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CHEMICAL REACTIONS IN CROSSED MOLECULAR BEAMS

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Contents

Abstract ................................................... vii

I. Chemical Kinetics and Molecular Beams
   A. Introduction ............................................ 1
   B. Evolution of Molecular-Beam Research ............... 1
   C. Chemical Applications of Beam Techniques .......... 2
   D. Crossed-Beam Studies of Reactions .................. 2

II. General Theory of Reactive Scattering
   A. Introduction ............................................ 5
   B. Mechanics of Binary Collisions ....................... 5
   C. Some Reaction Models ................................... 17

III. Experimental
   A. Introduction ............................................ 21
   B. Apparatus
      1. Vacuum System ........................................ 24
      2. Beam Sources ......................................... 28
      3. Detector ............................................... 35
   C. Experimental Procedure
      1. Preliminary Operations ................................ 41
      2. Measurement of Angular Distributions .............. 42
      3. Reduction of Data ..................................... 43

IV. Results and Analysis
   A. Summary of Data
      1. Experimental Data .................................... 44
      2. Calculated Results ................................... 50
   B. General Features of Analysis ......................... 67
   C. Detailed Analysis Based on Computer Program
      1. Center-of-Mass Distribution ........................ 69
      2. Recoil-Energy Distribution ........................... 71
      3. Angular-Momentum Considerations ................... 74
V. Discussion ........................................... 76
Acknowledgments ........................................ 78
Appendices
   A. Suppliers and Manufacturers ................. 79
   B. IBM 7090 Computer Program ......... 82
References ............................................. 84
"... When the intervals, passages, connections, Weights, impulses, collisions, movement, order, And position of the atoms interchange, So must the things formed from them change."

Lucretius, De Rerum Natura
CHEMICAL REACTIONS IN CROSSED MOLECULAR BEAMS

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Berkeley, California
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ABSTRACT

Crossed molecular beam studies are made of the reactions $K + RI \rightarrow R + KI$, where $R$ is $CH_3$, $C_2H_5$, etc. The experimental techniques and theoretical treatment necessary for this study are discussed.

From comparisons of the angular distributions of KI observed experimentally with computer-calculated distributions it has been possible to gain information about the angular distributions of products in the center-of-mass system and about the internal excitation of the products. The results show that 75% to 100% of the energy released in the reaction appears as internal excitation of the products and that the angular distribution is quite anisotropic, with most of the KI recoiling backward (and $R$ forward) with respect to the incoming $K$ beam. This anisotropic distribution indicates that a long-lived reaction complex is not formed and that any complex that is formed decomposes within a time not much longer than $10^{-12}$ seconds.
I. CHEMICAL KINETICS AND MOLECULAR BEAMS

A. Introduction

The theory of chemical equilibria has seen a very satisfactory development. By means of statistical mechanics and spectroscopic information, it has been possible to relate thermodynamics to molecular structure. The conceptual framework for a similar fundamental treatment of chemical kinetics was developed through statistical mechanics in the 1930's. Unfortunately, classical methods of kinetics have not been able to provide the analog of spectroscopic information, and accordingly, the molecular mechanics of reactions remains in a primitive state.

Molecular beam techniques allow us to study the molecular mechanics of reactions directly. It becomes possible to observe the products after they have been formed in a single collision. There are severe intensity limitations to these molecular-beam studies, but for a large class of reactions of alkali metals the experiments are feasible. It has been demonstrated in recent years that these reactions can be studied with almost rudimentary apparatus.\(^1\),\(^2\),\(^3\)

This study is the first in which information about the internal excitation and center-of-mass-system trajectories of reaction products has been obtained.

B. Evolution of Molecular-Beam Research

The first molecular-beam experiment was performed by Dunoyer\(^4\) in 1911. He verified that gas molecules travel in straight lines between collisions. The velocity distribution of molecules in a beam was first measured by Stern\(^5\) in 1920. To within the accuracy of his experiment the distribution was found to be Maxwellian. Subsequently, more accurate determinations have confirmed this result.

Until recently, most beam work was concerned with the deflection of atomic and molecular beams by electric and magnetic fields. In 1921, Stern and Gerlach experimentally verified the space quantization of angular momentum by observing the splitting of a beam of silver atoms in an inhomogeneous magnetic field. With the introduction of the
resonance method by Rabi in 1937, molecular-beam techniques have been extensively used to measure the electric and magnetic properties of atoms, molecules, and nuclei. The entire development of molecular beams is excellently presented in several books and review articles. An extensive bibliography of the published work in molecular beams has been compiled by the Berkeley group.

C. Chemical Applications of Beam Techniques

Molecular-beam methods have also been extensively used in studying gas-surface interactions. Studies of diffraction of beams from crystal surfaces as well as work on reflection, condensation, and surface migration have been summarized by Fraser. Recently, radio-tracer techniques have been used to measure condensation coefficients and heats of adsorption. The phenomena of surface ionization of molecules by heated surfaces has been of great importance to molecular-beam research for it serves as the basis for the detector most commonly used. The use of this effect in studies of adsorption dates from the work of Langmuir and Kingdon, and Taylor and Langmuir.

Intermolecular potentials have been studied by observing the elastic scattering that results when a beam is passed through a gas-filled scattering chamber. The repulsive electron-overlap forces have been studied by Amdur and co-workers using very high velocity (200-2000 eV) atomic beams. Experiments involving the relatively long range attractive forces have been carried out by Rothe, Bernstein, and Pauly.

D. Crossed-Beam Studies of Reactions

The first attempt to study a bimolecular reaction by using molecular beams was made by Kröger in 1925. Unfortunately, because of technical difficulties, and a poor choice of reactions, no information was obtained.

Polanyi's work in the 1920's with dilute-flame and diffusion-flame techniques showed that extremely high collision yields were obtained for alkali-metal-halogen reactions. Almost all subsequent
beam work has been concerned with these reactions.

Sasaki and co-workers\(^\text{23}\) have attempted to study the alkali-metal-halogen reactions but have been unsuccessful. Some work on the initiation of elementary chemical processes has been done by passing a high-temperature molecular beam into a low-temperature reaction gas.\(^\text{24,25}\) These studies were complicated by the possible presence of reactions on the walls. The reaction of a pulsed beam of CCl\(_4\) with Cs vapor contained in a scattering chamber has been studied by Bull and Moon.\(^\text{26}\) The CCl\(_4\) molecules were accelerated by a collision with the tip of a rotating blade. As a detector they used the standard surface-ionization detector, which was sensitive to both Cs and CsCl. Their data indicated that considerable reaction took place.

In 1955, the problem of detection was solved by Taylor and Datz,\(^\text{1}\) who used a surface-ionization detector sensitive to alkali atoms and not to alkali-containing molecules. They used this detector in the study of the reaction

\[
K + HBr \rightarrow H + KBr.
\]

They were able to arrive at an estimate of the reaction yield and the activation energy, but due to the unfavorable mass factors (see Sec. II) were unable to obtain any information about the distribution of products in the center-of-mass system. In 1960, Greene, Roberts, and Ross\(^\text{3}\) reported a further study of the K + HBr reaction; they made the important refinement of a mechanical velocity selector to select the K beam velocity. This has led, in recent work by Beck,\(^\text{27}\) to detailed information about the dependence of the reaction probability on the initial relative translational energy and impact parameter of the reactants.

In our experiment, we study the distribution of velocity vectors of products; from this we obtain information on the internal energy states of the products as well as the directions in which they recoil away from the center of mass. The experiments on the reactions of potassium with the alkyl iodides, discussed in this thesis, were done in collaboration with G. H. Kwei. Similar experiments on the reactions of Cs and of Rb have been performed by G. H. Kwei and J. L. Kinsey. The reactions
of Na are currently under study here by K. R. Wilson.

For all the reactions studied, most of the energy of reaction appears as internal excitation of the products. The angular distribution of reaction products is found to be quite asymmetric in the center-of-mass system and is peaked about the direction of the initial relative-velocity vector.
II. GENERAL THEORY OF REACTIVE SCATTERING

A. Introduction

The interpretation of the results of reactive scattering experiments is closely analogous to the theoretical interpretation of spectroscopic experiments. The problem divides into two parts: (a) the determination of the angular distribution of products in the center-of-mass system that led to the observed laboratory distribution, and (b) the explanation of this angular distribution in terms of a reaction model. A method of handling the first problem, based on conservation laws, has been described by D. R. Herschbach. His method has been used throughout this work and is summarized in Sec. II. B. The beginnings that have been made in the solution of the possible reaction model problem are discussed in Sec. II. C.

B. Mechanics of Binary Collisions

Figure 1 shows velocity-vector diagrams for the reactive collision of two molecules of masses $m_1$ and $m_2$ forming products $m_3$ and $m_4$, where, by convention, $m_1 \leq m_2$ and $m_3 \leq m_4$. The initial laboratory velocities $\vec{v}_1$ and $\vec{v}_2$ make an arbitrary angle $\gamma$ with one another,

$$\vec{v} = \vec{v}_1 - \vec{v}_2$$

(2-1)

is the relative velocity, and

$$\vec{v}_c = \frac{m_1 \vec{v}_1 + m_2 \vec{v}_2}{m_1 + m_2}$$

(2-2)

is the center-of-mass velocity. These velocity vectors refer to an asymptotic initial state far from the scattering center; however, it is convenient to draw them as if they were just emerging from the scattering center and to regard Fig. 1a as applying to an idealized encounter in which no interaction occurred.
Fig. 1. Velocity-vector diagrams. (a) Initial-velocity vectors; (b) final-velocity vectors. (c) This diagram includes both the final- and initial-velocity vectors and is drawn for the special case of $v'$ lying in the plane of $v_1$ and $v_2$ ($\phi = 0$).
When referred to a coordinate system which moves with the constant velocity of the center-of-mass, the velocity vectors of the reactants become

\[
\vec{u}_1 = \vec{v}_1 - \vec{c},
\]

and

\[
\vec{u}_2 = \vec{v}_2 - \vec{c}.
\]

Figure 1b. shows a possible final state for the collision. The final asymptotic velocity vectors are \(\vec{v}_3\) and \(\vec{v}_4\), and

\[
\vec{v'}_3 = \vec{v}_3 - \vec{v}_4,
\]

and

\[
\vec{c} = \frac{m_3\vec{v}_3 + m_4\vec{v}_4}{m_3 + m_4},
\]

where \(\vec{c}\) is a constant of the motion that results from the conservation of mass and linear momentum. The final relative-velocity vector, \(\vec{v'}\), may point in any direction. Accordingly, the plane containing the relative-velocity vectors will in general be rotated from that containing the initial vectors; the rotation is specified by the angle \(\psi\). In the center-of-mass system, in which the molecules collide along \(\vec{v}\), the scattering must be cylindrically symmetric about \(\vec{v}\). The magnitude of \(\vec{v'}\) is fixed by the conservation of energy:

\[
E' = E + Q,
\]

where

\[
E' = \frac{1}{2} \frac{m_3 m_4}{m_3 + m_4} (v')^2,
\]

and

\[
E = \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} (v)^2,
\]

and \(Q\) represents the energy converted from internal degrees of freedom (rotational, vibrational, or electronic) to relative kinetic energy of the emergent particles. For an elastic collision we have \(Q = 0\), and for an exothermic reaction we have \(Q > 0\). The range of values of \(Q\) accessible
in any particular case may be obtained from spectroscopic information on the internal energy levels of the reactant molecules. For the case of the reaction

\[ K + CH_3I \rightarrow CH_3 + KI \]  \hspace{1cm} (2-8)

see Fig. 2. As indicated in Fig. 3, the total energy available to the reaction products (omitting the constant energy of the center of mass) is \( E + W + \Delta D_{\text{ex}} \), where \( \Delta D_{\text{ex}} \) is the difference in dissociation energy of the K-I and C-I bonds, about 22 kcal/mole; \( E \) is the initial relative translational kinetic energy of the reactants and has a thermal distribution peaked at about 1 kcal/mole; and \( W \) is the internal energy of CH$_3$I, most of which is in the ground vibrational state, with a rotational energy peaked near 0.3 kcal/mole. About 7% of the CH$_3$I molecules have an additional 0.7 kcal/mole in thermal excitation of the C-I stretching vibration. Formation of the products CH$_3$ + KI therefore frees about 24 kcal/mole to be partitioned between \( E' \) (the final relative translational energy) and \( W' \) (the vibrational and rotational excitation of the products). If all of the available energy goes into internal excitation \( (W' = 24 \text{ kcal/mole}) \) there would be none left for the translational energy of separation \([E' = 0, Q = -(E + W)]\) the products would stick together and their angular distribution would coincide with that of the center of mass. If the other limiting case obtains, the products would be formed in their lowest internal states \( (W' = 0) \), all of the reaction energy would go into translational separation \( (E' = 24 \text{ kcal/mole}, Q = \Delta D_{\text{ex}}) \) and the products would recoil away from the center of mass with the maximum possible velocity.

Consider now collisions at the intersection of two crossed molecular beams, each homogeneous in velocity and of very small transverse dimensions. The final velocity vectors of the product molecules in the center-of-mass system,

\[ u_3 = \frac{m_4}{m_3 + m_4} v' \]

and

\[ u_4 = \frac{-m_3}{m_3 + m_4} v' \]  \hspace{1cm} (2-9)
Fig. 2. Energy-level diagram for the reaction

\[ K + CH_3I \rightarrow CH_3 + KI. \]
Fig. 3. Generalized energy-level diagram.
will have a range of directions with respect to \( v \) (angles \( \chi \) and \( \pi - \chi \), respectively), but for collisions of a given inelasticity, \( Q \), the magnitude of \( v' \) is fixed,

\[
v' = v\left(\frac{m_1 m_2}{m_3 m_4}\right)^{1/2} (1 + Q/E)^{1/2},
\]

(2-10)

and the end points of the \( u_3 \) vectors must lie on a sphere of radius \( \left[\frac{m_4}{m_3 + m_4}\right] v' \) and those of the \( u_4 \) vectors on a sphere of radius \( \left[\frac{m_3}{m_3 + m_4}\right] v' \), as indicated in Fig. 1c. Figure 38 is the analogous diagram for the reaction \( K + CH_3 I \rightarrow CH_3 + KI \). The c.m. differential cross-section is defined by the distribution of vectors over the surfaces of these spheres. The cross section depends on \( \chi \), and is independent of \( \psi \), just as in the theory of transport properties.\(^{29}\) In the center-of-mass system the direction of \( m_3 \) is given by \( \chi \), \( \psi \) and that of \( m_4 \) by \( \pi - \chi \), \( \pi + \psi \).

It is more convenient to use angles which refer to one of the incident beams rather than to the trajectory of the center of mass; \( \phi_i \) is the angle between \( v_i \) and a line perpendicular to the plane containing the initial vectors and \( \theta_i \) is the angle between \( v_i \) and the projection of \( v_i \) on this plane.

From Fig. 1b and 1c it is seen that the ratios \( c/u_3 \) and \( c/u_4 \) determine how confined the scattering of \( m_3 \) and \( m_4 \) is in the laboratory system.

When \( u_i > c \), the product \( m_i \) may scatter in any direction in the laboratory system, whereas, whenever \( u_i < c \), it is confined to a forward cone about the trajectory of the center of mass in the laboratory system. The maximum deviation of the angular distribution of \( m_i \) from the c.m. trajectory indicates how the energy of reaction is divided between relative translational motion and internal excitation of the products [see Eqs. (2-9) and (2-10)]. The interpretation of this is complicated, however, by the possibility that the form of the differential cross-section may also restrict the range of accessible laboratory angles. Another source of difficulty arises when \( u_i \) is less than one-half or one-third of \( c \). Then very high angular resolution is required if the differential cross-section
in the center-of-mass system is to be determined. For the reaction
\[ K + HBr \rightarrow H + KBr , \]  
mentioned in Sec. I, the most probable value of \( u_4 \) is less than \( c/7 \).
For the reaction (2-8), \( u_4 \) is near \( c/2 \). The relationship between the laboratory distribution and the center-of-mass distribution is further obscured by the blurring effect of the velocity distributions in the two beams. A graph of these distributions for the case of K and \( CH_3I \) beams is given in Fig. 4. For a certain class of recoil vectors the transformation from the laboratory to the center-of-mass system becomes singular. The locus of the tips of these recoil vectors is a "singular sphere" with the center-of-mass vector \( \mathbf{c} \) as a diameter, as indicated at the top of Fig. 5. Recoil vectors terminating on this sphere are perpendicular to the corresponding laboratory vectors, so that the ratio of solid-angle elements, \( \frac{d\omega_{\text{cm}}}{d\omega_{\text{lab}}} \), becomes infinite at all points on the sphere.
Those portions of the recoil spectrum that lie on or near this sphere are therefore strongly weighted in the observed scattering. Since the singularity is integrable, it is smoothed out by the experimental spread in velocity and beam dimensions. This effect always appears in reactive scattering (although it may be insignificant if the recoil spectrum is negligible near the singular sphere), and it can also appear in elastic or inelastic scattering. The actual center-of-mass distribution is best determined by comparing calculated laboratory distributions with experimental (see Sec. IV).

The preceding analysis has relied only on the classical conservation laws for energy and linear momentum. Those laws cannot explain the angular distributions observed experimentally nor can they explain why the products are in a given internal energy state. They do provide the general relationships which enable such features to be deduced from the observations.

Conservation of angular momentum is more intimately connected with the molecular mechanism of the reaction, because both position and momentum enter into the definition of angular momentum. Before and after a collision, the total angular momentum may be divided up into the momenta of the individual collision partners (denoted by \( J \).
Fig. 4. Maxwell-Boltzmann velocity distributions in the scattering center for the case of K and CH$_3$I beams.
Fig. 5. Illustration of the "edge effect." In the topmost velocity-vector diagram, the heavy circle indicates the "singular sphere." Lower diagrams show in more detail the edge effect for recoil vectors of the particular length given by the light sphere drawn about the tip of the center-of-mass vector \( c \); in this example, the singularity occurs at 33 deg from the direction of \( c \). The curves show the calculated intensity per unit solid angle in the laboratory system when the intensity in the center-of-mass system is uniformly distributed (differential cross section = \( \sigma_0 \) per steradian). The solid curve corresponds to infinite angular resolution.
before and $J'$ after) and the orbital angular momentum associated with their relative motion ($L$ before and $L'$ after). In the case of two colliding particles, the magnitude of the initial orbital angular momentum is given by

$$L = \mu v b.$$ \hspace{1cm} (2-12)

Here $b$ is the "impact parameter," which would be the distance of closest approach if the particles were merely to fly by one another without any interaction, and $\mu$ is the reduced mass of the reactants. For any given velocity there is presumably a wide range of impact parameters which might lead to a reaction. Small values of $b$ are much less probable than large ones, but the reaction probability must eventually become negligible at sufficiently large $b$. A representative value of $b$ can be estimated by equating $\pi b^2$ to the total reaction cross-section. Using this value of $b$ and the most probable value of $v$, a representative value for $L$ is found. For the reaction $K + CH_3I$ (see Sec. IV) this is approximately five times the most probable value of $J$.

The direction of $L$ is perpendicular to both the relative velocity and the impact parameter. As impact parameters with all possible azimuthal orientations about $v$ are equally likely to occur, the distribution of initial $L$ vectors may be visualized as occupying a disk with $v$ as axis. On the other hand, the orientations of the initial $J$ vectors are uniformly distributed in space regardless of the direction of $v$. Thus the total angular momentum $L$ and $J$ always has a distribution with cylindrical symmetry about $v$. These relationships are shown in Fig. 6a.

Under certain conditions the correlation between the product distribution and the direction of $v$ is greatly enhanced. Consider the limiting case in which orbital angular momentum is conserved, $L' = L$. In this limit, the motion of both reactants and products is confined to a plane perpendicular to $v$. The relation between the scattered intensity per unit angle in this plane, $d\sigma/d\chi$, and the differential cross-section is

$$I(\chi) = (2\pi \sin \chi)^{-1} \frac{d\sigma}{d\chi},$$ \hspace{1cm} (2-13)

where the first factor arises from integrating over the azimuthal orientations of $L$ about $v$. The situation is illustrated in Fig. 6b for
Fig. 6. (a) Orientation of initial angular-momentum vectors.
(b) Distribution of recoil vectors for "sticky-collision" model discussed in text.
the special case
\[
\frac{d\sigma}{d\chi} = \text{constant,} \tag{2-14}
\]
which distributes the products uniformly over the azimuthal angles about \( L \). The complete angular distribution is obtained by rotating this diagram about \( v \) so that the circle shown in Fig. 6b generates a sphere. On this sphere the recoil vectors of the products will fan out around the equator and accumulate along the poles, as required by Eq. (2-13). Equation (2-14) need not hold in general; the \( 1/\sin \chi \)

factor will produce strong forward peaking whenever the planar distribution does not vanish at \( \chi = 0 \) deg, and backward peaking whenever it does not vanish at \( \chi = 180 \) deg. This has been called the "glory effect" in discussions of elastic scattering. The peaking can be suppressed only when \( d\sigma/d\chi \) vanishes sufficiently rapidly at the poles.

In reactive scattering, it cannot be expected that \( L' = L \). However, deviations from planar motion are small when

\[
L \gg J \quad \text{and} \quad L' \gg J', \tag{2-15}
\]

and the glory effect will then enter prominently. The glory scattering will fade away if the inequalities in (2-15) are reversed; thus, if \( L \ll J \), the distribution of directions of the total angular momentum vector becomes nearly isotropic and hence no longer endows the products with a "memory" of the direction of \( v \).

C. Some Reaction Models

In the analysis of \( I(\chi) \) it is often appropriate to separate three factors: the partitioning of the total angular momentum (a) between \( L \) and \( J \), and (b) between \( L' \) and \( J' \); and (c) the distribution \( d\sigma/d\chi \), which now refers to a plane perpendicular to the total angular momentum vector.

A rough estimate of factor (a) (see Sec. IV) has shown \( L \gg J \) for most chemical reactions and in particular for reactions (2-8) and (2-11). Thus, (a) does not inhibit the glory effect. Therefore, factors (b) and (c) decide whether or not the angular distribution of products will show pronounced anisotropy.
The simplest model to treat assumes a "sticky" collision complex which lives long enough to make Eq. (2-14) hold. A characteristic feature of this model is that the angular distribution of products must be symmetrical about \( \chi = 90 \) deg. If it is assumed that \((b)\) is fixed by the population of rotational states of the complex,\(^{29}\) then we have \( L' \gg J' \) for reaction (2-8); hence, this model predicts strong scattering both forward and backward along \( v \). Figure 6 is a special case of the "compound nucleus model."\(^{31}\)

A long-lived complex in a reaction for which \( J' \gg L \) and \( L' \gg J' \) would lead to a spherically symmetric distribution of products about the center of mass (as would any model which led to \( L' \) spherically symmetric).

The case in which no complex is formed and the newly formed KI continues in the opposite direction that the K was initially moving can be called the stripping model.\(^{31}\) For this model the initial and final relative-velocity vectors are collinear with \( \chi = 0 \) (\( \chi \) being the angle between the center-of-mass velocities of K and \( \text{CH}_3 \), and \( \pi - \chi \) being the angle between the center-of-mass velocities of K and KI). The complete vector diagram is shown in Fig. 7. This model would predict a peak in the KI distribution in the center-of-mass system at \( \chi = 0 \) deg.

Blaise and Bunker have recently performed Monte-Carlo calculations of the product trajectories for the reactions of alkali-metal atoms with methyl iodide.\(^{32}\) In these calculations, the three interacting particles (\( \text{CH}_3 \) is treated as a single atom) are not restricted to collinearity, but for the sake of economy in computing time it was necessary to restrict the trajectories to a plane. (It is possible that this may affect their conclusions about the angular momentum and distribution of products.) Each collision is initiated with a randomly chosen impact parameter and angular orientation of the \( \text{CH}_3\text{I} \) molecule. The thermal distributions of relative velocity and rotation and vibration of the \( \text{CH}_3\text{I} \) are included. The effects of the qualitative features of the potential-energy surface upon the internal energy and angular distribution of the products have also been studied. Their results indicate that
Fig. 7. Velocity-vector diagram for the stripping model.
the reactions are not describable by the formation of a long-lived complex. A more complete description of the results of their work is given in Sec. V.
III. EXPERIMENTAL

A. Introduction

The apparatus was designed to measure the angular distribution of product molecules produced by reactive collisions at the intersection of two molecular beams.

Figure 8 shows the apparatus used in these experiments. As shown in Fig. 9, the beams are formed by thermal effusion from ovens suspended from a lid which is rotated to sweep the angular distribution past the detector. Replacement of the in-plane detector, shown in place in Fig. 9, with the out-of-plane detector, allows the scattering to be measured out of the plane (angle $\phi$, accessible from $+30$ deg to $-90$ deg) as well as in the plane of the incident beams (angle $\theta$, accessible over $-100$ deg to $+150$ deg from the alkali beam).

For a reaction to be studied by use of molecular-beam techniques, the products of the reaction must reach the detector in sufficient quantity to be measurable. The intensity of products at the detector is affected by three factors. These are: (a) chemical reactivity, (b) how the products are confined in the center-of-mass system, and (c) the geometric arrangement of ovens and detector. Restrictions that can arise from the center-of-mass distribution were discussed in Sec. II. The chemical factor is introduced because only a small fraction of the molecules entering the scattering center react. As is shown in Sec. IV, this fraction is approximately $10^{-3}$ for the most reactive molecules that can be studied with the surface-ionization detector. The geometric factor arises from the flux of a molecular beam through a given area decreasing by $1/r^2$ as its distance from the beam source is increased. Therefore, it is desirable to locate the beam sources and the detector as close as is feasible to the scattering center. However, the closer the sources are, the more poorly defined the incident beams will be and the more the angular distribution of products will be blocked by the ovens. The closer the detector is the poorer will be the resolution of the angular distribution. In these experiments, the distance from the
Fig. 8. Molecular-beam vacuum chamber. (A) Gas-feed line, (B) support column for K oven, (C) cold shield for K oven, (D) 6-in. diffusion pumps, and (E) part of copper liner.
Fig. 9. Cutaway sketch of apparatus showing lid, ovens, and in-plane detector.
scattering center to the alkali oven is 11 cm, to the gas oven slit 1.7 cm, and to the detector 10 cm for in-plane experiments and 5 cm for out-of-plane experiments. The detector subtends about $10^{-5}$ of the $4\pi$ steradians about the scattering center.

In the $K + \text{CH}_3\text{I}$ experiments, the concentration of $K$ within the volume defined by the intersection of the beams is about $10^{10}$ atoms cm$^{-3}$, equivalent to a pressure of $10^{-6}$ mm, and that of $\text{CH}_3\text{I}$ is about 100 fold greater. About $10^{14}$ K atoms/sec enter the reaction volume, of which roughly 0.1% react to form KI while about 10% undergo elastic scattering. The steady-state concentration of KI in the reaction volume is roughly $10^7$ molecules cm$^{-3}$, and the pressure is approx $10^{-9}$ mm. At the peak of the KI distribution about $10^7$ molecules/sec arrive at the detector.

B. Apparatus

1. Vacuum System

   a. Vacuum chamber. To ensure that molecules in the beam collide only at the scattering center, it is necessary that the mean free path of the background gas be greater than the apparatus dimensions. The low pressure required was obtained by using diffusion pumps of very large throughput (see Appendix A) and lining the vacuum chamber with a copper box that was kept at liquid-nitrogen temperature. For condensible reactants this liner provides a very high pumping speed (estimated at 200,000 liters/sec). The copper liner is connected to a 20-liter reservoir for liquid nitrogen (also inside the vacuum chamber). Both ends of the liner are supported on stainless steel knife edges to reduce conductive heat loss. The total rate of heat loss during an experiment was equivalent to six liters of liquid nitrogen per hour. The external liquid-nitrogen supply consisted of a pressurized 100-liter dewar and an off-on solenoid valve controlled by a gas thermometer located in the reservoir. The copper tank suspended from the stainless steel lid may be filled with liquid nitrogen to provide additional trapping
for the reaction chamber. In practice it was found both unnecessary and inconvenient to do so. When the tank was cooled, it became much more difficult to rotate the lid.

The angular position of the rotating lid was determined by means of degree marks on the lid and an adjacent vernier scale on the apparatus. The lid position could be determined within ±0.05 deg.

b. Pumps and traps. Figure 10 is a schematic of the pumping system. When the apparatus was warmed after a run, the cold trap shown in Fig. 10 was placed in the vacuum line. This helped prevent damage to the mechanical pumps from the vaporizing organic iodide. Even with this precaution, the pump oil was sufficiently decomposed at the end of six or seven days to require its being changed.

The nominal pressures obtained on the low-pressure side of the various pumps are given in Table I.

<table>
<thead>
<tr>
<th>Type of pump</th>
<th>No reactants</th>
<th>Crossed beams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical pump</td>
<td>15 µ</td>
<td>150 µ</td>
</tr>
<tr>
<td>Booster DP</td>
<td>0.1 µ</td>
<td>0.1 µ</td>
</tr>
<tr>
<td>Main DP</td>
<td>10⁻⁶ mm</td>
<td></td>
</tr>
<tr>
<td>Main DP with liquid-nitrogen trapping</td>
<td>5 × 10⁻⁸ mm</td>
<td>10⁻⁷ mm</td>
</tr>
</tbody>
</table>

When the apparatus was pumped down from atmospheric pressure, 15 minutes were required for the mechanical pumps to reduce the pressure to 500 µ. At this pressure, the booster diffusion pump was turned on. This pump reached operating temperature in twenty minutes and evacuated the system to approximately 1 µ in five minutes. At this point the main diffusion pumps were started, and within thirty minutes reduced the pressure to 10⁻⁵ mm. The copper liner was then cooled to liquid-nitrogen temperature. This required 75 liters of nitrogen and one-half hour.
Fig. 10. Schematic of vacuum system. (A) Vacuum chamber, (B) 6-in. oil-diffusion pumps, (C) 4-in. booster-diffusion pump, (D) 8-cfm mechanical pump, (E) 5-cfm mechanical pump, (F) cold trap.
c. **Pressure measurement.** Thermocouple gauges were used to measure pressures in the 1- to 1000-μ range. Below 1 μ, an ionization gauge was used. The ionization gauge was mounted on the side of the vacuum chamber with the liquid-nitrogen-cooled liner between it and the reaction region. The nominal pressure read by this gauge is therefore lower than that actually existing on the inside of the liner. These pressures are generally considered to differ by a factor of 10. The actual pressure in the reaction region during an experiment is therefore about 10⁻⁶ mm. The mean free path corresponding to this pressure is approximately 50 m, which satisfactorily meets the requirement of being greater than the apparatus dimensions.

d. **Vacuum seals.** UCRL vacuum connectors were most satisfactory for couplings of a semipermanent nature. Rubber gaskets of rectangular cross-section were used to make the vacuum seals between the vacuum chamber and the rectangular flanges. These gaskets were fabricated at the Lawrence Radiation Laboratory. Vacuum seals on the circular ports were made with standard O-rings. The seal between the rotating lid and the vacuum chamber consisted of two O-rings with the region between the O-rings externally evacuated. The lid was difficult to turn unless the O-rings were well coated with stopcock grease and the room temperature was above 75°F. (Fortunately, this was usually the case throughout the year in California.)

Electrical leads to the ovens were sealed in epoxy plugs which were pressed against O-ring fittings on the lid. Occasionally, a wire would break free from the surrounding epoxy. Such leaks were repaired with Glyptal. The power leads to the detector filaments were soft soldered to a Stupakoff seal fastened to the flange on which the detector was mounted. To prevent this seal from leaking, we covered it with 1/4 in. of epoxy. The same type of seal should be used for the filament leads as was used for the oven leads.

The vacuum seal for the lead from the detector-collector plate to the electrometer had to be of very high-resistance material. Two types of seals were used which were very satisfactory. The seal for the in-plane detector was a porcelain amphenol connector sealed to the
apparatus with an O-ring. The out-of-plane detector lead was passed through a glass- Kovar seal that was hard soldered to the detector mount.

The tubing connecting the internal gas oven to the external source passed through an O-ring seal in the center of the rotating lid (as shown in Fig. 11). Fortunately, leaks were not a frequent problem. Those leaks which did appear were located with a He mass-spectrometer leak detector.

2. Beam Sources

a. Ovens. The ovens were designed to produce an effusive flow of molecules over a range of temperatures. Double chamber ovens were used for both the potassium and the organic halides. This design permits the pressure and kinetic energy of the gas to be varied independently by adjusting the power input to the lower and upper chambers.

The design of the K oven is shown in Fig. 12. The positioning of the heater coils is such that the slits are slightly warmer than the rest of the upper chamber. This arrangement prevents clogging of the slits. The charge of potassium was contained in the removable thimble which was sealed into the lower chamber with a copper gasket.

Unlike the K oven, the gas-oven chamber that contained the beam material was located outside the apparatus. The gas source or barostat is shown in Fig. 13. The lower portion of the barostat was immersed in a constant temperature bath such as liquid nitrogen or dry-ice acetone. By varying the power input to the heating element, any temperature greater than or equal to the bath temperature could be maintained. Since the feed lines from the barostat to the apparatus were at room temperature, it was not possible to use compounds whose vapor pressure at room temperature was less than approximately 300 p. The pressure necessary varied with the substance and was determined by what attenuation of the K peak was desired. The barostat was connected to the gas oven as shown in Fig. 11. The 12-liter bulb in the feed line served to damp out any short-term pressure fluctuations. Two types of gas oven were used; the standard oven shown in Fig. 14, and the thin oven shown
Fig. 11. Gas manifold. (A) Barostat (see Fig. 13), (B) 12-liter ballast bulb, (C) rubber-connection tubing, (D) thermocouple vacuum gage, (E) rotating seal between gas manifold and rotating lid, (F) fitting for tube from lid, (G) block soldered to tube from manifold, (H) O-ring, (I) 3/8-in. copper tubing, (J) glass tubing, and (K) rotating lid.
Fig. 12. Potassium oven. (A) Upper chamber, (B) lower chamber, (C) yoke for holding thimble in place, (D) thimble.
Fig. 13. Gas barostat.
Fig. 14. Standard gas oven. (A) Support, (B) gas inlet, (C) slit assembly.
in Fig. 15. The standard oven was used for all out-of-plane runs and for most in-plane runs with $\gamma = 90$ deg. The thin oven was designed to subtend the smallest possible sector of the angular distribution. With its surrounding cold shield in place, it obstructs 30 deg of the angular distribution. It was used for in-plane runs when $\gamma$ was not equal to 90 deg.

The power and thermocouple leads for the ovens were contained inside columns that passed through holes in the lid and tank. These columns also served as supports for the potassium and gas ovens. Both supports could be rotated and the K-oven support could be raised and lowered by means of a micrometer type screw. All the ovens were heated with coils of 10-mil tantalum wire. Tungsten was not used because it becomes brittle when heated.

To maintain the lower K chamber at its operating temperature of 265°C required about 18 W of power. Approximately 45 W were necessary to maintain the upper chamber at its maximum temperature of 600°C. Direct-current power supplies with regulated input voltages were used for both the K and the gas ovens. All oven temperatures were read with calibrated chromel/alumel thermocouples using commercial meters (see Appendix A).

b. Slits. The K-oven slit consisted of two pieces of stainless steel foil held in place with two steel bars. The bars were held to the upper oven with screws. The slit size defined by the foil was 0.025 cm $\times$ 1 cm. At the operating temperature of the lower K oven, the vapor pressure of potassium is about 100 $\mu$. The mean free path at this pressure is 0.05 cm. The slit width satisfies the requirement of being less than this, therefore effusive flow was maintained.

The gas-oven slit was composed of a sandwich of Zacharias slits. Their use results in a much more directional beam than would be obtained with standard slits. The corrugations have a width of 7 mils, a depth of 4 mils, and a length of 1 cm. For these channels, pressures below 500 $\mu$ result in effusive flow. All gases were run at pressures less than this.
Fig. 15. Thin gas oven. (A) Support, (B) gas inlet, (C) well for thermocouple, (D) holes for heater coils, (E) Zacharias slit assembly.
c. Cold shields and beam flags. The beams were defined by 0.3 × 1.5 cm slits in the cold shields that surrounded each oven. The K oven had an additional collimating slit 1.5 inches in front of the cold shield. Radiation to the liquid-nitrogen-cooled copper liner kept the cold shields at a temperature of -40°C when the ovens were at operating temperature. Both the temperatures of the copper liner and the cold shields were measured with thermocouples.

A beam flag was located between the gas-oven slit and the cold-shield collimating slit. The beam flag is operated by a plunger above the lid. The vacuum seal around the plunger was a 1/8-in. i.d. O-ring. Initially, a beam flag was also located in front of the K-oven slit. It was found that the potassium would deposit on the track in which the flag moved, thereby freezing the two together. The gas-oven beam flag would freeze only when the lid was cooled.

3. Detector

a. Construction. The detector used in the in-plane and out-of-plane experiments is shown in Fig. 16. The support for the out-of-plane detector is shown in Fig. 17. In and out motion of the in-plane detector was achieved by mounting the detector on the end of a shaft around which was an O-ring seal. The hole through which the shaft moved was located in a flange that could be moved horizontally. The tracks against which this flange moved were bolted to another flange that could be moved vertically. The horizontal movement was used to position the desired filament on a line passing through the detector collimating slit and through the center of reaction. The support for the detector used in the out-of-plane measurements differs only in that the shaft can be rotated rather than moved in and out. Vacuum seals were provided by O-rings beneath the flanges and around the shaft hole.

Both detectors were surrounded by cold shields during actual experiments. These shields prevented most background gas molecules from striking the detector. The out-of-plane shield was cooled by radiation to the copper liner. The in-plane shield was cooled by
Fig. 16. Detector. (A) Filament support, (B) holder and guard rings, (C) collector plate.
Fig. 17. Out-of-plane detector and support assembly. (A) Lead from collector plate, (B) sliding flange, (C) rotating support, (D) detector.
direct contact with the liner. A collimating slit fixed in front of the in-plane shield restricted the molecules striking the detector to those emanating from the region of reaction. The out-of-plane shield had a rectangular slot 1/2 by 1 in. located in front of the filaments. It was not possible to have a collimating slit for this detector since the filaments would not have been movable with respect to it. The noise level of the out-of-plane detector without a cold shield was $10^3$ times greater than with one. There were also large drifts in the background. Under such conditions it was impossible to obtain any data.

It is also possible to have the in-plane detector fixed and the collimating slit attached to the movable detector mount. By adjusting the position of the slit either filament may be aligned with the center of reaction. However, this arrangement results in the two filaments, the collimating slit, and the ovens being in different positions with respect to the copper liner. This factor caused reflections from the apparatus to be detected by one filament and not the other. This was noticed by crossing K with CH$_3$OH under these conditions. Since no reaction can take place in the gas phase with these molecules, the peaks that were observed on both Pt and W in different regions were due to reflection. After it was realized that this was a source of error, all experiments made with this configuration were rerun with the detectors movable and the slit fixed. Running CH$_3$OH and K under these conditions leads to no such peaks (as can be seen in Fig. 26).

The electrical circuit for the detector is shown in Fig. 18.

b. Operating characteristics. The detector used consisted of two filaments, W and an alloy of 92% Pt-8% W; the filaments were heated by having direct current passed through them, and were biased positive with respect to a surrounding collector plate. The W filament ionizes both K and KI molecules essentially 100%, producing K$^+$ ions which are attracted to the collector plate. This ion current is therefore a direct measure of the sum of the K and KI molecules striking the W filament. At the temperature at which the Pt alloy filament is operated, 85% of the incident K atoms are ionized. By alternately
Fig. 18. Detector circuit. (A) Pt and W filaments, (B) collector plate, (C) vibrating-reed electrometer.
measuring on the W and Pt filaments the current resulting from an
incident KI beam, the ionization efficiency of KI on Pt was found to be
one-fiftieth of that for KI on W.

The temperatures at which it was desired to operate the W and
Pt filaments were obtained from R. W. Roberts' data on the tempera-
ture dependence of their ionization efficiencies. These temperatures
were 1800°K for W and 1200°K for Pt. The current-vs-temperature
information necessary for W was obtained from the tables of Jones and
Langmuir. By calibrating an optical pyrometer with the W filament
and making use of the emissivity of Pt, we obtained the current-vs-
temperature information needed for the Pt filament. The operating
currents for the filaments that were used are given in Table II.

Table II. Detector-filament operating currents.

<table>
<thead>
<tr>
<th>Filament</th>
<th>Operating current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0022 Pt</td>
<td>0.16</td>
</tr>
<tr>
<td>0.003 Pt</td>
<td>0.35</td>
</tr>
<tr>
<td>0.002 W</td>
<td>0.44</td>
</tr>
<tr>
<td>0.003 W</td>
<td>0.60</td>
</tr>
</tbody>
</table>

By aging the filaments for about six hours before each run, the noise
level on each filament was reduced to about 10^-14 A. The aging currents
were 10% higher than the operating currents.

When the Pt signal is normalized to the W at the beam peak, their
difference in all other angular regions was taken as the KI signal. This
procedure is valid when the ionization efficiencies of the W and the Pt
alloy filaments are not functions of the incident K or alkyl-iodide inten-
sity. The normalized Pt and W signals were everywhere equal when a
K beam was crossed with a CH_3OH beam, indicating that the ionization
efficiencies are not a function of the K intensity. However, when an
alkyl iodide was used as the crossed beam, the normalization was poor
in the region within 30 deg of the K beam. This indicates the ionization
efficiencies are in some way a function of the K intensity when an iodide is present. Fortunately, in the region of greatest interest (angles greater than 30 deg) the K intensity varies only slightly.

C. Experimental Procedure

1. Preliminary Operations

The preliminary operations can be divided into alignment of the apparatus and bringing the apparatus to equilibrium.

The alignment procedure for the ovens achieved the desired angle of intersection of the beams and ensured that the region of intersection was located at the center of rotation of the lid. Before the ovens were aligned, it was necessary to position the cathetometer on a line passing through the center of rotation. When the lid was rotated 180 deg, the two positions of the slit in the K-oven cold shield defined such a line. The K-oven cold shield was removed and, by using the positioned cathetometer, the K oven was located so that its slit was on the line. After replacing the K cold shield and positioning the outer collimating slit, the lid was rotated an amount equal to the desired angle of intersection, \( \gamma \). The gas-oven slit and cold shield were then aligned with the cathetometer. When a new detector was placed in the apparatus, it and the detector collimating slit were aligned through the port at the opposite end of the apparatus. The K thimble (capacity 5 cc) was filled in a nitrogen atmosphere inside a dry box and rapidly transferred to the lower chamber of the K oven. After the alignment of the K oven was rechecked the apparatus was pumped down.

When the pressure reached \( 10^{-6} \) mm, the aging of the detector filaments began. At the same time, the gas oven and upper K chamber were brought to operating temperatures. The process of heating the lower K-oven chamber was begun. The temperature of the lower chamber was increased slowly so that any vaporizing impurity would not cause the K to splatter into the upper chamber. Maintaining the lower chamber at 150° C overnight was generally sufficient.

When the detector filaments and potassium were aged, the K
oven was brought to operating temperature. The desired K flux at the
W detector corresponded to a signal of about $3 \times 10^{-8}$ A. Any short-
term fluctuations in the signal were taken either as evidence of insuf-
ficient aging of the K or as evidence of the presence of nonvaporized K
in the upper K-oven chamber. These fluctuations could always be cured
by lowering the temperature of the lower chamber to 150°C and waiting.
Generally a few hours were sufficient to establish a steady beam. When
the desired beam intensity was reached, the valve to the gas barostat
was opened and the apparatus was allowed to equilibrate. While equilib-
rium was being reached, the detector positions at which a line through
the detector collimating slit and the center of rotation would intersect
the filaments were determined. The position for each filament was
found by taking the mean of the detector positions at which the signal
was one-half of the maximum signal. The corresponding lid position
was found in the same way. The positions of both the filament and the
lid were redetermined until there were no changes in the mean positions.
The data taking was begun when the K-beam peak intensity and its attenu-
ation by the gas beam ($\approx 20\%$) became constant to within $1\%$ over a period
of ten minutes. To achieve such constancy generally required about six
hours from the time the gas beam was turned on.

During a series of runs, the temperature of any of the ovens or
of the gas-source material could be changed. Any such change neces-
sitated waiting for equilibrium to be reestablished.

When the K charge was consumed, the diffusion pumps on the
apparatus were turned off as was the automatic liquid-nitrogen supply.
The cold trap was brought to room temperature by circulating warm
air within the LN$_2$ reservoir. About six hours were required to warm
the apparatus. The mechanical pump and booster DP were then
isolated from the vacuum chamber which was then vented with dry
nitrogen.

2. Measurement of Angular Distributions

The data consisted of measurements of the effect of the gas-beam
flag on the detector signal as a function of the angle from the K peak.
 Approximately 1.5 hours were required to obtain these measurements on each filament. The second filament was aged for 15 min before it was used to obtain measurements. The distributions were measured until the desired data was obtained or the potassium ran out. With a peak intensity of $3 \times 10^{-8}$ A, the potassium would last about three days.

3. Reduction of Data

In Sec. III. C. 2 above, the experimental procedure for obtaining the Pt and W filament signals as a function of angle was described. Lowering the gas-oven beam flag eliminated the elastic and reactive scattering of the K caused by the organic halide beam. The beam flag did not affect any scattering because of possible cloud formation of organic halide or the presence of background gas. Therefore, the beam-flag attenuation as measured on the Pt or W filament corresponds to the amount of K, or K + KI, respectively, that was present at any given angle resulting from the crossed beams. The effects of fluctuations in the intensity of either beam are eliminated by plotting the beam-peak attenuation vs time and dividing all other readings by the appropriate peak attenuations. By normalizing each filament in this way, their different ionization efficiencies are taken into account. The angular distribution of KI is obtained by subtracting the normalized Pt readings from those of the W filament. Most of the elastically scattered K was confined to within 30 deg of the K beam. Because of this large elastic signal it was impossible to determine the amount of KI present in this region. Out-of-plane data is obtained in basically the same manner as in-plane data. The lid is kept fixed at each desired in-plane position while the out-of-plane region is scanned with the detector.

A K-beam peak and the effect upon it of a CH$_3$I beam is shown in Fig. 19. Typical normalized Pt and W filament signals for the reaction of K and CH$_3$I are shown in Fig. 21. The KI distribution obtained from these curves is also shown.
IV. RESULTS AND ANALYSIS

A. Summary of Data

1. Experimental Data

A typical potassium-beam profile and the effect upon it of a CH₃I beam are shown in Fig. 19. These curves represent the signal on the W filament. The difference between beam profiles (a) and (b) shows the effect of scattering by background gas. The K beam traverses approximately 20 cm of the region containing the background gas and only a fraction of a cm of the crossed beam which is at a higher pressure than the background gas. It can be seen that the crossed beam raises the general background considerably; however, because of the operation of the beam flag, this effect does not influence the data (see Sec. III).

A crossed-beam profile measured by using CCl₄ is shown in Fig. 20. The effect of the width of this beam upon the KI distribution is shown in Sec. IV. A. 2 to be unimportant.

In Fig. 21a are shown typical results for the K + CH₃I reaction. The parent K beam of 5 × 10⁻⁸ A is attenuated 7% by the crossed CH₃I beam. Readings on the platinum detector (solid circles) are normalized to those on tungsten (open circles) at the parent-beam peak. The curves in Fig. 21b are derived from Fig. 21a (circles) and a similar experiment done some months later (triangles).

Crossed beam studies have been made of the reactions

\[ K + RI \rightarrow R + KI \]  \hspace{1cm} (4-1)

For γ = 90 deg, the angular distributions of KI that result from the different alkyl radicals are shown in Fig. 22. The experimental conditions are listed in Table III. The peak heights have been normalized to unity in this figure. The actual peak values obtained experimentally are given in Table III. These actual peak heights varied from one run to another when the same experiment was repeated. During each run, however, the height remained constant. This effect is probably caused by poisoning of the filament (see Sec. III).
Fig. 19. Potassium-beam peak profile. (a) Signal with only K oven on, (b) signal with K and CH$_3$I ovens on but CH$_3$I beam flag closed, (c) signal with both ovens on and beam flag open.
Fig. 20. CCl\textsubscript{4} beam profile.
Fig. 21. (a) Typical Pt (•) and W (○) signals, (b) KI distributions. Dashed line refers to calculated KI distribution.
Fig. 22. KI distributions that result from reaction

\[ K + RI \rightarrow R + KI. \]
Table III. Experimental conditions for the reactions of K + RI.

<table>
<thead>
<tr>
<th>RI</th>
<th>Temperature of RI beam (°K)</th>
<th>Temperature of K beam (°K)</th>
<th>Experimental normalized peak intensity $\times 10^5$</th>
<th>(Normalization method is discussed in Sec. III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) methyl iodide</td>
<td>315</td>
<td>573</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![methyl iodide]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) ethyl iodide</td>
<td>311</td>
<td>573</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![ethyl iodide]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) n-propyl iodide</td>
<td>313</td>
<td>661</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![n-propyl iodide]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) i-propyl iodide</td>
<td>300</td>
<td>657</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![i-propyl iodide]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e) n-butyl iodide</td>
<td>313</td>
<td>613</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![n-butyl iodide]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(f) i-butyl iodide</td>
<td>308</td>
<td>575</td>
<td>3.9</td>
<td></td>
</tr>
</tbody>
</table>
The reaction of K with CH$_3$I has been studied at intersection angles of 60 deg, 90 deg and 120 deg. The KI distributions for these cases are shown in Fig. 23.

For $\gamma = 90$ deg, the results of a variation in the K-beam temperature for runs with CH$_3$I and C$_2$H$_5$I are shown in Figs. 24 and 25. These results were obtained in experiments performed immediately after one another to eliminate any effect of possible filament changes.

In Fig. 26 the experimental results of a run with K and CH$_3$OH (which cannot react in the gas phase) are compared with the results of a similar experiment with CH$_3$I. These distributions confirm that the observed peak results from reactive scattering and shows that there is no KI in the negative angular region.

A complete and satisfactory out-of-plane distribution has not yet been obtained. A preliminary distribution measured at 90 deg from the K peak and the corresponding in-plane distribution are shown in Fig. 27.

2. Calculated Results

An IBM 7090 computer program has been written that will calculate the in-plane laboratory distribution that results from any center-of-mass distribution. The output from the computer is in the form of a graph of product intensity vs $\theta$ (see Fig. 1). The program performs the necessary averaging to take into account the Maxwell-Boltzmann distribution of velocities in the beams. Appendix B contains a detailed discussion of the program. Unless otherwise specified, the following results pertain to the reaction of K with CH$_3$I.

The effect of the CH$_3$I beam width on the KI distribution is shown in Fig. 28. Each KI distribution in this figure is the result of a summation of individual KI distributions, each of which results from the intersection of a perfectly collimated K beam with CH$_3$I beams of different directions and intensities. The resultant KI peak is seen to be relatively insensitive to the width of the CH$_3$I beam. The effect of energy dependence of the reaction upon the laboratory distribution is
Fig. 23. KI distribution as a function of the intersection angle $\gamma$. 
Fig. 24. Effect of potassium temperature on the reactions with CH₃I.
Fig. 25. Effect of potassium temperature on the reactions with $C_2H_5I$. 
Fig. 26. Comparison of results when a K beam is crossed with a beam of CH$_3$I or CH$_3$OH.
Fig. 27. Out-of-plane distribution taken at $\theta = 90$ deg—shown with the corresponding in-plane distribution.
Fig. 28. Effect of CH₃I beam width on the KI distribution. The curves on the left are various CH₃I beam profiles and those on the right are the resultant KI distributions.
shown in Fig. 29. Varying the temperature of the K beam leads to the distributions shown in Fig. 30. The qualitative features of the KI peak are seen to be insensitive to the temperature of the K beam and unaffected by activation energies of less than approximately 1 kcal/mole.

The effect of $Q_1$, when $E = E^*$ (relative energy that results from collision between molecules having their most probable velocity) and when $\chi$ is uniformly distributed over that portion of the $4\pi$ steradians defined by $\chi = \chi_{\text{max}} = 50$ deg, is shown in Figs. 31, 32, and 33. Allowing $Q$ to be uniformly distributed from 0 to 4, 0 to 9, or 0 to 14 kcal/mole results in the curves shown in Fig. 31 for $\gamma = 60, 90,$ or $120$ deg. When $Q$ ranges from 0 to 4, 5 to 9, or 10 to 14 kcal/mole, for $\gamma = 90$ deg the distributions are as shown in Fig. 32. The effect of $Q$ on the reaction of K with $C_4H_9I$ is shown in Fig. 33.

The most interesting changes in the angular distribution result from variations in the center-of-mass differential cross section. The cross-section that distributes the reaction-product vectors uniformly over the portion of a sphere defined by $\chi \leq \chi_{\text{max}}$ leads to the distributions in Fig. 34. Here, we have $\chi_{\text{max}} = 5, 50, 90,$ and $180$ deg, with $\gamma = 60, 90,$ and $120$ deg. The KI distribution would appear as that shown in Fig. 35 for a differential cross-section $d\sigma/d\omega$ proportional to $1/\sin \chi$.

For $40 \leq \chi \leq 50$ deg and $13 \leq Q \leq 17$ kcal/mole the laboratory system distribution of KI appears as in Fig. 36.

The out-of-plane distribution that results from a spherically symmetric center-of-mass distribution and one value of $Q$ is shown in Fig. 37.
Fig. 29. Effect of activation energy on calculated KI distribution. All curves were calculated for \(0 \deg \leq \chi \leq 50 \deg\) and \(Q = 2 \text{kcal/mole}\). Each curve represents the KI distribution that results when reaction takes place only when the initial relative energy \(E\) is within certain limits. These limits are from the outermost curve to the inside curve: \(0.5 \leq E \leq 3\); \(0.8 \leq E \leq 3\); \(1.1 \leq E \leq 3\); \(1.4 \leq E \leq 3\); \(1.7 \leq E \leq 3\); \(2.0 \leq E \leq 3\) kcal/mole.
Fig. 30. Effect of variation in temperature of K beam on calculated KI distribution when CH$_3$I temperature is 300°K.

- K:600°K
- K:900°K.
Fig. 31. Effect of variation of maximum in $Q$ range when $0 \text{ deg} \leq \chi \leq 50 \text{ deg}$.

- $\delta = 60^\circ$
- $\delta = 90^\circ$
- $\delta = 120^\circ$

- $0 \leq Q \leq 4 \text{ kcal/mole}$
- $0 \leq Q \leq 9$
- $0 \leq Q \leq 14$. 
Fig. 32. Effect of variation in Q range when 0 deg \( \leq \chi \leq 50 \) deg and \( \gamma = 90 \) deg. (a) \( 0 \leq Q \leq 4 \), (b) \( 5 \leq Q \leq 9 \), (c) \( 10 \leq Q \leq 14 \) kcal/mole.
Fig. 33. Effect of variation in $Q$ range with $0 \text{ deg} \leq \chi \leq 50 \text{ deg}$ for the reaction of K with $\text{C}_4\text{H}_9\text{I}$.

- $-0.5 < Q < 5.0 \text{ kcal/mole}$
- $-0.5 < Q < 10$
- $0 < Q < 4$. 
Fig. 34. Effect of $\chi_{\text{max}}$ upon KI distribution when $0 \leq Q \leq 4$ kcal/mole.

- - - - - - $0 \text{ deg} \leq \chi \leq 5 \text{ deg}$
- - - - - - $0 \text{ deg} \leq \chi \leq 50 \text{ deg}$
- - - - - - $0 \text{ deg} \leq \chi \leq 90 \text{ deg}$
- - - - - - $0 \text{ deg} \leq \chi \leq 180 \text{ deg}$. 
Fig. 35. KI distribution when $d\sigma/d\omega \propto 1/\sin \chi$, and $Q = 2$ kcal/mole.
Fig. 36. KI distribution resulting from $13 \leq Q \leq 17$ kcal/mole and $40 \text{ deg} \leq \chi \leq 50 \text{ deg}$.
Fig. 37. Out-of-plane distribution of KI resulting from a spherically symmetric center-of-mass distribution with $Q = 2$ kcal/mole. Contour lines are curves of constant KI intensity.
B. General Features of Analysis

The angular distributions of KI (Fig. 21 for example) have been normalized so that the area under the curves gives the collision yield (see Sec. III), which is \(5 \times 10^{-4}\) and corresponds to a reaction cross-section of about \(7 \text{Å}^2\). The elastic cross-section has been estimated to be of the order of \(1000 \text{Å}^2\). The method used in estimating the cross-sections is summarized by Ramsey. The estimate of the elastic cross-section was obtained from the attenuation of the beam peak and from the data on source pressures and apparatus geometry summarized in Sec. III. The reactive cross-section was obtained by comparing the total K scattered from the beam peak with the total KI intensity, calculated by assuming the out-of-plane distribution to be cylindrically symmetric about the in-plane peak (justified by the data shown in Fig. 27).

The experimental results of varying the K-beam temperature (Figs. 24 and 25) when compared to the calculated results (Figs. 29 and 30) indicate that the activation energy for the reaction of K with CH\(_3\)I or C\(_2\)H\(_5\)I is less than 1 kcal/mole.

That the position of the KI peak remains near 90 deg for all R studied (Fig. 22) indicates that \(Q\) decreases as the mass of the R group becomes larger (see Eq. 2-10). There is no noticeable effect from steric hindrance as the R group becomes more complex, since the collision-yield remains about the same as for the CH\(_3\)I reaction (see Table III and Fig. 22).

The vector diagrams of Fig. 38 (drawn using the most probable initial velocities), enables a first comparison to be made between the observed angular distributions (Figs. 22 and 23) and that distribution which is allowed by the conservation laws. It is seen that the broad peak observed in the laboratory (for all R studied) corresponds to scattering in which an observer stationed at the center of mass would see KI recoil backward (and CH\(_3\) forward) with respect to the incoming K beam. Since the scattering is symmetric about the initial relative velocity, \(v\), the limits on the \(\chi\) and \(Q\) ranges are obtained from the more restrictive region below \(v\) and are bounded on either side by the
Fig. 38. Velocity vector diagrams for the reaction $K + CH_3I \rightarrow CH_3 + KI$. The circles represent different $Q$ values; $R$ denotes the $CH_3$ radical.
half-intensity lines (located at approximately $\theta = 45$ and 80 deg for $\gamma = 60$ deg). The qualitative features of angular distributions resulting from $\chi$ and $Q$ values allowed by the region in the vector diagram between the half-intensity lines and above $\gamma$, but not allowed by the region below $\gamma$, have been shown in Fig. 34 to be incompatible with the experimental results. The allowed values of $\chi$ and $Q$ must be such that the end points of the KI velocity vectors lie within the restricted region just described. Preliminary estimates of the ranges of $\chi$ and $Q$ can be obtained from the positions and widths of the KI peaks at different values of $\gamma$. On figures such as Fig. 38 (drawn using the procedure described in Sec. II) are lines indicating the location of the peak- and half-peak-intensity positions of the KI distribution (obtained from Fig. 23). Since part of the KI-peak width arises from the velocity distributions in the beams, the positions of the half-intensity lines in Fig. 38 (drawn for only one set of velocities) will actually be somewhat closer to the peak position. The estimated ranges of $\chi$ and $Q$ obtained from Fig. 38 are $0 < \chi < 50$ deg and $0 < Q < 5$ kcal/mole. The calculated distributions in Figs. 31 through 34 indicate that a broader $Q$ range is compatible with the experimental data but that the $\chi$ range estimated above is approximately correct.

C. Detailed Analysis Based on Computer Program

1. Center-of-Mass Distribution

The main points to be settled by the comparison of the experimental and calculated results are what is the distribution of KI as a function of $\chi$ (in particular, whether it is symmetric about $\chi = 90$ deg) and whether a substantial glory effect is indicated. In Sec. IV. C. 2, the determination of the level of product excitation is discussed.

As can be seen from Fig. 38, for large $Q$ much of any "forward" scattering of the alkali halide, corresponding to $\chi > 90$ deg, would appear in the region $-30 > \theta_{KI} > 30$ deg. As Fig. 21 shows, this region is hidden by elastic scattering from the parent K beam.
To determine whether the KI distribution is symmetric, the calculated distributions that result from several reaction models (previously discussed in Sec. II) will be compared with the experimental data. The calculated distributions in Fig. 37 indicate that a prominent shoulder would have been observed in the region $30 > \theta_{KI} > 50$ deg (see Fig. 23) if the scattering could be described by $d\sigma/d\omega \propto 1/\sin \chi$.

These distributions were calculated for one value of $Q$ (2 kcal/mole); however, from Figs. 31 and 32, it can be seen that changing the range of $Q$ would not result in qualitatively different calculated curves. The case of $d\sigma/d\omega = \text{constant}$ (corresponding to $\chi_{\text{max}} = 180$ deg in Fig. 34) leads to distributions much broader than those observed experimentally. A comparison of Figs. 34 ($\chi_{\text{max}} = 180$ deg) and 35 shows that any symmetric distribution intermediate between $d\sigma/d\omega = \text{constant}$ and $d\sigma/d\omega \propto 1/\sin \chi$ would also lead to a KI distribution inconsistent with the experimental data. In light of these observations, it seems very improbable that the KI distribution is symmetric about $\chi = 90$ deg.

That the distributions in Fig. 34 for $\chi_{\text{max}} = 90$ deg are broader than the experimental peaks indicates there is little scattering with $\chi > 90$ deg.

However, neither this fact nor the preceding discussion of symmetric distributions rules out the possible presence of a relatively small amount of forward-scattered KI.

At first glance, the vector diagrams in Fig. 38 do not eliminate the possibility that the KI peak arises from Q values near 15 kcal/mole and $\chi$ values near 45 deg. However, due to the cylindrical symmetry of the scattering about $v$ this would lead to the double peaking shown in Fig. 36. This is clearly at variance with the experimental results. The KI peak that would result from the simple stripping model ($\chi = 0$ deg) (see Fig. 34b, $\chi_{\text{max}} = 5$ deg) when compared with the corresponding experimental distribution (Fig. 23) is much too narrow.
Close agreement between experimental and calculated distributions occurs for two different cases. These are

\[
(a) \quad \frac{d\sigma}{d\omega} = \begin{cases} 
\text{const} & x \leq 50 \text{ deg} \\
\text{zero} & x > 50 \text{ deg}
\end{cases}
\]

and

\[
(b) \quad \frac{d\sigma}{d\omega} = \frac{1}{\sin x} \frac{d\sigma}{dx}, \quad \text{where} \quad \frac{d\sigma}{dx} = \begin{cases} \text{const} & x \leq 90 \text{ deg} \\
\text{zero} & x > 90 \text{ deg}
\end{cases}
\]

The calculated results for case (a) are shown in Fig. 34 for \(\chi_{\text{max}} = 50\) deg. This case could result from a short-lived collision complex that yields reaction products the orbital angular momentum of which is less than their internal angular momentum (in particular if the final orbital angular momentum is spherically symmetric over part of the \(4\pi\) steradians so that \(\gamma\) is uniformly distributed over the angular region defined by \(\chi < 50\) deg). The results to be expected from case (b) correspond to the KI peaks at large \(\theta\) shown in Fig. 35. Case (b) would result from a short-lived complex and a large glory effect. That is, with the reaction products having orbital angular momentum equal to that of the reactants.

2. **Recoil Energy Distribution**

An estimate of the \(Q\) ranges consistent with the experimental data can be obtained from a comparison of Figs. 31 through 33 with the experimental results in Fig. 23. From Fig. 31 it can be seen that the experimental data at \(\gamma = 90\) deg and 120 deg is consistent with \(Q\) ranges of 0 to 4, 0 to 9, or 0 to 14 kcal/mole, but that the \(\gamma = 60\) deg calculations indicate the maximum in the \(Q\) range must be less than 9 kcal/mole (due to the positions of the peaks). The positions of the calculated peaks in Fig. 32 indicate the \(Q\) range must include values between 0 and 4 kcal/mole. Similar calculations for the reaction of K with \(\text{C}_4\text{H}_9\text{I}\) (Fig. 33) show \(Q\) must range between -0.5 and 6 kcal/mole. The \(Q\) distribution for the reaction K + CH\(_3\)I indicates that the products are in excited states approximately 15 to 24 kcal/mole above their ground-states, since the difference between the ground levels of the reactants
and products is approximately 22 kcal/mole (see Figs. 2 and 3 and the discussion in Sec. II).

While the computer program calculates only in-plane distributions, it is possible to use it to assist in the calculations of the out-of-plane distribution that results from a spherically symmetric center-of-mass distribution. A qualitative picture of the in-plane distribution that results from a fixed orientation of \( \mathbf{v} \), but with a spread in the length of \( \mathbf{v} \), is shown in Fig. 39a. The out-of-plane distribution for this one orientation of \( \mathbf{v} \) is cylindrically symmetric about \( \mathbf{c} \) and can be represented by the contour map in Fig. 39b. If velocity averaging is added to the above calculations (that is, if the distributions resulting from several orientations of \( \mathbf{v} \) are averaged together, the in-plane distribution becomes the same as the curves in Fig. 34 for \( \chi_{\text{max}} = 180 \text{ deg} \)). The resultant out-of-plane distribution for one value of \( Q \) is shown in Fig. 37. It is seen that velocity averaging smears out the forward and accentuates the backward peak. Essentially this averaging consists of a superposition of many figures like Fig. 39b (each weighted with its relative Boltzmann probability) each of which has been calculated for a different orientation of \( \mathbf{v} \). Since the center-of-mass distribution is not affected by the orientation of \( \mathbf{v} \), only by its magnitude, and since the center-of-mass distribution is spherically symmetric, the \( \theta \phi \) contour map will be shifted in position along the \( \theta \) axis for new orientations of \( \mathbf{v} \) and will expand or contract as the magnitude of \( \mathbf{c} \) contracts or expands. This combination of factors leads to the smearing out of the forward peak and the accentuation of the backward peak.

It is also possible to obtain a qualitative picture of certain other out-of-plane distributions. The simplest case is that of the stripping model. Since \( \chi \) there would be near 0 deg, the scattering would be confined to the plane of the incident beams.

The distribution in Fig. 37 was obtained with only one value of \( Q \). If instead a range of \( Q \) values were used, this distribution would be smeared out and possibly monotonically decrease from a single peak located in the plane of the beams. The out-of-plane distributions corresponding to the other curves in Fig. 34 for values of \( \chi_{\text{max}} \leq 180 \text{ deg} \)
Fig. 39.  (a) In-plane distribution of Ki resulting from fixed orientation of \( \nu \).  (b) Out-of-plane distribution of Ki corresponding to fixed orientation of \( \nu \).
would in that case also decrease monotonically from a single peak. The differential cross-section \(d\sigma/d\omega \propto 1/\sin \chi\) (with \(d\sigma/d\chi = \text{const}\)) would lead to a double peaking in the plane and a monotonically decreasing intensity from these peaks out-of-the-plane.

3. Angular-Momentum Considerations

In Sec. IV. B, the total reactive cross-section was estimated at \(7\text{Å}^2\), which, when equated to \(\pi b^2\), yields 1 to 2Å as a representative range for \(b\) (see Sec. II). By using Eq. 2-12, \(100 \hbar\) is obtained as an estimate of \(L\). The range of the final impact parameter, \(b'\), like that of \(b\), is expected to be limited by the short range of the forces. The maximum values of \(b\) and \(b'\) in a reactive collision probably cannot be much greater than bond lengths in the reactants and product molecules. From the angular distribution of products in the laboratory system, \(v'\) may be estimated (a representative value being \(15 \times 10^4 \text{ cm/sec}\)) and a value of \(L'\) may be calculated (\(L' \approx 70 \hbar\) for the above \(v'\) and with \(b' \approx 3\text{Å}\)). The rotational partition function yields \(20 \hbar\) as a rough estimate of the internal angular momentum, \(J\), of \(\text{CH}_3\text{I}\) (see Figs. 2 and 3). The conservation of angular momentum enables an upper limit on the rotational momentum, \(J'\), to be calculated. If \(L'\) is assumed to be distributed isotropically with respect to \(L + J\), an average over-all orientation yields

\[
\left\langle J'^2 \right\rangle < \left| L + J \right|_{\text{max}}^2 + L'_{\text{max}}^2 ; \quad (4-1)
\]

whereas, if \(L'\) is oriented oppositely to \(L + J\), the limit is

\[
J' < \left| L + J \right|_{\text{max}} + L'_{\text{max}} . \quad (4-2)
\]

The limits estimated for the rotational excitation of the products from the reaction \(K + \text{CH}_3\text{I}\) from Eqs. (4-1) and (4-2) are 3.5 kcal/mole and 7 kcal/mole respectively. The above limits refer to the rotational excitation of KI and do not include any excitation of \(\text{CH}_3\). Since the small moment of inertia of the \(\text{CH}_3\) radical enables it to carry away large amounts of rotational energy with relatively low angular momentum
(e.g., 10 kcal/mole for $J_3 = 20 \hbar$, in contrast to KI, which has only 1.7 kcal/mole for $J_4 = 100 \hbar$), the observation that in reactions involving larger R groups the internal excitation does not decrease (but, rather, increases somewhat) suggests that CH$_3$ must have little rotational momentum. 34

The calculations of Bunker and Blaise, 32 on the other hand (see Sec. V), suggest that the final orbital angular momentum, L', is zero and that all the angular momentum appears as rotation of the KI molecule. As was shown in Sec. IV. C. 1, the results to be expected from $J' \gg L'$, with L' distributed uniformly over part of the $4\pi$ steradians, and from $L' \gg J'$ are both in agreement with the experimental data.
V. DISCUSSION

Some evidence for the products of exothermic reactions of the type

\[ A + BC \rightarrow AB + C \]

being in highly excited internal-energy states has been obtained from chemiluminescence and flash photolysis. M. Polanyi and co-workers\textsuperscript{35} inferred that the process

\[ X + N_2 \rightarrow NaX^* + Na \]

led to NaX molecules containing 50% to 90% of the heat of reaction as vibrational energy. Direct evidence for the formation of vibrationally excited products in reactions of the type

\[ A + BCD \rightarrow AB^* + CD \]

has been obtained by flash photolysis followed by absorption spectroscopy. These and other similar studies have recently been reviewed by Basco and Norrish\textsuperscript{36} and by Polanyi.\textsuperscript{35} In contrast to chemiluminescence and flash photolysis experiments which deal with steady-state distributions, beam experiments give information about the mechanics of the single reactive collision event.

For all the reactions studied in this research, the average relative translational energy of the products inferred from their angular distribution is from one to less than nine times that of the reactants. Thus, roughly 75% to 100% of the energy of reaction appears as internal excitation. The experimental results offer no information about the partitioning of this energy among various degrees of freedom, but presumably it is largely present as vibration of the newly formed bond.

The calculations of Bunker and Blaise\textsuperscript{32} (see Sec. II) indicate that a high level of product excitation is caused by a potential surface constructed so that most of the fall in potential energy is associated with attraction between the reactants as earlier suggested by Evans and Polanyi,\textsuperscript{37} and not repulsion between the products. The predicted angular distribution in the plane, \(d\sigma/d\chi\), falls off roughly linearly from
a maximum near $\chi = 0$ deg to a value about one-tenth the maximum at $\chi = 180$ deg. This leads to an angular distribution that is strongly peaked about the relative-velocity vector and asymmetric about $\chi = 90$ deg when $d\sigma/d\chi$ is averaged over azimuthal angles. Their calculations involved a hard-sphere repulsion between K and CH$_3$. Increasing the radius of this sphere caused the peaking to become more pronounced at $\chi = 0$ deg. They also tentatively conclude from their calculations that the angular distribution of products is not very sensitive to the form of the potential surface. That is, a surface which emphasizes attraction between the reactants and one which emphasizes repulsion between the products both lead to peaking at $\chi = 0$ deg. However, if the collisions are restricted to those with impact parameters, $b$, equal to zero, the reaction trajectory becomes very complicated and the KI distribution becomes peaked near $\chi = 90$ deg.

The experimentally observed asymmetric peaking of the angular distribution along the direction of the initial relative-velocity vector implies a reaction mechanism with specific properties. The lack of symmetry about $\chi = 90$ deg shows that the decomposition of the collision complex cannot be regarded as independent of its manner of formation (as in the compound nucleus model of nuclear reactions$^{31}$). The suppression of $\chi = 180$ deg scattering must be attributed to an anisotropy in the planar cross-section $d\sigma/d\chi$. Scattering near $\chi = 0$ deg evidently corresponds to a "hard" collision rather than a "grazing" one, as the K atom, the R group, and the center of mass of K and I must all reverse direction. The picture suggested by the asymmetry is that the complex decomposes before it can rotate through a half turn. As the rotational velocities estimated from Eq. (2-12) are very high, roughly half of the complexes would have to decompose within about $10^{-12}$ sec, a time not much longer than a vibrational period.
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APPENDICES

A. Suppliers and Manufacturers

1. Chemicals
   a. Potassium supplied by A. D. MacKay Company
      198 Broadway
      New York, New York
   b. Organic Chemicals – Eastman Organic Chemicals
      Eastman Kodak Company
      Rochester, New York

2. Vacuum Equipment
   a. Mechanical Pumps – Model No. KC 5 and KC 8
      Kinney Manufacturing Division
      New York Air Brake Company
      Boston, Massachusetts
   b. Diffusion Pumps
      (1) 4-in. Booster Pump; Model 900-150-1
      F. J. Stokes Corporation
      Philadelphia, Pennsylvania
      (2) 6-in. Main Pump; Model No. PMC 1440
      Consolidated Vacuum Corporation
      Rochester, New York
   c. Vacuum Valves
      Ball valves, type 2, size 415B
      Worcester ball valve
      Consolidated Vacuum Corporation
      Rochester, New York
2. Vacuum Equipment - continued

d. Vacuum Gages and Power Supplies

   (1) Thermocouple vacuum tube DV-3M
       Haystings - Raydist, Inc.
       Hampton, Virginia

   (2) Thermocouple power supply
       UCRL 5Z4994-3X8565
       Lawrence Radiation Laboratory
       Berkeley, California

   (3) Ionization gage and power supply
       Type RG-21A
       Veeco Company
       New Hyde Park
       Long Island, New York

3. Detector

   a. Filaments
      (1) Undoped W filament - Westinghouse Corporation
      (2) Alloy No. 479 (92% Pt and 8% W) - Sigmond Cohn Company

   b. Vibrating Reed Electrometer
      Cary Model 31
      Applied Physics Corp.
      Monrovia, California

   c. Recorder
      Speedomax Type G
      Leeds and Northrup Company
      Philadelphia, Pennsylvania

4. Oven Power Supplies

   a. Voltage Regulator
      Stabiline Type 1E5105RP
      Superior Electric Company
      Bristol, Connecticut
4. Oven Power Supplies - continued

b. K-Oven Supplies

(1) Upper chamber
UCRL 2X7273-3X8995-0142
Lawrence Radiation Laboratory
Berkeley, California

(2) Lower chamber
UCRL 2X7273-3X8995-0242
Lawrence Radiation Laboratory
Berkeley, California

c. Gas-Oven Supply

UCRL 3X8981
Lawrence Radiation Laboratory
Berkeley, California

5. Thermocouple Temperature Meters

a. K Oven, both chambers
Wheelco Capacitrol Model 241
Chicago, Illinois

b. Gas Oven
Sym-Ply-Trol RE-1 411-805
Assembly Products Inc.
Chesterland, Ohio
B. IBM 7090 Computer Program

The computer program calculates the laboratory angular distribution of the products \( m_3 \) and \( m_4 \) from any reaction of the type

\[
m_1 + m_2 \rightarrow m_3 + m_4,
\]

(B-1)
given the initial conditions (masses, beam temperatures, etc.) and the center-of-mass distribution of \( m_3 \). By reading into the computer suitable input data (described below), the Maxwellian distribution of velocities in the beams of reactants is also taken into account in the calculation.

The average over the velocity distributions of the reactants is accomplished with a set of angles read into the program as data. These angles (called AXI in the program) correspond to the various desired orientations of \( \mathbf{v} \) (the initial relative-velocity vector) with respect to \( \mathbf{v}_1 \) (the \( K \) velocity vector). A method of determining a satisfactory AXI set is as follows:

(a) Calculate the most probable velocities for molecules \( m_1 \) and \( m_2 \), \( a_1 \) and \( a_2 \), respectively.
(b) Calculate the magnitude of the relative-velocity vector, \( v \), for a collision between molecules having the most probable velocity.
(c) Find AXI max (resultant angle when \( v_2 = 2.2a_2 \)) and AXI min [resultant angle when \( v_2 = 0.2a_2 \) and \( v \) is as calculated in step (b) above].
(d) The set of AXI to be used should run between AXI min and AXI max in increments of one degree.

If values of \( E \) are to be used that are significantly different from the \( v \) calculated in step (b), it may be necessary to use a set of AXI covering a different angular range.

For each set of data the values of \( \theta \) resulting from all possible combinations of \( \chi \), \( Q \), \( E \), and AXI are calculated. For each such \( \theta \) the Boltzmann probability for the combination of \( v \) and AXI (\( v_1 \) and \( v_2 \)) that led to that \( \theta \) is stored in the \( \theta \) cell containing that \( \theta \). At the completion of the calculations for a given set of data, the contents of the \( \theta \) cells are normalized so that the maximum cell content is 99.
The output from the computer is a plot of $m_3$ and $m_4$ product-intensity vs $\theta$. The resolution in $\theta$ in the print-out and the size of the $\theta$ cells used during the calculation are equal and are determined by the operator. The length of time required for an average calculation is approximately five minutes.
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