ODIORNE, Truman J, 1944-
ENERGY DEPENDENCE OF A SIMPLE REACTION.

Rice University, Ph.D., 1971
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan
RICE UNIVERSITY

Energy Dependence of a Simple Reaction

by

Truman J Odlorne

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Ph. D.

Thesis Director's Signature:

Philip R. Brook

Houston, Texas 77001

May 1971
Please Note:

Some pages have very light type. Filmed as received.

University Microfilms.
ABSTRACT

Energy Dependence of a Simple Reaction

by

Truman J Odiorne

The reaction K + HCl → KCl + H has been studied using the crossed molecular beam technique. The reaction was investigated both for HCl \((v=0)\) and HCl* \((v=1)\). The K and HCl beams were formed by thermal effusion from 600°K and 300°K sources respectively. The product KCl was detected by differential surface ionization. The HCl* was produced by excitation of the HCl beam with the output from an HCl laser. This was a pulsed, flash photolysed, chemical laser utilizing the reaction HI + Cl₂ → HCl + I₂. The angular distribution of KCl and the reaction cross section for both reactions were measured.

The cross section for K + HCl was found to be \(0.15 \pm 0.03 \text{ Å}^2\). Because of the confinement of the product to be very near the center-of-mass little could be determined from the angular distribution. However, the low reactivity suggests a barrier to reaction (for the reaction \(\Delta E = +1.5 \pm .4 \text{ kpm. from thermochemical data}\) and two calculations were carried out to investigate the nature of this barrier. One of these investigated the centroid distribution and the other studied the role of angular momentum.

The reaction cross section for K + HCl* was found to be \(\sim 20 \text{ Å}^2\). This large increase in reactivity is in accord with other experimental
results and with theoretical calculations which suggest that vibrational energy should be especially effective for enhancing the reactivity of an endoergic reaction. In further agreement with these other works is the indication that a majority of the energy from the reaction goes into translation of the product.
ACKNOWLEDGEMENTS

I would like to thank the personnel of the machine shop, the electronics shop, and the glass shop for their work and patience.

Financial support for the thesis work was provided by The Robert A. Welch Foundation and by the United States Atomic Energy Commission and their assistance is gratefully acknowledged.

Also, I would like to thank my laboratory associates for their help and assistance. In particular, I express my appreciation to Professor Brooks without whose guidance and encouragement this work would certainly never have been completed.

For encouragement and moral support, I am in debt to my parents. And finally I wish to thank my wife, Ollive, for her help, her support, and her constant confidence in me.
FIGURES

1. Newton Diagram for K + HCl$_{(v=2)}$..........................9
2. Collision of Two Particles..................................12
3. Schematic of Molecular Beam Apparatus..................20
4. Picture of Molecular Beam Apparatus......................21
5. Schematic of Vacuum Pumping System......................24
6. Picture of K Detector .....................................26
7. Picture of Main Detector Location.........................26
8. Picture of K Oven Chamber..................................27
9. Picture of K Oven...........................................27
10. Picture of Gas Oven.........................................31
11. Schematic of Gas Collimator...............................33
12. Picture of Surface Ionization Detector..................36
13. Picture of Rotating Lid....................................36
14. Schematic of Rotating Lid Assembly.....................38
15. Picture of Main Detector Box...............................39
16. Schematic of Glass Rack..................................41
17. Schematic of Laser System.................................45
18. Electronic Schematic for Laser............................48
19. Detection Electronics for D.C. Signal....................52
20. Detection Electronics for Pulsed Signal................53
21. Timing Sequence for Counting Operation................66
22. Data from Single Run of K + HCl.........................75
23. Angular Distribution of KCl...............................76
24. Newton Diagram for K + HCl........................................77
25. Calculation results for the Cross Section of K + HCl..........................85
26. Distribution of Centroids.................................................91
27. Effect Parameter from Excitation.....................................94
28. Angular Distribution of Effect..........................................97
29. Angular Distribution of KCl from HCl*..............................99
30. Trajectory Calculation Results.........................................104
TABLES

1. Typical Scattering Sizes.................................11
2. Results from This Work..................................72
CONTENTS

Acknowledgements.................................i

Figures............................................i1

Tables.............................................iv

I. Introduction.....................................1

II. Collision Mechanics...........................5
   A. Data Representation.........................5
   B. Collisions..................................11
   C. Reactive Scattering.........................14

III. Experimental and Apparatus................19
   A. High Vacuum Beam System................19
      1. Chambers..................................19
      2. Pumping....................................23
      3. Control Box...............................25
      4. Potassium Beam............................25
      5. Gas Oven..................................30
      6. Beam Detection............................34
   B. Gas Handling System.......................40
      1. Secondary Beam Gas......................40
      2. Laser Gas................................42
      3. Pumping...................................43
   C. The Laser....................................43
1. Housing..............................................44
2. Gas Connections.................................44
3. Electronics....................................47
4. Optics............................................49

D. General Electronics.............................50
   1. Initial Detection.............................50
   2. Detection of D.C. Signal....................51
   3. Detection of Counted Pulse...............51
   4. General Support Equipment...............55

IV. Procedures......................................56
   A. Filament Preparation.......................56
      1. General.....................................56
      2. Tungsten Filament.......................56
      3. Platinum Filament.......................58
   B. Formation of the Gas Beam................59
   C. Formation of the Potassium Beam........59
   D. Operation of the Laser....................60
      1. Preliminary...............................60
      2. Optics....................................60
      3. Gas.......................................60
      4. Electronics..............................61
      5. Gas Cell..................................61
   E. Data Acquisition............................62
      1. D.C. Signal...............................62
      2. Pulsed Signal.............................65
   F. Shut Down....................................70

V. Data and Results...............................71
I. INTRODUCTION

If the field of chemistry is the study of chemicals (molecules and atoms) and the reactions they undergo, then physical chemistry is the study of the exact nature of these chemicals and the way in which they react.

When early chemists marveled at the new substances they could produce by mixing, heating, stirring, or otherwise, many other chemists wondered as to what was happening as a result of these stimuli. One of the earlier successful attempts to correlate reaction and stimulus was the empirical formula given by Hood (HO0 78).

\[ \log k = B - A'/T \]

where \( A' \) and \( B \) are constants, \( k \) the rate constant for the reaction and \( T \) the temperature. In 1884 van't Hoff (VAN 84) published his law stating the dependence of the equilibrium constant on temperature. Arrhenius (ARR 89) applied van't Hoff's argument for the equilibrium constant to the rate constant in each direction separately (since this establishes the equilibrium) and found,

\[ \frac{d \ln k}{dT} = \frac{E}{RT^2} \]

which upon integration yielded,

\[ k = A \exp \left( -\frac{E}{RT} \right) \]

In arriving at this expression the term \( E \) was considered a constant. Arrhenius showed that a number of reactions well known at that time did indeed fit this derived equation. This is perhaps the most significant single result in the study of stimulus on the rate of reaction and was
definitely the most significant at the time of development.

This equation not only contains the strong dependence of the rate constant on the temperature but also an unknown parameter with units of energy. Arrhenius suggested that perhaps the molecules can exist in two states. The first would be the normal energy state indicated by the temperature, and the second would be one occupied by only a few of the molecules having an extra amount of energy and thereby a changed character to reaction. This character change would have an effect on the rate at which the molecule could undergo reaction. This is of course the essence of an "energy barrier". The developments over the next 40 years strengthened the general idea of an energy barrier, especially with the quantum mechanical calculations of London, Eyring, Polanyi, and many others.

The next significant event was the advent of the theory of absolute reaction rates. While the general nature of such a theory was first suggested several years earlier, the first particularly clear statement of this theory was by Eyring (EYR 35) in 1935. This includes a mathematical formulation of the nature of a barrier and the role it plays in the reaction. This theory (LAI 65) presents the reaction as developing from an infinite amplitude vibration of the bond being broken in the reaction. This has been of the the most successfully applied theories to date.

Concurrent with the development of absolute rate theory was the observation by several investigators that many reactions could be stimulated by the use of light. At one time many chemists supported a "radiation hypothesis" where the extra energy necessary for reaction was gained by the absorption of radiation. Later it was shown, however, that
while this may be the case in some instances, the "radiation hypothesis" did not in general explain reaction behavior.

More recently investigators using chemical accelerators of varying styles have produced reactant molecules having energies many times greater than the 2-4 eV. energy of a typical molecular bond. These energies are helpful for some purposes (i.e., studying the potential energy curve of two species at distances less than the 1-3 Å of a molecular bond) but these are rather specialized. To learn more detail about the exact nature of the potential surface on which the reaction takes place it seems more informative to merely perturb the energetics of the reaction.

Thus it seemed interesting and potentially informative to add to a reaction system a fraction of an eV. of energy, and to add this energy to a particular mode. Furthermore, since absolute rate theory pictured the reaction as occurring through a vibration, increased vibrational energy should be favorable to cleavage of the bond and consequent reaction. For most simple molecules this excitation would amount to a few tenths of an eV. for a change of vibrational levels of 1 or 2 (0.4 eV. for $\Delta v = 1$ in HCl).

In recent years more and more chemical reactions have been studied using the molecular beam technique. This is a very powerful approach leading to information often otherwise unattainable and was first applied successfully to the reaction of K + HBr to yield H + KBr (TAY 55). Due to conveniences in detection much of the work done by this method has been limited to reactions involving the alkali metals. Furthermore, due to some of the problems of intensity of the products of the reactions,
most of the reactions studied have been those involving either very small or non-existent barriers to reaction.

The beam method had been used to study the reaction (among many others) of K and HI. However, attempts to study the reaction of K and HCl were hampered by an inability to directly observe the reaction product, KCl (ACK 64). This latter reaction is endothermic while both of the two previous hydrogen halide reactions with K were exothermic. This endothermicity is very close to the energy generally available in crossed thermal beams for reaction (0.1 - 0.2 eV). However, there is sufficient energy to expect reaction to occur unless there exists some additional energy barrier to reaction.

The purpose of this work was to measure the dependence of the K + HCl reaction cross section on vibrational energy. First the K + HCl (v=0) cross section was to be measured, and hopefully an estimate of any energy barrier beyond the endothermicity of the reaction would be gained. A quantum of vibrational energy would then be introduced and the reaction cross section for K + HCl (v=1) would now be measured. Any enhancement of the reactivity would therefore be directly attributable to the effectiveness of the energy increase in surmounting the energy barrier.
II. COLLISION MECHANICS

This chapter presents some of the mathematical mechanics used for the reduction and interpretation of the raw data resulting from molecular beam experiments. The discussion here will deal exclusively with the reactive scattering from perpendicularly crossed beams. This is not to suggest a lack of development in the mechanics for treating other collision event. Indeed, probably the most sophisticated treatment is that used for elastic scattering data. Treatments of this type are given by Present (PRE 58), Greene, Moursurd, and Ross (GRE 66), Toennies (TOE 68), McDaniel (McDA 64), and many others. However, since only reactive scattering was studied in this work, only the classical mechanics necessary for this will be discussed. The major topics to be considered are the representation of the data, the scattering collision, and the results from reactive scattering.

Data Representation

Let us assume that we have two point particles with masses \( m_1 \) and \( m_2 \) and that they are traveling in the lab with velocities \( v_1 \) and \( v_2 \) respectively. They, of course, intersect perpendicularly. The collision products will have masses \( m_3 \) and \( m_4 \) with velocities \( v_3 \) and \( v_4 \). One of the most effective ways of avoiding the many complications inherent in a given physical situation is to convert to center of mass coordinates. The basic purpose of this transformation is to use a frame of reference which moves with the center of mass (C.M.) of the colliding particles instead of the lab frame of reference.

Conservation of momentum requires that the total momentum be constant throughout the collision process (McDA 64, PRE 58, GoI 50).
\[ m_1v_1 + m_2v_2 = m_3v_3 + m_4v_4 = MV \]  \hspace{1cm} (1)

where

\[ M = m_1 + m_2 = m_3 + m_4 \]  \hspace{1cm} (2)

and

\[ V = (m_1v_1 + m_2v_2)/M \]  \hspace{1cm} (3)

so

\[ V = \text{the center of mass velocity.} \]

The velocity of each beam particle, in the C.M. system, is simply the
lab velocity less the C.M. velocity.

\[ v_1' = v_1 - V \]  \hspace{1cm} (4)

where \( v_1' \) is the velocity of the \( i \)'th particle in the C.M. system and
\( v_1 \) is the velocity in the lab. The relative velocity is defined as

\[ v_r = v_1 - v_2 = v_1' - v_2' \]  \hspace{1cm} (5)

and the reduced mass is defined in the customary manner

\[ m_r = m_1m_2/(m_1 + m_2) \]  \hspace{1cm} (6)

If MV is the C.M. momentum then

\[ 1/2 MV^2 = \text{C.M. energy} = E_{C.M.} \]  \hspace{1cm} (7)

The initial total energy \( E_t \) is

\[ E_t = 1/2 m_1v_1^2 + 1/2 m_2v_2^2 \]  \hspace{1cm} (8)

Conservation of energy requires this also to be constant. The energy
of the two particles in the C.M. system will be the original energy less
the C.M. energy or

\[ e = E_t - E_{C.M.} = 1/2 m_1v_1^2 + 1/2 m_2v_2^2 - 1/2 MV^2 \]  \hspace{1cm} (9)

It can be shown that

\[ e = 1/2 m_r v_r^2 \]  \hspace{1cm} (10)
Because the C.M. momentum and energy are constant throughout the collision, only the relative energy of the two particles is considered during the collision.

Since the C.M. reference frame is moving with the total momentum of the two particles, their total relative momentum must be zero.

\[
m_1 \dot{v}_1 + m_2 \dot{v}_2 = m_3 \dot{v}_3 + m_4 \dot{v}_4 = 0
\]  
(11)

Or,

\[
m_1 \dot{v}_1 = - m_2 \dot{v}_2
\]  
(12.a)

and

\[
m_3 \dot{v}_3 = - m_4 \dot{v}_4
\]  
(12.b)

Let

\[
m_r = m_3 m_4 / M
\]  
(13)

and

\[
\dot{v}_r = \dot{v}_3 - \dot{v}_4
\]  
(14)

then

\[
e = 1/2 m_r \dot{v}_r^2
\]

which yields

\[
(v_3 - v_4)^2 = e / (1/2 m_r)
\]  
(15)

then

\[
\dot{v}_3 = \left[ \frac{2 m_4 e}{m_3 M} \right]^{1/2}
\]  
(16)

This, however, is not an accurate description of most reactive collisions. Molecules and atoms are not point particles and we must consider some of their properties in greater detail. It was stated earlier that the energy was constant throughout the collision, but at the time only translational energy was included. Molecules and atoms have other
forms of energy which must be included since it is the total energy only which is constant. Also there is an energy change upon reaction between the energy zero of the reactants and the products and this must be considered. Using the following definitions,

\[ e = \text{relative initial kinetic energy} \]
\[ I = \text{initial external energy} \]
\[ e' = \text{relative final kinetic energy} \]
\[ I' = \text{final external energy} \]
\[ D = \text{the zero energy change upon reaction} \]

we can express the total energy relation as

\[ T = e + I = e' + I' + D \]  \hspace{1cm} (17)

Now

\[ e' = T - I' - D \]  \hspace{1cm} (18)

and with

\[ W = -(I' + D) \]  \hspace{1cm} (19)

then

\[ e' = T + W \]  \hspace{1cm} (20)

If this is now used for the energy term in Eq. (16), we find

\[ v_3' = \left[ \frac{2m_4}{m_3 m} (T + W) \right]^{1/2} \]  \hspace{1cm} (21)

A graphical method of representing the C.M. transformation is the "Newton diagram". This is shown in Fig. 1. The diagram shown is for the reactive collision of K + HCl to form KCl. The HCl reactant is chosen to be in the second vibrational state. The K velocity is \( 6.5 \times 10^4 \) cm/sec. and the HCl velocity is \( 4.5 \times 10^4 \) cm/sec. The K and HCl velocity vectors, \( v_K \) and \( v_{HCl} \), are perpendicular in the lab system. \( V \) is
Figure 1. Newton Diagram for $K + HCl_{(v=2)}$ with reaction.
calculated according to Eq. (3) and the relative vectors, \( v'_k \) and \( v'_\text{HCl} \), for the C.M. system are shown. The relative velocity vector calculated from Eq. (6) is shown to be just the combined lengths of \( v'_k \) and \( v'_\text{HCl} \). Finally the maximum magnitude of the KCl product velocity vector, \( v'_{\text{KCl}} \), is indicated by the dashed line. This was found by the use of Eq. (21). Unfortunately this equation depends on the quantity \( W \) for determining the velocity \( v'_3 \). Since \( W \) (a measure of the energy partitioning between internal and translational modes in the product) is unknown before the experiment, Eq. (21) can only be evaluated for chosen values of \( W \). A particularly useful choice of \( W \) is the one which yields a maximum limiting value for \( v'_3 \) corresponding to \( I' = 0 \). This is indicated in Fig. 1. Furthermore Eq. (21) is incapable of suggesting the direction of the product relative velocity vector and consequently it could be scattered in any direction from the scattering center. This would include a full \( 2\pi \) steradians of solid angle since the product is not confined to the plane of the original beams. The circle in Fig. 1 is a section cut through the sphere whose radius is the maximum size of the \( v'_3 \) vector. Of course it is not the relative velocity vector that is observed in an experiment but the lab product velocity vector \( v'_3 \) which is the vector sum of the relative velocity vector and the C.M. velocity. This would be \( v'_{\text{KCl}} \) in Fig. 1. Because of this vector summation, even though the relative velocity vector may come off with any angle with respect to the \( K \) beam, the lab product velocity vector (the observed product in an experiment) may still be restricted to limited angles. In Fig. 1 the product KCl is limited to the region between \( 12^0 \) and \( 55^0 \).
Collisions

Because the collision (in the C.M. system) takes place in a rather head on fashion along the relative velocity vector, it may be pictured as a projectile--target collision with one particle being the target and the other the projectile. Fig. 2 is a representation of a target--projectile collision.

The primary interest here is how close the projectile must come to the target (or the effective size of the target) to produce the type of collision of interest. We are concerned with reactions and therefore with the reactive size or as it is more commonly called, the reactive cross section, \( Q_r \). The reaction cross section \( Q_r \) is equal to the cross sectional area of a sphere with radius \( b \).

\[
Q_r = \pi b^2
\]  

(22)

The impact parameter, \( b \), is the distance of closest approach between the two particles, if there were absolutely no interaction between them.

The cross section for different types of scattering are different and the impact parameters they correspond to are also different. Typical values are shown in Table 1.

<table>
<thead>
<tr>
<th>Scattering</th>
<th>( Q (\text{A}^2) )</th>
<th>( b (\text{A}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic</td>
<td>500 - 5000</td>
<td>13 - 40</td>
</tr>
<tr>
<td>Inelastic</td>
<td>200 - 2000</td>
<td>8 - 25</td>
</tr>
<tr>
<td>Reactive</td>
<td>10 - 200</td>
<td>1 - 8</td>
</tr>
</tbody>
</table>
Figure 2. Target--projectile representation of scattering.
In order to know the collision cross sections there must be some mechanism for calculating them from the observed data. The most common description of the measurement of the collision cross section is based on the more common measurement of the absorption of light. Here the incident light beam is considered to be the projectile and the medium it travels through, the target. There is a flux of light or projectiles traveling through the target just as in the molecular beam situation there is a flux of atoms or molecules traveling through the target atoms or molecules. The scattering for both cases has been shown to follow Beer's law,

\[ \frac{dI}{I_0} = - n Q dx \]  

(23)

where

\[ I_0 = \text{the initial flux of projectiles before scattering} \]  
\[ (#/cm^2 \text{ sec.}) \]

\[ dI = \text{the loss of projectiles through scattering} \]  
\[ (#/cm^2 \text{ sec.}) \]

\[ n = \text{the number density of the target} (#/cm^3) \]

\[ Q = \text{the cross section for scattering} (cm^2) \]

\[ dx = \text{the length of the scattering path (cm) and the units shown are typical. This equation can be integrated to yield,} \]

\[ \frac{I}{I_0} = \exp(- n Q x) \]  

(24)

where \( I \) is now the final intensity of projectiles, and \( x \) is the length of the scattering path. Rearrangement of this equation with

\[ I' = I_0 - I \]
yields,
\[
\frac{I_0 - I'}{I_0} = \exp(-nQx)
\]
(25)

If \(nQx\) is large with respect to \((nQx)^2\) then the exponential term may be approximated by
\[
1 - \frac{I'}{I_0} = 1 - nQx
\]
or
\[
\frac{I'}{I_0} = nQx
\]
(26)

This equation describes the relation between the cross section and the scattered intensity. It must be pointed out that both \(Q\) and \(I'\) must be for the same particular process.

So far this discussion has considered the perpendicular collision of two mono-energetic beams with specified internal energies. This is unfortunately an idealized situation never found in the lab. Both of the beams are usually formed by thermal effusion from a source and have a modified Maxwell-Boltzman velocity distribution (RAM 56). These velocity distributions can be approximated by the most probable velocity, but this may lead to erroneous predictions based on the Newton diagram and caution must be used. In some cases, one or both of the beams may be velocity selected and this greatly reduces the velocity distribution depending on the exact construction of the velocity selector.

Reactive Scattering

Now we shall consider the application of these collision mechanics to some reactive scattering and shall look at some of the more general results of reactive scattering measurements.
One of the more persistent problems in the analysis of molecular beam reactive scattering results lies in the determination of the product velocity vector. The formal mechanics (Eq. (21) and Eq. (19)) are only able to predict an upper limit on the magnitude of $v_3'$, since the final internal energy is seldom known. The actual size of $v_3'$ is dependent upon the energy partitioning (during reaction) between the internal and translational modes of energy in the products. The more customary way of gaining knowledge as to the energy partitioning in the reaction has been to measure the velocity distribution of the product and then solve for $I'$ in Eq. (19).

Another of the unknown quantities which at present must be determined experimentally is the direction of the $v_3'$ vector. It can be seen that since the direction of the product velocity is unspecified, the conservation laws do not restrict the direction and the particle may scatter into a full sphere. The circle shown in the Newton diagram is only a section cut through this sphere. In some experiments such as $K + HCl (v=0)$ the upper limit given by Eq. (21) is sufficiently small in comparison to the C.M. velocity vector $V$, that the location of the product in lab coordinates is still well known. (This is discussed further in Chap. V. Indeed, for the $K + HCl$ case, the error introduced in approximating the total velocity distribution of the thermal beams by the most probable velocity is much greater than the uncertainty in not knowing the energy partitioning in the products.) Due to the exothermicity of most of the reactions studied by the molecular beam technique, the uncertainty in energy partitioning is a major consideration.

In addition to the angular distribution of reaction products the other measurable quantity of primary interest to investigators has been
the reaction cross section. As pointed out in Table I reaction cross sections typically run from 10 - 200 Å² in size. The upper limit of these are much, much larger than simple viscosity cross sections which are considered to be a measure of the actual physical size of the particles. The size of these cross sections suggests that the future result of the collision (that reaction occur) has already been determined when the particles are still approaching each other from a distance many times larger than the size of the particles themselves.

As early as 1932 Michael Polanyi in his work with "flame" experiments (POL 32) pointed out this extreme reactivity. He states (POL 32), "...reactions take place at least as rapidly, and often at a noticeably greater speed, than that calculated on the supposition that every collision is effective." In using the term "calculated", Polanyi is referring to a calculation using the viscosity cross section to determine the number of collisions.

A description of the details of reactions of this type which has been most successful in explaining the observed cross sections is the "Harpooning Model" (HER 66). The reactions where very large cross sections have been found are those between particles with very low ionization potentials (alkali atoms) and particles with high electron affinities. An example is the reaction of Cs + Br₂ with Q_r ~ 200 Å². The "Harpooning Model" proposes basically that because of the low ionization potential and high electron affinity, an electron may be transferred from the alkali atom to the other particle when the two particles are still at rather large separation distances. Of course the coulombic attraction then present brings the collision partners together to complete the re-action.
A crude description of the electron transfer process predicts the separation distance for transfer to be given by,

\[(e^-)^2/r_t = I(M) - E(X)\]  

(27)

where \(e^-\) is the charge of the electron, \(r_t\) is the transfer distance, \(I(M)\) is the ionization potential of the alkali atom \(M\), and \(E(X)\) is the electron affinity of the collision partner. Since \(I(M)\) is well known the accuracy of the predicted transfer distance \(r_t\) is determined by the accuracy of \(E(X)\) and the accuracy of the description of the process itself. Unfortunately the uncertainty in the appropriate value of \(E(X)\) has precluded any real evaluation of the accuracy of the model itself.

Another study of interest in the interpretation of reaction collisions is the dependence of the cross section upon the collision energy \(e\). This was first done by Greene, Roberts, and Ross (GRE 60) on the \(K + HBr\) reaction. Earlier, Present (PRE 55) had proposed an energy dependence of the form

\[Q_r(e) = b_c(1 - (E_a/e)) \quad e > E_a\]  

(28.a)

\[Q_r(e) = 0 \quad e \leq E_a\]  

(28.b)

This formulation assumed that the reaction partners must approach within a critical distance \(b_c\) for reaction to occur and that for sufficiently small approach distances the potential, \(V(r)\), will become repulsive. The energy of activation \(E_a\) then is equal to the repulsive potential at \(V(b_c)\).

Finally in recent years there has arisen an interest in the angular dependence of the cross section. This effect is present whenever either of the collision partners lacks spherical symmetry. Then the reaction cross section may depend not only on the energy but also on the exact
orientation of one of the particles to the other at the time of the collision. This was first shown by Brooks and Jones (BRO 66) for the K + CH₃I system where they found the cross section to be larger for K colliding with the iodine end of the molecule than with the methyl end. Beuhler, Bernstein, and Kramer (BEU 66) have studied this effect in detail for the Rb + CH₃I reaction.

This brief description of some of the interests in reactive collisions is not even a sampling of all the fields of present investigation and the references cited in this chapter are suggested as a source of both greater breadth and detail.
III. EXPERIMENTAL AND APPARATUS

There were four main groups of experimental apparatus. These were the A) high vacuum beam system, B) vacuum glass rack for gas handling, C) a chemical laser, and D) the general electronics system.

High Vacuum Beam System

1. Chambers The central portion of these four sections was the high vacuum beam system. The basic necessity for a molecular beam apparatus is to eliminate molecular collisions which would cause the individual beam particles to travel in an other than parallel direction and thus not be a beam. This is accomplished by reducing the pressure (i.e., the gas density) in the beam apparatus. Consequently the beam system is operated as a vacuum chamber usually at $10^{-6}$ - $10^{-7}$ torr (mm. Hg). Actually during the course of the work, two separate systems were employed. The more recent of the two will be described here. All of the work on potassium plus excited hydrogen chloride was done in the more recent system (which was constructed during the course of the thesis work). Also, the work reported earlier (ODI 69) was repeated in this system. The two systems were very similar except as pointed out in section 4 of this division. The more recent system will hereafter be referred to as the vacuum beam system.

As shown in Fig. 3 and 4, this system was comprised of three sections: the main reaction and detection chamber, the potassium oven chamber, and the potassium catcher. The fabrication and operation of the system followed generally accepted vacuum techniques for operation in the $10^{-7}$ torr region. These are discussed in several available sources, of which Gutherie (GUT 63) is typical. The main chamber was
Figure 3. Schematic of molecular beam apparatus: a) main chamber, b) K chamber, c) K catcher, d) gas oven, e) K oven, f) main detector, g) guage tube, h) K detector.
Figure 4. Picture of molecular beam apparatus.
constructed from 1.0 cm thick 6061 T6 aluminum plate. The wall plates were machined for an inside dimension of 38 cm x 33 cm x 69 cm with an inside bevel of 15° on all joints to facilitate cleaning and to help eliminate possible virtual leaks. After pre-machining, the plates were commercially cleaned and the joints heli-arced on the outside for a vacuum weld. After welding the box was leak checked, stress relieved, and finally machined with ports and O-ring surfaces to receive flanges. After the chamber was completely machined and after O-ring surfaces were prepared, it was anodized and helicoils inserted into the bolt holes. The anodizing left the O-ring surfaces with a finish much more resistant to scratches. The heli-coils prevented stripping of the tapped holes by the bolts, which happens easily if the bolts are tightened directly into aluminum threads.

The potassium oven chamber was constructed from type 304 stainless steel pipe with 27 cm o.d. x .34 cm wall with flanges welded to each end. From one side of the pipe there was welded a smaller pipe, 6.4 cm o.d. x .32 cm wall, whose axis was perpendicular to the axis of the larger tube. This with a flange welded to the free end then formed a pumping port for a 2" pump. This chamber was bolted directly on to the side of the main chamber.

The potassium catcher was also fabricated from a piece of stainless steel tube, 12 cm o.d. x .5 cm wall. Again suitable end flanges were welded to the ends of the tube which allowed it to be bolted on to a larger side flange and this in turn was bolted onto the side of the main chamber. The catcher and the oven chamber were designed and built by John Langeberg, whose help is appreciated.
2. **Pumping** The vacuum pumping for the system was accomplished by oil diffusion pumps (Fig. 5) and by LN\textsubscript{2} cryopumping. The main chamber was pumped by two nominal 6" oil diffusion pumps with an originally listed speed of 1360 l./sec. purchased from Tri-Metal Vacuum Products, a most unfortunate experience both in purchase and operation. However, they did continue to work after being rebuilt. To reduce backstreaming, the two diffusion pumps were topped off with chilled water cooled chevron baffles which were made in the Department machine shop. They were designed along the general lines of the ambient temperature optical baffles now being offered by various companies. The potassium oven chamber was pumped separately by its own diffusion pump which was a PMCS-2C (104 l./sec.) purchased from C.V.C. and was used without baffling. All three pumps were attached through separate bellows valves to a common foreline equipped with an Edwards Model SVAR8-4 isolation and vent valve. This then was connected to a Welch #1402B mechanical vacuum pump.

In addition to this, the vacuum system was pumped by four LN\textsubscript{2} traps. Gases which have a vapor pressure much less than the pressure inside the chamber (10^{-6} - 10^{-7} torr) at liquid nitrogen temperature (this condition includes most gases) will be condensed on the LN\textsubscript{2} surface and removed from the gas phase. Thus a LN\textsubscript{2} surface is a vacuum pump with a rated speed of approximately 10 l./sec. cm.$^2$ for condensable gases. The traps containing LN\textsubscript{2} are especially useful for condensing the potassium from the gas phase. There was one trap in the potassium catcher which was shaped like a 20 cm thick donut. The catcher trap was (Fig. 6) used to freeze out the entering potassium beam and help eliminate multiple
Figure 5. Schematic of vacuum system A) main chamber B) K oven chamber C) water cooled baffles D) nominal 6" oil diffusion pumps E) nominal 2" oil diffusion F) foreline G) thermocouple gauge tube I) isolation and vent valve W) mechanical vacuum pump.
reflections which increased the background at the main detector. The potassium oven chamber had an LN₂ trap (Fig. 8) from which hung strips of copper ("copper hangers") on all sides except the rear to allow access through the cover flange. In the main chamber there was a large rectangular trap (Fig. 7) hanging 2 cm below the top flange with again "copper hangers" extending down from it. Finally hanging from the rotating lid there was a cylindrical trap with one flattened side onto which the rectangular detector housing was attached by screws. The trapping was primarily for reducing the overall background from scattered potassium because its pumping speed for HCl gas is rather low.

3. Control Box The vacuum control was mounted on the support rack for the chamber. This housed the simple on-off controls for the various pumps and all of the various protection shut down systems. The system was designed for protection against power failure, water failure, loss of vacuum, short circuits, or overheating of the pumps. The electrical power to the instrument racks was also interlocked on this system to protect the electrical components (filaments, heaters, etc.). This control was designed and built by Ken Smith, whose help with it is appreciated.

4. Potassium Beam The oven (Fig. 9) was a 4 cm x 4 cm x 10 cm block of monel with a small snout on it. The oven had a large cavity in the central portion to hold the molten potassium at a given temperature, and a snout portion was heated separately and usually kept 20°C - 50°C hotter than the main body. The potassium gas effused from a slit sealed onto the snout by an annealed copper gasket. The typical size of the the exit hole was 0.0153 cm. Earlier ovens made of stainless steel had
Figure 6. Picture of K beam detector.

Figure 7. Picture of main detector arrangement with LN$_2$ traps, copper hangers, detector box, and gas oven.
Figure 8. Picture of K oven chamber with oven in place.

Figure 9. Picture of K oven showing central will, snout, heaters, and screw holes for attachment of exit slit.
been used, but it was found that the potassium attacked the stainless
leaving a combination of impurities which would plug the small exit hole
in the slit. The attack and resulting loss of beam were well eliminated
by the use of the monel oven. The oven was heated by small tantalum
springs, wound in the lab from .051 cm tantalum wire and insulated with
ceramic tubing (.32 cm o.d. x .025 w.) cut to the proper length. The ends
of the springs were then spot welded to a common nickel lead. The oven
was surrounded by several layers of stainless steel foil. This was used
as a radiation or heat shield to minimize heat loss of the oven to the
LN\textsubscript{2} trap and copper hangers forming a shell around the oven. This is
important because the oven is operated at 600\textdegree K while the LN\textsubscript{2} trap is at
77\textdegree K. The oven with radiation shield is shown in place in Fig. 8.

The oven rested on three peg feet laid out in a triangle. The feet
were placed on a kinematic mount for relocation as described by Strong
(STR 38). Also on the mount platform was the heated slit which was 1.6 cm
in front of the leading edge of the snout. The heated slit was simply a
piece of stainless .254 cm thick spot welded to a heated brass plate with
a coinciding hole in each. The hole in the stainless (.028 cm x .120 cm)
was the defining slit, being appreciably smaller than the other. Midway
between the snout and the heated slit was a copper plate attached to and
suspended from the cold trap. This plate had a hole in it whose center
was on the beam axis. The hole was 1 cm x 1.3 cm and was used to trap or
freeze out some of the excess potassium leaving the oven slit. At the
front of the chamber, next to the wall of the main chamber was still
another LN\textsubscript{2} cooled copper hanger with a hole in it for the beam to pass.
Of course the wall of the main chamber had a hole to admit the potassium
beam and this hole was a little larger than the hole in the copper plate.
Attached to the opposite side of this wall was a cylinder extending out some 5.4 cm. Directly on the opposite side of the reaction chamber was the beam catcher and at the far end of the catcher was the potassium detector used for monitoring the potassium flux of the beam. (The details of the detector will be discussed in section 6 of this division.) The previously described combination of slits yielded a ribbon shaped beam with a vertical divergence of $3.8^\circ$ and a horizontal divergence of $0.5^\circ$. This produced a beam shape at the reaction center of $1.34 \text{ cm} \times 0.214 \text{ cm}$. The potassium beam intensity at the main detector was at a constant maximum for a spread of $3.5^\circ$, leaving this region the intensity dropped two orders of magnitude thru the first two degrees. The potassium was obtained from Mine Safety Appliances Research Corporation as $99.95\%$ pure metal in 5 gm. ampoules under argon and was used directly by simply breaking the ampoule and placing it in the oven.

The only really significant difference between the earlier and final apparatus was in the addition of a small salt oven in the former. This earlier system had a potassium beam system very much similar to the described one, but it also had an extra heated oven system. The second one was located about 7 cm. directly above the primary oven and used to generate a low intensity beam of the salt product of the primary reaction (KCl). The oven was a cube of copper 2.5 cm. on a side. It had a central well the salt was held in and holes were drilled along the side to receive the tantalum spring heaters. A thermocouple was silver soldered on the side and a .15 cm. hole drilled from the face to the well forming an exit channel. The oven was mounted with a thin walled stainless steel tube to minimize heat loss and the oven was directed to produce a beam in the same plane as the two original reactant beams. The oven was
heat shielded and completely enclosed except for a small exit hole which could be opened or closed with a beam flag. The salt beam ran slightly below the reaction center and impinged on the detector arc at $45^\circ$. The beam was so broad that the intensity was essentially constant from 35 to 50 degrees. This eliminated the need to know precisely the detector position when simply reading the salt flux. The salts used were reagent grade, shelf stock potassium chloride, potassium bromide, and potassium iodide. These were used after an initial vacuum bake out in the salt oven.

5. **Gas Oven** The gas for the secondary beam flows into an oven inside the main chamber through a vacuum tight passage and then out into the main chamber as a beam. The oven was unheated because all of the secondary beam reactants had a sufficient vapor pressure at room temperature. This oven will be referred to as the "gas oven".

The gas oven is shown in Fig. 10. It consisted principally of a stainless steel cube with a gas line leading to it, a fitting on the face for a collimator, and adjusting gears and worms.

These gears were attached to the oven for adjustments in either plane and the mating worms were then rotated from the outside of the vacuum chamber by .64 cm. brass shafts with flexible ends to accommodate the necessary motion. The other ends of the shafts ran external to the vacuum and were controlled by standard ten-turn dials. This arrangement allowed for the "aiming" of the beam while operating. The worm-worm gear combination led to a reduction ratio of 80:1 in the vertical plane and 100:1 in the horizontal plane. This combination yielded a resolution of at least $0.05^\circ$ in either plane. The adjustments were designed such that the center of the collimator underwent no displacement except under extreme
Figure 10. Picture of gas oven
movement of the oven, which was not necessary. This meant that the origin of the gas beam never moved, only the direction of its travel.

Fig. 11 shows the detail of the front of the gas oven including the collimator, cover plate, and teflon gasket. The collimator was sealed into the oven body with an O-ring and the output beam shape was defined by the 0.16 cm x 0.90 cm slit cut in the cover plate and teflon gasket. This collimator itself was a glass capillary array purchased from Mosaic Fabrications, Inc. It had a pore diameter of two microns with a pore length (or thickness) of .254 cm. The overall diameter was .95 cm and it had a 50% transparency.

The characteristics of the array were taken from those published by Johnson (JOH 66). A portion of these had been checked in our own lab and found to agree within experimental tolerances, and this particular array was used without further testing. One of the difficulties encountered in the use of these arrays was that the pores were not necessarily perpendicular to either face of the array. This was one of the reasons for building a device which would be adjusted externally.

An ionization gauge tube (which was used as a gas beam detector) was placed at the far end of the box opposite the gas oven. The ionization gauge tube was operated from a commercial controller with the collector output fed into an electrometer. This technique has been described fully elsewhere (JON 69, BRO 69).

The gas oven was aligned by simply admitting some gas into the oven (P ~ 200 μ Hg) and monitoring the signal at the electrometer. The dials were adjusted in an iterative manner to maximize the signal. The gauge tube was located 36.2 cm. from the gas oven.
Figure 11. Gas collimator assembly.
The divergence of the beam leaving the gas oven was calculated using equations given by Johnson, Stair, and Pritchard (JOH 66). This gave a divergence of 0.3°. Measurement of the beam profile suggested a divergence of less than 0.5° (the width of the source and detector limited the sensitivity to this resolution) and so 0.3° was accepted. This divergence yielded a rectangular beam, 0.17 cm. x 0.93 cm., at the reaction zone.

Three gases were studied: methyl iodide, hydrogen bromide and hydrogen chloride. The methyl iodide was reagent grade shelf stock and was used after vacuum degasing. The hydrogen bromide was obtained from a Matheson Gas Products lecture bottle with a stated purity of 99.8% and was used without further purification. The hydrogen chloride was Air Products and Chemicals Inc. electronic grade with a stated purity of 99.9% and was used as received.

6. Beam Detection Each of the two different types of species encountered in the beams required its own type of detector for measuring the beam flux. The detector for the gas beam has been described in the previous section and no further account of it will be given here. The other reactant beam and the product were detected by a different type of detector which will now be described.

This detector was a surface ionization detector. It has been described fully elsewhere (DAT 56A, DAT 56B, KAM 65) and only a brief description will be given here. If an atom with a low ionization potential collides with a surface with a much higher work function, then an electron will be removed from the atom yielding an ion. If, furthermore, the surface is sufficiently hot, the resulting ion will be sublimed from the
surface as a gaseous ion which may then be collected. If the work
function of the surface is appreciably higher than the ionization poten-
tial of the colliding atom, then this process may have a very high
efficiency. For potassium atoms colliding on tungsten at 1600°K the
efficiency is 83% with a difference between the work function and ioni-
zation potential of .31 eV. In the case of a potassium halide molecule
colliding with the surface, it appears that the molecule is first dis-
sociated, and the resulting potassium atom then undergoes the process
just described. If the surface used is platinum instead of tungsten,
only potassium is ionized (with a lower ionization potential) but the
potassium halides are not ionized. (The efficiency is also changed for
the potassium). The detector then should contain a hot filament and a
means of collection of the ions.

The basic mechanical components can be seen in Fig. 12. There was
a filament support which could hold multiple individual filaments, oper-
ating each one individually. The filaments were spot welded to the
common post at one end and at the other end to individual springs which
served as electrical connections and to hold the filaments taut. Also,
there was a plate which collected ions to be detected as a small positive
current, and finally a body to provide overall support and unity. The
filaments used were .0076 cm. in diameter and were heated by passing an
electric current through them from a regulated D.C. power supply. The
electronics are more fully discussed in that section of this chapter.
This type of detector was used as the potassium beam detector in the
potassium catcher and was equipped with two tungsten filaments (one plus
a spare) which would detect potassium and potassium halides. The main
detector used at the reaction center was the same type of detector but
Figure 12. Picture of surface ionization detector.

Figure 13. Picture of rotating lid showing angular readout and feedthroughs.
with some differences and the description of the whole rotating lid assembly (of which the detector was a part) follows.

The rotating lid assembly was made up of three parts: the rotating lid, the trap, and the detector can (Figs. 14 & 7). The rotating lid was an O-ring sealed, rotating, stainless steel table. It had a 14 cm. skirt with angular position readout in $1^\circ$ increments coupled with a x 10 vernier to give $.1^\circ$ resolution on the readout (Fig. 13). The body of the table had a double O-ring groove with pumppout in between. Mounted on the top were two hermetically sealed electrical feedthroughs (Amphenol #67-04H14-5P(105) & #67-04H 14-61P(105) which carry power to the detector box and a Cajon Ultra-Torr fitting for a rotary shaft which also ran to the detector box. The trap was suspended from the center with its axis passing through the reaction center and perpendicular to the plane of the reactant beams. The trap was flattened on one side and had a small block near the bottom which was drilled and tapped for screws. This allowed attachment of the detector box.

The detector box (Fig. 15) contained a movable filament holder (supported by and moved by the rotating shaft) a Bendix 306 magnetic electron multiplier, a collector plate, an exit slit, and a removable entry slit. The two principal differences between this detector and the one just described was that 1) the ions could be collected (and subsequently detected) by either the electron multiplier (e/m) or the collector plate, and 2) the filament holder contained a tungsten (detected potassium and its halides) and a platinum/tungsten alloy (detects only potassium atoms). The tungsten wire was obtained from General Electric through the courtesy of Mr. S. R. Blumberg as high purity, undoped tungsten wire and a length
Figure 14. Schematic of rotating lid assembly. A) lid skirt B) screw holes D) detector box L) lid body P) pumpout R) o-ring grooves S) removable slit T) LN₂ trap.

Figure 15. Picture of inside of detector box showing filaments and e/m.
Figure 15. Picture of inside of detector box showing filaments and e/m.
of single crystal tungsten wire necessary for portions of the work was obtained from Professor J. L. Kinsey at M.I.T. The platinum/tungsten alloy filament (which will hereafter be referred to as the platinum filament) was purchased from Sigmund Cohn Manufacturing Company, Inc. as alloy #479.

Since the detector used more than one filament and the slits allowed only one filament to be in the product beam at any given time, the filament holder had to be moved from side to side. This allowed one of the filaments to "see" the incoming product beam. The holder position was adjusted by the external hand wheel and gear arrangement on the top of the rotating lid. The combination of linkages allowed the filament position to be reproduced to within one quarter of a filament width. This was used when changing from one filament to another.

The Gas Handling System

1. Secondary Beam Gas

The gas handling system (Fig. 16) was a rather awkward, tricky device hereafter referred to fondly as the glass rack. The glass rack served as a central distribution and control facility for the supply of gas to the gas oven and to the laser. The gas supply for the secondary beam needed to be held at a rather constant pressure to eliminate signal drift. It was customary to obtain a constant pressure source of gas by simply holding the liquid in a thermostatic bath. Since there was no convenient bath for a reasonable pressure of HCl, a large volume, low pressure reservoir was used instead. (Low pressure was desirable due to the lack of an adequate leak. The large volume avoided a constant downward drift due to depletion of the gas in
Figure 16. Schematic of glass rack. A) laser manifold including laser and large trap B) secondary gas supply C) central trunk of the rack D) fill port for the reservoir E) needle valve F) oil manometer G) 2" oil diffusion pump H) large reservoir I) connections to trunk J) mechanical vacuum pump.
the reservoir.) The Granville-Phillips (#9100) leak (used for methyl iodide) was unusable because of the corrosive effect of the HCl (and HBr). However, later in the experiment a Heraeus needle valve was obtained which worked well. The HCl for the gas beam was held at 50-100 torr in a 60 l. tank, bled out through a Heraeus-Engelhard Fine Needle Valve and into the gas oven. From the gas oven it passed through the collimator and finally into the reaction chamber. The pressure of the gas going into the gas oven was measured with a Heraeus Diavac Diaphragm Vacuum Gauge.

2. Laser Gas  The other purpose of the glass rack was to handle the gas going to the laser. This involved carrying three gases to two separate systems. One system was the flash lamp which used xenon. This merely required emptying and filling the flash tube occasionally with xenon. The other system was used to supply fresh reactant gas to the actual laser tube; this required the oil manometer, the separate manifolds for the two reactant gases, and the exit tube with a large trap joining back on to the trunk of the glass rack. The HI and the Cl₂ were leaked directly out of the lecture bottle and used. The Cl₂ had a stated purity of 99.5% and the HI a stated purity of 98%. It was found necessary when starting a new bottle of either gas to immerse the bottle in a dry ice-acetone bath and pump on the bottle for quite some time to remove the impurities. The presence of these was indicated by a rise in the pressure on the pump side of the large LN₂ trap at moderate flow rates. This was substantiated by small or no output powers from the laser. Once a Cl₂ bottle was "cleaned up" by this process it was found to remain satisfactory sitting on the shelf until almost empty. On the other hand, the HI left at room temperature was found to continue to presumably decompose
and need cleaning, so it was stored in the dry ice bin and used at room
temperature. The exit trap for the laser was specially built for this
purpose. Over a period of hours (the length of time of a run) a large
quantity of gas, deposited as a solid, was built up in the trap and
could lead to surprising results. On one occasion it exploded! This
solid consisted of HCl, HI, Cl₂, I₂, and during a "clean up" some H₂
could be trapped out in the lattice of the other gases. At normal
throughput rates there was no pressure rise after the first trap with
clean gas and no observed condensation in the second and final trap. The
stopcocks on all portions of the glass rack except the laser reactant gas
manifold were standard pyrex series 7540 high vacuum stopcocks. The laser
reactant gas manifold utilized Kontes O-ring stopcocks. These exhibited
some obvious defects in design but after modification were used with less
trouble than the constant use of grease.

3. Pumping Of course the central necessity for the glass rack
was vacuum pumping. This was done by a Cenco Supenvac OD-25 oil dif-
fusion pump backed by a Welch 1400 mechanical pump. Pressure was measured
with the previously mentioned Heraeus diaphragm gauge or a Hastings Thermo-
couple Gauge with sensing tubes located at various points on the glass
rack.

The Laser

The laser used was designed and built by Professor Jerry Kasper pre-
ently at U.C.L.A., Department of Chemistry. The instrument was built
while Dr. Kasper was working with Dr. Kenneth Pitzer here at Rice. A
similar instrument had been used earlier by Dr. Kasper (KAS 64, KAS 65).
It was a pulsed, flash photolysized, chemical laser. The reactant gases, HI and Cl₂, were allowed to continuously flow through the laser tube which acted also as a reaction chamber. The laser tube was optically coupled to an adjacent flash tube (with aluminum foil) which would initiate reaction. The reaction (by photolysis) produces vibrationally excited HCl which lases down to the ground state. Various portions of the unit are shown in Fig. 17.

1. **Housing**  The optical portion of the laser system was set up on a heavy wooden table. This is completely encased in the large framework of angle iron covered with 20 gauge galvanized steel. This encasement not only provides a cover for the equipment but also helps to eliminate electrical noise generated by the firing of the flash tube from interfering with the operation of the rest of the instruments in the lab.

2. **Gas Connections**  Passing through this covering were four gas lines. One was a .64 cm. copper line coming from the xenon manifold and joined to it by a vacuum fitting. The xenon was controlled by a Nupro bellows valve connected to the flash tube. The other tubes (all glass) were for the flow of laser gas. Two carried gas from the manifolds to the entry of the laser tube where they were allowed to mix and flow down the laser tube. The third formed the exhaust at the lower end of the tube and carried the exhausted gases to the large cold trap. This emptied into the trunk of the glass rack. Due to the spontaneous reaction of the gases it was necessary to use as high a gas flow conductance through the laser tube as possible. This is critical because the spontaneous reaction gives HCl in the ground state and reduces the population inversion on photolysis
Figure 17a. Schematic of laser system.

Diagram showing components labeled as Flash, Mirror, Windows, Laser, HI, Cl₂, and Exhaust.
Figure 17b. Picture of laser and housing.

Figure 17c. Picture of laser cavity.
and consequent power of the laser.

3. **Electronics** The laser was pumped by a xenon flash lamp. The electronics (Fig. 18) for this were a high voltage transformer supplying up to 19 kv., appropriate rectifiers, a high voltage capacitor, and finally a high voltage switch. The line voltage to the transformer was controlled by relays and a variac. The transformer then fed the diode and resistor string, and they in turn fed into the discharge capacitor. When the comparator sensed the set voltage on the capacitor, it triggered the line control to shut down and started the time delay. At the end of the delay time (0.1 - 4.0 sec.) the timer pulsed the ignitron trigger unit and the high voltage pulser. The high voltage pulser was basically an E.G. & G. TR-69 high voltage pulse transformer which put out a low energy pulse of 50 kv. to initiate high voltage breakdown of the xenon immediately prior to the main discharge. The ignitron trigger unit provided a 2.5 kv. pulse to the trigger of the ignitron which would then discharge the main capacitor through the flash tube. The ignitron was capable of handling the full maximum load of the large working capacitor which was 3 kjoules (15 Mfd. @ 20 kv.) in approximately 1 microsec. or 3,000 Megawatts. The ignitron was a Westinghouse #WL-8306. To simplify data taking and control, the laser also had control facilities at the electronics rack.

Two detectors were used for detection of the laser beam. An older P.E.M. detector was used extensively due to convenience (required no power and was not overly sensitive to light). However, the absolute sensitivity of this detector was unknown and a PbSe detector was purchased from Santa Barbara Research Center with a stated detectivity of
Figure 18. Electronic circuit for laser.
\[ D^* = 2.8 \times 10^8 \text{ cm. Hz}^{1/2} \text{ watt}^{-1} \] and with a blackbody responsivity of \( 5.2 \times 10^2 \). This detector was used as an absolute measure of the output power of the laser and as a standard to normalize the P.E.M. detector.

4. **Optics** The flash tube was a 150 cm. length of quartz tubing with an o.d. of 1.6 cm. and i.d. of 1.4 cm. It was sealed on to electrode fittings at each end by O-ring Swagelok fittings. The fitting at one end had a small hole through which the xenon was carried. These seals were tight to testing by a Helium leak detector, and the flash tube was found to hold a charge (16-18 torr) of xenon sufficiently well to last 2-4 months with light usage and a month with heavy usage. The laser tube was also quartz tubing, 9 cm. o.d. by 7 cm. i.d., and 170 cm. long. Each end was cut at the Brewster angle (30° with respect to the tube axis) on to which a sapphire window was sealed with black wax. Eight cm. from each end there was a side port with an O-ring stopcock for the movement of the lasing gas. Creating the laser cavity were two Perkin-Elmer gold mirrors with maximum reflectivity. They were spherical mirrors of borosilicate glass, 2.5 cm. in diameter, and with a 2 meter radius. The laser tube and the cavity mirrors were all mounted on an Ealing optical bench. The flash and laser tubes were optically coupled by wrapping them with aluminum foil. The take-out of radiation was by means of a take-out window of sapphire mounted on the optical bench between one end of the laser tube and the cavity mirror. This gave both a forward and backward reflected beam. The taken-out portion of the beam in the forward direction was passed through a hole in the housing which could be covered with a filter to block off the shorter wavelength radiation from the flash tube and pass only the longer wavelength radiation such as the HCl radiation
(3.5 microns). The beam, after leaving the housing, traveled over to the vacuum chamber where it was caught by a mirror system and directed through a sapphire window into the vacuum box and there crossed the molecular HCl beam.

General Electronics

1. Initial Detection  A description has been given previously (in section 6 of the division describing the high vacuum beam system) of the surface ionization detector. For this detector to operate, the surface used for ionization must be heated. The heating was by resistance of the filament. The current was supplied by a Sorensen QRS 15-2 power supply for both the potassium and main detectors. This was a .01% regulation supply. In the potassium detector the filament was biased + 45 volts with respect to ground to drive the ions over to the collector. The voltage is provided by a fixed voltage power supply purchased from acdc. These controls were all brought in through (Fig. 6) a ten conductor hermetically sealed connector from Amphenol. The collector current of the potassium detector was taken out through a single conductor Amphenol M.H.V. connector. External to the vacuum chamber the collector current was carried by a low noise Amphenol cable #21-537. When the main detector was operated in the collector configuration it was also operated this way. When the main detector was operated with the electron multiplier, e/m, the filament was grounded due to the high voltage on the front of the e/m next to it. The high voltage operating power for the e/m was obtained from a Fluke power supply #405B and controlled by the e/m control circuit. It was brought in to the vacuum chamber through one of the two
hermetic connectors on the rotating lid and from there run to the e/m. The ions were reflected from the forward surface of the filament and thus the e/m, a Bendix M.E.M. #306, was positioned to detect the re- flected ions. This unit was found to be fairly good for the purpose except for a very broad distribution of pulse heights from the output apparently dependent on the exact position of entrance of the incoming ion (BAR 64). This gave a negative output pulse for each incoming ion with a charge gain under normal operating conditions of $10^5$-$10^6$.

2. Detection of D. C. Signal When using simply the collector configuration (Fig. 19) the signal was a D.C. current which was combined with a zero supression circuit and fed into a Keithly #610BR Electrometer. The output from the Keithley was then used to drive an L&N Speedomax W to record the signal. The current from the potassium detector was run directly into a Boonton Model 95A DC Meter and measured. The e/m was not used at all in the measurements taken at the main detector in the original vacuum chamber.

3. Detection of Counted Pulse When the main detector was being operated in the pulse counting mode (Fig. 20), the e/m fed out through a coax hermetic connector to the pre-amp. located just above the rotating lid. All of the counting equipment was from Mech-Tronic Nuclear except the gate generator which was from Ortec. The pre-amp. (#404) had a conversion gain of .45 v./picocoulomb. This fed into and was powered from the main shaping amplifier (#501). The amplifier was used with a .2 microsec. clipping and integrating time constant. Because of the rather high count rates at some angles, the pulses were kept as narrow as possible to minimize dead time. The gain was set to give the maximum
Figure 20. Detection circuit for counting pulsed signal.
signal at a given e/m gain but never more than X500 and usually about X200.

From the main amplifier the signal went to an integral discriminator, (#604), with the output finally going into the scalers (#703). When data had been collected these were printed out on an ASR 33 Teletype by the #801 Teletype Interface.

The scalers were gated on and off by signals originating at the time of the laser pulse. The flash detector located in the laser housing triggered a triple pulser at the instrument rack. The first pulse out of the pulser was an immediate one and was followed by a second a set time later (usually 1.25 millisecond.), both being fed into the Ortec Gate and Delay Generator #416-S. The third pulse exited from a separate connector and went into the input of the third scaler where it was counted. This third pulse occurred an independently set time after the second pulse (1.5 millisecond.). The Ortec 416-S after receiving each pulse in, delayed a set time and then sent out a set length pulse for gating, which gated on one or the other of the #703's. Because the gating pulse for each scaler came from the same generating circuit it was expected the length of time "on" for each scaler should be identical. This was checked and found to be the case within 10 ppm. The gate pulses after leaving the generator were put through a gate router and finally went to each of the scalers. The #705 scaler counting the laser pulses was a pre-set type shutting the laser and counting system down after reaching the pre-set number of laser shots. This would also cause the data to be printed on the Teletype. All of the NIM modules were housed and powered by two Mech-Tronics NIM bins.
4. General Support Equipment  In addition to the preceding equipment, there were other necessary pieces. The snout of the potassium oven was heated by a variac and the body temperature was controlled by a Gardsman temperature controller. The slit was heated by a small un-regulated D.C. supply. The beam flag was opened and closed by a low voltage D.C. power supply. The pressure was measured with a Granville-Phillips model 236 and an N.R.C. model 831 Ionization Gauge Controller operating standard Bayard-Albert gauge tubes.
IV. PROCEDURES

Unfortunately the apparatus described in Chapter III was not as computer automated as some that have appeared in laboratories recently, consequently a rather large amount of running procedures were necessary to have the machine print out the data desired. This chapter will describe the operation of the equipment in the manner required for obtaining meaningful data (and in some instances not so meaningful data). The presentation will be in a general chronological order. An experiment consisted of preparation of the filaments, formation of the gas beam, formation of the K beam, operation of the laser, data taking, and shut down.

Filament Preparation

1. General The first preparation for running was the mechanical arrangement of the components inside the vacuum chamber and then pumping the chambers down to operating pressure. This pump down time was usually 3-4 days. Normally the pressure at this time would be $0.5 - 1.0 \times 10^{-6}$ torr and with the filling of the LN$_2$ traps the pressure would be reduced to $4 - 8 \times 10^{-8}$ torr. At this time the first step was to start ageing the filament(s).

2. Tungsten Filament The tungsten filaments required an initial ageing procedure to put them in the correct condition for beam detection. This also served to remove much of the impurities from near the surface, thereby reducing the noise and overall background. If the filament had not been used before then this required a full ageing treatment, which was to heat the filament to $2400^0\text{K (}.95 \text{ Amp.) for 24 hours, 2600^0\text{K (1.09 Amp.) for 1 hour, and finally to 2800^0\text{K (1.23 Amp.) for 0.25 hour. At the end of this ageing procedure the temperature was lowered to the}}$
operating temperature and the filament used. The temperatures for the filament were based upon the values given in the Jones-Langmuir tables (JON 27) for the current passing through the .0075 cm. diameter filament. If the filament had been used before (since being installed in the detector) then it was operated at 2000\(^{0}\)K for 2-3 hours, and then at 2400\(^{0}\)K for 1 hour after which the temperature was reduced to the operating temperature.

There were two operating temperatures used for the tungsten filament. When measuring the ground state HCl reaction or the reaction of either of the other two gasses used, the operating temperature was 1600\(^{0}\)K. This temperature is very convenient because the ionization efficiency is not particularly sensitive to the temperature in this region (DAT 56A), the background coming from the impurities within the filament is fairly low, and the filament has a rather long operating life. When trying to detect the products of the reaction of excited HCl it was necessary to run the filament at an elevated temperature.

As was described in Chapter III the method of detection of the product from the reaction of excited HCl was to turn on the counting scalers only when the reaction product arrived at the detector and at no other time. The timing sequence then was of upmost importance if one was to accurately measure the product intensity. One of the difficulties encountered was that the ionization which takes place on the surface of the filament is not instantaneous. At the normal temperature of 1600\(^{0}\)K (.45 Amp.) the residence time was hundreds of microseconds compared to timing sequence requirements of a few microseconds. More important, because this residence time is energy dependent, there was a range of residence time. This would add to the smearing out of the arrival of the
product already inherent in using a thermal beam with its velocity dis-
tribution. Although very little reliable data is available on residence
times for ionization of KCl (BUL 51, KNA 48, STA 49), it appeared that
the residence time could be reduced to merely several (10-30) micro-
seconds with probably a comparable narrowing of the distribution by
raising the temperature to 2000°K. After measuring the effect of tem-
perature on the background from the filament, 2000°K was then adopted as
the operating temperature when operating a timing sequence. It should
also be noted that a decrease in temperature caused a loss of signal
during an actual experiment.

3. **Platinum Filament** As was mentioned earlier the filament
referred to as the platinum filament is actually an alloy of 92% platinum
and 8% tungsten. The tungsten principally helps prevent melting of the
filament since platinum's melting point is low (2050°K). This filament
also required a conditioning procedure. The one used was that of Touw
and Trischka (TOU 63). This calls for heating of the filament for 1
minute in an environment of 1 - 3 x 10^-4 torr of methane at 2000°K
(.35 Amp.) and reducing the temperature to 1570°K (.2 Amp.) for operation.
After the temperature has been reduced the chamber may be evacuated.
This renders the filament sensitive to K but not to KCl, KBr, or
KI.

Again when operating the electronics in the timing mode the filament
was operated at an increased temperature (~ 1900°K) to minimize residence
time. Unfortunately this led to a much greater increase in background
than in the case of the tungsten filament, and thus to overall poorer data.
Formation of the Gas Beam

The formation of the gas beam was a relatively simple matter. Gas was allowed to pass from the reservoir at the glass rack through the needle valve to the gas oven where it effused into the chamber to form the beam. The pressure at the gas oven was 7 torr, 3 torr and 0.6 torr for CH$_3$I, HBr, and HCl respectively for typical conditions. This gas oven pressure gave a main chamber pressure of from $1.5 - 5.0 \times 10^{-6}$ torr and a flux of $10^{18}$/cm$^2$ sec. at the source. One of the main reasons for formation of the gas beam early in the experiment was that in the case of HCl and HBr which are partially pumped by the LN$_2$ trapping, steady state was slowly approached.

Formation of the Potassium Beam

Formation of the K beam amounted to heating the K oven. This was generally started some 24 hours before the run was to begin. It had been found helpful to simmer the K in the oven at 350 - 400$^\circ$K before running. The reason for this was not well defined but it seemed to reduce plugging of the slit, and lead to a steadier beam. Once the gas beam had reached a steady state condition, the heated slit was turned on and heated to 170$^\circ$C requiring 20 watts of power. The snout and oven temperatures were raised gradually to 350$^\circ$C and 305$^\circ$C respectively. The snout dissipated 70 watts and the oven 30 watts. This temperature produced a current of $3 - 4 \times 10^{-9}$ Amp. at the K detector ($10^{13}$/cm$^2$ sec. at the reaction zone) unattenuated. The normal gas beams caused attenuations of the K beam of 20 - 30%. Stabilization of the K beam required 30 minutes after gaining the desired intensity.
Although the K beam was formed after the gas beam in most cases, sometimes the opposite order was used so as to accurately know the K intensity unattenuated. This is essential for the calculation of the cross section. This was not the preferred order because the finite lifetime (customarily 6 hours) of the K beam versus the much longer lifetime of the gas beam.

Operation of the Laser

1. **Preliminary** The previous chapter mentioned that the gases for use in the laser had to be "cleaned up" prior to usage. This was always done a day or two in advance when a new lecture bottle was started and then done again before every run. In addition the flash tube was checked for the lowest voltage at which it would fire since this provided a measure of the purity of the xenon. If the xenon would not discharge below 4.5 kV. then it was replaced.

2. **Optics** Shortly before running, the laser mirrors and tube alignment were rechecked and the alignment to the vacuum chambers, the detector, and through the gas sample cell was all checked. This was done with a small HeNe laser.

3. **Gas** After the gas lecture bottles were well degased the HI needle valve was adjusted for 0.7 cm of oil pressure at the manometer and the Cl$_2$ valve was adjusted for 5 cm of oil total pressure. A higher pressure, with the same ratio of reactants, had been used earlier with moderate output powers (millijoules) but this had been found to give very small amounts of the 1 - 0 transition that is necessary for excitation of the ground state molecular beam. This had been corrected by increasing the flow conductance of the total flow system from the point of mixing
of the two gases to the exit trap where they are pumped and by keeping
the concentration of the reactant gases low. This did not appreciably
affect the total power output. It did change the ratio of usable power
\( v = 1 - v = 0 \) to total power from approximately 0% to about 50-70%.

4. **Electronics**  
After all of these parameters were adjusted the
various electronic components were turned on, the flash voltage set
(6-7 kV.) and the laser was test fired. It was operable in either a
continuously pulsed mode or a single shot mode. In the continuously
pulsed mode the system could be controlled either from the general con-
trol console or at the laser itself. The output from the PEM detector
was fed into a Techtronix 555 oscilloscope. If the output pulse appeared
normal (.2 - .4 millijoule), then the exact intensity of the total power
and of the 1 - 0 transition was measured by the absorption cell.

5. **Gas Cell**  
The total power of the laser was measured by inte-
gration of a photograph of the output trace from the scope. The power
of the 1 - 0 transition was measured by the use of an I.R. gas sample
cell. The attenuation of the laser beam by the empty cell was first
measured and then the attenuation by the cell filled with 3 - 4 torr. of
the HCl used to supply the gas oven. This density of absorbing mole-
cules coupled with the 10 cm path length of the gas sample cell provided
complete attenuation of the 1 - 0 transition line with no effect on the
other output lines. Thus using the empty cell as a correction blank, the
fraction of power in the frequency of interest could be calculated. If
the total power and the power in the 1 - 0 transition were in the normal
range then the laser was used. Practice showed that a failing in
either of these quantities was an indication of a problem. The problem
almost invariably got worse rapidly with time and to try to start a run
without correction of the problem was a fallacy. Some of the typical problems arising were dirty gases, improperly aligned mirrors, leaks in the vacuum line, and having a gas bottle run dry.

Data Acquisition

There were basically two modes of obtaining data. The first was detection of the signal as a simple D. C. current and this was used in the measurement of the angular distribution of the products from the ground state reactions. The second mode was to detect each of the product molecules arriving at the detector as a separate pulse and to count the number of pulses. This was used for the measurement of the angular distribution of KCl from the K and excited (v = 1) HCl reaction and, inadvertently, of the K and ground state HCl reaction on a couple of occasions.

1. D. C. Signal

There were three reactions run by this method. They were:

\[ K + CH_3I \rightarrow CH_3 + KI \]
\[ K + HBr \rightarrow H + KBr \]
\[ K + HCl (v = 0) \rightarrow H + KCl \]

The operating procedure for all three of these was the same and the following explanation will be equally applicable to all three, however, the actual description will be that of the HCl reaction. Of course when any of these reactions were run there was no need for the laser, and data acquisition began after stabilization of the two reactant beams.

Once the two reactant beams had stabilized in intensity the main detector was positioned at 35° (measured from the K beam) with the tungsten filament operating. The zero offset circuit (Fig. 19) was turned on
and the offset adjusted for a sensitivity increase on the electrometer of from 3 to 30. The signal was recorded while the gas beam flag was opened and closed. For the sensitivity used, the flag change produced from 20 - 100% full scale deflections. The detector was then rotated to a new angle and the process repeated. After every fourth new angle the detector was returned to 35° to measure any drift in one or both of the reactant beams. After taking a complete angular scan of the reactive scattering on the tungsten filament, it was turned off (no longer heated). The filament holder was now moved to position the platinum filament in the center of the detector slit system, where the tungsten filament had been positioned. The main chamber pressure was raised to 2 x 10^{-4} torr by admitting methane. The platinum filament conditioning procedure was carried out as described previously in this chapter and the chamber reevacuated. This entire step could be performed without affecting the reactant beams. Once the new filament had been operated for some 15 - 30 minutes the noise and background fell to a level allowing data to be taken. The detector was moved to 35° and the whole procedure just executed with the tungsten was repeated with the platinum filament. This then constituted a full experiment. If this had been accomplished rapidly and the K beam still appeared strong, then this procedure might be repeated or the gas used as the gas beam might be changed and the procedure repeated. Data acquisition never began until at least 11:00 p.m. This seemed to produce a better and more stable signal. The following is a schedule of the times involved in a run. This presumes the filaments and the K oven have been turned on earlier as described previously in this chapter.
p.m. 1:00 Filaments ageing, K oven heating at 150°C, pressure is 0.8 x 10^{-6} torr.

2:30 Put LN2 in all traps. Pressure goes to 0.8 x 10^{-7} torr. Finish filament ageing and reduce temperature to operating point.

4:30 Raise K oven temperature to 200°C.

8:30 Start letting gas into gas oven.

10:30 Gas beam starts to stabilize, increase K intensity (raise temperature of K oven) to 10% of operating.

11:30 Gas beam has stabilized, increase K beam to full intensity.

a.m. 12:10 Start data acquisition.

2:30 Change to platinum filament.

4:30 Finish with platinum filament; decide to redo tungsten data.

4:35 Turn off platinum filament and turn on tungsten to 2500°C.

5:00 Increase to 2600°C.

5:05 Reduce to 1600°C.

5:15 Resume data acquisition on the tungsten filament.

7:30 Finish second run with the tungsten filament, change gas from HCl to HBr.

8:00 Have started beam of HBr. K beam dies.

8:05 Shut down.
As was suggested here the experiment was almost always terminated by a loss of intensity in the K beam. This resulted from three problems: the K oven had simply run out of K, the exit slit on the snout of the oven had plugged, or the K deposited on the LN₂ cooled plate immediately in front of the snout had become large enough to bridge across to the snout. This latter item provided a large heat sink on the snout which cooled it enough for the exit slit to become clogged with K.

2. **Pulsed Signal** This mode of signal handling and detection was used for the measurement of the reactive cross section for

\[ K + HCl (v = 1) \rightarrow H + KCl \]

The electronics used for this are those illustrated in Fig. 20. The description of these are found at the end of Chapter III. The preparations necessary were the same as those for the preceding section on a D. C. Signal except that for this reaction the laser was also used. Thus the laser preparations were involved.

The first step after filament preparation, formation of the two beams, and checking of the laser, was to check the timing sequence of the electronics. This is shown in Fig. 21. The operating voltage was applied to the e/m to produce a gain of \(10^6\), the detector set at a given angle for investigation, and the laser turned on. The laser would fire for the number of times shown on the pre-set scaler, after which the laser would be stopped, and all three scalers printed out on the teletype. After print out, the counting system and the laser would all start again. During print out the beam flag would be closed, and the same number of laser shots would then be counted with the flag closed. This number would usually be between 10 and 40 depending on the drift of the
Figure 21. Timing sequence for counting pulsed signal
signal. This sequence of counting first with the flag open and then with the flag closed was repeated until a total of about 200 shots in either condition was accumulated. This would give a total time on for the signal counting scalers of only 0.12 sec. At this point the angle would be changed and the whole process repeated. Normally only three angles could be run at a time and with only one filament. The power out of the laser both in the total mode and in the l - 0 mode was checked at random times during the experiment with an average time interval of 15 - 20 minutes.

The signal from the main amplifier was fed into the discriminator and into a linear rate meter with the output from the ratemeter being recorded on the L & N Speedomax recorder. This gave a constant visual display of the signal level, the change due to the beam flag, and anything else that might take place. The recorder chart was useful as a real time display only and not as a record.

Since only a fraction of the total data necessary for a total angular distribution of the product could be collected during a run, operating conditions were kept very similar from run to run. This was fairly simple in the case of the K intensity since it meant holding the K oven at the temperature used previously. The adjustment of the HCl beam to the intensity used previously was a little more difficult and this was complicated by the long stabilization time. This was the situation that made formation of the gas beam a preliminary to formation of the K beam. A schedule of these procedures is shown for reference.
p.m.  1:00  Filaments ageing, K oven heating at 150°C, pressure is 0.8 x 10^{-6} torr.

1:30  Put LN₂ in all traps. Pressure goes to 0.6 x 10^{-7} torr. Finish filament ageing and reduce temperature to operating point.

4:30  Start letting gas into gas oven, with rise in main chamber pressure. Raise K oven temperature, start monitoring K intensity.

5:30  Gas beam stabilizing, main chamber pressure at 1.6 x 10^{-6} torr. Oven chamber pressure is 2 x 10^{-7} torr.

8:30  Increase K beam to 10% of final intensity. Start degasing laser gas bottles. Check out laser mirrors and beam alignment.

10:30 Increase K intensity to full running level. Turn on all laser electronics and make connections to scope.

11:00 Let K beam stabilize. Adjust laser gas flow, fire laser, and check power output.

11:45 Check electronics timing sequence. Move detector to position. Recheck laser power.

a.m. 12:15 Start data acquisition.

2:45 Move to new angle. Continue.
4:00  Move to new angle. Continue.

5:15  Signal beginning to show strong downward drift. Gas beam steady, check K beam and find it weakening.

5:30  Shut down.

This was the procedure for actual data acquisition. After reaction of excited molecules was confirmed much time was spent varying such operating parameters as the laser power and the filament temperature. Decreasing the filament temperature caused a loss of signal as has been mentioned.

Changing the flash voltage from 10KV. to 6 KV. (corresponding to a change in laser power of more than a factor of 10) had no effect (greater than statistical fluctuation) on the amount of reaction from excited molecules. The flash voltage could not be lowered below 6 KV. because the laser power became very unstable at the lower flash voltages. Another capacitor (0.5 mfd.) was used for the flash power, but even at the highest voltages used there was no increase in reactively scattered KCl. The calculations done earlier had predicted for this laser energy (0.5 erg.) that the population of the beam in the excited state would be low (10%) and the reaction probably undetectable.

Since it was not possible to detect the excited HCl molecules directly, another procedure was employed as a check on the validity of the excitation process. This consisted of simply starting a run in the normal manner and measuring the increase in reaction signal by excitation. The laser was then detuned (by varying the reactant gas pressure) to eliminate the 1 - 0 transition power while holding the total power approximately constant (less than a 20% decrease). This caused the
signal difference from the two counting scalers to go to 0. The laser
was finally retuned and again a net increase on one scaler was observed.

The gate generator was set to provide a gate "on" pulse (285 µ sec.)
sufficient to collect 75% of the product beam. Because of the velocity
spread a much longer on time would have been necessary to collect more
than this, with a concomitant decrease in S/N ratio.

Shut Down

The gas beam was "turned off" by simply closing a valve. The K
beam was not immediately turned off, but instead the temperature of the
whole oven was gradually lowered keeping the snout hotter than the body
until the temperature was below 200°C. This insured no K in the snout
region in case the slit should be removed later. At this temperature the
heaters were turned off.

The laser electronics were turned off and so was the gas supply.
The HI lecture bottle was returned to the dry ice bin for storage. The
large cold trap that was a part of the laser system was removed and
placed in a fume hood to warm.
V. DATA AND RESULTS

Four reactions were studied.

\[ \text{K + CH}_3\text{I} \rightarrow \text{CH}_3 + \text{KI} \]
\[ \text{K + HBr} \rightarrow \text{H} + \text{KBr} \]
\[ \text{K + HCl} \rightarrow \text{H} + \text{KCl} \]
\[ \text{K + HCl}^* \rightarrow \text{H} + \text{KCl} \quad \text{HCl}^* = \text{HCl}(v=1) \]

The reaction cross sections for these reactions from this work and from the literature are shown in Table 2.

The last two of these were of principal interest and the first two were run primarily as a calibration procedure for the apparatus and the operator. Therefore the results for \( \text{CH}_3\text{I} \) and \( \text{HBr} \) will be considered together.

\( \text{CH}_3\text{I} \) and \( \text{HBr} \)

The \( \text{K + HBr} \) reaction was run in the original apparatus and under the conditions described in an earlier note (ODI 69). The angular distribution of \( \text{KBr} \) reproduced that measured by Taylor and Datz (TAY 55).

In addition to serving as a general check out procedure the \( \text{K + HBr} \) experiment helped develop a method for the determination of the gas beam flux. It is necessary to know the flux and/or density of each of the reactant beams for the calculation of the reaction cross section. The \( \text{K} \) beam intensity is measured by the ion current at the \( \text{K} \) detector. The gas intensity is more difficult to measure since the gas beam detector cannot differentiate between background gas in the vacuum chamber and the gas beam.

The collimator used for the gas beam had a transmission which could
Table 2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Literature</th>
<th>$Q_r(\AA^2)$</th>
<th>$\Delta E$(Kpm)</th>
<th>Detected Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K} + \text{HBr}$</td>
<td>34$^a$</td>
<td>This Work</td>
<td>- 4</td>
<td>K</td>
</tr>
<tr>
<td></td>
<td>46$^b$</td>
<td></td>
<td>- 4</td>
<td>K</td>
</tr>
<tr>
<td>$\text{K} + \text{CH}_4\text{I}$</td>
<td>10$^c$</td>
<td>39</td>
<td>- 4</td>
<td>KBr</td>
</tr>
<tr>
<td>$\text{K} + \text{HCl}$</td>
<td>4$^b$</td>
<td>7$^*$</td>
<td>-25</td>
<td>KI</td>
</tr>
<tr>
<td></td>
<td>.15</td>
<td></td>
<td>+1.5</td>
<td>KCl</td>
</tr>
</tbody>
</table>

$a$ - [BEC 62], $b$ - [GRE 66], $c$ - [HER 61]

*In plane measurement only
be calculated if one knew the driving pressure. Unfortunately at the start of these experiments a thermocouple gauge was the only pressure measuring device available for the pressure range in question. These gauges are of moderate accuracy for most low molecular weight gases with the exception of those containing a halogen atom. For all of the gases to be used then, the thermocouple gauge was unreliable. Thus an opposite tack was taken to measure the gas beam density. The pumping speed of the diffusion pump with baffle was known, and the effective pumping speed of the LN$_2$ trapping for each of the gases was determined. This gave the total pumping speed of the system for each of the gases. The pressure of the vacuum chamber was read at the start of an experiment. Gas was admitted to the gas oven and after the pressure of the chamber had stabilized, the pressure read again. The flux then was

\[
\text{Flux} = \text{Effective Speed} \times \text{Pressure Increase.}
\]

Area of the Source

The reading from the ionization gauge was corrected for its sensitivity (DUS 49) to each gas. This flux was then used to find the gas beam density.

When the experiment was moved into the apparatus described in Chapter III, the CH$_3$I experiment was performed. At this time the Divac pressure gauge had been purchased and was used to measure the driving pressure behind the collimator. Using this pressure and the equations of Johnson, Stair, and Pritchard (JOH 66), the gas flux was calculated (in agreement with experiment) and this value used to calculate the reaction cross section for CH$_3$I.
The angular distribution for the KI product matched that published by Kwei et al. (KWE 67). It was felt this was sufficient testing of the apparatus in each case and studies of the reaction of interest were begun.

HCL (v=0)

1. Data Because of the difficulties encountered in an earlier investigation (MOU 65) of this reaction and the small reaction cross section predicted from elastic scattering analysis (GRE 66), the sensitivity of the detector was monitored during data acquisition. This will be described in addition to the data.

Fig. 22 shows the angular distribution of signal from the tungsten and platinum (normalized) filaments in a single experiment for thermal beams \((T_K = 600^0 \text{K}, T_{\text{HCL}} = 290^0 \text{K})\). The resulting angular distribution of KCl from this experiment and the average distribution from all runs are shown in Fig. 23. Fig. 24 is the Newton diagram for this reaction constructed from the most probable beam velocities. The laboratory angular distribution of product is displayed on the relative velocity vector. This is a particularly good example example of how the predictions from "most probable" values may be misleading when broad distributions are present. According to Fig. 24 the product should be limited to lab angles of from 29\(^0\) to 34\(^0\), whereas product was found in the experiment from 20\(^0\) to 65\(^0\).

Integration of the angular distribution of KCl yielded a total KCl intensity of \(10^9\) molecules/sec. This resulted from a K density of \(10^9\) atoms/cc. and a gas flux of \(\times 4 \times 10^{17}\) molecules/cm\(^2\) sec. These values, used in the equation for the reactive scattering cross section,
Figure 22. Angular distribution of signal intensity.
Figure 23. Angular distribution of detected KCl intensity.
Figure 24. Newton diagram for the $K + HCl$ reaction with the angular distribution of KCl shown.
\[ \frac{I}{I_0} = nQx \]

(26)

give the reaction cross section of 0.15 Å\(^2\) in Table 2.

During data acquisition the filament sensitivity was checked by using the primary K beam and the low intensity salt beam. The flux of particles from either oven was calculated for the operating temperature and this expected intensity was compared with the ion current at the main detector. This was done before admission of gas to the chamber and with gas in the chamber in varying concentrations.

Both filaments were checked in this way for sensitivity to K and KCl. The sensitivity of the tungsten filament to K and KCl was found to be the same as that given by Datz and Taylor (DAT 56A, DAT 56B) regardless of the concentration of HCl. The platinum filament after conditioning yielded an ionization efficiency of 65\% for K and no signal resulting from KCl could ever be detected, setting an upper limit for ionization efficiency for KCl of 0.1\%. The ionization efficiencies for the platinum filament were also found to be independent of the gas concentration.

There was one effect the platinum filament displayed rather prominently. When the main detector was operated with the platinum filament for the first time a small titanium sublimation pump had been installed directly in the path of the gas beam. This location placed it just below the main detector. For the first couple of months the data taken from the platinum filament resembled a random walk, until it was realized that the filament was being contaminated by titanium. When this was realized the pump was retired from use and the problem stopped.

2. **Interpretation** The K + HBr reaction, exhaustively studied in other laboratories, is exothermic by 4 kpm. and requires no collision
energy to react. Since the endothermicity of the K + HCl reaction was almost equal to the collision energy (2 kpm.), the reaction cross section was expected to be less than that for K + HBr. The reaction cross section for the K + HCl reaction had been predicted to be $4 \text{A}^2$ by elastic scattering analysis (GRE 66) or about an order of magnitude less than for the K + HBr reaction. The cross section actually measured for the K + HCl reaction was a factor of 20 less than predicted or a factor of 200 less than the hard sphere cross section. This suggested that the requirements for a collision to lead to reaction are more stringent than merely supplying the reaction energy. We have adopted the traditional approach of considering these requirements to be an energy of activation.

For the reaction of an alkali atom plus a hydrogen halide molecule, almost all of the momentum must be carried away by the very massive (relative to the other product) alkali halide molecule. Because of the similarity in the endothermicity and available energy for the K + HCl reaction, there is very little energy left for translation of the KCl product away from the center-of-mass (Fig. 24). Consequently we expected and found the scattered KCl product angular distribution to be reproduced by the distribution of centroids (ODI 69).

The cross section measured for K + HCl is much less than the hard sphere size of the HCl molecule based on viscosity data. Consequently, it no longer seemed justified to think of the reaction merely as occurring from impact parameters less than or equal to some given distance. The assumption was made that the reaction cross section was essentially the hard sphere cross section of K colliding with HCl which we took to be,

$$Q_{\text{h.s.}} = \pi r_e^2 = 27 \text{A}^2$$

(29)

where $r_e$ is the equilibrium bond length for KCl. This cross section would
have been measured if all collisions with \( b < r_e \) led to reaction. The measured cross section was consequently interpreted as the hard sphere cross section times a factor for the probability of the collision going to reaction or,

\[
Q_r = P(e) \times Q_{h.s.} \tag{30}
\]

where we let the probability factor be dependent upon the energy. The factor \( P(e) \) then will be the fraction of collisions having sufficient energy to meet the reaction energy requirements. It is necessary now to try to understand the nature of this energy restriction.

The most widely applied function for an energy of activation is the Arrhenius equation.

\[
\frac{Q_r}{Q_{h.s.}} = P(e) = \exp(-E/RT) \tag{31}
\]

Using \( Q_r = .15, Q_{h.s.} \), and \( T = T_{HCl} \), this equation suggests an energy barrier of 3 kpm. (Kcal./mole). The best data (JAN 71) yields an endothermicity (\( \Delta E \)) of 1.5 ± .4 kpm. and this would leave an equal amount for the activation energy (Ea). This interpretation, while admittedly crude, did offer some suggestion for the lack of reactivity and had the advantage of producing its result only 30 minutes after the cross section for the reaction was first calculated from the data.

A more refined explanation of the energy dependence was obtained by consideration of the kinematics of the collision. In addition to the requirements of conservation of energy and momentum in all collisions, there is also the requirement of conservation of angular momentum for all collisions. Thus, for all reactive collisions of \( K + HCl \),

\[
m_K v_K + m_{HCl} v_{HCl} = m_{KCl} v_{KCl} + m_H v_H = MV \tag{1}
\]
\[ e + I = e' + I' + D \]  
\[ m_r v_r b + P_{HCl} = m'_r v'_r b' + P_{KCl} \]  
\[ (17) \]
\[ (32) \]

where all quantities are as defined in Chapter II. For the reactions of the hydrogen halides, Eq. (32) can often be greatly simplified (HER 61, GRE 66, TOE 68). Consider the l.h.s. of Eq. (32): \( m_r v_r b \) is sufficiently greater than \( P_{HCl} \) to approximate the l.h.s. by simply \( m_r v_r b \). In the r.h.s., \( m'_r \) is the reduced mass of H and KCl and thus \( m'_r << m_r \) or \( m_r v_r b >> m'_r v'_r b' \), since both \( b' \) and \( v'_r \) are constrained. (\( b' \) must approximately equal \( b \) and \( v'_r \) is energy limited (GRE 66)). The result of this is,

\[ m_r v_r b \approx P_{KCl} \]  
\[ (33) \]

and the approximation (Eq. (33) is even better since

\[ P_{HCl} \approx m'_r v'_r b' \]  
\[ (34) \]

Thus the collisions must have sufficient energy to not only overcome the energy requirement \( D \), but also the resulting KCl must have sufficient energy (rotational) to carry away all of the initial orbital angular momentum, \( m_r v_r b \). The cross section is now calculated with the use of these results.

The mechanics we use are based on a derivation by Present (PRE 58), and are given in detail in Appendix C. The rate of reaction of beam molecules with a single velocity \( v_1 \) colliding with beam molecules in a velocity range \( v_2 \) to \( v_2 + dv_2 \) with impact parameters in the range \( b \) to \( b + db \) is

\[ \frac{d^2 R}{\alpha^4 v_1} = 4 I_1 I_2 v_r v_2^2 \exp(-v_2^2/\alpha^2)P(e)P(b)b \, db \, dv_2 \]  
\[ (35) \]
where \( P(e) \) and \( P(b) \) are the probabilities of reaction for a given \( e \) or \( b \) respectively. The other quantities are defined in Appendix C.

Because

\[
P_{\text{KCl}} \approx m_r v_r b = b(2m_r e)^{1/2}
\]

the final internal energy is,

\[
I' \approx b^2 m_r e/L_{\text{KCl}}
\]

Eq. (17) then becomes

\[
e + I = e' + D + b^2 m_r e/L_{\text{KCl}}
\]

For threshold conditions, the final reaction product velocity would be 0 so,

\[
e' = 0
\]

Thus the minimum energy requirements for reacting particles are

\[
e = e' + D - I
\]

\[
1 - b^2 m_r / L_{\text{KCl}}
\]

and with Eq. (39) for the threshold,

\[
e \geq (D - I) / (1 - b^2 m_r / L_{\text{KCl}})
\]

Rearrangement produces

\[
b \leq \frac{L_{\text{KCl}}}{m_r} \left( \frac{1}{2} \right)
\]

where

\[
\delta = \left( \frac{e + I - D}{e} \right)^{1/2}
\]

The integration in Eq. (35) over the impact parameter reduces to,

\[
K = \int_0^\infty P(b) b \, db
\]
and
\[ P(b) = 1 \quad b < b^* \]  \hspace{1cm} (44.a)
\[ P(b) = 0 \quad b > b^* \]  \hspace{1cm} (44.b)

where
\[ b^* = \left[ \frac{L_{KCl}}{m_r} \right]^{1/2} \delta \quad I \leq D \]  \hspace{1cm} (45.a)
\[ b^* = \left[ \frac{L_{KCl}}{m_r} \right]^{1/2} \quad I > D \]  \hspace{1cm} (45.b)

Now
\[ \int_{b^*}^{\infty} P(b) \, b \, db = 0 \]  \hspace{1cm} (46)

so,
\[ K = \int_{0}^{b^*} P(b) b \, db = (b^*)^2 / 2 \]  \hspace{1cm} (47)

or
\[ K = L_{KCl} \delta^2 / 2m_r \quad I \leq D \]  \hspace{1cm} (48.a)
\[ K = L_{KCl} / 2m_r \quad I > D \]  \hspace{1cm} (48.b)

We have assumed that for the reaction to occur the particles must approach to within a certain critical distance \( r_c \). Present has shown that for this situation,
\[ P(E) = (1 - E_a/E) \quad E > E_a \]  \hspace{1cm} (28.a)
\[ P(E) = 0 \quad E \leq E_a \]  \hspace{1cm} (28.b)

where \( E_a \) is the repulsive potential between the particles evaluated at \( r_c \) (PRE 55).

With the use of Eqs. (28.a) and (28.b) we can now complete the integration of Eq. (35) over the velocities and over each rotational state populated in the primary HCl beam. The contribution from each state is weighted by the population of that state and then summed to produce an average cross section. This cross section is now a function
of e, the relative initial translational energy (RIKE); $E_a$, the energy of activation; and D, the energy of reaction.

The calculation was done in each of four different ways. Two of the procedures resulted from the use of either the total relative energy for E or the use of RIKE only. The energy difference in these two procedures was simply the rotational energy of the HCl (since vibrational and electronic energy contributions at these temperatures are negligible). The other half of the variation in calculation procedure came from allowing the impact parameter function $P(b)$ as used in Eq. (44) to be defined either by Eq. (48) or by Eq. (49).

$$K = \frac{L_{KCI}}{2m_r}$$  \hspace{1cm} (49)

The effect of the use of Eq. (49) instead of (48) is to simply ignore the specific use of the angular momentum constraint. The four procedures used to calculate the cross section were these.

1. Exclusion of angular momentum restrictions and use of RIKE only in Eq. (28).

2. Exclusion of angular momentum restrictions and use of RIKE plus rotational energy in Eq. (28).

3. Specific use of angular momentum and use of RIKE only for Eq. (28).

4. Specific use of angular momentum and use of RIKE plus rotational energy in Eq. (28).

The cross section calculated by each of these procedures was dependent upon the initial energy of the particles, the reaction energy, and any further activation energy $E_a$ beyond the reaction energy. Figs. 25a, 25b, and 25c show the results of these calculations. It can be seen
Figure 25a. Variation of cross section as a function of $E_A$ for an endothermicity of 1.0 kpm.
Figure 25b. Variation of cross section as a function of $E_A$ for an endothermicity of 1.5 kpm.
Figure 25c. Variation of cross section as a function of $E_A$ for an endothermicity of 2.0 kpm.
that if angular momentum is specifically included and only RIKE is used for E in Eq. (28) (this corresponds to mechanism #3) our measured cross section is predicted by using a reaction energy \( D \), of 1.5 kpm. and \( E_a = 0.8 \) kpm.

One of the main purposes of these calculations was to try to provide some clarification of the discrepancy between our observations and the cross section which had been predicted by Greene, Moursund, and Ross (GRE 66). Their method compared the elastic scattering of K from the \( K + HCl \) system to the elastic scattering of K from a non-reactive \( K + K\alpha \) system. At small scattering angles (large impact parameters) they found the elastic scattering for the two systems to be very similar, after appropriate normalization. At large scattering angles (small impact parameters) they found less elastic scattering in the reactive system than in the non-reactive system. They ascribed the loss in elastic scattering to reaction and measured the reaction cross section by measuring this loss in elastic scattering. This was first applied to the \( K + HB\alpha \) system and the resulting cross section is shown in Table 2. Because of the initial success of the method, it was applied to the \( K + HC\alpha \) reaction and that result is also shown in Table 2.

The calculation results in Fig. 25b, with \( D = 1.5 \) kpm., predict our observed cross section from the use of mechanism #3 and an \( E_a = 0.85 \) kpm. From the same value of \( D \) and \( E_a \) energies, mechanism #2 predicts the same cross section given by the elastic scattering experiment with the use of their initial energies. These initial relative energies were different for the two types of experiment.

While there is a difference in cross section arising from the use of the total energy versus RIKE, this is seldom greater than a factor of 2.
Close to an order of magnitude is found to be the effect from the inclusion or exclusion of restrictions due to angular momentum conservation. This suggests that many of the collisions have the energy necessary to surmount the energy barrier (D + Eₐ of 2.0 - 2.5 kpm.) but do not react because of the lack of sufficient additional energy to fulfill the angular momentum constraint. To try to characterize the elastic scattering from this type of system by the elastic scattering from a non-reactive system such as Kr + K would seem questionable. The real difference between our cross section and that predicted appears to be that the method used for the prediction counted as reactive all collisions in which the K was not scattered according to the fitted potential. In contrast, we have counted as reactive only collisions from which we detect KCl.

As explained earlier the KCl product was constrained to a laboratory angle very near the center-of-mass velocity. A calculation was performed to try to reproduce the observed angular distribution of KCl. This was basically a distribution of centroids calculation. An arbitrary velocity was chosen for the particles in each beam. The angle of the center-of-mass velocity vector (with respect to the K vector) was calculated.

$$\theta = \text{Arccsin} \left[ 1 + \frac{m_K v_k}{m_{HCl} v_{HCl}} \right]^{-1}$$  \hspace{1cm} (50)

The contribution (to the angular distribution) at this combination of velocity vectors was calculated from the fractional populations of each of the beams at those velocities by

$$\Omega_\theta (v_k, v_{HCl}) = n(v_k) \cdot n(v_{HCl})$$  \hspace{1cm} (51)
Once these contributions are calculated for all of the significantly populated velocities of each beam, the contributions at each angle are summed

$$\Omega_\theta = \sum_{i,j} \Omega_{\theta} (i,j)$$

(52)

These simple considerations were made more flexible by the addition of two energy parameters, $D$ and $E_a$, and a center-of-mass angular dependence, $\theta$. The collision energy for each combination of particle velocities was calculated as in Chapter II.

$$e = \frac{1}{2} m_r v_r^2$$

The energy of the products was then

$$e' = e - D$$

(53)

If this quantity was less than the specified $E_a$ there was no contribution (reaction) in Eq. (51). The KCl velocity vector in the C.M. system could be oriented at any angle relative to the C.M. velocity and the contribution for the velocity populations was for the angle obtained from the vector addition of the C.M. velocity vector and the KCl velocity vector in the C.M. system. Because of the very small magnitude of the KCl velocity vector in the C.M. system the angular dependence never showed appreciable effect and was excluded from the calculation after a short time. The final contribution at a given lab angle then was

$$\Omega_\theta (v_k, v_{\text{HCl}}) = n(v_k) \cdot n(v_{\text{HCl}}) \quad e' \geq E_a$$

(54.a)

$$\Omega_\theta (v_k, v_{\text{HCl}}) = 0 \quad e < E_a$$

(54.b)

and this was again summed as in Eq. (52) to create a predicted angular distribution based on the distribution of centroids and the two energy parameters. The result of this calculation is shown in Fig. 26.
Figure 26. Distribution of centroids for different endothermicities and activation energies. Points are experimental results.
The energies necessary to reproduce the experimental product distribution are approximately the same as those predicted from the cross section calculation just described or 2.0 - 3.0 kpm. total energy. This calculation did not account for the product broading due to the finite width of the reactant beams and for greater accuracy this should be included.

\[
\text{HCl}^* \ (v=1)
\]

1. **Data** The data for the $\text{K} + \text{HCl}$ reaction was measured as an "effect" produced by the laser excitation. This effect was measured by the net increase in signal on the "A" scaler compared to the "B" scaler. The A scaler was turned on (see Fig. 2) at a time appropriate for the arrival of the product from the reaction of the HCl*. The B scaler was turned on at a sufficiently later time to see only the product of the reaction with HCl. Thus the signal on scaler A was

\[
A = \text{K} + \text{KCl}^* + \text{KCl} + \text{K}^* + \text{N} \quad (55)
\]

where,

- $A$ = signal on scaler A
- $\text{K}$ = elastically scattered K from HCl
- $\text{K}^*$ = elastically scattered K from HCl*
- $\text{KCl} = \text{reaction product from K + HCl}$
- $\text{KCl}^* = \text{reaction product from K + HCl}^*$
- $\text{N}$ = general background from filament and electronics

and the signal on scaler B was

\[
B = \text{K} + \text{KCl} + \text{N} \quad (56)
\]

The difference was

\[
A - B = \text{K}^* + \text{KCl}^* \quad (57)
\]

The criteria used to make a measurement of this effect was to plot the
fractional increase in signal at each angle
\[(A-B)/B\]  \hspace{1cm} (58)

versus the number of laser shots used to produce the average value.
\[
\left(\frac{A-B}{B}\right)_w = \frac{K^* + KCl^*}{K + KCl + N} \hspace{1cm} (59)
\]

Plots of this type are shown in Figs. 27a and 27b. Fig. 27a is for the measurement taken at 25°. It is evident that a non zero equilibrium value is being approached. Fig. 27b is this same type of plot for the data taken at 40° and shows no effect within statistical tolerances. It should be noticed the sensitivity of the ordinate scale in Fig. 27b has been increased by a factor of 2-1/2 over that of 27a. More laser shots (not shown here) were used to reduce the uncertainty of these values and accumulate the same data for all lab angles studied.

The platinum filament, of course, does not detect KCl, so the signals on the scalers were
\[
A_p = K + K^* + N \hspace{1cm} (60)
\]
\[
B_p = K + N \hspace{1cm} (61)
\]
\[
A_p - B_p = K^* \hspace{1cm} (62)
\]

One could conclude that all that was necessary for the measurement of the KCl* intensity was to subtract the A-B quantity of the platinum filament, from the same quantity of the tungsten filament,
\[
(A-B)_w - (A-B)_p = KCl^* \hspace{1cm} (63)
\]

Unfortunately if this procedure is used directly a great number of problems arise due to the uncertainties in trying to determine absolute intensities of the KCl*, HCl*, and other important factors.
Figure 27a. Plot of the "effect parameter" versus the number of laser shots accumulated to produce the average value shown. This is from the data taken at 25 degrees.
Figure 27b. Plot of the "effect parameter" versus the number of laser shots accumulated to produce the average value shown. This is from data taken at 40 degrees.
The procedure used was to measure the effect \((A-B)/B\) with each filament at each angle (Figs. 28a and 28b) and subtract this ratio.

\[
\left(\frac{A-B}{B}\right)_w - \left(\frac{A-B}{B}\right)_p = \frac{KCl^*}{K + KCl + N}
\]  \hspace{1cm} (64)

For this procedure \(B_p\) was approximated as \(B_w\) because \(K \gg KCl\). The ratio of \(KCl\) to total signal was well known from the ground state experiments, thus,

\[
\frac{KCl^*}{K + KCl + N} \times \frac{K + KCl + N}{KCl} = \frac{KCl^*}{KCl}
\]  \hspace{1cm} (65)

Equ. (65) had to be corrected for the relative densities (see Appendix D for details) of reactants \((HCl\) and \(KCl^*)\). The result of this correction

\[
\frac{KCl^*}{KCl} \times \text{Correction} = \frac{KCl^*'}{KCl}
\]  \hspace{1cm} (66)

was then proportional to the reaction cross sections,

\[
\frac{KCl^*'}{KCl} = \frac{Q_r(HCl^*)}{Q_r(HCl)}
\]  \hspace{1cm} (67)

and the angular distribution of this ratio is shown in Fig. 29. The absolute reaction cross section for \(K + HCl^*\) was then

\[
\frac{KCl^*'}{KCl} \times Q_r(HCl) = Q_r(HCl^*)
\]  \hspace{1cm} (68)

With a ratio of 120 this equation yields,

\[
Q_r(HCl^*) = 18 \pm 9 \text{ A}^2
\]

After the increase in the size of the reaction cross section, probably the most noticeable feature of the angular distribution in Fig. 9 is its narrowness. Even though more energy is available for translation of the KCl product in the \(K + HCl^*\) reaction and the product does contain
Figure 28. Angular distribution of effect for the W and Pt filaments.
Figure 29a. Angular distribution of KCl from HCl and HCl*. 

K + HCl†

K + HCl (x 25)
Figure 20b. Newton diagram for K + HCl* with detected KCl shown.
more translational energy, the spread in the distribution of this energy is much smaller than in the K + HCl reaction. In an attempt to understand this limited spread in translational energy the centroid distribution calculation used in the ground state reaction description was also run for the K + HCl* reaction. While the center angle of the distribution could be fitted by the correct choice of the scattering angle in the C.M. system and/or the correct choice of the portion of the relative energy going into translation of the reaction products, the calculation was unable to reproduce the extreme narrowness of the angular distribution by variation of either of these parameters. The precision of the experimental data is not sufficiently great to rule out experimental error, so this has not been pursued further.

2. Interpretation While the addition of energy to an endothermic reaction might be expected to increase the reactivity, a more detailed examination is necessary if this is to be understood. A closer analysis is especially desirable in light of the results various groups have obtained in the last 2 - 3 years. These results have been both experimental results and theoretical predictions based on model calculations. The first experimental study of the variation of reactivity on vibrational energy was the work of Schmeltekopf, Ferguson, and Fehsenfeld (SCH 67). They studied certain ion-molecule reactions as a function of vibrational energy level and found a strong dependence in reactivity on the vibrational energy. More recently Jaffe and Anderson (JAF 68, JAF 69) have studied the reaction cross section for the HI + DI reaction as a function of translational energy. Chupka, Berkowitz, and Russell (CHU 69) have done a particularly nice study of the ion-molecule reaction of \( \text{H}_2^+ \) + He varying both the vibrational and translational energies independently.
A potential surface has been calculated for the Chupka work by Brown and Hayes (BRO 71) which indicates certain significant characteristics in the light of recent trajectory calculations on generalized potential surfaces by Polanyi (POL 69, MOK 69) and colleagues. Finally, a very interesting procedure has been used by Anlauf et al. (ANL 69) for the prediction of the energy dependence of endothermic reactions.

Jaffee (JAF 68, JAF 69) and Anderson studied the reaction of HI and DI,

\[ \text{HI} + \text{DI} \rightarrow \text{HD} + \text{I}_2 \]

as a function of translational energy. A molecular beam of HI was produced with translational lab energies of 40 - 125 km/s. This was passed through a chamber containing DI at 10^{-4} torr. The energy of activation for the HI + DI reaction is 44 km/s. The mean RIKE was varied from 20-109 km/s or from 1/2 to 2-1/2 times the activation energy. The product was to have been detected by a mass spectrometer whose sensitivity coupled with operating conditions, yielded a detectable cross section lower limit of 0.04 Å². The investigators were unable to detect reaction at any energy used. While it is possible that other problems may have arisen (surface effects, competing reactions, etc.) precautions were taken to avoid this. Although this reaction is not of the simple A + BC exchange type as the one studied in this work, the total lack of reactivity when more than a sufficient amount of energy to overcome the E_a barrier is present is significant. The apparent inability of translational energy to promote reaction in this case has led the authors to state (JAF 69), "...translational energy alone is not sufficient to produce appreciable reaction...The energy requirements for activation are specific: vibrational
or rotational excitation of collision partners is required for an appreciable reaction probability of HI with DI."

A very thorough and detailed investigation of the energy dependence of the reaction

\[ \text{H}_2^+ + \text{He} \rightarrow \text{HeH}^+ + \text{H} \]

has been conducted by Chupka, Berkowitz, and Russell (CHU 69). Using photoionization they were able to produce H\(_2^+\) ions in specific vibrational states and the reaction of these ions with Helium was studied as a function of the RIKE from 0 to 150 kpm. The most prominent feature of their results was that for a RIKE of approximately 10 - 12 kpm, the cross section for the \( v = 0 \) state is less than 0.05 Å\(^2\), while for the \( v = 3 \) state the cross section is almost 5 Å\(^2\), a gain of a factor of 100! This is especially interesting since the cross section increased by only a factor of 2 when the RIKE (for the \( v = 0 \) state) was changed from 25 - 125 kpm. This 100 kpm. increase is more than the dissociation energy of H\(_2^+\).

Brown and Hayes (BRO 71) have done a non-empirical LCAO-MO-SCF calculation for the potential energy surface for the \( \text{H}_2^+ + \text{He} \) reaction in the ground electronic state. They find the only barrier to reaction is the exit channel itself. The highest energy state for the system is asymptotically approached for infinite separation of the reaction products, so the energy barrier is as "late" in the reaction transition state as possible. The importance of this result is evident only in the use of result for the calculations of Polanyi et al.

This group has made classical trajectory calculations (POL 69) for two slightly different model energy surfaces. These are shown in Fig. 30. The feature of interest is that the barrier (7 kcal.) for
one surface has been placed in the entrance channel and the same barrier for the other surface has been placed an equal distance into the exit channel. The surface in each case still represents the simple A + BC exchange reaction.

The results of the calculations are shown in b, c, e, and f of Fig. 30. The reaction was pictured for each surface as approaching from the lower right hand corner and exiting in the upper left hand corner.

The main results of interest here are the following:

1. For Surface I (barrier in the entrance channel) the reactivity was enhanced equally by either an increase in the translational energy or an increase in the translational and vibrational modes of energy corresponding to a given temperature. However, the reactivity for a certain energy was always higher with all of the energy in translation.

2. For Surface I vibrational energy was totally ineffective for reaction.

3. For Surface I most of the energy after reaction went into vibrational or rotational excitation of the newly formed bond.

4. For Surface II (barrier in the exit channel) the reactivity was enhanced only slightly by an increase in the energy in both the translational and vibrational modes corresponding to a given temperature. However, it was enhanced greatly by an increase in the vibrational energy.

5. For Surface II translational energy was totally ineffective for reaction.

6. For Surface II most of the energy after reaction went into translational excitation of the newly formed molecule.
Figure 30. Results of trajectory calculations on the indicated potential energy surfaces.
In a second paper (MOK 69) an attempt was made to correlate the location of the barrier to other characteristics of the surface which might be known. Following is a list of the important results.

1. For an exothermic reaction the barrier was in the approach coordinate.

2. As the reaction becomes more endothermic the barrier was shifted along the reaction coordinate to a later position.

3. For an endothermic reaction the barrier was in the exit coordinate.

Combining these results with the results from paper I yielded these conclusions for the model surface used.

1. An exothermic reaction has its energy barrier in the entrance valley and the reactivity is increased when the translational energy of the colliding particles is increased. This results in a product molecule with a large fraction of the available energy in the internal modes.

2. An endothermic reaction has its energy barrier in the exit valley and the reactivity would be increased by vibrational energy of the bond to be broken. This results in translational excitation of the products and little internal excitation.

This description (based on an assumed, although realistic, potential) correlates the results from this work, the lack of reaction seen by Jaffe and Anderson, and the combined work of the two groups dealing with the \( \text{H}_2^+ + \text{He} \) system. In both the first and third cases the reactions were endothermic. They both have shown an extremely strong dependence in reactivity on the vibrational energy. Furthermore in the case of \( \text{K} + \text{HCl}^* \) a majority of the energy carried off by the reaction products appear to
be used for translation. Again this result would have been predicted by Polanyi's trajectory calculation for the endothermic reaction. In the HI + DI system there was no reaction even though the energy available in translation was 2-1/2 times the barrier height. In Fig. 10 f. Polanyi and Wong's calculations predicted no reaction even though the translational energy was more than twice the barrier height.

Finally an interesting procedure has been applied by Anlauf, Maylotte, Polanyi, and Bernstein (ANL 69). The authors have taken data from chemiluminescence regarding the distribution of energy in the products from the exothermic reaction,

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

applied detailed balancing, and made predictions about the reactivity of the reverse endothermic reaction. The two endothermic reactions considered were

\[ \text{HCl} + I \rightarrow \text{HI} + \text{Cl} \]
\[ \text{HCl} + \text{Cl} \rightarrow \text{H} + \text{Cl}_2 \]

Their predictions were basically as follows: for vibrational levels less than \( v = 4 \), an increase in vibrational level led to a rapid increase in reactivity; for vibrational levels of 2, 3, or 4 the reactivity maximized for a rotational energy of about 5 kpm; and translational energy showed no consistent effect. One interesting item was that in both reactions it appeared the reactivity was maximized for some specific vibrational and rotational level and that as the level (of either) of these energies was increased beyond this the reactivity was lowered.

Our present results are, therefore, in very good accord with the results of investigations from other laboratories. Our results specifically support the concept that the reactivity of an endoergic reaction
(as K + HCl was shown to be) is greatly enhanced by vibrational excitation \((K + HCl^*)\). Furthermore a majority of the relative energy of the products will be released into the translational mode of excitation.
VI. CONCLUSIONS

The angular distribution of KCl resulting from the reaction of K and HCl in crossed molecular beams has been measured. Due to the constraint of the product to be near the center-of-mass no attempt was made to interpret the spacial distribution of reaction product in the C.M. system. However, the scattered intensity was integrated over all space to yield a reaction cross section of 0.15 $\text{Å}^2$. This extremely small cross section has been interpreted as a combination of endothermicity and energy of activation barrier totaling 2.0 - 3.0 kpm. It also appears that this energy barrier may be emphasized due to conservation of momentum restrictions as described in Chapter V.

In addition the angular distribution of KCl resulting from the reaction of K and HCl* ($v = 1$) under the same conditions has been measured. The reaction cross section has been greatly enlarged to about 20 $\text{Å}^2$. This has been expected in accord with the basic hypothesis of absolute reaction rate theory through its interpretation of a reaction occurring by an infinite amplitude vibration of the bond that must be broken. This result was also predicted by calculations of Polanyi and colleagues who have suggested that the rate of an endothermic reaction, such as this, will be increased most effectively by vibrational energy.

A comparison to this situation is that of Jaffe and Anderson who sought to measure the dependence of reactivity on translational energy for the reaction of HI and DI. Though they increased the mean relative translational energy from 1/2 of the known energy of activation to 2-1/2 times this quantity they could observe no reaction. Again this is in accordance with the calculations of the Polanyi group. One more test
for the possible validity of the trajectory calculations is that they predict for the endoergic reaction (such as K + HCl) excess energy should go into translation of the reaction product away from the center-of-mass. The only energy analysis that could be made on the reaction products in our study of the K + HCl* reaction (which was far from conclusive) suggests that some 70-80% of the energy available does go into translation of the reaction products.
APPENDIX A

Suppliers and Manufacturers

1. Chemicals
   Potassium
   100 gm. Mine Safety Appl. 99.95%
   Methyl Iodide
   10 gm. Fisher Scientific 99.5%
   Hydrogen Bromide
   20 gm. Matheson Gas 99.8%
   Hydrogen Chloride
   100 gm. Air Products 99.99%
   Coffee
   120 lbs. Maryland Club Drip Gr.

2. Vacuum Equipment
   Oil Diffusion Pumps
   2 Tri-Metal TM6
   1 C.V.C. PMCS-2C
   1 Cenco OD-25
   Vacuum Valves
   1 Granville-Phillips 9100
   1 Leybold-Heraus Fine
   1 Edwards Vacuum D21401
   3 Norton Research 1251
   Mechanical Pumps
   1 Welch Scientific 1400
   1 Welch Scientific 1402
<table>
<thead>
<tr>
<th>Dewars</th>
<th>Gardner Cryogenics</th>
<th>GNS-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gauges</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Granville-Phillips</td>
<td>236</td>
</tr>
<tr>
<td>1</td>
<td>Norton Research</td>
<td>831</td>
</tr>
<tr>
<td>3</td>
<td>Vacuum Industries</td>
<td>BA100P</td>
</tr>
<tr>
<td>1</td>
<td>Hastings Vacuum</td>
<td>GV-3RST</td>
</tr>
<tr>
<td>1</td>
<td>Norton Research</td>
<td>803</td>
</tr>
<tr>
<td>1</td>
<td>Leybold-Heraus</td>
<td>Divac</td>
</tr>
</tbody>
</table>

3. **Electronics**

<table>
<thead>
<tr>
<th>Power Supplies</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fluke</td>
<td>405B</td>
</tr>
<tr>
<td>2</td>
<td>Sorensen</td>
<td>QRS15-2</td>
</tr>
<tr>
<td>1</td>
<td>acdc</td>
<td>Bx46NO.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Recorders</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Heath</td>
<td>EU-20B</td>
</tr>
<tr>
<td>1</td>
<td>Leeds &amp; Northrup</td>
<td>W</td>
</tr>
<tr>
<td>1</td>
<td>Parsons</td>
<td>31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Counting Equipment</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ortec</td>
<td>416-S</td>
</tr>
<tr>
<td>1</td>
<td>Mech-Tronics</td>
<td>404</td>
</tr>
<tr>
<td>1</td>
<td>Mech-Tronics</td>
<td>501</td>
</tr>
<tr>
<td>1</td>
<td>Mech-Tronics</td>
<td>604</td>
</tr>
<tr>
<td>1</td>
<td>Mech-Tronics</td>
<td>705</td>
</tr>
<tr>
<td>2</td>
<td>Mech-Tronics</td>
<td>703</td>
</tr>
<tr>
<td>1</td>
<td>Mech-Tronics</td>
<td>801</td>
</tr>
<tr>
<td>2</td>
<td>Mech-Tronics</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Electrometers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Tele-Type</td>
<td>ASR-33</td>
</tr>
<tr>
<td>1</td>
<td>Keithley</td>
<td>610BR</td>
</tr>
<tr>
<td>1</td>
<td>Boonton</td>
<td>95A-R</td>
</tr>
<tr>
<td>Temperature Controller</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Gardsman</td>
<td>90110</td>
</tr>
<tr>
<td>Thermocouple Readers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Assembly Products</td>
<td>I/C</td>
</tr>
<tr>
<td>Oscilloscope</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Tektronix</td>
<td>561A</td>
</tr>
<tr>
<td>1</td>
<td>Tektronix</td>
<td>555</td>
</tr>
<tr>
<td>Pressure Relays</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Mercoid</td>
<td>DA-427</td>
</tr>
</tbody>
</table>
APPENDIX B

In order to calculate the reaction cross section for the K + HCl* reaction it was necessary to know the concentration of HCl* in the HCl beam. This is in turn dependent upon the density of the HCl beam, the energy density of the laser beam and various physical parameters. Kemble (KEM 58) relates these quantities for the equilibrium condition

\[ N_n [A_{n,m} + B_{n,m}\rho(\nu_{n,m})] = N_m B_{m,n}\rho(\nu_{n,m}) \]  

where

\[ N_n = \text{the population of the lower state} \]
\[ N_m = \text{the population of the higher state} \]
\[ A_{n,m} = \text{coefficient of spontaneous emmision} \]
\[ B_{n,m} = \text{coefficient of induced emmision} \]
\[ B_{m,n} = \text{coefficient of induced a sorption} \]
\[ \rho(\nu_{n,m}) = \text{energy density per unit frequency interval at frequency } \nu_{n,m} \]

Because the times for absorption and induced emmision are short compared to the length of the laser pulse \(10^{-5} \text{ sec.}\), a steady state condition should be approximated.

Eq.(1) can be rearranged to produce

\[ N_m/N_n = (A + \rho B)/\rho B \]  

where we have abbreviated \( A_{n,m} \), \( B_{n,m} \), \( B_{m,n} \), and \( \rho(\nu_{n,m}) \) by \( A \), \( B \), \( B \), and \( \rho \) since we are only working with and interested in the equations for a particular frequency and only two states. Futhermore

\[ B_{n,m} = B_{m,n} \]
The relationship between A and B is given by Herzberg (HER 50)

\[ \frac{A}{B} = 8\pi \hbar \tilde{v}^3 \]  

(4)

where \( \tilde{v} = \nu/c \), and c is the velocity of light. Then

\[ \frac{N_m}{N_n} = 1 + \left( \frac{8\pi \hbar \tilde{v}^3}{\rho} \right) \]  

(5)

For HCl, \( \tilde{v}_{0,1} = 2886 \text{ cm}^{-1} \), and this yields

\[ \frac{N_m}{N_n} = 1 + \left( 4.02 \times 10^{-15} \text{ erg. sec.}/\rho \text{ cc.} \right) \]  

(6)

If the population ratio is set at 1.1, \( \frac{N_m}{N_n} = 1.1 \), then the population percentages are \( N_m = 52.4 \% \) and \( N_n = 47.6 \% \) and

\[ \rho = 4 \times 10^{-14} \text{ erg. sec.}/\text{ cc.} \]

A pulse volume is

\[ V = Act \]  

(7)

where A is the cross sectional area of the laser beam. This yields

\[ V = 10^6 \text{ cc.} \]

Now

\[ \rho = E/(\Delta \nu x V) \]  

(8)

and the line width is no more than the Doppler width so,

\[ E/\Delta \nu = \rho V = 4 \times 10^{-8} \text{ erg. sec.} \]  

(9)

and with a Doppler width of \( 10^9 \text{ sec.}^{-1} \), \( E = 40 \text{ ergs.} \)

Eq. (6) can be checked for limiting conditions. Letting \( \rho \) go to 0 allows the r.h.s. of (6) to become infinite and all the population will be in the lower state. Thus with no incident radiation all of the molecules must fall to the lowest state. Letting \( \rho \) go to infinity eliminates the second term in the r.h.s. of (6) and the population is equally distributed between the upper and lower states. This is of course, just what would be expected from Eq. (1) with \( \rho \) equal to infinity.
The most important feature was that the population would reach the saturation limit of 50% asymptotically at infinite energy. Thus if one is at an energy to produce a much greater percentage of HCl* than approximately 45% the amount of HCl* actually produced becomes rather insensitive to the energy of the laser. The conclusion that 50% of the HCl beam was HCl* was based on the insensitivity of the effect parameter $(A - B)/B$ upon the power within the upper power range of 200 to 1000 ergs. and a total loss of effect in the lower power range of 0.1 to 10 ergs.
APPENDIX C

In this appendix we show the details of the derivations used for the calculation of the cross section for \( K + HCl \rightarrow H + KCl \). This was done to try to gain a better insight into the extremely small reaction cross section observed, and into the discrepancy between our results and those from elastic scattering data (GRE 66).

The reaction collision is governed by the same laws of conservation as any collision. These are conservation of energy (1), of momentum (2), and of angular momentum (3).

\[
e + I = e' + I' + D \\
m_K v_K \pm m_{HCl} v_{HCl} = m_{KCl} v_{KCl} + m_H v_H = MV \\
m_r v_r b + P_{HCl} = m_r' v_r' b' + P_{KCl}
\]

where, \( P_i \) is the rotational angular momentum of the particle \( i \) and all other quantities are as defined in Chapter II. The values for \( m_r \) and \( m_r' \) are,

\[
m_r = (m_K m_{HCl})/M = 18.85 \\
m_r' = (m_H m_{KCl})/M = 0.994
\]

Comparing equation (3) and (4) with \( b' \approx b \), we have

\[
m_r v_r b \approx P_{KCl}
\]

Thus,

\[
P_{KCl} \approx b (2m_r e)^{1/2}
\]

or

\[
J_{KCl} \hbar = b (2m_r e)^{1/2}.
\]
Then rewriting equation (1) using (b)
\[ e + B_{\text{HCl}} \hbar J(J + 1) - D = \frac{e' + b^2 m_r e}{L} \]
where \( L \) = moment of inertia of KCl, and rearranging
\[ e = e' + D - I \]
\[ \frac{1}{1 - b^2 m_r L^{-1}} \]
For minimum energy conditions
\[ e' = 0 \]
\[ e > \frac{D - I}{1 - b^2 m_r / L} \] (8)
Since electronic and vibrational energy of HCl @ room temperature are negligible let
\[ R = I \]
where
\[ R = \text{initial rotational energy of HCl.} \]
Consider a beam of molecules traveling at one speed, \( v_1 \), and intersecting at right angles with a beam with a modified Maxwell-Boltzmann distribution. The rate at which collisions occur in the collision volume is related to
\[ v_1 \quad \text{the velocity of the selected beam} \]
\[ v_2, \, dv_2 \quad \text{the velocity and range of the second beam} \]
\[ I_1 \quad \text{the intensity of the selected beam} \]
\[ I_2 \quad \text{the intensity of the cross beam} \]
\[ \text{Intensity in Molecules/sec crossing unit area} \]
The rate at which molecules with speed \( v_1 \) collide with molecules whose speeds lie in the range \( v_2 \) to \( v_2 + dv_2 \) for which the impact parameter is between \( b \) and \( b + db \) is
Rate = n_1 \cdot \frac{d n_2}{d v_2} \cdot 2 \pi b d b \cdot v_r \tag{9}

where \( d n_2 \) = density of molecules with \( v_2 + v_2 + dv_2 \)

\[ n_1 = \frac{I_1}{v_1} \]

The intensity of the cross beam in the velocity range \( v_2 + v_2 + dv_2 \), is given by Ramsey (RAM 56).

\[ I(v) dv = \frac{2 I_0}{\alpha^4} \cdot \frac{v^3}{\alpha^2} \exp \left(-\frac{v^2}{\alpha^2}\right) dv \]

\[ d n_2 = \frac{I(v_2) dv_2}{v_2} = \frac{2 I_0}{\alpha^4} \cdot \frac{v_2^2}{\alpha^2} \exp \left(-\frac{v_2^2}{\alpha^2}\right) dv_2 \]

So the number of collision per second per cc with \( b + b + db \) and \( v_2 \) to \( v_2 + dv_2 \) is

\[ \text{Rate} = \frac{I_1 I_2(v)}{v_1 v_2} \cdot 2 \pi b d b \cdot dv_2 \cdot v_r \]

\[ = \frac{2 \pi I_1 I_2}{\alpha^4} \cdot \frac{v_r}{v_1} \cdot \frac{v_2^2}{\alpha^2} \exp \left(-\frac{v_2^2}{\alpha^2}\right) dv_2 \cdot b d b \]

Not all of these collisions produce reaction. Certain minimum energy requirements are necessary and these also depend on \( b \). There is thus some probability of reaction, \( p(E, b) \) or

\[ \text{Reaction rate} = 4 \pi I_1 I_2 \cdot \frac{v_r}{v_1} \cdot \frac{v_2^2}{\alpha^2} \exp \left(-\frac{v_2^2}{\alpha^2}\right) b d b \cdot p(E, b) dv_2 \]

For the functional form of the reaction probability, we consider two criteria:

1) The reaction has some "energy of activation" \( \epsilon_A \), and the cross section is given by Present (PRE 58), p. 153:
\begin{equation}
\sigma(\varepsilon) = \sigma_0 \left(1 - \varepsilon_A / \varepsilon\right) \quad \varepsilon > \varepsilon_A \tag{15}
\end{equation}
\begin{equation}
\sigma(\varepsilon) = 0 \quad \varepsilon \leq \varepsilon_A
\end{equation}

2) For impact with an impact parameter \( b \), the RIKE must be such that angular momentum is conserved according to (8)

\begin{equation}
e > \frac{D - R}{1 - m_r b^2} \tag{16a}
\end{equation}

or, for a given energy, \( e \)

\begin{equation}
b > \left[ \frac{L}{m_r} \right]^{1/2} \delta \tag{16b}
\end{equation}

where \( \delta = \left[ \frac{e - D + R}{e} \right]^{1/2} \)

The total number of reactions is the integral of (14) over all allowed \( e \) and \( b \):

\begin{equation}
\text{Total Rxn Rate} = \frac{4 \pi I_1 I_2}{\alpha^4} \int_0^\infty v_r v_2^2 \exp \left(-v_2^2 / \alpha^2\right) (1 - \varepsilon_A / \varepsilon) \, dv_2 \kappa
\end{equation}

where \( \kappa = \int_0^{b^*} bdb = \frac{(b^*)^2}{2} \)

and \( b^* = \left[ \frac{L}{m_r} \right]^{1/2} \delta \)

unless \( R > D \) in which case \( b^* = \left[ \frac{L}{m_r} \right]^{1/2} \)

So \( \kappa = \frac{L}{2 m_r} \delta^2 \)
The total Rxn Rate is then:

\[
TRR = \frac{4 \pi I_1 I_2 L}{2 \alpha^4 m_r} \int_{A = \varepsilon A / \varepsilon}^{\infty} v_r v_2^2 \exp\left(-\frac{v_2^2}{\alpha^2}\right) (1 - \frac{\varepsilon A}{\varepsilon}) \delta^2 dv_2
\]  

(18)

(all symbols are positive)

change variables:

\[v_r^2 = v_2^2 + v_1^2\]

\[v_2^2 = v_r^2 - v_1^2 \quad (v_1^2 \text{ is a constant})\]

\[d(v_2^2) = d(v_r^2)\]

Let \(\varepsilon A = a\quad \varepsilon = \varepsilon\)

\[
\frac{TRR}{2 \pi I_1 I_2 \cdot \exp\left(\frac{v_1^2}{\alpha^2}\right)} = \frac{L}{m_r} \int_{a}^{\infty} v_r^2 \left(v_r^2 - v_1^2\right)^{1/2} \exp\left(-\frac{v_r^2}{\alpha^2}\right) (1-a/\varepsilon) \delta^2 dv_r
\]

(19)

collecting terms, we get:

\[
\frac{TRR}{(2 \pi I_1 I_2 \exp\left(\frac{v_1^2}{\alpha^2}\right))^{1/2}} = \frac{L}{m_r} \int_{a}^{\infty} e^{1/2} \left(2\varepsilon/m_r - v_1^2\right)^{1/2} \exp\left(-2\varepsilon/m_r \alpha^2\right)(1-a/\varepsilon) \delta^2 de
\]

\[
\frac{m_r}{m_r \alpha^4 v_1}
\]

(20)

It should be noted here that \(a\) is to be interpreted as the minimum RIKE necessary for reaction to take place. Thus,

\[a = "Activation\ Energy" + D - R.\]
Now let us consider the experimental rate. For a typical crossed beam experiment, the attenuation of the primary beam is given by,

\[
\frac{I}{I_0} = \exp\left(-nQ\ell\right)
\]  
(21)

\(I = \text{Final Intensity}\)
\(I_0 = \text{Initial Intensity}\)
\(n = \# \text{ density of second beam}\)
\(Q = \text{appropriate scattering cross-section}\)
\(\ell = \text{scattering length}\)

When \(nQ\ell\) is small this expression can be approximated by

\[
\frac{I}{I_0} = 1 - nQ\ell
\]  
(22)

then with \(\Delta I = I_0 - I\)

\[
\frac{\Delta I}{I_0} = nQ\ell
\]  
(23)

Now for convenience of calculations, assume each beam is 1 cm.² in cross-section and \(\ell = 1\) cm., then we have

\[\Delta I = I_0 nQ\ell\quad \Delta I = \frac{I_0 I_2}{V_2} Q\]

To relate this to the reaction rate, let the density of each species in the intersection volume be

\[n_i = \frac{I_i}{V_i}\]
giving
\[ \frac{dN}{dt} = k n_1 n_2 = k \frac{I_1}{v_1} \frac{I_2}{v_2} \]  \hspace{1cm} (24)

and with
\[ k = Q \sqrt{v} \]
\[ \frac{dN}{dt} = \frac{Q \sqrt{v} I_1 I_2}{v_1 v_2} \]  \hspace{1cm} (25)

From Ramsey p. 21 (RAM 56) the average value for the velocity in a molecular beam is
\[ <v> = \frac{3}{4} \sqrt{\pi} \alpha \]

thus the average relative velocity is
\[ <v_r> = <\sqrt{v_1^2 + v_2^2}>^{1/2} = <\frac{v_1^2 + 9 \pi \alpha^2}{16}>^{1/2} \]  \hspace{1cm} (26)

and the inverse is
\[ <\frac{1}{v_2}> = \frac{2}{\alpha^4} \int_{0}^{\infty} v_2^2 \exp(-v_2^2/\alpha^2) \, dv = \sqrt{\frac{\pi}{2}}/2 \alpha \]  \hspace{1cm} (27)

Combining these with eqn. (25)
\[ TRR = \frac{dN}{dt} = Q \frac{I_1 I_2}{v_1} \sqrt{\frac{\pi}{2 \alpha}} \left( \frac{v_1^2 + 9 \pi \alpha^2/16}{16} \right)^{1/2} \]  \hspace{1cm} (28)

When one combines this with Eqn. (20) and performs a dimensionality analysis consistency is found. Also a limiting value simplification was done and is note 1.

Using the resultant from combining Eq. (20) and Eq. (28), Q for each rotational level is given by
\[ Q_r = \binom{5/2}{m_r} \frac{L \sqrt{\pi} \exp(v_1^2/\alpha^2)}{(v_1^2 + 9 \pi \alpha^2/16)^{1/2} \alpha^3} \int_a^\infty \varepsilon^{1/2} (2\varepsilon/m_r - v_1^2)^{1/2} \exp(-2\varepsilon/m_r \alpha^2)(1-a/\varepsilon)^{1/2} \delta^2 \, d\varepsilon \quad (29) \]

The overall average cross-section is

\[ Q_T = \Sigma_r f_r Q_r \]

where \( f_r \) is the fraction of the total population in a given rotational state.

Now with given beams, temperatures, and velocity \( (v_1) \), the quantities in front of the integral in the r.h.s. of equ. (29) are all constant, so let

\[ \Lambda = \binom{5/2}{m_r} \frac{L \sqrt{\pi} \exp(v_1^2/\alpha^2)}{(v_1^2 + 9 \pi \alpha^2/16)^{1/2} \alpha^3} \quad (30) \]

Then rewriting (29),

\[ Q_r = \Lambda \int_a^\infty \varepsilon^{1/2} (2\varepsilon/m_r - v_1^2)^{1/2} \exp(-2\varepsilon/m_r \alpha^2)(1-a/\varepsilon)^{1/2} \delta^2 \, d\varepsilon \quad (31) \]

and

\[ Q_T = \Lambda \Sigma_r f_r \int_a^\infty \ldots \, d\varepsilon \]

This expression can now be simplified by substituting the following quantities:

\[ y = 2\varepsilon/m_r \alpha^2 \quad A = \left( \frac{a}{kT} \right) \left( \frac{m_1 + m_2}{m_1} \right) \]

\[ c = v_1^2/\alpha^2 \quad B = \left( \frac{D - R}{kT} \right) \left( \frac{m_1 + m_2}{m_1} \right) \]
Eqn. (31) is then rewritten as,

$$Q_r = \pi^{1/2} \frac{2L}{m_r \alpha^2} \int_{0}^{\infty} (v_1^2 + 9\pi \alpha^2/16)^{-1/2} y^{1/2} \exp(-y+c) \int_{A,C} y^{1/2} \exp(-y+c) (1 - A)(1 - B) \frac{dy}{y}$$

(32)

This equation is now complete for the description of the elastic scattering data. In our experiment, however, the K beam was not velocity selected and, therefore, Eq. (32) had to be integrated over all potassium atom velocities.

$$Q_r = \pi^{1/2} \frac{2L}{m_r \alpha^2} \int_{0}^{\infty} (v_1^2 + 9\pi \alpha^2/16)^{-1/2} y^{1/2} \exp(-y+c) \int_{A,C} y^{1/2} \exp(-y+c) (1 - A)(1 - B) \frac{dy}{y}$$

(33)

$$dv_1$$
Note I

Taking equ. (20)

\[
\frac{\text{TRR}}{\left(\frac{2}{m_r}\right)^{1/2} 2\pi I_1 I_2 \exp \left(\frac{v_1^2}{\alpha^2}\right)} = \frac{L}{m_r} \int_a^\infty \epsilon^{1/2} \left(2\epsilon/m_r - v_1^2\right)^{1/2} \exp(-2\epsilon/m_r\alpha^2) (1-a/\epsilon) \delta^2 d\epsilon
\]

and letting \( a \to 0 \), \( \delta \to 1 \)

and with \( \frac{L}{m_r} = \frac{\sigma}{\pi} \)

the right hand side of (20) goes to

\[
= \frac{\sigma}{\pi} \int_{m_r v_1}^\infty \epsilon^{1/2} \left(2\epsilon/m_r - v_1^2\right)^{1/2} \exp(-2\epsilon/m_r\alpha^2) d\epsilon
\]

then with rearrangement and letting \( v_1 \to 0 \) for simplification this reduces to

\[
\text{TRR} = \frac{\sigma I_1 I_2}{v_1} \int_0^\infty \frac{2\epsilon}{m_r\alpha^2} \exp\left(-\frac{2\epsilon}{m_r\alpha^2}\right) \frac{2d\epsilon}{m_r\alpha^2}
\]

And finally

\[
\text{TRR} = \frac{\sigma I_1 I_2}{v_1} \Gamma (2) = \frac{\sigma I_1 I_2}{v_1}
\]
APPENDIX D

In Chapter V it was mentioned that the ratio of KCl* to KCl had to be corrected for the relative densities of the two reactants HCl* and HCl. It can immediately be seen that if the HCl beam was single valued in velocity, the the "A" scaler (counting product from the reaction of HCl*) should only be on a time equal to the length of the excited molecular beam divided by the velocity. Since the excited molecules have a range of velocities they will arrive at the reaction zone and their reaction product at the detector over a range of times corresponding to their velocities. Consequently to collect an appreciable portion (75%) of the product, KCl*, coming from the excited reactant, HCl*, it is necessary to leave the scaler on approximately an order of magnitude longer than would have been necessary had the HCl beam been single valued in velocity. This causes a dilution of the KCl* signal on Scaler "A" with KCl (reaction product of HCl) of an order of magnitude, equal to the time on. This becomes important since the amount of reaction of K + HCl* is not measured directly but as a ratio to the amount of reaction from the ground state reaction. The KCl* signal on scaler "A" then had to be corrected for this since it was to be compared to the KCl signal on scaler "B". This scaler was on the same length of time but did not suffer the dilution problem. In addition to this correction, it was necessary to account for the fact that the laser only excites the higher rotational levels \( J \geq 4 \) which includes \( \approx 50\% \) of the beam population. In addition to these factors, it was pointed out in Appendix B that no more than 50% of the population of an excited state may actually be excited. Thus the total correction was a factor of approximately 40.
APPENDIX E

References


GOL 50 H. Goldstein, Classical Mechanics, Addison-Wesley, 1950.


HOO 75  J. J. Hood, Phil. Mag., 6, 371 (1878).


VAN 84  J. H. van't Hoff, Etudes de Dynamique Chimique, (1884).