Hg(^1S) + 2H(^2S) \quad (52)$$

The surfaces relevant to this reaction may now be considered as a second example of the procedure. The curves on the left-hand face of the cube in figure 4 correspond to an infinite H–H separation; those on the right-hand face to an infinite Hg–H separation.

The homopolar curves on the left-hand face may be constructed from the spectroscopic data (143). An $Hg^+(^2S)$ ion interacts with an $H^-(^1S)$ ion with the formation of a polar $^2\Sigma^+$ state, but the corresponding curve can not be constructed, owing to lack of information from crystal data. An excited mercury atom, $Hg(^3P)$, reacts with $H(^2S)$ to give attractive $^2\Sigma^+$ and $^2\Pi$ states; experimentally it has been found that the $^2\Pi$ state is the lower one, although this is not at all obvious when the term manifold is determined from the states of the separated atoms (see, e.g., Fig. 152 in reference 80). This, incidentally, emphasizes the need for caution in predicting which one of the electronic states will be the lowest one; if at all possible, recourse should always be had to any available experimental evidence. The ionic curve cuts the lowest $^2\Pi$ curve at a separation of about 3 Å., as shown on the left-hand face of figure 4. There is no difficulty about the intersection of the ionic and nonionic $^2\Sigma^+$ curves. Since the point of intersection lies at an internuclear separation where the nonionic curve approaches the asymptote (i.e., the molecule is practically dissociated), the interaction of the ionic $Hg^+H^-(^2\Sigma^+)$ and the nonionic $HgH(^2\Sigma^+)$ state is so weak that the curves may be considered as crossing even in higher approximation. There is thus no violation of the noncrossing rule (*cf.* Section III B, page 168). The curves on the right-hand side of figure 4 are, of course, analogous to those in figure 3.

The surfaces connecting the two sets of curves in the interior of the figure may now be discussed. If a hydrogen atom (^2S) approaches linearly an HgH molecule in its lowest ($^2\Sigma^+$) state the resulting states are $^1\Sigma^+$ and $^3\Sigma^+$ and of these, on account of the correlations

$$Hg(^1S) + H_2(^1\Sigma_g^+) \rightarrow HgH_2(^1\Sigma^+) \quad (53)$$

$$Hg(^1S) + H_2(^3\Sigma_u^+) \rightarrow HgH_2(^3\Sigma^+) \quad (54)$$

the $^1\Sigma^+$ state arises from the attractive ($^1\Sigma_g^+$) state of hydrogen and the $^3\Sigma^+$ from the repulsive ($^3\Sigma_u^+$). The curves for $HgH(^2\Sigma^+)$ and $H_2(^1\Sigma_g^+)$ are therefore connected by a $^1\Sigma^+$ surface, which has the same general form as the lowest surface in the Na + H_2 reaction. A second surface ($^3\Sigma^+$) connects the curves for $HgH(^2\Sigma^+)$ and $H_2(^3\Sigma_u^+)$; this is a highly repulsive surface. The lowest state of HgH which arises from $Hg(^3P)$ and a normal hydrogen atom (^2S) is $^2\Pi$ and this interacts with a second hydrogen atom to give $^1\Pi$ and $^3\Pi$ states. In view of the further relationships

$$Hg(^3P) + H_2(^1\Sigma_g^+) \rightarrow HgH_2(^3\Pi, {}^3\Sigma^+) \quad (55)$$

and

$$Hg(^3P) + H_2(^3\Sigma_u^+) \rightarrow HgH_2(^5\Pi, {}^3\Pi, {}^1\Pi, {}^5\Sigma^+, {}^3\Sigma^+, {}^1\Sigma^+) \quad (56)$$

it is evident that only the $^3\Pi$ curve is of importance; it connects the $HgH(^2\Pi)$ curve with the $H_2(^1\Sigma_g^+)$ curve.

The lowest state of the H_2^- molecule is $^2\Sigma^+$, and this interacts with a normal (^2S) Hg^+ ion to give $^3\Sigma^+$ and $^1\Sigma^+$ states. Similarly, the lowest ionic state of $Hg^+H^-(^2\Sigma^+)$ interacts with $H(^2S)$ to give $^3\Sigma^+$ and $^1\Sigma^+$ states. Two surfaces therefore connect the $Hg^+H^-(^2\Sigma^+)$ and $H_2^-(^2\Sigma^+)$ curves, and of these the $^1\Sigma^+$ is lower and corresponds roughly to the electrons being on the hydrogen atom nearer to the mercury atom; the $^3\Sigma^+$ state corresponds to the electrons being on the farther atom.

Detailed consideration (103) of the behavior of the connecting surfaces in the interior of the cube indicates that the reaction between an excited mercury atom (^3P) and a hydrogen molecule ($^1\Sigma_g^+$) probably proceeds *via* the formation of an ionic complex on the ionic $^3\Sigma^+$ surface. The system then moves to the repulsive homopolar $^3\Sigma^+$ curve connecting the $HgH(^2\Sigma^+)$ and $H_2(^3\Sigma_u^+)$ curves. The system then slides down this surface until it reaches the part corresponding to $HgH(^2\Sigma^+)$ and $2H(^2S)$. The detailed reaction path is thus

$$\begin{aligned} Hg(^3P_1) + H_2(^1\Sigma_g^+) &\rightarrow HgH_2(^3\Pi) \rightarrow Hg^+H_2^-(^3\Sigma^+) \rightarrow HgH_2(^3\Sigma^+) \\ &\rightarrow HgH(^2\Sigma^+) + H(^2S) \rightarrow Hg(^1S_0) + 2H(^2S) \qquad (57) \end{aligned}$$

The examples discussed above indicate the usefulness of potential-energy surfaces in tracing the course and mechanism of a reaction involving excited species. Pringsheim (179) has expressed the opinion that the above use of potential-energy surfaces is " . . . only a more elaborate formulation of a general idea which has been enunciated at a much earlier date by Franck and Eucken . . . " (44). What is referred to here is the principle that the exchange of energy accompanying these reactions is not primarily a mechanical problem of collisions, but that the efficiency of the energy transfer will depend upon the strength of the interactions of the electronic fields of the colliding species. The use of potential-energy curves, which take this electronic interaction into account explicitly, is, however, more than just a more elaborate formulation; their use offers one of the most practical *quantitative* approaches to the general problem of energy interchange (and chemical reactions) whose basic *qualitative* formulation was laid down by Franck and Eucken. Potential-energy surfaces have proved useful not only in discussing the mechanism of reactions involving electronically excited species, but also in an understanding of the specific magnitudes of quenching cross-sections (102, 141, 206) (see Section III B). Potential-energy surfaces have also been utilized in discussing the interconversion of translational and vibrational energies (18, 33, 61, 88), and further progress in the general field of energy interchange in inelastic collisons, a problem intimately connected with the mechanisms of reactions, may well be made by a study of the pertinent potential surfaces in the manner outlined above.

B. RATE EQUATIONS

According to the formulation developed by Eyring (32, 62) the specific rate of a chemical reaction can be expressed as

$$k = \kappa \frac{\mathbf{k}T}{h} \frac{F^{\ddagger}}{F_A F_B \ldots} e^{-E_0/RT} \qquad (58)$$

where κ is the transmission coefficient, $\mathbf{k}$ and h are the Boltzmann and Planck constants, T is the absolute temperature, $F^{\ddagger}$ is the partition function for the activated state, and F_A, $F_B \cdots$ those for the initial states (reactants), E_0 is the energy of activation per mole at the absolute zero, and R is the gas constant. E_0 is approximately equal to the experimental energy of activation obtained from an Arrhenius plot of log k against $1/T$. In terms of the above expression, the main factors influencing the rate of a reaction are (*1*) the transmission coefficient, (*2*) the relative magnitudes of the partition functions F, and (*3*) the energy of activation E_0. Reactions involving electronically excited states exhibit some special features with respect to these factors, and special consideration must therefore be given to the study of rates in such systems. The above factors as related to electronically excited states will now be considered in some detail.

1. The transmission coefficient

The transmission coefficient κ is introduced to take account of the fact that not all species which have acquired the necessary free energy to cross the potential-energy barrier actually do so; some of these species will return to the initial state after having reached the activated state at the top of the barrier. The transmission coefficient is defined as the ratio of the number of systems which attain the final state to the number which reach the activated state. An equivalent definition is that κ gives the probability that a system which has reached the activated state will continue to the final state. The evaluation of κ in reactions involving molecules in their ground states has been discussed in detail by Hirschfelder and Wigner (83), who have shown that for a large number of such reactions it is close to unity. It is, however, very frequently less than unity in reactions involving electronically excited states, for reasons now to be considered.

In reactions in which no electronically excited states are involved, the potential-energy surface on which the reaction occurs is the lowest for the system, and the reaction can be represented by a smooth movement over this surface. When a reactant or a product is excited, on the other hand, it is necessary to take upper surfaces into consideration. As has been seen in Section III A, the number and spectroscopic designation of potential-energy surfaces for a given system of interacting atoms and molecules can be obtained by making use of the vector model and the Wigner–Witmer correlation rules. This procedure, however, gives rise to surfaces that may cross and takes no account of the resonance splitting that occurs at the "crossing" point. In order to treat reactions involving excited states it is necessary to take into account this resonance splitting and so to obtain a set of noncrossing surfaces.

The extent of the resonance separation at the "crossing" of two surfaces depends in a marked manner on whether the states corresponding to the two surfaces are of the "same species" or are of "different species." States of the same species (80, 145) are those with the same symmetry properties and the same Λ and S values, and give rise to a large resonance separation (153, 209), as shown in figure 5. When this is the case the probability of a crossing between the two surfaces is very small, so that, for example, a reaction system on a lower surface has little probability of passing to the upper one.

For states of different species (i.e., states which do not have the same symmetry properties and the same values of Λ and S), the resonance separation is extremely slight (figure 6); the probability of transition between the upper and lower surfaces is now close to unity, while that of staying on the upper or lower surface is close to zero. This is equivalent to saying that the reaction system behaves as if the surfaces really crossed. One special aspect of this is that systems resist any change in spin angular momentum and hence of multiplicity; this principle is often known as the Wigner spin-conservation rule (227). The value of the transmission coefficient for a reaction involving a change in multiplicity is probably always less than 10^{-4}, so that such processes rarely are important in reaction mechanisms, being overwhelmed by more efficient ones.

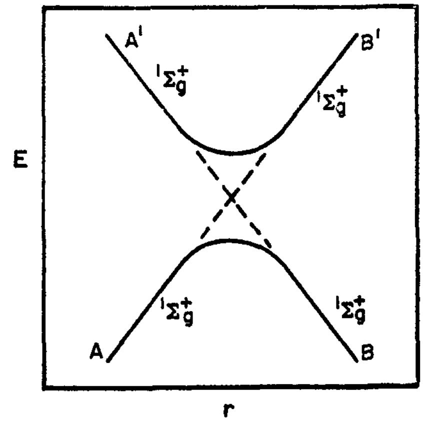

FIG. 5

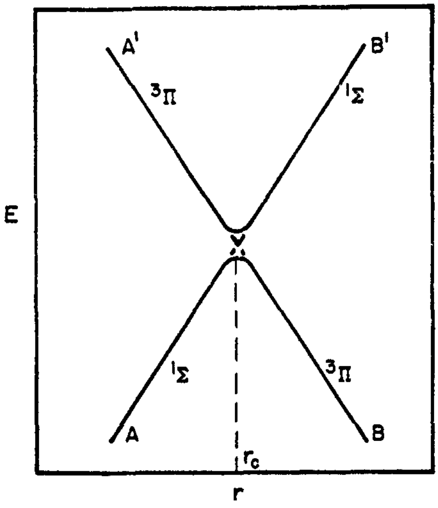

FIG. 6

FIG. 5. Schematic potential-energy surfaces for states of the same species, showing large resonance splitting.

FIG. 6. Schematic potential-energy surfaces for states of different species, showing small resonance splitting.

The foregoing qualitative statements may now be expressed in quantitative form. The resonance splitting ϵ_{12} at the "crossing" point is given by the matrix element $\int \psi_1 H \psi_2 \, d\tau$, where ψ_1 and ψ_2 are the eigenfunctions for the two states and H is the Hamiltonian operator. For states of the same species the integral is large, and the resonance separation is generally of the order of several kilocalories. For states of different species, on the other hand, the integral is small (101) and generally of the order of a few small calories. Actually it is found that if in the construction of the Hamiltonian the spin-spin and spin-orbital interactions are neglected the integral vanishes; the actual resonance separation is therefore due to these interactions.

The probability of a transition between surfaces corresponding to states of the same species showing strong interactions has not been treated quantitatively[5]; as has been seen, the probability is very low, and that of staying on the surface is therefore close to unity. In the case of states of different species the probability of crossing is given by the Landau–Zener equation (37, 108, 231) as:

$$P = e^{-4\pi^2\epsilon_{12}^2/hv|s_1-s_2|} \tag{59}$$

Here v is the velocity with which the system passes the point of closest approach of the surfaces, and $|s_1 - s_2|$ is the absolute magnitude of the difference of the slopes with which the surfaces would cross if resonance interaction were not taken into account. This expression is seen to be smaller the larger the resonance splitting, ϵ_{12}; if ϵ_{12} were zero, P would be unity, and the surfaces would then behave as if they really crossed. This is approximately the situation with states of different species. The probability that the system will remain on an upper or a lower surface is given in general by

$$P' = 1 - e^{-4\pi^2\epsilon_{12}^2/hv|s_1-s_2|} \tag{60}$$

For states of different species, for which ϵ_{12} is small, this is approximately equal to

$$P' = \frac{4\pi^2\epsilon_{12}^2}{hv\,|s_1 - s_2|} \tag{61}$$

A similar treatment of the probability that a system remains on a higher-order approximation noncrossing surface (225), carried out in connection with radiationless transitions in predissociation processes and applicable to states of different species, gave rise to

$$P' = \frac{4\pi^2\epsilon_{12}^2}{h} \tag{62}$$

If, for example, two zero-order approximation intersecting surfaces are of designation $^1\Sigma$ and $^3\Pi$, the higher-order approximation noncrossing surfaces will differ in spectroscopic designation for $r < r_c$ and $r > r_c$. This is illustrated in figure 6, in which the lower surface is $^1\Sigma$ for $r < r_c$ and $^3\Pi$ for $r > r_c$, and the upper is $^3\Pi$ for $r < r_c$ and $^1\Sigma$ for $r > r_c$. If the system remains on one of these surfaces there will therefore be a change in both S and Λ; the probability of remaining on a surface is, according to equation 61, very low, and is approximately proportional to the square of the matrix element ϵ_{12}. The conditions for nonvanishing ϵ_{12}, i.e., for high probability of remaining on a surface, can be expressed as selection rules for perturbations (101), and these are also the selection rules governing the occurrence of the reaction. The most important of these in connection with chemical reactions and physical quenching are that the initial and final states of the reaction system must have the same *total* spin (i.e., $\Delta S = 0$), and that the Λ differ by only 0 or ± 1 (i.e., $\Delta\Lambda = 0, \pm 1$). For such processes the perturbation selection rule $\Delta S = 0$ is usually stated as the

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[5] The Landau–Zener equation 59 is only valid for $\epsilon_{12} \ll \frac{1}{2}\mu v^2$, and is not applicable to the ϵ_{12} values found with states of the same species.

Wigner spin-conservation rule (227), which says that the total spin of collision partners must remain unchanged before and after collision.

The relationship between the transmission coefficient κ and the probability P of a transition from one surface to another depends upon the form of the surfaces. A common case is represented in figure 7. The system may pass from A to B in two different ways. The first way involves its remaining on the upper surface in the first vibration and going to A′, followed by a transition to B in the second vibration. The probability of its remaining on the upper surface in the first vibration is $1 - P$, and that of the transition to B is P; by the theorem of compound probabilities of independent events the probability A → B by this route is thus $P(1 - P)$. Alternatively the system may first cross to B′, with a probability of P, and then remain on the lower surface, the probability of which is $1 - P$; the net probability of the transition A → B by this mechanism is therefore also $P(1 - P)$. The total probability of the transition A → B by both mechanisms is therefore $2P(1 - P)$, i.e.,

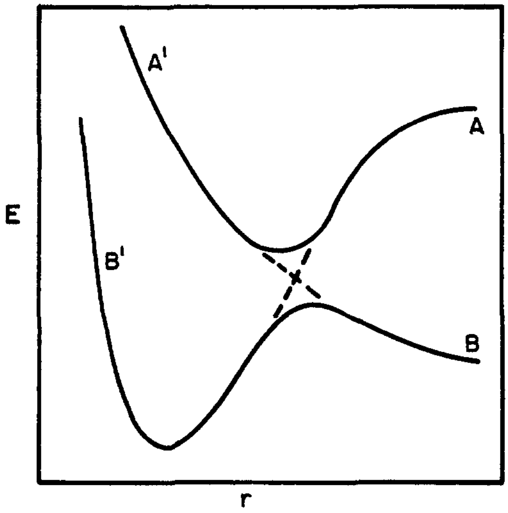

FIG. 7. Potential-energy surfaces relevant to certain quenching reactions

$$\kappa = 2P(1 - P) \tag{63}$$

For this case κ will have a maximum value of 1/2 when $P = 1/2$, and will be very small when P is either close to unity or close to zero (i.e., for either a very small or a very large value of ϵ_{12}). This fact explains the low efficiency of quenching by atoms (102).

Relationships between κ and transition probabilities for cases where more than two potential-energy curves are necessary to describe the reaction have been discussed by Magee (125) and by Laidler (102), and κ has been evaluated explicitly by Magee (125) for the system alkali atom plus halogen atom. Since the transmission coefficient for systems of several surfaces may depend upon the various crossing probabilities in a rather complicated manner (102), no general statement can be made as to its probable magnitude under these conditions.

Calculations have been made (128) of the transmission coefficient for the reaction

$$C_2H_4(^1B) \rightarrow C_2H_4(^3B) \rightarrow C_2H_4(^1B) \qquad (64)$$

for the reaction (224)

$$O(^3P) + CO(^1\Sigma) \rightarrow CO_2(^1\Sigma) \qquad (65)$$

and for the reaction (204)

$$N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O(^3P) \qquad (66)$$

In the first reaction κ was found to have the value of about 10^{-6}, in the second and third of 10^{-4}. Such processes with $\Delta S \neq 0$, due to their very slow rate, will therefore rarely play a part in reaction mechanisms, being superseded, if at all possible, by more efficient ones with $\Delta S = 0$. The Wigner spin-conservation principle is thus of great value in excluding certain mechanisms which might otherwise be considered to be of importance. The other selection rules, such as $\Delta\Lambda = 0, \pm 1$, do not impose too serious a restriction on the occurrence of reaction; an inspection of table 2 shows that the orbital angular momenta can combine in so many ways that the condition $\Delta\Lambda = 0, \pm 1$ can usually be met.

The following are some reactions involving excited electronic states which have been shown fairly conclusively to occur in reaction mechanisms; as may be seen, these reactions take place without change in total spin:

$$O(^3P) + CO(^1\Sigma) \rightarrow CO_2(^3\Pi) \qquad (67)$$

$$C_2H_4^*(^3B) \rightarrow C_2H_2^*(^3B) + H_2(^1\Sigma_g^+) \qquad (68)$$

$$Hg^*(^3P) + Tl(^2P) \rightarrow Hg(^1S) + Tl^*(^2X) \qquad (69)$$

$$OH^*(^2\Sigma^+) + O_2(^3\Sigma_g^-) \rightarrow OH(^2\Pi) + O_2^*(^3\Sigma_u^-) \qquad (70)$$

$$Hg^*(^3P) + C_2H_4(^1A) \rightarrow Hg(^1S) + C_2H_4^*(^3B) \qquad (71)$$

$$O(^3P) + O(^1D) \rightarrow O_2^*(^3\Sigma_u^-) \qquad (72)$$

$$Na(^2S) + H(^2S) + H(^2S) \rightarrow Na^*(^2P) + H_2(^1\Sigma_g^+) \qquad (73)$$

The following reactions, showing a change in total spin, have sometimes been postulated as playing a part in reaction mechanisms. Because of the small transmission coefficient the rate of these reactions is, however, probably too low for them to be of much importance in the overall reaction:

$$N_2O_5(^1A) \rightarrow N_2O_3(^1A) + O_2(^3\Sigma_g^-) \qquad (74)$$

$$O(^3P) + CO(^1\Sigma) \rightarrow CO_2(^1\Sigma_g^+) \qquad (75)$$

$$Hg^*(^3P) + H_2(^1\Sigma_g^+) \rightarrow Hg(^1S) + H_2(^1\Sigma_g^+) \qquad (76)$$

It may be noted that the words "adiabatic" and "nonadiabatic," usually employed in a discussion of these topics, have not been used in the above discussion. This omission has been made intentionally, since we feel that the use of these terms, unless they are stringently defined, may lead to some unnecessary confusion.

According to the so-called adiabatic principle, first formulated by Ehrenfest (31) for classical systems, a molecule will remain in a given energy eigenstate when changes in an external parameter, such as the internuclear distance, are made at a vanishingly slow rate (215). Interactions between electronic states which in a low approximation are degenerate will only be effective if the nuclear motion is slow compared with the electronic, so that the avoidance of crossing of the potential curves indicated in figures 5 and 6 will only be realized for a very slow change of internuclear distance. For a small dr/dt, a molecular system starting at A will thus move along the lower potential curve and end up in state B, and according to the above discussion such a reaction would be adiabatic. If dr/dt is large, the potential curves behave as if they crossed (dotted lines in figures 5 and 6), and a system starting at A will end up at B′; this would correspond to a nonadiabatic process.

The terms "adiabatic" and "nonadiabatic" have, however, not always been used in this sense, and in particular the term "nonadiabatic reaction" has frequently been used synonymously with "reaction in which there is a change of multiplicity." Thus the reactions

$$N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O(^3P) \qquad (77)$$

$$O(^3P) + CO(^1\Sigma^+) \rightarrow CO_2(^1\Sigma_g^+) \qquad (78)$$

have been referred to as nonadiabatic, although from the above discussion they should be called adiabatic, since the system remains at all times on the lowest surface (A–B in figure 6). On the other hand, reactions like $O(^1D) + CO(^1\Sigma^+) \rightarrow CO_2(^1\Sigma_g^+)$ are often regarded as adiabatic; since they do not violate the Wigner spin-conservation rule and occur with high transmission coefficients; according to our previous discussion, however, they are nonadiabatic.

This discrepancy arises when the approximation used in constructing the potential curves is not specified. While there will be no difficulty for states of the same species where the potential curves will avoid a crossing even in a very low approximation (figure 5), there is this danger of confusion for states of different species (figure 6). In a low approximation where the potential curves will cross, an "adiabatic" reaction goes from A to B′, while in a higher approximation, where the crossing is avoided, an "adiabatic" reaction would go from A to B. In considering these concepts from the point of view of the approximation used in constructing the potential curves, the question of the rate of change of external parameter no longer enters into the discussion, and the validity of the application of the terms "adiabatic" and "nonadiabatic" would seem to be questionable.

In view of the difficulties revealed by the above discussion in the case of states of different species, we are in favor of abandoning the use of these terms in this connection.

2. *Evaluation of the partition functions*

(a) The electronic partition functions

In order to calculate the rates of chemical reactions by means of absolute rate theory it is necessary to evaluate the partition functions appearing in equation 58. The form of these partition functions for molecular systems of various complexity and methods for evaluation have been discussed in detail in several monographs (see, e.g., references 62 and 133) and there is thus no need to enter into any extended treatment in this review. There are, however, some special points to be noted in connection with the internal partition function for some electronically excited states.

The ground state of most common molecules with the exception of $O_2(^3\Sigma_g^-)$ and $NO(^2\Pi)$ is $^1\Sigma$ and the first excited state is usually energetically quite far removed. The electronic contribution to the internal partition function, $\Sigma g_{el}e^{-\epsilon_{el}/kT}$, is thus unity, the statistical weight g_{el} being unity for the ground state owing to its Σ character, and the exponential factor being unity for the ground state owing to its singlet character. The excited electronic states will usually make no contributions, since $\epsilon_{el}^* \gg kT$. Many excited states, however, are not of the $^1\Sigma$ type; this is the case both for systems with $^1\Sigma$ ground states and for those with ground states of other designation. Some common examples are $CH^*(^2\Delta)$, $CO^*(^1\Pi)$, $CO_2^*(^3\Pi)$, $H_2^*(^3\Sigma_g^+)$, $NO^*(^2\Sigma^+, {}^2\Pi)$, $OH^*(^2\Sigma^+)$, $HgH^*(^2\Pi, {}^2\Sigma^+)$, $O_2^*(^3\Sigma_u^-, {}^1\Delta)$, and it is necessary to take these electronic structures into account in evaluating the partition functions of electronically excited reactants.

Since the energy separation of the spin-split levels in the doublet and triplet states is very small, depending upon the spin-coupling constant, it may be necessary to evaluate the electronic partition function explicitly. In the case of $O_2^*(^3\Sigma_u^-)$ their contributions to the partition function may be taken as identical so that $\Sigma g_{el}e^{-\epsilon_{el}/kT} = 3$; in this case, the total partition function has to be multiplied by this factor 3. For states with $\Lambda \neq 0$, i.e., Π, $\Delta \cdots$, the interaction between the rotation of the molecule and the electronic orbital angular momentum produces a splitting of each rotational level into two closely spaced sublevels, the so-called Λ-type doubling. In these cases, the electronic statistical weight g_{el} is equal to 2, owing to the double degeneracy of the rotational levels; furthermore, for states of higher multiplicity the spin splitting must again be taken into account. For $CO^*(a^3\Pi)$, for instance, the electronic partition function is equal to 6; this is due to the Λ-type doubling ($g = 2$) and the triplet spin splitting into rather close-lying levels, each exponential term, corresponding to one of the three levels, being approximately unity.

Similar considerations also hold for atoms which are not in $^1S_0$ states. For atoms, the electronic statistical weight is given by $g_{el} = 2J + 1$, where J is the total angular momentum resulting from the vector addition of the spin angular momentum S and the orbital angular momentum L. The number of levels into which each term level is split owing to the spin-orbit interaction is given by $2S + 1$ or $2L + 1$, depending respectively upon whether $L > S$ or $L < S$, the separation of the split levels increasing rapidly, as in the case of diatomic molecules, with increasing nuclear charge. For $O(^3P_2, {}^3P_1, {}^3P_0)$, with level separations of 0.45 kcal. and 0.64 kcal., the electronic partition function is given by $5 + 3e^{-0.45/kT} + e^{-0.64/kT}$; at about 3000°K., the approximate temperature of many flames, its value is 8.7.

For the flame reaction

$$O(^3P_{2,1,0}) + CO^*(^3\Pi) \rightarrow CO_2^*(^3\Pi) \qquad (79)$$

the denominator of the rate equation will thus contain a factor of the order of magnitude 50, while for the reaction

$$O^*(^1D_2) + CO(^1\Sigma^+) \rightarrow CO_2(^1\Sigma_g^+) \qquad (80)$$

the factor due to the electronic partition will only be 5, this being g_{el} for $O(^1D_2)$. For a rate calculation it will, of course, also be necessary to determine $F^{\ddagger}_{el}$, the electronic partition function of the activated complex. This can at best be only a rough estimate, since it is frequently difficult to say whether the activated state partakes more of the nature of loosely coupled reactants or of a rather stable association complex. For reaction 80, for instance, $F^{\ddagger}_{el}$ may be either 5 (corresponding to $CO(^1\Sigma^+) + O^*(^1D_2)$) or 1 (corresponding to $CO_2(^1\Sigma_g^+)$); for purposes of rough calculation, in the absence of more definite information, an intermediate value may be used.

(b) The rotational partition function and the quenching cross-section

For bimolecular reactions the rate constant k is given by collision theory as

$$k = Ze^{-E/RT} \qquad (81)$$

where Z, the frequency of collisions per cubic centimeter per unit concentration, is given by

$$Z = \sigma_{AB}^2 \left[\frac{8\pi kT}{\mu_{AB}}\right]^{1/2} \qquad (82)$$

In this equation σ_{AB} is the mean collision diameter of molecules (or atoms) A and B and μ_{AB} is the reduced mass of the reaction system. Comparison of equations 58 and 81 shows that

$$Z = \kappa \frac{\mathbf{k}T}{h} \frac{F^{\ddagger}}{F_A F_B} \qquad (83)$$

provided that $E_0 = E$, which is certainly the case to a good approximation. If the reacting species are atoms, it can readily be shown by writing out the partition functions that the relation

$$\sigma_{AB}^2 = \kappa r_{\ddagger}^2 \qquad (84)$$

will hold (81); $r_{\ddagger}$ is the distance between the atoms A and B in the activated complex.

Experimental rate determinations can be expressed in terms of collision "cross-sections" σ_{AB}^2 by means of equations 81 and 82, and the applicability of collision theory can then be tested by comparing these experimental cross-sections with those estimated from kinetic theory using viscosity data. The transmission coefficient and $r_\ddagger$ can be calculated from basic structural and spectroscopic data after the potential-energy surfaces have been constructed. These calculated values are admittedly subject to quite an uncertainty, owing to the various approximations which have to be made in constructing the potential surfaces; however, *in principle* the collision cross-sections are now amenable to exact *a priori* calculation.

For quenching reactions of electronically excited atoms it has been possible to carry out such calculations for the collision cross-section, which in these types of reactions is frequently referred to as the "quenching cross-section." Quenching reactions frequently proceed without any—or with only a very small—energy of activation, and this suggests that the interactions between the excited atom and the quencher in forming an activated complex must be quite weak. The quenching molecule may then be considered as retaining its rotational and vibrational degrees of freedom in the very loosely bound activated complex; it will behave as a virtually free entity. To this approximation one of the vibrations in the activated complex corresponds to a rotation of the quencher in its initial state. When these approximations are applied to the reaction between an excited atom and a diatomic quencher, i.e., a reaction such as

$$A^* + BC \rightarrow A + BC \tag{85}$$

the absolute rate expression will reduce to that for a reaction between two atoms and equation 84 will be found to hold (62, 102, 125). The quantity $r_\ddagger$ now denotes the distance between A and B (or C, depending upon the "bonding") in the activated complex.

For quenching reactions proceeding with very small or zero activation energies it might be quite reasonable to suppose that the activated state is located at the "crossing" point of the potential surfaces. The potential surface connecting the excited and quenched states should be smooth and downhill except for the potential "ripples" introduced by the perturbation of crossing surfaces. The activated state is probably to be located at the top of one of these potential ripples at the crossing point of the potential surfaces. If this analysis is correct, then $r_\ddagger$ is identical with r_c, the internuclear separation at the crossing points.

The determination of the internuclear separations $r_\ddagger$ in the activated state is of course a prerequisite to the evaluation of the rotational partition function $F_r^\ddagger$. For reactions not involving electronically excited states there is usually no difficulty in locating the activated complex on the one potential surface for the system, since the path of the reaction is clearly marked out through the potential valleys and across the potential barrier. For reactions involving electronically excited states the system of potential surfaces may be quite complex (see, e.g., figure 3). This difficulty has already been emphasized (228) in connection with the calculation of activation energies; a similar difficulty exists also in locating unequivocally the activated complex and thus fixing the internuclear separations in the activated state. This problem is rather specific to the particular reaction being investigated and some thought should be given to the question of the location of the activated complex in constructing the potential-energy surfaces upon which the reaction proceeds.

The problem of accurately locating the activated state enters also into the evaluation of the vibrational partition functions of the activated complex. If the vibrational frequencies $\nu_‡$ are to be determined from the properties of the potential-energy surface, using the theory of small vibrations, it is necessary that the equilibrium internuclear distances in the activated state be known. In the rather simple case of

$$N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O(^3P) \tag{86}$$

it is possible to determine the dimensions of the activated complex, since it most probably is located at the crossing point of the potential curves for $N_2(^1\Sigma) + O(^1D)$ and $N_2(^1\Sigma) + O(^3P)$, and for this reaction $F_v^‡$ can thus be evaluated explicitly (204). There seem to be no other instances of explicit calculations of $F_v^‡$ for reactions involving electronically excited states. The evaluation of vibrational and rotational partition functions of electronically excited reactants poses no special problems, since the internuclear distances, configurations, and vibration frequencies are usually known from spectroscopic analysis.

3. *The activation energy*

It is difficult to take explicit account of the factors which may influence the activation energies for reactions involving excited electronic states. Calculation of activation energies by the semiempirical method (36, 62) will give only very approximate values even for reactions not involving electronically excited species. The approximations of this method, such as considering only linear or planar complexes with s electron bonding and taking a fixed ratio ρ of coulomb to exchange energy, would seem to be particularly unsuitable for systems with electronically excited reactants or products.

Excited atoms and molecules are usually not in S or Σ states and the electrons involved in the bonding of the activated complex are liable to be p electrons or higher. In these cases, the configuration of lowest potential energy may be no longer linear but triangular, or staggered in a zigzag fashion in the case of polyatomic activated complexes, depending upon the directional properties of the various orbitals involved in the bonding. Some calculations of Magee (124) on a system of two s electrons and one p electron seem to indicate that the directed valence introduced by the p electron lowers the activation energy for the formation of the resulting triangular complex below that which is obtained for a linear complex. This is in line with the findings of Bartlett (3) that for p electrons the coulombic interactions are much more important than exchange contributions, the activation energy being due to the exchange interactions, since the coulombic terms are always attractive. Owing to the arduous nature of the calculations for nonlinear complexes, activation energies for systems involving electronically excited states have hitherto been calculated for linear complexes (102, 127); it is not known with certainty how much this approximation will affect the value of the calculated activation energies.

In reactions involving electronically excited species, the reactants may "move" along a number of potential-energy surfaces, both polar and homopolar, before arriving at the configuration of the activated complex. In such a system of surfaces, with the possibility of transitions, it seems quite evident that the procedure of taking a constant ratio of coulombic to exchange energy for varying internuclear distances is quite inadequate. Since no activation energies seem to have been calculated for any but the simplest systems of potential surfaces, this problem has not had to be faced as yet; if explicit calculations are to be made however, this variation of ρ with r would have to be taken into account.

It is clear from the above discussion that experimental activation energies should preferably be used in rate calculations whenever they are available. Considering the difficulties and doubtful validity of calculations of activation energies for even the simplest three-center reactions of ground-state atoms and molecules, there is not too much hope that any significant improvements with respect to reactions involving electronically excited species will be made in the near future.

4. The validity of rate calculations

There is one problem which should be mentioned at this point, since it affects the whole concept of rate calculations in reaction systems containing electronically excited species. Rate calculations, whether they be collision theory calculations or absolute rate calculations, are essentially based on the assumption that an equilibrium distribution is maintained in the system during the reaction (43). It has been shown (37) that this equilibrium prerequisite can be reduced to the condition that the reactants are at all times in an equilibrium distribution among themselves. While calculations have indicated that a disturbance of this equilibrium distribution by the reaction itself will be rather small and will not affect the calculated rate to any great extent (38, 89, 100, 177, 178), the problem is somewhat different if there is no equilibrium distribution of reactants to start with.

Such a nonequilibrium distribution of reactants may be found when electronically excited reactants are produced by photochemical excitation (158, 180), in discharges (137, 138, 159), and in flames (51, 184). Apart from the question of the validity of equilibrium rate calculations for these systems, there is the related problem of the "temperature" of the reaction system, since there may be different rotational, vibrational, and electronic "temperatures," not to mention mass-equilibrium "temperatures" or electron "temperatures." There is no question but that much more work needs to be done on the statistical mechanics and chemical kinetics of these nonequilibrium systems. In the meantime, one can assume provisionally that these nonequilibrium distributions will be only a small "perturbation," so that equilibrium rate calculations are still essentially valid. In any case, the postulated reaction mechanisms for systems containing electronically excited species should not be affected by a possible nonequilibrium distribution of reactants or products.

IV. The Production of Electronically Excited Species

A. PHOTOCHEMICAL AND RADIOCHEMICAL EXCITATION

The primary step in both photochemical and radiochemical reactions is the excitation of one or more of the chemical species in the reaction system. In photochemical work this excitation is usually brought about by the absorption of electromagnetic radiation with an energy in the range 2 to 6 e.v. (50 to 140 kcal.), corresponding to a spectral region of about 7000 to 2000 Å. Since the ionization potential of most atoms (78) and practically all molecules (208) is considerably higher than the energy of this incident radiation, the excitation is usually to one of the discrete energy levels. In radiochemical work, the incident radiations (x-rays, γ-rays) or particles (α-particles, protons, etc.) are usually of sufficient energy ($\gg$6 e.v.) for their passage through the reaction system to produce ionization; however, measurements have shown that only about one-half of the energy of the incident radiation is utilized in this process, a large portion of the remaining energy being taken up in excitation to discrete levels and in dissociation, with possible consequent excitation of the dissociation fragments. As might be expected, the electronically excited species produced in a given system by either photochemical or radiochemical excitation are generally the same. The most significant difference is the fact that in the photochemical case there is resonance excitation to specific energy levels, in contrast to the rather random excitation to a great variety of energy levels by high-energy particles or photons in radiochemical systems. Another consequence of this nonspecificity of radiochemical excitation is the greater variety of excited species produced per incident particle as compared to photoexcitation; however, if the incident radiation in photochemical systems were varied over a wide enough range of frequency, a comparable profusion of electronically excited species might readily be obtained.

It is not the purpose of this paper to discuss in any detail the general features of photochemistry and radiation chemistry, both of which have been treated recently in a thorough manner (23, 116, 157, 181). The primary processes of photochemistry and radiation chemistry leading to electronically excited species, i.e., the absorption of radiation by matter and the inelastic collisions of high-energy charged particles and photons with atoms and molecules, are of a predominantly physical nature and fall outside the scope of this review. In the next three subsections will be discussed the types of electronically excited species produced by the photochemical irradiation of various reaction systems. As far as the radiochemical excitation processes are concerned (pages 183 and 185), the discussion will deal mainly with the production of electronically excited species by the interaction between electrons and atoms, molecules, and ions, since some of these processes may, under certain conditions, be treated by the methods discussed in this paper.

1. *Photoexcitation of atoms*

The excitation of atoms by incident monochromatic radiation is a rather simple process from the standpoint of the excited species produced. The importance of excited atoms in photochemical reactions lies in their ability to initiate secondary reactions (photosensitization). In this connection the lifetime of the excited state is of consequence, since excited species with long lifetimes will be more effective in initiating these secondary reactions. While at higher pressures the controlling factor in the lifetime of an excited species is its ability to survive quenching collisions (Section V), at sufficiently low pressures these collisions are of less significance and the controlling factor is the radiative lifetime. It is therefore of importance that in some systems the excited species is produced—either by direct absorption or by absorption with a consequent collision-induced radiationless transition—in a state which is metastable with respect to radiative transition to the ground state. A well-known example is the excitation of mercury vapor by irradiation with the 2537 Å. line, the processes being (157):

$$\mathrm{Hg}(6^1S_0) \xrightarrow[2537\text{Å.}]{h\nu} \mathrm{Hg}^*(6^3P_1) + \mathrm{M} \rightarrow \mathrm{Hg}^*(6^3P_0) + M \qquad (87)$$

The $\mathrm{Hg}(6^3P_0)$ state is metastable with respect to the transition to the 6^1S_0 ground state, since the transition $J = 0 \rightarrow J = 0$ is forbidden for dipole radiation.

Another interesting effect in atomic photoexcitation is the "cascading" observed when certain atoms are irradiated with light corresponding to a high energy level (10). In this case, the radiative transition may not be directly to the ground state, but the emission electron may "cascade" to the ground state *via* intermediate energy levels, and various excited electronic states of the atom may thus be produced. It may be possible in this manner to produce an excited state which may be reached directly only with difficulty owing to the lack of a suitable light source of sufficient intensity.

2. *Photoexcitation of diatomic molecules*

The products of the photoexcitation of diatomic molecules are determined by the energy of the incident radiation and the relative position of the potential curves for the ground and excited states, the transition being governed by the Franck–Condon principle. This can be seen most readily by an examination of figures 8 and 9. If the upper electronic state is repulsive (figures 8b and 9b), photoexcitation will lead to photodissociation and the end products will be the constituent atoms of the molecule. This is the reverse process to the radiative two-body association reactions discussed in more detail on page 188. The resulting electronic states of the atoms will depend upon whether or not the repulsive upper state correlates with the ground states of the atoms; if so (figure 8b), the photodissociation will lead to normal atoms, otherwise (figure 9b) to one or two excited atoms. If the upper state is a stable state (figures 8a and 9a), photoexcitation may lead either to an excited diatomic molecule or to photodissociation, depending upon the energy of the incident radiation and the relative position of the potential curves. In the case of photodissociation, the electronic states of the dissociation products again depend upon the nature of the potential curves (figures 8 and 9). Photoexcitation and dissociation products of diatomic molecules for various energy regions of the incident radiation are listed by Noyes and Leighton (157).

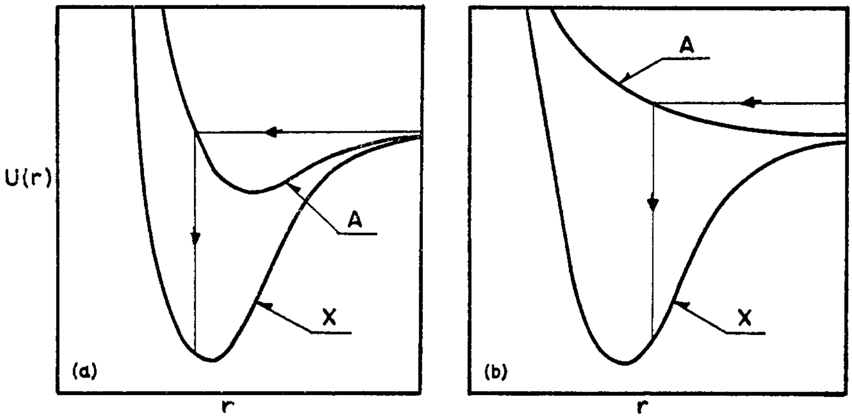

FIG. 8. Potential-energy curves for a diatomic molecule in its lowest state and in an excited state, the latter dissociating into two normal atoms. (a) The upper electronic state is stable. (b) The upper electronic state is unstable.

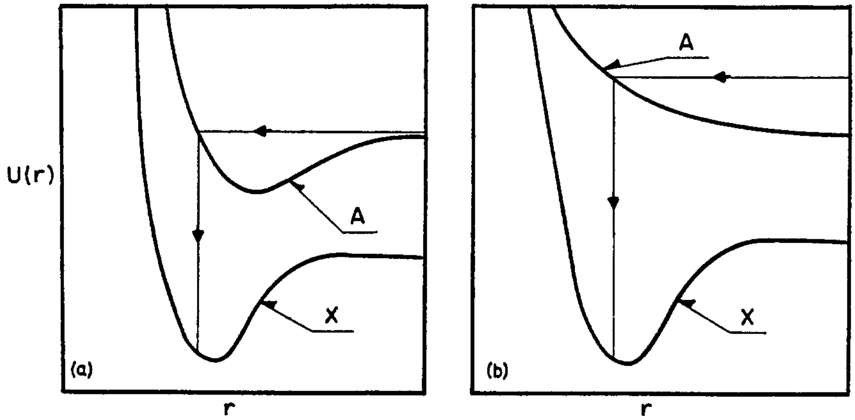

FIG. 9. Potential-energy curves for a diatomic molecule in its lowest state and in an excited state, the latter dissociating into excited atoms. (a) The upper electronic state is stable. (b) The upper electronic state is unstable.

The above discussion has neglected the possibility of predissociation due to the perturbation of closely lying energy levels of the several electronic states. This topic has been treated in detail elsewhere (80, 157, 181), and certain aspects of it are discussed in Sections III (page 170) and V (page 203).

3. Photoexcitation of polyatomic molecules

The photoexcitation and photodissociation of polyatomic molecules, while in principle rather similar to that of diatomic molecules, is in actuality a rather complex phenomenon posing a number of unanswered questions as to the nature and electronic state of the product species. While the Franck–Condon principle is still applicable, the two-dimensional potential curves of the diatomic molecules must now be replaced by polydimensional surfaces corresponding to the variety of bonds in the molecules. As the molecule becomes more complex, the number of crossings of these surfaces will increase, so that the opportunities for predissociation will be greatly increased as compared with the case of the diatomic molecules.

Another complicating factor in the photoexcitation of polyatomic molecules is the possibility of internal conversion of the excitation energy (45). Because of the close packing of vibrational and rotational levels in polyatomic molecules, and because of the large number and rather small separation of the electronic energy levels, resonance may exist between some of the levels in the excited and ground states. If this resonance occurs in conjunction with a common nuclear configuration for both states, a radiationless transition is possible, and the excitation energy which might be sufficient to raise the molecule to an excited electronic state will be found instead as excess vibrational and rotational energy of the ground state.

Owing to the greater number of bonds in polyatomic molecules, photodissociation may lead to a variety of products—both excited and in their ground states—depending upon the mode of dissociation of the molecule. This in turn is a function of the energy of the incident radiation and its mode of absorption, i.e., whether it will be absorbed primarily by one bond or will be distributed over several bonds of the molecule. While application of the Wigner spin-conservation rule should be of help in designating the electronic states of the dissociation products, our lack of knowledge of the electronic states of most of the polyatomic molecules prevents the use of this principle to its full extent. This is particularly true of nonlinear polyatomic molecules, for which correlations with atomic or diatomic states have not yet been worked out to any extent.

In view of these difficulties it is not surprising that little progress has been made in the elucidation of photoexcitation processes in polyatomic molecules. An appreciation of the difficulties involved can be gained from a study of the work of Sponer and Bonner (191) on the photodissociation of the comparatively simple molecule N_2O. A table of photodissociation products of molecules containing OH, CN, NH_2, and NO, giving the electronically excited species, is given by Pringsheim (179), based on the work of Terenin (152, 211); the data contained therein are, however, subject to considerable uncertainty. Of particular interest, in view of some of the discussion to follow, is the finding, in the HCHO fluorescence (30), of the hydrocarbon flame bands attributed (220) to excited HCO.

4. Excitation by impact of charged particles and high-energy photons

Excitation occasioned by the impact of massive charged particles (α-particles, protons, deuterons, etc.), electrons, or high-energy quanta (x-rays, γ-rays) can proceed by several mechanisms. The massive charged particles in their passage through matter lose a good part of their energy in inelastic collisions with the molecules of the reaction system, and thus bring about dissociation, excitation, and ionization of the collision partners. These types of collision processes have been discussed in detail by Bohr (12) and by Mott and Massey (142). This topic is of particular interest at present in connection with the effects of fission fragments and accelerated elementary particles in their passage through various media. The deleterious physiological effects of high-energy massive particles on human tissues is due mostly to ionization and dissociation, with electronic excitation playing only a minor and secondary role.

The absorption of high-energy quanta by atoms and molecules brings about the emission of photoelectrons; in the case of photons of very high energy ($\sim 10^3$ e.v.) Compton scattering also plays a role. In either case, the primary effect of this high-energy radiation is the production of ions and free electrons; most of the electronic excitation (to bound states of the electron) observed in these systems is due to secondary reactions between the emitted electrons and the ions and molecules of the reaction system. It is also possible, of course, that the photon of originally high energy will have its energy so reduced by repeated Compton scattering that it can undergo resonance absorption and thus bring about electronic excitation in a more direct manner.

Electronic excitation due to the interaction of incident electrons with molecules and ions can proceed by three principal mechanisms: (*i*) inelastic collisions between bound and free electrons, (*ii*) exchange between a bound and a free electron, and (*iii*) electron capture by ions. The first of these processes is of importance in excitation in arcs and discharges, and the second process in the case of slow electrons ($\sim$20–50 e.v.). Mechanism (*iii*) is important in the secondary processes following the primary production of electrons by the passage of high-energy particles; the majority of these secondary electrons will have approximately thermal energy by the time they undergo capture.

Excitation by electron impact is, in the same way as photoexcitation, governed by the Franck–Condon principle. The incident electron, upon collision with a bound electron, will "knock" the bound electron into an outer orbital, the whole process taking place so rapidly that there is no change of position or momentum of the nuclei. A knowledge of the energy of the incident electrons and the relative positions of the potential curves of the various relevant electronic states will thus permit a prediction as to the nature and energy state of the excitation product; the detailed picture of the actual collision must be obtained from a quantum-mechanical treatment of the collision process (12, 142). Excitation by electron impact thus results in excited molecules or dissociation fragments—excited and normal—in a manner similar to photoexcitation. This is shown graphically for the excitation of H_2 by electron bombardment in an interesting review article by Condon (19) on the Franck–Condon principle, and is discussed in more detail for the continuous spectrum of H_2 by Coolidge (20).

One of the consequences of this Franck–Condon type of excitation by electron impact is that one would not expect to obtain electronically excited molecules whose equilibrium nuclear configuration differs appreciably from that of the ground state. As pointed out by Gaydon (50), and as will be discussed in more detail in Section IV B, the nuclear configuration of excited carbon dioxide is probably considerably different from that of normal carbon dioxide, and one would thus not expect to find excited carbon dioxide in arcs or discharges. Similar considerations would appear to hold for the production of O_2^* in the $^3\Sigma_u^-$ state by electron bombardment of ground state $O_2(^3\Sigma_g^-)$, since the equilibrium nuclear separation of the two states is quite different (80):

$$r_e(^3\Sigma_g^-) = 1.207 \text{ Å.}; \qquad r_e(^3\Sigma_u^-) = 1.604 \text{ Å.}$$

However, CO flame bands, attributed to excited CO_2^*, have been found in a high-voltage arc in carbon dioxide (42); similarly, Schumann–Runge bands of $O_2^*(^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-)$ have been observed in arcs (41) and discharges (134) in oxygen. The formation of these excited species in discrete levels in these high-pressure arcs is probably due, as pointed out by Feast (41, 42), to three-body recombinations following the decomposition of the molecules by the electron impact. In the case of carbon dioxide the recombination process will be

$$CO(^1\Sigma^+) + O(^3P) + M \rightarrow CO_2^*(^3\Pi) + M \tag{88}$$

For oxygen the recombination reaction is

$$O(^3P) + O^*(^1D) + M \rightarrow O_2^*(^3\Sigma_u^-) + M \tag{89}$$

In excitation brought about by impact with high-energy electrons ($\geqslant$200 e.v.), the Born approximation, applicable to this collision process, indicates that excitation will take place predominantly to optically allowed levels. It has, however, been found that for impacts of low-energy electrons ($\sim$20–100 e.v.), where the Born approximation no longer holds, excitation to a different term system takes place quite readily; thus, for instance, electrons with an energy of $\sim$35 e.v. will excite ground state 1^1S helium atoms preferentially to the 3^3P rather than to the 3^1P state (110). As pointed out by Mott and Massey (142), this indicates that in these low-velocity collisions an electron exchange between the impinging and the orbital electron takes place in such a way as to change the symmetry of the orbital electron spin function. This phenomenon is of importance in that it emphasizes the need for caution in treating processes between molecular or atomic species and electrons in a manner similar to chemical reactions. If one considers excitation by electron impact as a collision of the first kind, i.e.,

$$A + e \rightarrow A^* + e \tag{90}$$

the results obtained for helium (110), i.e., $He(1^1S) + e \rightarrow He^*(3^3P) + e$, would seem to indicate a violation of the Wigner spin-conservation rule, even though the coupling between the spin and the orbital motions in helium is small enough for this prohibition of intercombination to hold quite strongly. Phenomena such as electron exchange and the possible penetration of potential barriers by electrons should be taken into account in any consideration of interactions of matter and electrons leading to electronically excited states.

5. Excitation by electron capture

One of the processes in radiochemical systems by which electronically excited species can be produced is the discharge of ions by electrons:

$$A^+ + e \rightarrow A^* \tag{91}$$

$$A^+ + e + M \rightarrow A^* + M \tag{92}$$

Process 91, as written, can be considered as the inverse of a spontaneous radiationless ionization, i.e., a pre-ionization analogous to the atomic Auger process. Like it, it can be discussed on the basis of the overlapping and crossing of certain electronic states. Process 92, which is a bimolecular capture process, is the inverse of a quenching reaction with ionization of the quenched species; it too can be treated by a consideration of the relevant potential curves.

Unimolecular capture processes of the type of 91 have recently been discussed for the hydrogen system by Magee and Burton (126). They considered a nonradiative electron capture as a chemical reaction where a thermal electron (with energy of the order of kT), treated as a spherical wave filling all the container but essentially at infinity most of the time, is captured from its standing wave eigenfunction at the crossing of the potential curves of the various pertinent electronic states. The probability P of the occurrence of such a process is given by the Landau–Zener equation (37, 108, 231) discussed on page 170. As pointed out by Magee and Burton, the advantage of this treatment over the more usual treatment in terms of "cross-sections" and "collision probabilities" is the unification of the process of electron capture with that of chemical reactions involving excited electronic states, with the concomitant possibility of discussing in more detail the reaction mechanisms and products.

The general approach may be exemplified by the consideration of the reaction:

$$H_2^+ + e \rightarrow H + H^* \tag{93}$$

The potential curves for some representative states of the system H_2 are shown in figure 10. As pointed out by Magee and Burton, these are by no means all the possible states of the system. In particular, no states of the same species which, owing to resonance interaction, will not show any "crossings" at all, are represented here, and it is quite possible that these states may modify the ensuing reactions considerably. This, however, has no bearing on the validity and applicability of this general approach. The following points may be noted:

(*1*) The capture of an electron by the system $H^+ + H$ will lead either to $H^+ + H^-$ or to $H^* + H$, but not to H_2 or two normal H atoms, since the states of H_2^+ do not cross either the ground or the excited state of H_2. It seems that the ${}^2\Sigma_g^+$ state of H_2^+ might cross the ${}^3\Sigma_u^+$ state of H_2 at a high energy value. However, capture at this crossing is extremely unlikely because of the high value of the activation energy E_a of ~80 kcal. for this reaction, the activation energy being reckoned from the zero-point level of the initial state to the crossing point.

(*2*) Capture of the electron by the molecule-ion H_2^+ may take place at the two crossings of $H_2^+(^2\Sigma_g^+)$ and the polar state $H^+H^-(^1\Sigma_g, {}^1\Sigma_u)$, with activation energies of ~20 and ~40 kcal. with respect to the $H^+ + H^-$ state. Both of these crossings are above the dissociation limit of H_2^*, and the products, owing to further crossings of the Σ states of H^+H^- with the Π states of H_2^*, would most probably be $H(1^2S) + H^*(2^2S, 2^2P)$ with a kinetic energy of ~10–20 kcal.

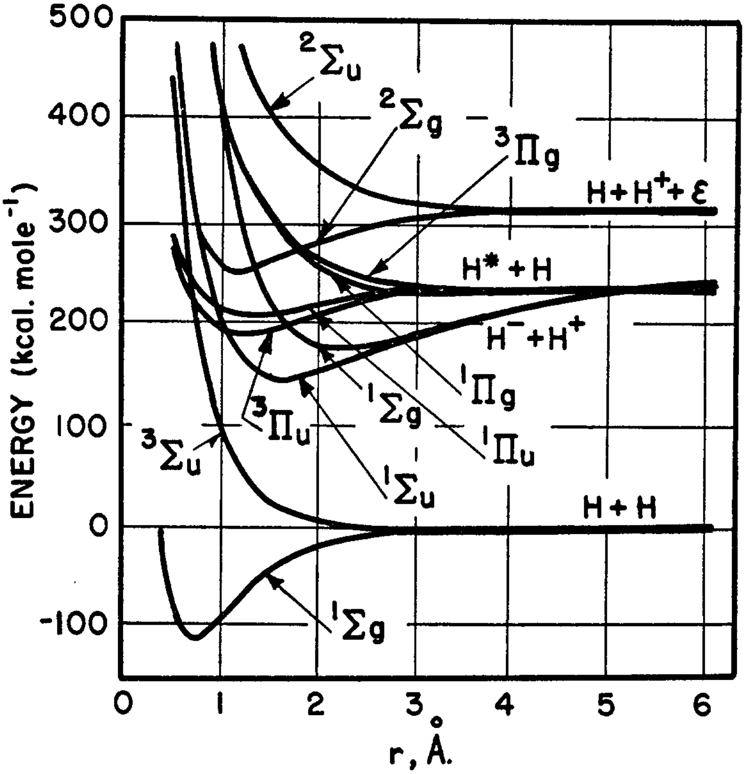

FIG. 10. Potential-energy curves for the system H_2, relevant to the mechanism of electron capture by H_2^+ (after Magee and Burton (126)).

(*3*) Capture of an electron may take place at the crossing between $H_2^+(^2\Sigma_g^+)$ and one of the excited H_2 states such as $H_2^*(^1\Pi_g, {}^3\Pi_g)$. This would seem to require considerable activation energy, but there are most probably other states of H_2^* which cross the $^2\Sigma_g^+$ state of H_2^+ nearer to its minimum, the capture thus resulting as before in $H + H^*$. This would just be an alternative path to the reaction discussed in paragraph (*2*) above.

The general conclusions reached by Magee and Burton on the basis of these and similar considerations are that the capture of an electron by an isolated polyatomic molecule-ion leads in most cases to immediate dissociation into two particles, one of which will be excited, dissociation into radicals being favored over dissociation into molecules. The basis for this conclusion is the greater number of possible radical dissociation processes with some of the fragments in excited electronic states, compared to the number of dissociation processes leading to molecular pairs in either normal or excited states.

Several points with regard to this treatment would have to be considered more explicitly before quantitative calculations could profitably be undertaken. In order to establish the complete reaction mechanism it will be necessary to investigate the possible influence of all the relevant potential-energy curves on which the various elementary steps of the overall reaction may proceed. This may be a rather difficult undertaking, since the exact form of the ionic surfaces, i.e., surfaces for states such as A^+A^-, and surfaces of charged species, i.e., A_2^+ or A_2^-, is not too well known for many systems. Furthermore, it will be necessary to investigate the magnitude of the matrix element ϵ_{12} of the Landau–Zener equation, where ϵ_{12} here refers to the interaction between the free and a bound electron. While the value of the matrix element is probably small in any case, owing to the diffuse nature of the free-electron orbit, it will still be necessary to decide whether the capture of the free electron takes place in one of the outlying or one of the inner orbitals of the ion, since this will have an important effect on the absolute value of ϵ_{12}. It may be possible that some quantitative information on the strength of interaction between bound and free electrons in electron capture processes can be obtained from a consideration of the inverse process of pre-ionization. In connection with the hydrogen systems discussed by Magee and Burton, the work of Beutler and Jünger (7) on pre-ionization of H_2 and H_2^+ is of interest.

In bimolecular capture processes of type 92 the previous discussion about capture process products will need to be modified because of the possibility that the molecule M may stabilize one of the resulting electronic states by inelastic collisions. An examination of figure 10 will make this clear. The crossing points of $H_2^+(^2\Sigma_g^+)$ and $H_2^*(^1\Pi_g)$ are above the dissociation limit $H + H^*$, and electron capture at this crossing should lead to a normal and an excited hydrogen atom. However, in a bimolecular capture process, the molecule M can stabilize the capture complex H_2^*, leaving it in the stable $^1\Pi_u$ state, so that the end product will be H_2^* rather than the atoms. The general conclusions of Magee and Burton as to the probable dissociation of species formed by electron capture thus hold only, as also emphasized by them, for systems at such low pressures that bimolecular capture processes can be neglected.

B. EXCITATION BY CHEMICAL REACTION

The production of electronically excited species during the course of a chemical reaction is usually indicated by the luminescence of the reaction mixture, which therefore constitutes a flame. Information as to the identity and mode of production of these excited species is given by spectroscopic investigations of the emitted radiation. The identification of the radiating species by analysis of their spectrum is, in principle, a rather straightforward matter (80), and for most of the diatomic emitters there is not much question as to their identity. The problem is in practice considerably more difficult for the case of polyatomic emitters, and much work remains yet to be done on the analysis and interpretation of the electronic spectra of polyatomic molecules (192). An example in point is the uncertainty still surrounding the identity of the emitter, presumably polyatomic, responsible for the so-called hydrocarbon flame bands in the oxyhydrocarbon flames (50, 53, 77, 220).

The question of the mode of production of these electronically excited species in flames is more difficult to answer. The excited species may be produced in various ways: (*i*) by chemical reactions such as association or exchange reactions, (*ii*) by energy-transfer mechanisms in which excess internal or kinetic energy is transferred as electronic energy to a suitable collision partner (collisions of the first kind), or (*iii*) by purely thermal collisions. One possible method of obtaining information as to the mechanism by which the excited species are produced is that of kinetic spectroscopy in which, by following the change of intensity in the spectra of the various species under varying conditions of fuel ratio and pressure, and in the presence and absence of inert diluents, the desired information may be deduced (50). Another approach to this problem is by a study of the energetic distribution of the excited radicals (56–58, 184, 185, 229). If a spectroscopic investigation of the emitted radiation indicates that the excited radicals are in a nonequilibrium or nonequipartition distribution, there is good reason to believe that they were formed in such a distribution by a chemical reaction; one is then dealing with a true case of chemiluminescence (51, 99). The existence of an equilibrium (equipartition) distribution would indicate either a purely thermal production of electronically excited radicals or equilibration by collisions of chemically produced radicals, and further investigations would be necessary before any definite conclusions as to their modes of production could be reached. Work along these lines should be very valuable in elucidating some of the processes by which the electronically excited radicals are produced in various reaction systems.

The work reviewed here deals mainly with those species and reactions which have been investigated in some detail. Many of the processes supposedly involved in the production of electronically excited species have never been subjected to an adequate theoretical study, and the following discussion will indicate the large amount of work still to be done before there will be an adequate body of knowledge concerning the nature and production of electronically excited species in flames.

1. *Two-body association reactions*

Association reactions of the type

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB} \tag{94}$$

where A and B are atoms or very simple radicals such as OH, are not common; to conserve linear momentum the energy of recombination goes into the vibrational modes of the association complex, which then dissociates unless stabilized by a collision with a third body. If, on the other hand, the association complex is formed in an electronically excited state it can become stabilized by emitting a large part of the energy of recombination as radiation and returning to a lower electronic state. The probability of such a two-body association reaction is, however, still rather small. The radiative lifetime of a diatomic electronically excited radical is usually of the order of 10^{-8} sec.; the average dissociation lifetime of a diatomic association complex is about 10^{-13} sec., corresponding to dissociation of the complex by vibration with a frequency of 10^{13} sec.$^{-1}$ Consequently, two-body association with radiative stabilization will take place in only one out of about every 10^{5} collisions.

Two-body association or recombination reactions involving electronically excited states are characterized by the "recombination continuum" emitted in the radiative stabilization of the association complex (figures 8 and 9). Radiative two-body association reactions in which the two reacting atoms are in their ground states (figure 8) would be expected to be rare, since a transition in which the upper state goes to configurationally unexcited atoms upon dissociation (the so-called sub-Rydberg transition) will have a rather small probability (146–148). This view is supported by the fact that no radiative two-body association reactions seem to be known in which the two reacting species are both in their ground states.

Atomic two-body association reactions in which one of the atoms is in an excited state (figure 9) have been proposed to account for some of the continua observed in flames and discharges. An example is the recombination of halogen atoms (98, 219),

$$\mathrm{X}(^2P_{3/2}) + \mathrm{X}(^2P_{1/2}) \rightarrow \mathrm{X}_2 + h\nu \tag{95}$$

where the excited halogen atom is supposedly produced by the dissociation of X_2 under the high temperatures employed in the experiments. Another example is the recombination of tellurium in a discharge through Te_2 (182).

Two-body association reactions between an atom and a molecule or between two molecules leading to electronically excited states have been postulated to account for various emission continua in flames and discharges. One would suppose that radiative stabilization of polyatomic association complexes would take place more readily than that of diatomic products, since in the polyatomic case there is a greater probability of the loss of excitation and recombination energy, owing to the breakdown of electronic selection rules by the excitation of certain unsymmetrical vibrations (192, 210). The requirement that the excited electronic state combine with the ground state (or some other lower state) is, of course, one of the factors limiting the occurrence of radiative recombination processes. It is, however, very difficult to associate with certainty the observed emission continua accompanying the overall chemical reaction with the various elementary steps postulated. This arises largely from the present paucity of knowledge of the electronic states of polyatomic molecules, particularly those of low symmetry. Consequently, not too many examples of molecular association reactions leading to electronically excited products are to be found in the literature, and those that are discussed here are not known with certainty to occur.

(a) The carbon dioxide continuum

One of the most thoroughly investigated reactions in which a two-body association process is believed to play a role is the carbon monoxide flame (50, 63, 86). The continuum appearing in this flame has been attributed (49) to the association reaction:

$$CO + O \rightarrow CO_2^* \rightarrow CO_2 + h\nu \tag{96}$$

This identification is plausible on energetic grounds, since the formation of carbon dioxide in its ground state is exothermic by 126.7 kcal., which is sufficient to extend the continuum down to the observed 2500 Å. The ground state of carbon dioxide is $^1\Sigma_g^+$ (144), and since there is no evidence that electronic excitation of the carbon monoxide precedes the formation of carbon dioxide, some $CO_2(^1\Sigma_g^+)$ may be produced by

$$O(^1D) + CO(^1\Sigma^+) \rightarrow CO_2(^1\Sigma_g^+) \tag{97}$$

According to Mulliken (144) the first excited states of carbon dioxide are probably $^1\Pi$ and $^3\Pi$, where the $^3\Pi$ state produced by

$$O(^3P) + CO(^1\Sigma^+) \rightarrow CO_2^*(^3\Pi, {}^3\Sigma) \tag{98}$$

is probably the lower-lying one (63). The continuum then would be due to the transition

$$CO_2^*(^3\Pi) \rightarrow CO_2\,(^1\Sigma_g^+) + h\nu \tag{99}$$

where the CO_2^* is produced in the continuous energy region of the $^3\Pi$ state by reaction 98.

The assignment of the carbon monoxide flame continuum to reaction 99 is in agreement with Hornbeck's observation (84) that the intensity of the continuum decreases as the intensity of the banded structure increases with increasing oxygen:carbon monoxide fuel ratio. A large fraction of this banded structure, which appears most prominently as the oxygen is increased above the stoichiometric ratio, has been identified (86) as the Schumann–Runge system $O_2(^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-)$ and the formation of the electronically excited oxygen *via* a nonlinear complex has been postulated (105) to be due to the reaction (see also page 210).

$$CO_2^*(^3\Pi) + O_2(^3\Sigma_g^-) \rightarrow CO_2O_2 \rightarrow CO_2O^+O^- \rightarrow CO_2(^1\Sigma_g^+) + O_2^*(^3\Sigma_u^-) \tag{100}$$

Reaction 100 accounts for the results of Hornbeck: as the proportion of oxygen in the fuel mixture increases, more excited O_2 will be produced by the transfer of electronic energy from the carbon dioxide, and the Schumann–Runge system will increase in intensity. At the same time, the electronically excited carbon dioxide is brought to the ground state by this radiationless transition, and less $CO_2^*(^3\Pi)$ will be at hand to give the continuum reaction 99. The lowered flame temperature brought about by the addition of excess oxygen may also be partly responsible for the suppression of the continuum as the $O_2:CO_2$ ratio increases.

(b) The nitrogen dioxide continuum

Another case of a two-body association reaction leading to an electronically excited product is the reaction between nitric oxide and oxygen:

$$NO + O \rightarrow NO_2^* \rightarrow NO_2 + h\nu \qquad (101)$$

It is believed that the afterglow of air in a discharge tube is due to this reaction (190). There is not much information on the electronic states of nitrogen dioxide or on the transitions involved in the continuum. Nitrogen dioxide is not a linear molecule and it is difficult to correlate the electronic states of NO_2 with those of NO and O. An experimental investigation of the electronic spectrum of nitrogen dioxide has been made by Harris and King (72) and the results have been discussed in terms of possible energy levels by Mulliken (149).

The nitrogen dioxide continuum has been used as a test for atomic oxygen in flames (48, 49). A small amount of nitric oxide is added to the flame, and the appearance of a yellow-greenish color is taken as evidence for the presence of atomic oxygen. The test is, however, not a quantitative one, since reactions such as

$$NO_2 + O \rightarrow NO + O_2 \qquad (102)$$

will change the atomic oxygen concentration. Furthermore, the addition of the radical NO may modify or change the mechanisms of the flame reaction, as is observed in the case of free-radical mechanisms in pyrolysis and photolysis.

(c) Inverse predissociation

Another possible way in which electronically excited association products can be formed in two-body collisions is by inverse predissociation. This process, involving the radiationless transition of the association complex from a continuous energy range to a discrete level of energy, with the consequent appearance of a discrete spectrum in the electronic transition, has been postulated to account for the formation of electronically excited $AlH(^1\Pi)$ when aluminum is heated in a hydrogen atmosphere (205). It can readily be shown (80) that inverse predissociation can be no more efficient than the ordinary radiative recombination in the formation of electronically excited association products.

2. *Three-body association reactions*

There are two types of reactions which must be considered in the discussion of three-body association reactions:

$$\text{(a)} \quad A + B + C \rightarrow AB^* + C \qquad (103)$$

$$\text{(b)} \quad A + B + C \rightarrow AB + C^* \qquad (104)$$

Reaction 103 is the inverse of the main secondary process in photolysis and reaction 104 is the inverse of a photosensitized dissociation reaction. In either case, A, B, and C may be atoms or molecules. These three-body reactions producing electronically excited species differ from the analogous two-body association reactions in that they give rise to a discrete spectrum: the third body can serve to remove some of the excess vibrational energy of the newly formed electronically excited molecule, leaving it in one of its discrete vibrational states. The transfer of energy by or to the third body C must, however, not be thought of as a purely mechanical process involving inelastic collisions: the work of Eyring, Gershinowitz, and Sun (33) on three-body reactions involving hydrogen, of Castellan and Hulburt (18) on the interchange of translational and vibrational energy, and of Laidler (103) on photosensitized dissociation reactions has shown that the ability of the third body to transfer energy from the newly formed molecule is dependent upon its specific chemical interaction in forming, a complex with the reacting species. In type (*a*) reactions the function of the third body is the removal of excess vibrational energy from the newly formed, electronically excited molecule; the specific mechanism of this type of energy transfer is not very relevant to the discussion of the formation of electronically excited molecules by association reactions and will therefore not be discussed in this review. In type (*b*) association reactions, however, the third body is formed in an electronically excited state *via* complexes of the type ABC, AB^+C^-, etc. and the overall process represented by reaction (*b*) must be decomposed into several elementary steps which must be discussed separately for a thorough understanding of the overall reaction.

(a) Processes of the type $A + B + C \rightarrow AB^* + C$

The only atomic association reaction of type (*a*) which seems to have been investigated in detail is the recombination of nitrogen atoms, giving rise to the characteristic yellow nitrogen afterglow consisting mostly of bands of the first positive system $N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+)$. Owing to the large number of potential surfaces for N_2 (thirty-two are listed by Herzberg (80)), and because of the complication introduced by the various metastable atomic and molecular states, it has not been possible so far to arrive at a detailed mechanism for this reaction. The origin of this afterglow and the mechanism of excitation have been discussed recently in great detail (135) with many references to the original literature. In view of this thorough discussion, and of the uncertainty still surrounding this reaction, a discussion of the various proposed mechanisms for the formation of electronically excited $N_2(B^3\Pi_g)$ at this point would not be of much value.

(*i*) *Excited* $O_2(^3\Sigma_u^-)$ *in flames:* The recent observation of Schumann–Runge bands in the hydrogen–oxygen flame (52, 85, 186), the carbon monoxide flame (86), and the ammonia–oxygen flame (85) raises the question of the production of electronically excited O_2 in these flames. While it is of course possible that the mode of formation is a specific one for every different reaction system, the fact that $O_2^*(^3\Sigma_u^-)$ has been found in so many different flames burning with oxygen would seem to argue that the reactions leading to the production of $O_2^*(^3\Sigma_u^-)$ are common to all the reaction systems and thus independent of the nature of the fuel.

In view of the above suggestion, the association reaction

$$O(^3P) + O^*(^1D) + M \rightarrow O_2^*(^3\Sigma_u^-) + M \tag{105}$$

must be considered as a possible source of electronically excited oxygen molecules· The presence of atomic oxygen in the hydrogen–oxygen and carbon monoxide–oxygen flames has been suggested by the nitric oxide test (48, 49); in the absence of specific information to the contrary, atomic oxygen might also be assumed to be present in the ammonia–oxygen flame. The atomic oxygen in the ^1D state may be produced thermally, the excitation energy from the ground state being only 1.97 e.v., or it may result from the dissociation of one of the reaction intermediates such as $OH^*(^2\Sigma^+)$. In the carbon monoxide flame, the $O^*(^1D)$ may conceivably be produced by the thermal dissociation of $CO_2(^1\Sigma)$:

$$CO_2(^1\Sigma^+) \rightarrow CO(^1\Sigma^+) + O^*(^1D) \tag{106}$$

Since the ^1D level is metastable with respect to radiative transitions to the ^3P ground state, the ^1D oxygen atom may well undergo a chemical reaction such as reaction 105 before it has an opportunity to lose its energy *via* a radiative transition.[6]

Recent experimental and theoretical work on the relative concentrations of $O_2^*(^3\Sigma_u^-)$ and $OH^*(^2\Sigma^+)$ in hydrogen–oxygen flames burning with various fuel ratios has given definite evidence that $O_2^*(^3\Sigma_u^-)$ and $OH^*(^2\Sigma^+)$ are in thermal equilibrium (186). While this finding is no direct proof that the excited O_2 is produced thermally, it at least indicates that the thermal production of $O_2^*(^3\Sigma_u^-)$ in these flames, which has also been suggested by Gaydon (52), is a distinct possibility. This hypothesis could also be tested by making the measurements described in reference 186 in low-pressure flames where there would be less of a problem in respect to the collisional equilibration of possibly chemiproduced $O_2^*(^3\Sigma_u^-)$.

(*ii*) *Excited* $CO_2(^3\Pi)$ *in the carbon monoxide flame:* Few association reactions of type (*a*) in which one or both of the associating species are molecules are known, and fewer still have been discussed in any detail. The reason for this is the difficulty of the spectroscopic identification of the possible polyatomic emitter. Many of the as yet unresolved and unidentified banded spectra in flames and discharges may well be due to electronically excited polyatomic species formed in such three-body association reactions.

About the only three-body association reaction giving rise to a polyatomic molecule which has been studied theoretically in any detail is the formation of

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[6] Since reaction 105, leading to $O_2(^3\Sigma_u)$ in a discrete vibrational state, is a three-body reaction, its importance in the production of $O_2(^3\Sigma_u^-)$ may be assessed by investigating the change of intensity of the discrete Schumann–Runge bands as the pressures of fuel and oxygen are decreased. According to reaction 105 there should be no Schumann–Runge bands in low-pressure flames, corresponding to their absence in low-pressure arcs (41).

electronically excited carbon dioxide in the carbon monoxide flame (63).[7] This is one of the most luminous of all flames, and the high quantum yield (1 quantum for every 125 molecules of carbon dioxide) indicates that the electronically excited carbon dioxide is not of thermal origin but has been produced chemically by one of the elementary reactions occurring in the flame, the most probable being

$$O(^3P) + CO(^1\Sigma^+) + M \rightarrow CO_2^*(^3\Pi) + M \qquad (107)$$

The consequent transition

$$CO_2^* \rightarrow CO_2 + h\nu \qquad (108)$$

is then responsible for part of the banded spectrum observed in the flame.

The presence of atomic oxygen in the carbon monoxide flame has been established by Gaydon (48, 49). Since normal carbon monoxide is in a $^1\Sigma^+$ state, reaction with ^3P oxygen atoms cannot give rise to carbon dioxide in its ground state ($^1\Sigma_g^+$) but only in a triplet excited state; the first excited state (probably $^3\Pi$) is produced by reaction between carbon monoxide and a ^3P oxygen atom, a reaction which has been shown to occur rather rapidly (175). Using the semi-empirical scheme, it is possible to construct schematic surfaces corresponding to reactions

$$O(^3P) + CO(^1\Sigma^+) \rightarrow CO_2(^3\Pi)$$

and

$$O^*(^1D) + CO(^1\Sigma^+) \rightarrow CO_2(^1\Sigma_g^+)$$

The potential-energy surfaces for the three-body system O^α–C–O^β may be represented in a three-dimensional diagram in which the coördinates are potential energy, O^α–C distance, and C–O^β distance. The two profiles which correspond to infinite separation of O^α and C and of O^β and C are shown as two sides of a cube in figure 11; the curves in this profile, which are in this case identical to one another, are the ordinary potential-energy curves for the carbon monoxide molecule. The system $O^\alpha(^3P) + CO(^1\Sigma^+)$ is represented by the curve AP on the left-hand face of the diagram, and the process of the reaction is represented by penetration of the surface until the configuration reaches a basin, corresponding to excited carbon dioxide, in the interior of the cube. The initial configuration for the reaction $O^\alpha(^1D) + CO(^1\Sigma^+)$ is represented by curve BQ, which lies 45.4 kcal. above AP.

In constructing the potential-energy curves for carbon monoxide, which are shown in more detail in figure 12, the dissociation energy of carbon monoxide into carbon and oxygen in their ground states was taken as 256.1 kcal. (11.11 e.v.), the value favored by Gaydon and Penney (54, 55). This corresponds to a value of 170 kcal. for the latent heat of sublimation of carbon, a value which seems to be favored by most of the available evidence (15, 54, 107, 193).[8]

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[7] It should be noted that there is as yet no certain spectroscopic evidence that the carbon monoxide flame bands are actually due to CO_2^*; however, what evidence there is points in this direction.

[8] Objections to this value have been put forward, particularly by Long and Norrish (120–122), but we consider their arguments to contain serious errors.

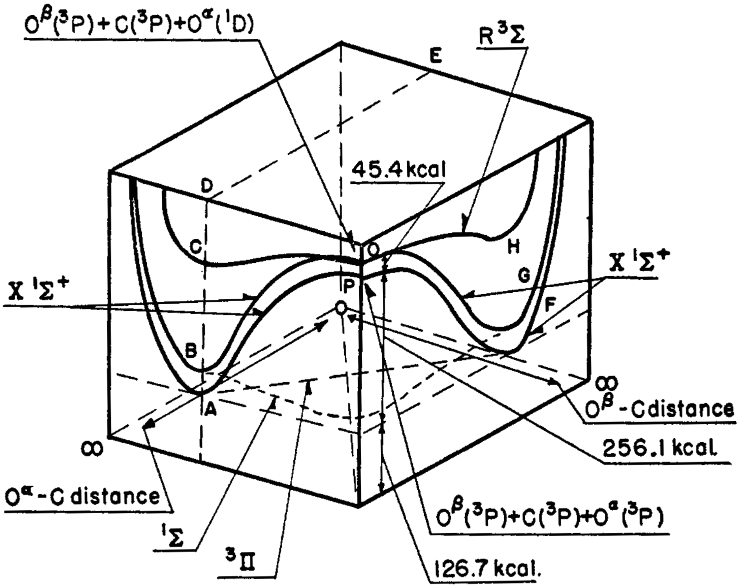

FIG. 11. Schematic potential-energy surfaces for the system O^{α}–C–O^{β}. Potential-energy curves for C–O^{β} and C–O^{α} are shown on the left-hand and right-hand faces of the cube, and are connected by surfaces, indicated by dotted lines, in the interior of the model. Only curves and surfaces relevant to the kinetics are included (after Griffing and Laidler (63)).

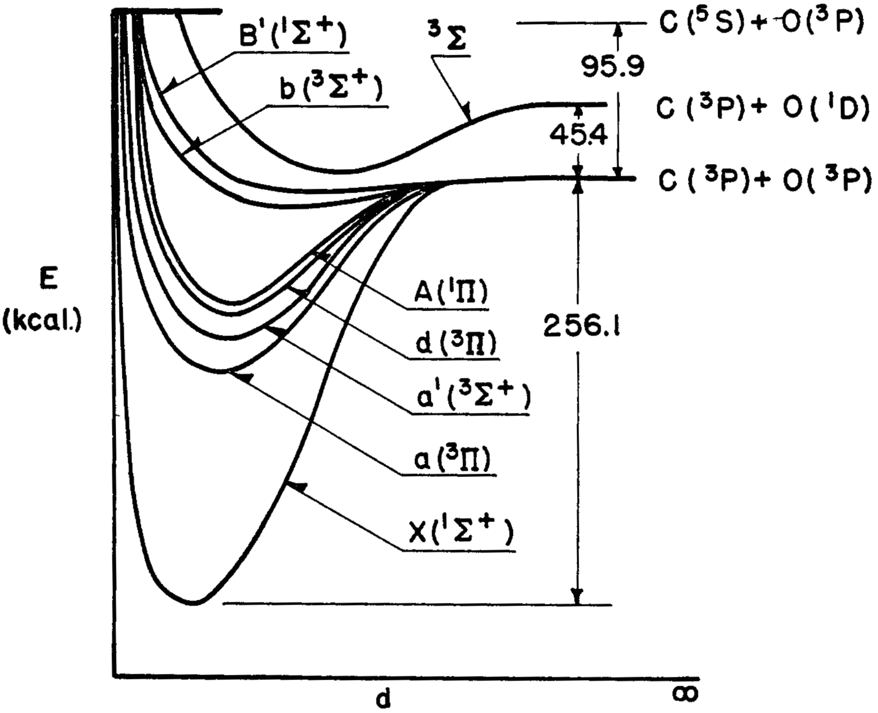

FIG. 12. Schematic potential-energy curves for the carbon monoxide molecule. These curves have been drawn so as to be consistent with the value of 256.1 kcal. for the energy of dissociation of the molecule into the ground-state atoms.

Carbon and oxygen atoms in their lowest states are both ^3P, and may therefore combine to give $\Sigma^+(2)$, Σ^-, $\Pi(2)$, and Δ states of carbon monoxide, each of these states occurring as singlets, triplets, and quintets. The lowest state is evidently a $^1\Sigma^+$, and this is identified with the $X^1\Sigma^+$ state found experimentally to be the ground state of the molecule. This is at variance with the view (121, 122) that apart from the possibility of crossing to other curves, the $X^1\Sigma^+$ state correlates with a carbon atom in the ^5S state, but agrees with the ideas of Long and Walsh (123) and Coulson (21) who, on the basis of a molecular orbital treatment, have shown that the bond in normal carbon monoxide is approximately double, and that the molecule can therefore dissociate, even in zero approximation in which interaction with other states is neglected, into normal carbon (^3P) and oxygen (^3P) atoms. Accordingly, the potential-energy curve for normal carbon monoxide ($X^1\Sigma^+$) may be constructed as a Morse curve, using the values $\omega_e = 2170.2$ cm.$^{-1}$, $r_e = 1.128$ Å., and $D_0^0 = 11.11$ e.v.; the first two values are taken from Herzberg (80), and the dissociation energy is that given by Gaydon (54). The potential curves for the various states of carbon monoxide are shown in figure 12; they are qualitative and show correlations only.

It is now necessary to consider how the curves shown on the two faces of the cube in figure 11 are connected in the interior of the diagram. When an oxygen atom in its lowest (^3P) state approaches a carbon monoxide molecule in its lowest ($X^1\Sigma^+$) state, the resultant states are $^3\Sigma$ and $^3\Pi$, i.e., $O(^3P) + CO(^1\Sigma^+) \rightarrow CO_2(^3\Sigma, {}^3\Pi)$, and both represent excited states of the carbon dioxide molecule. The $X^1\Sigma^+$ curves (*AP* and *PF*) on the two faces of the cube are therefore connected by two surfaces, the $^3\Pi$ surface apparently being lower. About the shape of this surface there is very little information of a definite character. The fact that carbon dioxide is transparent down to below 1700 Å. (176) would suggest that the first excited state lies at least 140 kcal. above the ground state. However, the carbon monoxide flame shows bands in the region of 3000–5000 Å., corresponding to energies of 55–95 kcal., which are at least partly due to carbon dioxide emission (47). The big difference between the region of absorption and emission has been explained by the fact that the molecule has very different configurations in the normal and excited states (50); according to this idea the most highly populated vibrational levels in the surface of the excited state are separated from the lower surface by 55–95 kcal., while the most populated levels of the lowest state are separated from the upper surface by about 140 kcal.

This situation is represented in the potential-energy profile shown schematically in figure 13. This profile corresponds to the normal C–O distance in carbon monoxide and is a section through *ABCDE* of figure 11. The conclusions as to the shape of the carbon dioxide surface are consistent with the kinetic result that reaction between $O(^3P)$ and $CO(^1\Sigma^+)$ occurs with an activation energy of not more than 3 kcal. (70, 90), a result which imposes an upper limit of $127 + 3 = 130$ kcal. on the excitation energy measured with respect to the surface minimum. There seems to be no obvious method of establishing a lower limit for the excitation energy from the available information, and the depth of the minimum in the $^3\Pi$ state of carbon dioxide (assuming that this is the upper state for the transition giving rise to the banded carbon dioxide spectra and therefore an attractive state) must remain an open question for the time being.

(b) Processes of the type $A + B + C \rightarrow AB + C^*$

Reactions of the type

$$A + A + X \rightarrow A_2 + X^* \tag{109}$$

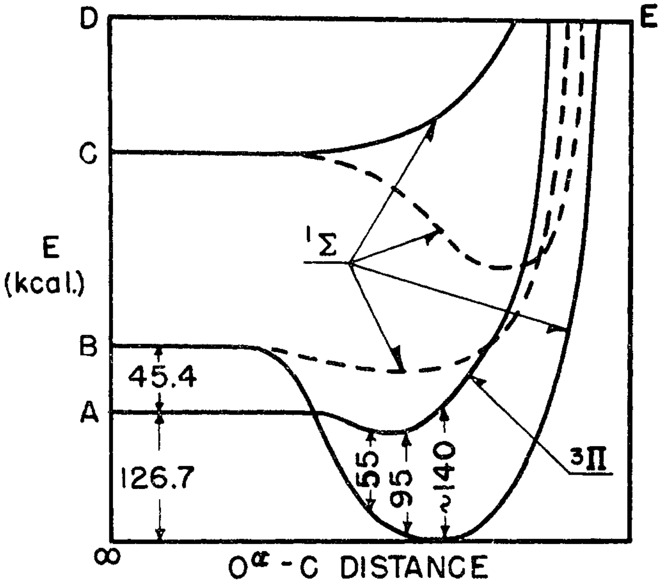

FIG. 13. Schematic potential-energy profiles through the section *ABCDE* in figure 11. The shapes of the curves for the lowest ($^1\Sigma_g^+$) state and the first excited state ($^3\Pi$) of carbon dioxide are consistent with the data on absorption and emission of carbon dioxide. The lowest state may be regarded as arising from resonance between the states represented by dotted curves, of which the one passing through *B* corresponds to $O^\beta(^3P) + C(^3P) + O^\alpha(^1D)$ and the one through *C* to $O^\beta(^1D) + C(^3P) + O^\alpha(^3P)$ (after Griffing and Laidler (63)).

have been investigated most thoroughly for the case of A = hydrogen. This is partly due to the ease with which hydrogen atoms can be prepared by Wood's method in a discharge tube, and partly to the fact that the comparatively long lifetime of active hydrogen in vessels poisoned against wall recombination facilitates the investigation of the recombination reactions. It has been noted (13, 14) that admixture of various gases with hydrogen atoms produced in a discharge tube results in the electronic excitation of these added gases. Examples of this are the emission of the sodium D line and of the 2537 line of mercury. Somewhat different is the behavior of hydrocarbons added to a stream of hydrogen atoms: in that case the hydrocarbons decompose to give electronically excited radicals.[9] The addition of ethane, pentane, or acetylene to a stream of hydrogen atoms gives rise to the Swan system of C_2 and some of the CH band system. The reaction between hydrogen atoms and benzene, which has been studied by Geib and Vaidya (60), also gives electronically excited C_2 and CH. It has also been suggested (50) that the excited S_2 observed in hydrogen flames containing sulfur as impurity might be due to the reaction:

$$H + H + S_2 \rightarrow H_2 + S_2^* \tag{110}$$

Another reaction of this type is

$$H + H + OH \rightarrow H_2 + OH^* \tag{111}$$

which has been proposed to explain the abnormal excitation of OH to the $v' = 2$ level in low-pressure flames of hydrogen (51, 99). It is, however, somewhat doubtful if there is a sufficient concentration of hydrogen atoms and hydroxyl radicals at low pressures ($\sim$5 mm.) for three-body collisions to be of much importance. This preferential excitation of OH to the $v' = 2$ level is a most interesting observation; further study of this phenomenon may throw light on some of the elementary reactions taking place in the hydrogen–oxygen flame.

The excitation of a third body during the recombination of hydrogen atoms may also take place as a heterogeneous reaction. When hydrogen flames are brought into contact with certain solids, particularly those containing various activated oxides, a luminescence (candoluminescence) is observed. While there is considerable uncertainty as to the mechanism responsible for this candoluminescence, it has recently been suggested (2) that the luminescence may have its origin in the reaction

$$H + H + S \rightarrow H_2 + S^* \tag{112}$$

where S represents the oxide surface. Evidence for this type of mechanism is adduced from the observation that the candoluminescence is suppressed coincidentally with the luminescence of sodium added to the flame, so that the controlling reaction in either case may be the removal or destruction of hydrogen atoms. In the same way that the formation of excited nitrogen dioxide can serve as a test for the presence of oxygen atoms, the presence of hydrogen atoms may thus be indicated by the appearance of candoluminescence.

It has been emphasized earlier in this section that the transfer of energy to the third body must involve the prior formation of an association complex with some type of chemical bonding of the various reacting species; this will also hold true for these heterogeneous reactions. It has been pointed out that the recombination of hydrogen atoms on surfaces involves the formation of surface hydrides (187), and the luminescent association reaction discussed above should thus be broken down into elementary steps of the type

$$H + S \rightarrow H\text{—}S \tag{113}$$

$$S\text{—}H + H \rightarrow (S\text{—}H\text{—}H)^{\ddagger} \rightarrow S^* + H_2 \tag{114}$$

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[9] It is not known if the hydrogen atoms in these reactions collide with hydrogen atoms stripped from the hydrocarbons, or if the hydrocarbon acts as a third body for the recombination of free hydrogen atoms, dissociating after the excitation.

where the symbol ‡ denotes the activated complex and the asterisk the electronically excited third body, i.e., the luminescent surface.

The most thoroughly studied case of a three-body association reaction of type (*b*) is the excitation of alkalies in the presence of hydrogen atoms:

$$\mathrm{H + H + X \rightarrow H_2 + X^*} \tag{115}$$

Excitation takes place readily with sodium atoms, with difficulty in the case of potassium, and not at all for rubidium and cesium (136). The energy of excitation to the first upper level of these atoms is in the order Na > K > Rb > Cs; there is clearly no correlation between the ease of occurrence and ease of excitation. On the basis of these data, Mohler (136) first suggested that hydrides are formed as intermediates, and this view has since been developed in more detail by Magee and Ri (127).

The potential-energy surface (127) for the reaction $\mathrm{Na + 2H \rightarrow Na^* + H_2}$ is shown in figure 14. It was constructed for linear complexes Na–H–H and Na*–H–H, but calculations show that the semiquantitative conclusions of this study are not too much affected by the shape of the complex, which should probably be triangular. Magee and Ri found an activation energy of $\sim$6.5 kcal. for the luminescent reaction. The details of the reaction can probably best be followed by means of the potential-energy surfaces (figure 3) constructed (102) for the system Na–H–H in a study of the quenching of excited sodium.

The reaction

$$\mathrm{Na(^2\mathit{S}) + 2H(^2\mathit{S}) \rightarrow Na^*(^2\mathit{P}) + H_2(^1\Sigma_g^+)} \tag{116}$$

corresponds to a transition from M to B *via* the curve $\mathrm{NaH(^1\Sigma^+) + H(^2\mathit{S})}$ This curve is connected with the $\mathrm{Na(^2\mathit{P}) + H_2(^1\Sigma_g^+)}$ curve by a surface of designation $^2\Sigma^+$, and it is on this surface that the luminescent reaction takes place. Reaction 116 may thus be written:

$$\mathrm{Na(^2\mathit{S}) + 2H(^2\mathit{S}) \rightarrow NaH(^1\Sigma^+) + H(^2\mathit{S}) \rightarrow Na\text{–}H\text{–}H(^2\Sigma^+)}$$
$$\mathrm{\rightarrow Na^*(^2\mathit{P}) + H_2(^1\Sigma_g^+)} \tag{117}$$

The association reaction $\mathrm{Na(^2\mathit{S}) + 2H(^2\mathit{S}) \rightarrow Na(^2\mathit{S}) + H_2(^1\Sigma_g^+)}$, which proceeds without excitation of the sodium, corresponds to a transition between M and A and takes place on a lower $^2\Sigma^+$ surface connecting the curves $\mathrm{H(^2\mathit{S})}$ + $\mathrm{NaH(^1\Sigma^+)}$ and $\mathrm{Na(^2\mathit{S}) + H_2(^1\Sigma_g^+)}$.

Magee and Ri (127) attribute the low activation energy of 6.5 kcal. for the luminescent sodium reaction to the strong interaction between sodium and hydrogen. The weak luminescence or complete absence of luminescence for potassium, rubidium, and cesium is then attributed to the higher activation energies for the reaction of these alkalies with hydrogen atoms, the M—H bond energies being in the order Na > K > Rb > Cs. It would, however, seem that the more important factor governing the activation energy is the interaction of the reaction surface with the polar state $\mathrm{M^+\text{–}H^-\text{–}H}$. The upper $^2\Sigma^+$ surface on which the luminescent reaction takes place is perturbed by the low-lying ionic state, the perturbation producing an activation-energy hump on the reaction surface. The increased activation energy for the reaction of potassium, rubidium, and cesium would then seem to be due to the greater amount of ionic character in the bonding of these alkali hydrides. The nonluminescent reaction proceeding along the lower surface will probably have zero activation energy, since the lower surface is too far removed to interact with the ionic state. Using $E = 6.5$ kcal. for the luminescent reaction and $E = 0$ for the nonluminescent reaction, and making reasonable assumptions about the magnitude of the transmission coefficient, Magee and Ri have calculated that about fifteen out of every one thousand sodium atoms will be found in the electronically excited ^2P state.

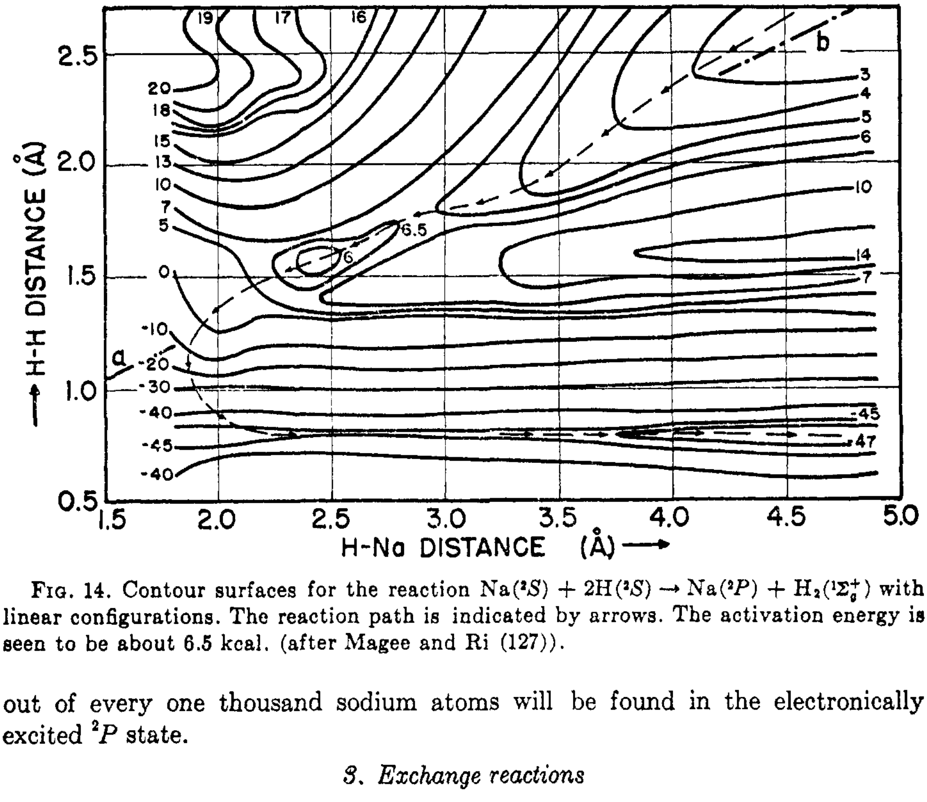


Fig. 14. Contour surfaces for the reaction $Na(^2S) + 2H(^2S) \rightarrow Na(^2P) + H_2(^1\Sigma_g^+)$ with linear configurations. The reaction path is indicated by arrows. The activation energy is seen to be about 6.5 kcal. (after Magee and Ri (127)).

3. *Exchange reactions*

Electronically excited species can be produced in exchange reaction of the type

$$\text{(c)} \quad A + BC \rightarrow AB + C^* \qquad (118)$$

$$\text{(d)} \quad AB + CD \rightarrow AC^* + BC \qquad (119)$$

or various modifications thereof. Reactions of type (*c*) have been studied for the systems

$$Na_2 + Cl \rightarrow NaCl + Na^* \qquad (120)$$

and

$$NaH + H \rightarrow H_2 + Na^* \qquad (121)$$

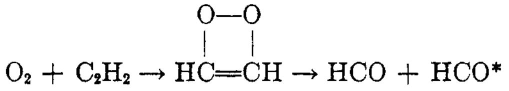
by Magee (125, 127), and these reactions are discussed in more detail on pages 202 and 199.

Exchange reactions of type (*d*), involving diatomic and polyatomic molecules, have been proposed as mechanisms responsible for the production of electronically excited radicals in hydrocarbon flames (50, 53); examples are

$$CH + O_2 \rightarrow CO + OH^* \qquad (122)$$

$$C_2 + OH \rightarrow CO + CH^* \qquad (123)$$

The exchange reaction



$$O_2 + C_2H_2 \rightarrow \overset{\displaystyle \mathrm{O{-}O}}{\underset{}{\mathrm{HC{=}CH}}} \rightarrow HCO + HCO^* \qquad (124)$$

has been suggested (77) as a possible mechanism for the production of electronically excited HCO in the oxyacetylene flame.[10] Walsh (223) has proposed the reaction

$$RCH_2O + OH \rightarrow ROH + HCHO^* \qquad (125)$$

to account for the formation of electronically excited formaldehyde in the cool flames of hydrocarbons.

Many more exchange reactions of the type listed above could be written down to account for the appearance of various electronically excited species. While it is, of course, desirable to study these exchange reactions in more detail from a theoretical point of view, it would be a rather difficult undertaking, since the number of atoms involved in the formation of the activated complex may be quite large. Four-atom reactions, similar to some of the examples mentioned above, have been investigated by Altar and Eyring (1), using potential surfaces in bond space. Their treatment, however, did not extend to a consideration of possible electronically excited states, and it is not clear if their method would lend itself to a satisfactory detailed treatment similar to that of three-body reactions in coördinate space. Some work along these lines would be very valuable.

C. EXCITATION BY INELASTIC MOLECULAR COLLISIONS

There is very little quantitative information on the efficiency of transfer of kinetic or internal energy into electronic energy in the inelastic collision of atoms or molecules. In the case of atomic collisions, the resonance principle of energy transfer in collisions of the second kind (79, 131) will, supposedly, also hold for the inverse process (i.e., collisions of the first kind), and the transfer of the kinetic energy of translation into the electronic energy of one of the collision partners is probably a very rare and inefficient process. No example of such an atomic excitation reaction seems to be known. In collisions of atoms with mole-

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[10] As pointed out by these authors there is as yet no unequivocal spectroscopic evidence that the emitter of the so-called "hydrocarbon flame bands" is HCO; for a discussion on that point see reference 53.

cules and in bimolecular collisions, electronic excitation of one of the colliding species may take place under certain conditions.

It has been pointed out (102) that in the physical quenching of electronically excited species the quenching molecule is often left in a vibrationally excited state. This is particularly the case if the amount of electronic energy to be changed into the internal modes of the colliding molecule is not too large. By the principle of microscopic reversibility, the reverse process, i.e., electronic excitation by collision with vibrationally excited species, should therefore also be possible.

A well-known example is the excitation of sodium by *vibrationally* excited sodium chloride

$$\mathrm{NaCl} + \mathrm{Na}(^2S) \rightarrow \mathrm{NaCl} + \mathrm{Na}^*(^2P) \tag{126}$$

first suggested by Polanyi (173) and discussed in more detail later by Magee (125). A consideration of the various potential-energy surfaces involved in the production of $\mathrm{Na}(^2P)$ atoms in the reaction

$$\mathrm{Na_2} + \mathrm{Cl} \rightarrow \mathrm{NaCl} + \mathrm{Na}^* \tag{127}$$

led Magee to the conclusion that the production of excited sodium atoms took place partly by reaction 126 and partly by reaction 127. Comparison of calculated and experimental luminescence yields showed that not every sodium chloride molecule with sufficient vibrational energy (~48.3 kcal.) could excite a sodium atom.

Since the efficiency of energy transfer from the vibrational to the electronic degrees of freedom is most probably $\ll 1$, it is necessary that the vibrationally excited molecules have a fairly long lifetime to be at all effective in energy-transfer reactions. While molecules in high vibrational states are metastable with respect to radiative transition, they would seem to be highly unstable with respect to loss of vibrational energy by collisions, since the energy in the closely spaced higher vibrational levels can be removed in small quanta to the internal or translational degrees of freedom of the collision partner. The metastability—or persistence—of excited vibrational states found in sound-dispersion and absorption experiments is not relevant to the reactions discussed here, since in the sound-dispersion experiments only the lower, widely spaced, vibrational levels with large energy separations are involved (160). The important consideration, however, seems to be that although the excess vibrational energy is removed quite rapidly and efficiently by collisions, it is removed by such small quanta at a time that even after several collisions there may still be sufficient vibrational energy residing in the molecules to cause an electronic excitation in a suitable collision partner. If this picture is correct, the transfer of vibrational to electronic energy should be possible only if the excited electronic state is not too far above the ground state. This is the case in the excitation of $\mathrm{Na}(^2S)$ to $\mathrm{Na}(^2P)$, the energy required for this transition being 48.3 kcal. The excitation of C_2 to the $C_2(A^3\Pi_g)$ state by collision with vibrationally excited molecules, recently postulated by Gaydon and Wolfhard (58) to account for the energy distribution of

C_2 in the low-pressure oxyacetylene flame, also meets this requirement, the energy required for the transition $C_2(X^3\Pi_u) \rightarrow C_2^*(A^3\Pi_g)$ being 55.1 kcal.

It has been suggested (53) that a large fraction of the electronically excited species found in flames are produced by this type of vibration-electronic energy transfer. Before this mechanism can be accepted, however, as an important source of electronically excited species, more theoretical work on the efficiency of this type of energy interchange will be necessary. Experimental evidence available at present would seem to indicate that vibration-electronic energy transfer is of importance only in excitation of molecules or atoms with low-lying (40–60 kcal.) excited electronic states.

V. Reactions of Electronically Excited Species

A. UNIMOLECULAR PROCESSES

1. Spontaneous dissociation

Spontaneous radiationless dissociation of electronically excited species from inherently stable configurations can take place unimolecularly by means of predissociation. This predissociation is brought about by the overlap of the discrete levels of one electronic state by the continuum of another electronic state; the mixing of the eigenfunctions of the overlapping vibrational levels introduces a perturbation which brings about the transition of the molecule. The reverse process of a transition from a continuous range to the discrete state, i.e., inverse predissociation, has been considered in Section IV B.

Predissociation can be discussed in terms of intersecting potential-energy curves analogous to the discussion in Section III B; a more complete treatment for diatomic molecules is given by Herzberg (80) and for polyatomic molecules by Sponer and Teller (192). The important points to be noted in connection with reaction mechanisms are that the selection rules $\Delta S = 0$, $\Delta\Lambda = 0, \pm 1$, $+ \nleftrightarrow -$ and $g \nleftrightarrow u$ must be obeyed for the reaction to take place at any appreciable rate. These selection rules are the same as those for optical transitions, with the exception of the $g \rightarrow g$ rule, which is the reverse of that for radiative transitions. Another factor influencing the occurrence of predissociation and spontaneous dissociation is the necessity that the Franck–Condon principle be obeyed. This limits the nuclear configuration where predissociation takes place to the region about the point of intersection of the potential curves, and in general requires that the (zero-order approximation) potential curves of the pertinent states do intersect. It is only in the case of moderate interaction of the zero-order potential curves that there will be any appreciable predissociation; if there is a large resonance separation in higher-order approximation, the probability of a spontaneous dissociation will be very small.

This last point is of particular interest in connection with predissociation in polyatomic molecules. In these cases, certain molecular states which for symmetrical nuclear configuration do not interact at all with one another—and thus show no predissociation—may be made to interact and thus to undergo predissociation by the excitation of nontotally symmetrical vibrations. This, together with the fact that there are a larger number of rather closely spaced electronic levels in polyatomic molecules than in diatomic molecules, and thus more chance for the intersection of potential-energy surfaces, accounts for the observation that predissociation (i.e., spontaneous transition and dissociation) is more prevalent in the former than in the latter.

Spontaneous dissociation of electronically excited molecules produced in a photosensitized reaction has also been observed experimentally. This was first done by Steacie and coworkers (65, 111), who found that in the mercury-photosensitized reactions of various olefins the rate of polymerization is decreased by increasing the total pressure. The suggested explanation of this phenomenon was that the excited molecular MH_2 produced by collision with an $Hg(^3P_1)$ atom may either be deactivated

$$MH_2^* + MH_2 \rightarrow MH_2 + MH_2 \tag{128}$$

or decompose spontaneously into free radicals

$$MH_2^* \rightarrow MH + H \tag{129}$$

the latter being responsible for the polymerization. This type of behavior has also been observed with 2-methylpropene or "isobutene" (66) and with the 1- and 2-butenes (67, 113, 114). It has been pointed out (104) that with these molecules the presence of low-energy carbon–hydrogen bonds, which are next but one to a double bond, favors the splitting-off of the hydrogen atom.

With ethylene (111, 113) and butadiene (64), on the other hand, in which there are no such weak carbon–hydrogen bonds, dissociation proceeds in another manner with the formation of the acetylene and a hydrogen molecule:

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \tag{130}$$

This reaction has been found to proceed readily when the $C_2H_4^*$ is produced by $Hg(^3P_1)$ (111, 113) but not at all when it is formed by $Cd(^3P_1)$ (113, 201, 203). This has been interpreted (104) in terms of the energies involved in the reactions. For conservation of spin angular momentum the excited ethylene produced from triplet mercury and triplet cadmium atoms must be in a triplet state, and the acetylene produced by the reaction

$$C_2H_4^*(^3B_1) \rightarrow C_2H_2^*(\text{triplet}) + H_2(^1\Sigma_g^+) \tag{131}$$

must therefore also be in a triplet state. It is estimated that the heat of a reaction analogous to reaction 131 in which the molecules are in their normal states is about 85 kcal.; hence, if the excitational energies of C_2H_4(triplet) and C_2H_2(triplet) are x and y kcal., respectively, the heat of reaction 131 will be about $85 + y - x$ kcal. Since the energy released by the deactivation of the $Cd(^3P_1)$ atom is 87.3 kcal., the energy other than electronic in the triplet-excited C_2H_4 molecule in reaction 131 is $87.3 - x$ kcal. If $y > 2.3$ kcal., there will be an activation energy, and reaction will be slow. The slow rate with which the reaction actually proceeds suggests that this is correct. Since the reaction proceeds readily with triplet mercury it can further be concluded that $y < 25.3$ kcal., this figure being the difference between the excitational energy for triplet mercury and 87.3 kcal.

2. Spontaneous isomerization

Certain spontaneous isomerizations may be classed as processes involving excited electronic states, the overall *cis-trans* reaction proceeding *via* an electronically excited intermediate state. Experimental work by Kistiakowsky and coworkers (93–97, 151; see also 106, 129) on the kinetics of *cis-trans* isomerization reactions has shown that they are unimolecular and fall into two distinct categories. One group, including dimethyl maleate, dimethyl citraconate, and maleic acid, has a frequency factor of about 10^5 and an activation energy of about 20–25 kcal.; the other group, which includes isostilbene, methyl cinnamate, and β-cyanostyrene, has a frequency factor of about 10^{11} and an activation energy of about 40–45 kcal. The reactions investigated by Kistiakowsky were thermal isomerizations; photochemical isomerizations, i.e., isomerizations initiated by irradiating the reaction system with light of the proper frequency, have been studied in detail by Olson (164–167). Since the workers in the photochemical field were apparently primarily interested in the photostationary state of these *cis-trans* reactions, no rate measurements comparable to those for the thermal isomerization reactions are available.

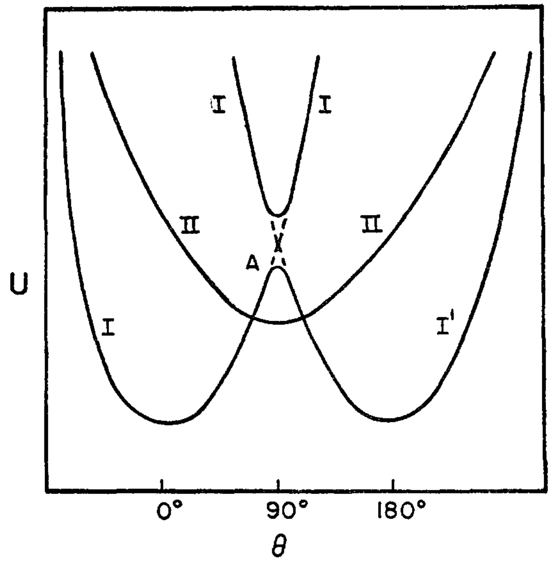

FIG. 15. The variation of the potential energy with the angle of twist θ about a double bond. Curves I and I′ are for the lowest, singlet, state; curve II for a triplet state.

The thermal isomerization reactions with a frequency factor of about 10^{11} are normal unimolecular reactions, in that this frequency factor corresponds to an entropy of activation close to unity. The explanation which has been put forth for the other class of reactions (i.e., low frequency factor and low activation energy) is that the reaction proceeds *via* a triplet excited state of the ethylenic derivatives. The variation in potential energy on rotation about the double bond for the singlet ground state is represented by curves I and I′ in figure 15, where

θ represents the angle of rotation. Owing to the strong resonance interaction of these states of the "same species," both being $^1B_1$, there will be a rather large splitting of the zero-order approximation curves at the "crossing" point A. The normal reaction can then be represented by a movement of the reaction system along the potential surface I and I′. The potential-energy curve for the triplet excited (^3B) state is shown as curve II. If it can be assumed that the triplet surface cuts the singlet surface about 20–25 kcal. above the ground level, a possible mechanism for the reactions with low frequency factor involves a transition of the reaction system from I to I′ *via* II. As discussed on page 170, the probability for the transition between the two zero-order crossing surfaces (i.e., I → II and II → I′) is given by the Landau–Zener equation (equation 60); since the interaction between the singlet and triplet surfaces will be very small, being due to spin–orbit interaction, the transition $^1B \rightarrow {}^3B \rightarrow {}^1B$ involving a change in multiplicity will take place only with difficulty, and the frequency factor $A = \kappa F^{\ddagger}/F$ will be low. It may be noted from figure 15 that this hypothesis also accounts for the different activation energies for the two classes of isomerization reactions.

There has been considerable discussion in regard to the energy of the triplet state of ethylenic compounds and similar olefins. On qualitative grounds, a fairly low lying state is to be expected, corresponding to the uncoupling of one of the electrons of the double bond in the triplet state; to account for the activation energies of the low-frequency-factor isomerization reactions, the triplet excited state has been postulated to be about 20 kcal. above the ground state (128). These conclusions appear to disagree with the values of the excitational energy given by the experiments of Lewis and Kasha (91, 115) (74 kcal.) and the theoretical calculations of Hartmann (73) (72 kcal.), Craig (22) (95 kcal.), and Mulliken and Roothaan (150) (44–62 kcal.). The values of these investigators, however, refer to excitation without change of configuration, while the value of 20 kcal. refers to the lowest state of the excited olefin in which the molecule has the "staggered" configuration, i.e., the excitation is accompanied by a rotation of the bond through 90°. The two sets of values are therefore not actually in disagreement; in particular, the data on the isomerization seem to require a low excitation energy for these twisted triplet olefins.

B. BIMOLECULAR PROCESSES

1. *Physical quenching*

Most of the experimental work on quenching has been done with excited sodium, mercury, and cadmium. The simplest reactions to interpret theoretically are those of sodium, because the quenching of a ^2P sodium atom must involve the formation of sodium in its lowest, ^2S, state, since this is the only lower state; with mercury and cadmium, on the other hand, quenching often occurs by the transfer of the atoms from their $^3P_1$ levels to the metastable $^3P_0$ levels. A further simplification in the case of sodium arises from the fact that the amount of energy, 48.3 kcal. per mole, liberated when an excited (^2P) sodium atom becomes deactivated to the normal (^2S) state is not sufficient to dissociate the average quenching molecule.

The quenching of excited (^2P) sodium by a number of gas molecules has been studied by Norrish and W. MacF. Smith (155). Some of the data are given in table 3, which also includes, for comparison, the data for mercury and cadmium. The values given for sodium are those of Norrish and Smith (155) and of Terenin and Prileshajewa (212) (the halogens).

If an atom quenches without itself becoming excited electronically, the electronic energy could only pass into translational energy; the almost complete failure of atoms to quench, as seen in table 3, indicates that this type of energy transition takes place only with great difficulty. This behavior has been explained (102) in terms of transition probabilities between potential-energy curves.

Appreciable quenching of sodium by most molecules is observed, and this must be of the physical type as there is insufficient energy available to bring about dissociation. The quenching cross-sections of hydrogen and the halogens have been interpreted quantitatively from the standpoint of potential-energy surfaces (102). It is found that the process proceeds *via* an ionic intermediate complex and may be represented, in the case of quenching by hydrogen, as follows (see also figure 3):

TABLE 3

Quenching cross-sections (Å.^{2}) *for* Na(^2P), Hg($^3P_1$), *and* Cd($^3P_1$)

QUENCHING GAS	Na(^2P)	Hg($^3P_1$)	Cd($^3P_1$)
Inert gases	0	0	0
H_2	7.4	6.01	0.67
N_2	14.5	0.192	0.021
CO	28.0	4.07	0.14
I_2	40.0		
Br_2	100.0		
CH_4	0.11	0.059	0.012
C_2H_6	0.17	0.421	0.024
C_3H_8	0.2	2.32	0.012
C_2H_4	44.0	48.0	
C_3H_6	52.0		

$$\mathrm{Na}^*(^2P) + \mathrm{H}_2(^1\Sigma_g^+) \rightarrow \mathrm{NaH}_2(^2\Sigma^+) \rightarrow \mathrm{Na}^+\mathrm{H}^-\mathrm{H}(^2\Sigma^+) \rightarrow \mathrm{NaH}_2(^2\Sigma^+) \rightarrow \mathrm{Na}(^2S) + \mathrm{H}_2(^1\Sigma_g^+) \qquad (132)$$

The activated complex corresponds to the transition between the first covalent complex and the ionic complex. A similar type of mechanism is applicable to quenching by halogen molecules. It can be inferred from the form of the potential-energy surfaces that the electronic energy passes mainly into vibrational energy of the quenching molecule.

From the point of view of the efficiency with which they quench excited sodium atoms, the hydrocarbons appear to fall into two distinct classes, corresponding to whether or not an unsaturated group is present (155). The saturated hydrocarbons are only weakly effective, their quenching cross-sections being only a fraction of a square Ångström, while the unsaturated hydrocarbons have quenching cross-sections of 40–50 Å. (see table 3). The explanation of these differences can be inferred only from a consideration of the evidence with regard to the quenching of excited mercury and cadmium atoms, which is discussed later. From the fact that triplet mercury and cadmium atoms remove hydrogen atoms from saturated hydrocarbons, one may conclude that a saturated hydrocarbon molecule interacts with an excited sodium atom in the same manner as does a hydrogen molecule, the sodium atom approaching one of the hydrogen atoms of the hydrocarbon (HR) to give a complex $Na(^2P)$–H–R, with a slight extension of the carbon–hydrogen bond. The surface corresponding to this complex is cut by a polar surface for Na^+–H^-–R, and reaction is completed by a transition, probably with a considerable extension of the carbon–hydrogen bond, from the polar to the lowest surface. The explanation of the low quenching efficiency is not clear; W. MacF. Smith and Southam (189) have shown that the reaction has no energy of activation, so that either a restricted transition probability or a low entropy of activation must be involved.

The simple saturated hydrocarbons do not absorb except at very low wave lengths; they therefore have no singlet levels of excitational energy less than the excitational energy of sodium. It is thus clear that electronic excitation of the hydrocarbons does not take place; probably most of the energy passes into vibrational energy, with a small amount going into translational and rotational degrees of freedom.

As it does not appear that triplet mercury or cadmium atoms in general remove hydrogen atoms from unsaturated hydrocarbons, it is concluded that the interaction, with these atoms and with sodium, is not between the metal atom and a hydrogen atom but rather between the metal atom and the double bond. It would again seem likely that the first surface is cut by a polar surface, which is probably low-lying since the double-bond system readily takes up an additional electron; the crossing point of the two surfaces corresponds to a high value of r_c, the internuclear distance at the crossing point, so that the quenching efficiency is high (104).

From the fact that ethylene does not absorb at wave lengths greater than about 2100 Å. (139) it can be concluded that there is no electronic state of ethylene which will combine with the ground state (i.e., no singlet state) having an energy less than about 135 kcal. Since only a singlet state could be produced by collision with an excited sodium atom, electronic excitation cannot take place, all of the energy going into vibrational, rotational, and translational degrees of freedom, the majority probably going into vibrational.

2. Transfer of electronic energy to a colliding molecule

The first example of a reaction of the type

$$A^* + B \rightarrow A + B^* \qquad (133)$$

was discovered by Cario and Franck (17), who found that excited mercury atoms would excite thallium atoms:

$$\mathrm{Hg}^*({}^3P_1) + \mathrm{Tl}({}^2P_{1/2}) \rightarrow \mathrm{Hg}({}^1S) + \mathrm{Tl}^* \tag{134}$$

Thallium atoms in a number of excited electronic states have been produced by this reaction. Triplet mercury and doublet thallium will combine to give quartet and doublet complexes, and the latter will dissociate to give $\mathrm{Hg}({}^1S_0)$ together with thallium in a doublet state:

$$\begin{gathered}\mathrm{Hg}({}^3P_1) + \mathrm{Tl}({}^2P_{1/2}) \rightarrow \mathrm{HgTl}(\text{doublets} + \text{quartets}) \\ \mathrm{HgTl}(\text{doublet}) \rightarrow \mathrm{Hg}({}^1S_0) + \mathrm{Tl}(\text{doublet})\end{gathered} \tag{135}$$

A number of such doublet excited states of thallium were observed spectroscopically by Cario and Franck.

The situation regarding the quenching of triplet mercury atoms by oxygen molecules is an interesting one. Triplet mercury and the triplet oxygen molecule combine to give singlet, triplet, and quintet complexes:

$$\mathrm{Hg}({}^3P_1) + \mathrm{O}_2({}^3\Sigma_g^-) \rightarrow \mathrm{HgO}_2(\text{singlets, triplets, quintets}) \tag{136}$$

Of these the triplets will correlate with $\mathrm{Hg}({}^1S) + \mathrm{O}_2(\text{triplet})$, so that the process

$$\mathrm{Hg}^*({}^3P_1) + \mathrm{O}_2({}^3\Sigma_g^-) \rightarrow \mathrm{Hg}({}^1S_0) + \mathrm{O}_2(\text{triplet}) \tag{137}$$

is a possible one. The O_2(triplet) could be in the lowest state, in which case the quenching would be of the physical type discussed earlier, but the formation of an excited triplet state would be more probable.

The production of oxygen in an excited singlet state can also occur, and this would take place *via* a singlet surface; thus the mechanism for the formation of O_2^*(singlet) would be

$$\mathrm{Hg}^*({}^3P_1) + \mathrm{O}_2({}^3\Sigma_g^-) \rightarrow \mathrm{HgO}_2({}^1\Sigma, {}^1\Pi) \rightarrow \mathrm{Hg}({}^1S) + \mathrm{O}_2^*(\text{singlet}) \tag{138}$$

In all of the above processes the possibility that ionic surfaces are involved must be borne in mind.

Reactions 137 and 138 as written are based on the assumption that the Wigner spin-conservation principle (Section III) governs the allowed spins of the products of these energy-transfer reactions. This "collision selection rule," $\Delta S = 0$, should, however, like the analogous optical and radiationless transition selection rule $\Delta S = 0$, depend upon the coupling conditions in the collision complex. Just as the prohibition of intercombination lines, such as ${}^3P_1 \rightarrow {}^1S_0$, is violated in mercury, since the coupling there is no longer of the pure Russel–Saunders type, it is also possible that a similar breakdown of the $\Delta S = 0$ collision selection rule will take place for collision systems involving mercury, the increasing interaction here being between S and Λ. This possibility should be kept in mind for all collision systems (i.e., energy-transfer reactions), where one or both of the collision partners are of high atomic or molecular weight and where the collision complex may have a strong quasi-chemical binding.

Unfortunately in these reactions involving excited mercury there does not appear to be any experimental evidence relating to the formation of any of these excited electronic states of oxygen. There is, however, some evidence for closely analogous processes occurring in the carbon monoxide flame. The luminescence of this flame has for a long time been thought to be due principally to the fluorescence of electronically excited carbon dioxide, the formation of which has been discussed on page 193; it has now been found, however, that the luminescence is due to a great extent to radiation by excited oxygen (86). One possible explanation (105) of the formation of these excited oxygen molecules is that they are produced by reactions of the type:

$$CO_2^* + O_2 \rightarrow CO_2 + O_2^* \qquad (139)$$

This explains not only the formation of excited oxygen but the disappearance of excited carbon dioxide, which is known from direct evidence to be formed in the flame.

Two excited electronic states of oxygen have been detected in the flame; one is the $^3\Sigma_u^-$ state which, by passing to the lowest state, gives the Schumann–Runge bands. This state may be formed *via* nonlinear triplet complexes (see footnote 4):

$$CO_2^*(^3\Pi) + O_2(^3\Sigma_g^-) \rightarrow CO_2O_2(\text{triplet}) \rightarrow CO_2^+O^-O(\text{triplet}) \rightarrow CO_2(^1\Sigma_g^+) + O_2^+(^3\Sigma_u^-) \qquad (140)$$

The other state detected is the $^1\Sigma_g^+$, produced on singlet surfaces *via* nonlinear complexes:

$$CO_2^*(^3\Pi) + O_2(^3\Sigma_g^-) \rightarrow CO_2O_2(\text{singlet}) \rightarrow CO_2^+O^-O(\text{singlet}) \rightarrow CO_2(^1\Sigma_g^+) + O_2^*(^1\Sigma_g^+) \qquad (141)$$

This type of transfer of electronic energy is also found to occur with excited mercury and cadmium atoms on collision with the unsaturated hydrocarbons. Evidence for this was first obtained by Le Roy and Steacie (111, 113), who studied the mercury($^3P_1$)-photosensitized reactions of ethylene. The most significant feature of the reaction is that the rate decreases with increasing ethylene concentration, indicating a deactivation to be involved, and Le Roy and Steacie suggested the scheme:

$$Hg(^3P_1) + C_2H_4 \rightarrow C_2H_4^* + Hg(^1S_0) \qquad (142)$$

$$C_2H_4 + C_2H_4^* \rightarrow 2C_2H_4 \qquad (143)$$

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \qquad (144)$$

The ethylene produced in reaction 142 must clearly be in a triplet-excited state for conservation of momentum. As noted in the discussion on the spontaneous isomerization of olefinic compounds, the energy of the triplet state is not known with certainty; however, the energy of the transition $Hg(^3P_1) \rightarrow Hg(^1S_0)$, equal to 112.6 kcal., is ample for excitation.

The results for the photosensitization of ethylene by triplet cadmium atoms

(201) differ significantly from those with triplet mercury in that the quantum yield is much lower, being only about 0.015. The high quenching efficiency, on the other hand, indicates that the reaction

$$\mathrm{Cd}^*({}^3P_1) + \mathrm{C_2H_4} \rightarrow \mathrm{C_2H_4^*} + \mathrm{Cd}({}^1S_0) \tag{145}$$

proceeds at a normal rate, and it therefore appears, as discussed earlier (page 204), that the subsequent reactions to give acetylene take place only slowly. The results with triplet zinc are very similar to those with cadmium.

The reactions of ethylene photosensitized by singlet zinc (4^1P_1) (71) and singlet cadmium (5^1P_1) (197) have also been studied. With cadmium, reaction occurs readily with a quantum yield of about unity, the products being olefins together with small amounts of acetylene and hydrogen. These facts suggest that the reaction proceeds mainly by a free-radical mechanism and that the excited molecule mechanism takes place to a small extent only. The reason for the low rate of the excited molecule reaction is not immediately clear; it is not to be explained, as it was with triplet cadmium, in terms of insufficient energy for the formation of acetylene, since there is now ample energy (124.4 kcal.) and the acetylene does not have to be excited electronically as there is no change of multiplicity. This suggests strongly that the low rate of production of acetylene is due to the low rate of the reaction:

$$\mathrm{Cd}^*({}^1P_1) + \mathrm{C_2H_4} \rightarrow \mathrm{Cd}({}^1S_0) + \mathrm{C_2H_4} \tag{146}$$

The ethylene formed in reaction 146 must, for conservation of spin angular momentum, be in a singlet state, and this must be its lowest electronic state, since there is no excited singlet state of ethylene with sufficiently low energy. The excitational energy of the ethylene must therefore be entirely in the form of nonelectronic energy, and most will be vibrational energy. It therefore appears that the transfer of large amounts of electronic energy into vibrational energy proceeds only slowly.

The results with singlet zinc are similar to those with cadmium, except that the amount of acetylene produced is even smaller. With zinc more electronic energy has to be converted into vibrational energy, and the rate will be even further reduced on this account. The singlet mercury reaction has not yet been investigated, but as the electronic energy available is still higher than with zinc (153.9 as compared with 133.4 kcal.), it might be anticipated that the rate of the excited-molecule reaction would be still lower. These findings are in agreement with those for the inverse of the process discussed here, i.e., the transfer of vibrational to electronic energy. As noted on page 202, electronic excitation of a molecule by collision with a vibrationally excited one appears to take place only if the amount of energy to be transferred is not too large (i.e., is less than about 60 kcal.).

It is to be noted that this interpretation of the reactions of the singlet atoms, postulating as it does that the primary reaction which forms the vibrationally excited molecule proceeds slowly, implies that the quenching rates (which have not been measured) would be low. The mechanism of quenching would in fact be similar to that of the saturated hydrocarbons, and it is to be expected that the cross-sections would be of the same order as those found with the saturated hydrocarbons.

Evidence for similar transfers of energy to other unsaturated hydrocarbons has also been obtained. 1,3-Butadiene ($CH_2{=}CH{-}CH{=}CH_2$) is structurally analogous to ethylene in that its C—H bonds are all olefinic, and it is therefore to be expected that its photosensitized reactions will be similar. That this is so with triplet mercury has been shown by Gunning and Steacie (64) (*cf.* Volman (222)), who found that the initial rate of polymerization decreases with increasing pressure. The reaction products were principally a dimer, hydrogen, and an acetylenic compound (C_4H_4). The results are consistent with the hypothesis that the main initial step is the formation of an excited butadiene molecule which may either dimerize on collision with another butadiene molecule or split off hydrogen to give C_4H_4. Similar evidence for the production of excited molecules has been obtained with propene (65, 68), isoprene (65), "isobutene" (66), 1-butene (67, 113, 114), 2-butene (67, 113, 114), cyclopropane (69), and ethylene oxide (172).

3. Quenching with dissociation of the quencher: $A^* + BC \rightarrow A + B + C$ *and* $A^* + BC \rightarrow AB + C$

It is convenient to discuss together these two variations of quenching with dissociation of the quenching molecule, since the association or nonassociation of the quenched species with a product of the dissociation depends largely upon the energetics of the reaction.

The best-investigated reactions are those involving triplet mercury and triplet cadmium atoms with hydrogen and the hydrocarbons; the quenching cross-sections for these systems were included in table 3. The mechanisms of these reactions have been discussed in some detail from the standpoint of potential-energy surfaces (103) (figure 4). The initial steps of the processes can be represented as (*cf.* reaction 57):

$$A^*(^3P) + H_2(^1\Sigma_g^+) \rightarrow AH_2(^3\Pi) \rightarrow A^+H^-{-}H(^3\Sigma^+) \rightarrow AH_2(^3\Sigma^+) \qquad (147)$$

The $AH_2(^3\Sigma^+)$ can now decompose either into $AH(^2\Sigma^+)$ and $H(^2S)$, or into $A(^1S) + 2H(^2S)$. It is likely that the latter will generally happen if there is sufficient energy available; otherwise the former will occur.

In the case of $Hg^*(^3P)$ and hydrogen, the reaction

$$Hg^*(^3P_1) + H_2(^1\Sigma_g^+) \rightarrow HgH(^2\Sigma^+) + H(^2S) \qquad (148)$$

would liberate 18.9 kcal. of energy. Although the details of the potential-energy surfaces for the reaction are not known, one can be fairly certain that a large fraction of this energy set free will pass into vibrational energy of the HgH molecule, the dissociation energy of which is 8.5 kcal. per mole. The HgH molecule will therefore decompose within the period of one vibration, so that the overall reaction is indistinguishable from the reaction (9, 46):

$$Hg^* + H_2 \rightarrow Hg + 2H \qquad (149)$$

This conclusion is in accord with the findings of Olsen (163), who showed spectroscopically that HgH is not produced in the reaction in the normal state, but only excited presumably by secondary reactions. The work of Masson and Steacie (132) is also consistent with the view expressed above.

The mechanism of the reaction of hydrogen may also be considered from a slightly different point of view. The "physical" type of reaction

$$\mathrm{Hg}^*({}^3P_1) + \mathrm{H}_2({}^1\Sigma_g^+) \rightarrow \mathrm{Hg}({}^1S_0) + \mathrm{H}_2({}^1\Sigma_g^+) \qquad (150)$$

analogous to that which takes place with sodium, is here restricted by the necessity for conservation of spin angular momentum unless the hydrogen on the right-hand side is in a triplet state; if this condition is satisfied, however, the molecule at once dissociates, so that the reaction is not of a physical nature. There is therefore little possibility of the hydrogen molecule taking up the excitation energy in the form of vibrational, rotational, or translational energy, as it was able to do with excited sodium; reaction can only proceed effectively by a dissociation of the hydrogen.

The potential-energy surfaces for the quenching of cadmium ${}^3P_1$ by hydrogen are similar in general form to those for the mercury reaction. The chief difference arises because, owing to the fact that only 87.3 kcal. of energy is liberated in the transition $\mathrm{Cd}({}^3P_1) \rightarrow \mathrm{Cd}({}^1S_0)$, the process

$$\mathrm{Cd}^*({}^3P_1) + \mathrm{H}_2 \rightarrow \mathrm{Cd}({}^1S_0) + 2\mathrm{H} \qquad (151)$$

is endothermic to the extent of 15.9 kcal. and therefore slow, since the activation energy is at least this amount. The reaction which forms CdH,

$$\mathrm{Cd}^*({}^3P_1) + \mathrm{H}_2({}^1\Sigma_g^+) \rightarrow \mathrm{CdH}({}^2\Sigma^+) + \mathrm{H}({}^2S) \qquad (152)$$

is much faster, since it is about thermoneutral, the dissociation energy of $\mathrm{CdH}({}^2\Sigma^+)$ being 15.6 kcal. The quenching reaction is therefore largely reaction 152.

The chief difference between the mechanism of the quenching of cadmium and that of mercury is that in the former case very little energy can pass into vibrational energy of the hydride, any that does so having to be paid for as activation energy. The hydride CdH will therefore not dissociate and should be detectable in its normal state; this has been done spectroscopically by Bender (6).

The evidence from recent investigations on the reactions of methane (140), ethane (25, 92, 195, 199, 200, 202), propane (132, 196, 198, 202), butane (74, 202), isobutane (28), neopentane (25, 26), dimethyl ether (130), diethyl ether (27), and methyl alcohol (171) photosensitized by triplet mercury and cadmium in all cases indicates an initial carbon–hydrogen bond split. From the theoretical point of view these reactions are very similar to the reactions of hydrogen, the normal state of the hydrocarbons being a singlet state. Quenching of the physical type, the energy being taken up as vibrational energy, is again excluded by the necessity for conservation of spin angular momentum. The possibility that the hydrocarbon is excited to a triplet state has to be considered, but this would probably be unstable and decompose to give a hydrogen atom and a free radical.

The mechanism is probably much the same as for hydrogen, reaction proceeding *via* a polar complex.

The question of whether the hydrides HgH and CdH are formed is of interest in connection with the strengths of the carbon-hydrogen bonds in the hydrocarbons. It has been seen that with hydrogen the hydrides are initially formed, but that if there is enough energy available, as in the case of triplet mercury, the hydride decomposes at once. Presumably the situation is much the same with the saturated hydrocarbons; the hydride is formed but may decompose. In the absence of additional information, therefore, the upper limit to the strength of the bond is that which corresponds to the energy of excitation of the mercury or cadmium plus the heat of formation of the hydride. If, however, it could be satisfactorily proved that the hydride was not formed, the energy of excitation of the metal atom might be accepted as a maximum.

The situation with regard to unsaturated hydrocarbons is less clear. In the case of Hg($^3P_1$) and ethylene, for example, there are two competing initial steps

$$\mathrm{Hg}^*(^3P_1) + \mathrm{C_2H_4} \rightarrow \mathrm{Hg}(^1S_0) + \mathrm{C_2H_4^*} \qquad (153)$$

and

$$\mathrm{Hg}^*(^3P_1) + \mathrm{C_2H_4} \rightarrow \mathrm{Hg}(^1S_0) + \mathrm{H} + \mathrm{C_2H_3} \qquad (154)$$

of which at 25°C. the former, which was discussed earlier, probably occurs about a hundred times as rapidly as the latter. The evidence for this is based on quenching data and also on the fact that the formation of acetylene, from $C_2H_4^*$, occurs to a very much greater extent than polymerization, which involves the free-radical mechanism. With cadmium ($^3P_1$), where there is 102.9 kcal. available when the hydride is formed

$$\mathrm{Cd}^*(^3P_1) + \mathrm{C_2H_4} \rightarrow \mathrm{CdH}(^2\Sigma^+) + \mathrm{C_2H_3} \qquad (155)$$

the situation is even less certain; this is unfortunate, as otherwise a limiting value for the C—H dissociation energy in ethylene would be provided. It has been suggested (104) that the evidence somewhat favors the hypothesis that the above reaction proceeds readily, which would imply a value of less than 102.9 kcal. for the dissociation energy. However, a higher value of perhaps about 106 kcal. seems to be indicated by other evidence.

The situation is clearer with ethylene and singlet-excited cadmium and zinc ($^1P_1$), owing to the fact that the formation of electronically excited ethylene is here excluded by the absence of a low-lying singlet-excited electronic state of ethylene. With cadmium, reaction occurs readily with a quantum yield of about unity, the products being olefins together with small amounts of acetylene and hydrogen (71); these facts indicate that the reaction involves as the main primary process the step:

$$\mathrm{Cd}^*(^1P_1) + \mathrm{C_2H_4} \rightarrow \mathrm{Cd}(^1S_0) + \mathrm{H} + \mathrm{C_2H_3} \qquad (156)$$

The results with singlet zinc are similar; the singlet mercury reaction has not yet been investigated.

Another reaction of this type is

$$OH^*(^2\Sigma^+) + H_2(^1\Sigma_g^+) \rightarrow OH(^2\Pi) + H(^2S) + H(^2S) \qquad (157)$$

a process that is endothermic by 10.4 kcal. It has been discussed by Farkas (39) and Herzberg (80) as a possible chain-branching process in the hydrogen–oxygen flame. Another example which has been suggested (63) is

$$CO_2^* + O_2 \rightarrow CO_2 + 2O \qquad (158)$$

the detailed course of the reaction being

$$CO_2^*(^3\Pi) + O_2(^3\Sigma_g^-) \rightarrow CO_2O_2(^3\Pi) \rightarrow CO_2{}^+O^-O(^3\Pi)$$
$$\rightarrow CO_2(^1\Sigma) + O(^3P) + O(^3P) \qquad (159)$$

If the energy released by the transition $CO_2^*(^3\Pi) \rightarrow CO_2(^1\Sigma)$ is about 99 kcal. (see Fig. 3 of reference 63), reaction 158 will be endothermic by about 23 kcal. Owing to the high temperatures (2000–3000°K.) at which flame reactions take place, it is quite possible that many endothermic dissociative quenching processes may take place which will not occur in low-temperature (~300–500°K.) photochemical systems. Various other steps of this type could readily be postulated for flame reactions; whether they are of any importance in flame kinetics is, however, not at all clear. Experimental work on this question would be rather difficult, since a large part of the free atoms in flames is unquestionably due to thermal dissociation.

4. Quenching with dissociation of the quenched species

This type of reaction can take place in essentially three ways: namely, as an induced predissociation, by the transfer of vibrational energy from the quencher to the quenched molecule, or as a chemical reaction. The induced predissociation can be of two types: a pressure-induced and a field-induced predissociation. A few examples of these types of reaction are known, or have been postulated, and will now be discussed briefly.

Pressure-induced predissociation was suggested by Turner (216, 218) to account for the quenching of certain I_2 bands in the presence of argon. He found that I_2 bands whose upper states lie above the dissociation limit of the ground state, and which have a normal intensity distribution in the absence of argon, are quenched by the addition of ~30 mm. of argon. The presence of free iodine atoms in the ground state $I(^2P_{3/2})$ was verified by absorption experiments. Turner suggested that this predissociation was allowed by the breakdown of the selection rule $\Delta J = 0$, which was derived for the free undisturbed molecule by Kronig (101). In the case of pressure-induced predissociation the conservation of angular momentum is applicable to the system-excited molecule plus quenching molecule; what must be considered therefore is not only the angular momentum of the rotating I_2^* molecule and the iodine atoms, but also the relative angular momentum of the iodine atoms and the outgoing argon atom after the collision. For such a system there can thus be an overall conservation of angular momentum even though the selection rule $\Delta J = 0$ is no longer obeyed for the dissociating molecule.

The possibility of inducing predissociations depends not only upon the "classical" effect of the conservation of angular momentum by the "billiard ball" collisions of the quenching atom, but also upon the distortion of the potential curves of the excited molecule by the inhomogeneous electric field of the impinging atom, provided it is strong enough. Thus, for instance, while helium very often does not induce predissociation, the stronger electric fields of the heavier rare gases are quite effective in inducing predissociation.

Turner (217) also found that dissociative quenching of I_2^* could be produced by the application of a magnetic field. This has been examined in detail by Van Vleck (221), who showed that the selection rule $\Delta J = 0$ no longer holds in a magnetic field so that I_2^* can go over into normal iodine atoms:

$$I_2^*({}^3\Pi_{ou}) \xrightarrow{H} I({}^2P_{3/2}) + I({}^2P_{3/2}) \qquad (160)$$

Predissociation induced by magnetic fields has also been observed in the resonance spectra of Se_2 and Te_2, although the evidence here is not as convincing as in the case of I_2.

Whereas induced predissociation involves the transfer of the electronically excited species from one electronic state to another, dissociative quenching may also be obtained by transferring collisions within one electronic state. Transferring collisions of the type where the electronically excited species gains or loses vibrational or rotational energy within one excited state have been investigated in some detail in photochemical systems (179); the results seem to indicate that while there may be a considerable change in rotational energy, the vibrations usually only changed by one or two quanta ($\Delta v = \pm 1, 2$). This is readily understood on the basis that the vibrational quanta, particularly in the lower vibrational levels, are so much larger than the rotational quanta that a given transfer of energy will give a $\Delta J \gg \Delta v$, and the persistence of vibration and nonpersistence of abnormal rotation have been explained on this basis (160, 184). The higher vibrational levels in a molecule do not, however, have such a large energetic separation and the transfer of vibrational energy will thus take place more readily. In particular, if an electronically excited molecule is produced in a chemical reaction in a flame it is likely that at the high temperature (2000–3000°K.) at which this reaction proceeds some of these molecules will be formed in highly excited vibrational states just below the dissociation limit of the excited state. If they then suffer a collision—or collisions—with other highly vibrationally excited molecules in the flame, it is quite likely that enough vibrational energy will be transferred to the electronically excited molecule so that it will undergo dissociation. A similar dissociation by rotation from a highly excited rotational state would also be a possibility.

One of the prerequisites for the occurrence of such a type of dissociative quenching is that the radiative lifetimes of the electronically and vibrationally excited molecules be rather long; they then have the opportunity to gain vibrational energy before going to a lower electronic or vibrational level by a radiative transition. Herzberg (80) has stated that "the higher vibrational levels of a molecule must be regarded as metastable" so that at least a part of the above prerequisite seems to be fulfilled. In the case of $OH^*(^2\Sigma^+)$, for instance, there is also a metastability with regard to electronic transitions (161, 162) with a radiative lifetime of about 4×10^{-6}, compared to the usual value of $\sim 10^{-8}$ for dipole transitions. This is due to the fact that the transition $OH(^2\Sigma^+) \rightarrow OH(^2\Pi)$ is half-forbidden, since the corresponding transition $O(^1D) \rightarrow O(^3P)$ of the separated atoms is not allowed. Dissociative quenching by transferring collisions of the type discussed above should therefore be possible for OH*, and the reaction

$$OH^* + H_2 \rightarrow O + H + H_2 \qquad (161)$$

suggested by Farkas (39) and Herzberg (80) may be understood on this basis. This reaction could then be written as

$$OH^*(^2\Sigma^+) + H_2(^1\Sigma_g^+) \rightarrow O^*(^1D) + H(^2S) + H_2(^1\Sigma_g^+) \qquad (162)$$

Reaction 161 as written by Herzberg (80) is given an endothermicity of 7.6 kcal. It is possible that it occurs by the following steps: The first reaction is

$$OH^*(^2\Sigma^+) + H_2(^1\Sigma_g^+) \rightarrow OH(^2\Pi) + H(^2S) + H(^2S) \qquad (163)$$

which would be endothermic by 9.7 kcal., since T_e for $OH(^2\Sigma^+) \rightarrow OH(^2\Pi)$ is 93.9 kcal. and $D_0^0(H_2) = 103.2$ kcal. Reaction 163 is then followed by

$$OH(^2\Pi) + H(^2S) \rightarrow O(^3P) + H_2(^1\Sigma_g^+) \qquad (164)$$

which is exothermic by 2.9 kcal. if the value of $D_0^0 = 100.3$ for $OH(^2\Pi)$ is accepted (29). The overall process

$$OH^\alpha(^2\Sigma^+) + H^\beta\text{-}H^\beta(^1\Sigma_g^+) \rightarrow O(^3P) + H(^2S) + H^\beta\text{-}H^\alpha(^1\Sigma_g^+) \qquad (165)$$

would then be endothermic by 6.8 kcal. Reactions of this type, leading to dissociation of the quenched molecule, may well occur in flames where the temperature is high enough to provide the energy for these slightly endothermic reactions. However, just as in the case of the similar process (reaction 158), leading to the dissociation of the quenching molecule, there is no direct experimental evidence bearing on this point.

5. *Quenching with isomerization of the quenched species*

Few examples of this type of process have been investigated, but an interesting case has been studied by Steacie and his coworkers (67, 113). The products formed in the mercury-photosensitized reaction of 1-butene ($CH_2{=}CHCH_2CH_3$) are chiefly 2-butene ($CH_3CH{=}CHCH_3$) and a polymer. It was found that increasing the pressure increases the rate of isomerization but decreases the rate of polymerization. This indicates that isomerization depends upon collisions between excited 1-butene molecules and normal molecules, and the only plausible mechanism would seem to be that of Gunning and Steacie (67), as follows:

$$Hg^*(^3P_1) + 1\text{-}C_4H_8 \rightarrow 1\text{-}C_4H_8^* + Hg(^1S_0) \qquad (166)$$

$$1\text{-}C_4H_8^* + 1\text{-}C_4H_8 \rightarrow 2\text{-}C_4H_8 + 1\text{-}C_4H_8 \qquad (167)$$

$$1\text{-}C_4H_8^* \rightarrow C_4H_7 + H \qquad (168)$$

Reaction 168 is supposed to be followed by chain processes resulting in polymerization. This reaction is of interest, in that it appears to have been the first to give concrete evidence that in photosensitized reactions free radicals may be produced from an excited molecule in a stable electronic state. On the basis of their kinetic results Gunning and Steacie (67) conclude that deactivation without isomerization takes place only to an insignificant extent compared with reaction 167.

6. Association between the excited molecule and the colliding molecule

This type of reaction is very similar to those discussed on page 188, i.e., two-body association reactions, with the exception that one of the collision partners is now in an excited state. The same considerations apply as before: if the associating species are of a rather simple structure the recombination energy must be removed, either as radiation or by a third body, for the association complex to be stable; if the associating species have enough degrees of freedom, the recombination energy may be distributed throughout the newly formed molecule without causing its dissociation. The Wigner spin-conservation rule will apply so that, if the excited molecule is in a triplet state and the normal molecule in a singlet state, the association complex, in the absence of a third body, must either remain in the triplet state by redistribution of the energy or go to a lower state by a radiative transition; in the latter case the prohibition of intercombinations (i.e., triplet → singlet) may be violated if the newly formed molecule is of sufficiently high molecular weight.

It is evident that if the association product is to be formed in its lowest electronic state, the energy to be removed or redistributed in the association complex will be the greater the higher the electronic excitation of the collision partners. If the excited molecule is produced by photoactivation, the association reaction to be successful must take place with a high frequency factor, i.e., rapidly, or otherwise the photoactivated molecule will return to its ground state by a radiative transition before it has undergone any successful collisions. This is due to the fact that a molecule which absorbs light readily will in general have only a short radiative lifetime unless it can go into a metastable state before returning to the ground state. No such restriction as to the rapidity of the association reaction would seem to be necessary for excited molecules produced by photosensitization.

Some association processes involving an electronically excited reactant have been discussed for flame reactions. Excited (^1D) oxygen atoms have been found (175) to combine with normal $CO(^1\Sigma^+)$ molecules to give carbon dioxide in its lowest state:

$$O^*(^1D) + CO(^1\Sigma^+) \rightarrow CO_2(^1\Sigma_g^+) \tag{169}$$

the reaction probably requiring a third body for the stabilization of the product. As mentioned in Section IV A, the production of $O_2^*(^3\Sigma_u^-)$ in the high-pressure arc has been explained (41) as due to the recombination of excited and normal oxygen atoms (equation 106), the reaction again requiring a third body for stabilization of the excited O_2.

Interesting examples of this type of reaction are found in photochemical or photosensitized polymerizations. In these the excited monomer adds on to a normal monomer molecule with the formation of a dimer radical:

$$M^* + M \rightarrow M_2 \qquad (170)$$

Little information is available as to the kinetics of such reactions, as in the usual treatment of polymerization reactions (5, 106) an average value is obtained for the rates of the various chain-propagating steps. Some of the polymerization reactions involving electronically excited species which have been postulated by various authors may be found discussed by Rollefson and Burton (181).

The authors are indebted to Dr. F. T. McClure, Dr. R. C. Herman, and Mr. G. A. Hornbeck of the Applied Physics Laboratory for helpful discussions and suggestions in connection with this review. One of them (K. E. S.) wishes to thank the National Research Council for the award of an Atomic Energy Commission Post-Doctoral Fellowship (1949–50) and the Applied Physics Laboratory of The Johns Hopkins University for the award of a Research Fellowship (1950–51). Many thanks are also due to Miss Angela Crimi and Miss Shirley Thomas for their assistance in the preparation of this manuscript, and to Miss Doris Rubenfeld for preparing the illustrations.

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