1950

Mass spectrometry: I Theory and construction of mass spectrometers: II Kinetics of the reaction of uranium with H₂, HD and D₂

Harry John Svec
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UMI
MASS SPECTROMETRY

I. THEORY AND CONSTRUCTION OF MASS SPECTROMETERS

II. KINETICS OF THE REACTION OF URANIUM WITH $\text{H}_2$, HD AND D$_2$

by

Harry John Svec

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

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In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

Iowa State College

1950
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I. INTRODUCTION AND HISTORICAL REVIEW

During the last decades of the 19th century scientific attitude towards the existing atomic theories started to undergo a complete and radical change. The causes for these changes are best ascribed to the discovery of radioactivity (1). Fundamental physical theories underlying the applied science of chemistry which formed a solid mathematical basis for its formulae were suspected of hitherto hidden flaws. These suspicions began to be realized when in 1906 Boltwood (2, 3) failed to separate ionium from thorium. In the non-radioactive field J. J. Thompson (4) a few years later observed the anomalous behavior of neon when subjected to positive ray analysis.

However to become orientated a review of the history back of the atomic theory is in order. In 1803 Dalton (5, 6) generalized his ideas about fundamental particles in what is known as the Atomic Theory. Of the five original postulates only the validity of one is in question today. This postulate is that: Atoms of the same element are similar to one another and equal in weight. Even this is a statement in two parts. One part deals with the similarity of the atoms making up elements. If we admit a similar chemical nature of
the atoms of an element then only the second part of the statement is pure hypothesis. In the light of present knowledge then we can say that the first four and half of the fifth postulate of Dalton's Atomic Theory are sufficient to define the word "element."

Prout (7) about ten years later suggested the idea that all atoms were made up of multiples of hydrogen atoms. At the time this seemed quite plausible considering what was known about atomic weights. However, when more and more careful atomic weight determinations were made this idea was dropped since it did not account for fractional atomic weights of elements such as chlorine and copper. In due course Prout's Hypothesis was abandoned.

It is interesting to consider the reasoning behind this decision. Two alternate views presented themselves. Either the atoms of elements all weighed the same, in which case the weights of the individual atoms would be fractional, or the element was actually a mixture of atoms of several different unit weights in such proportions as to give the observed atomic weight for the element. In the latter case one had to account for a similarity of chemical properties despite a difference in weight. On the face of it this idea is not readily
acceptable in view of the evidences of different weights for elements with the consequent different chemical properties. Chemical methods could not be used to challenge the idea concerning identity of weight since by definition elements were made up of atoms similar in chemical properties. There could be no positive chemical support for this hypothesis. There were not even any theoretical doubts until first Schützenborger (8) and then Sir William Crookes (9) in 1886 urged the possibility of heterogeneity of atoms in an address before the Chemical Section of the British Association for the Advancement of Science at Birmingham. Crookes stated that it was not inconceivable to him that calcium should have an atomic weight of 40 and be made up primarily of atoms of weight 40 but that there be also present atoms of weights 39 and 41 or 38 and 42. He went on further to state that these heavier and lighter atoms may even be sorted out in some sort of chemical fractionation. This, he said, may have taken place "while atomic matter was condensing out in the primal state of intense ignition." It might further have been partly effected in geological ages by successive solutions and precipitations of the various earths.

Crookes expanded the above concept in his pioneer
work on the separation of rare earths (10, 11) from the mixture yttria. The individual elements he separated which varied in weight by only a small amount but varied slightly in chemical properties he called "meta-elements." When it later developed that these were actual elements his hypothesis was abandoned and the riddle of fractional atomic weights remained unsolved.

As time went on the atomic weight determinations became more and more accurate and the question of why so many elements had combining weights very nearly integers (0 = 16) was still a very difficult question to answer.

It was not until the discovery of radioactivity that the true reason for fractional weights was suggested to be later confirmed by positive ray analysis of stable elements.

By 1910 Soddy (12) suggested the possibility of elements behaving similarly with respect to chemical properties but having different weights. Evidence (13, 14) was piling up of elements of similar chemical properties but different radioactive properties. At the same time positive ray analysis was being improved and in 1912 (4) the first results on neon were obtained which carried the idea into the region of non-radioactive
elements. In 1913 two papers were read before the British Association for the Advancement of Science, one on the "Radio Elements and the Periodic Law" (15), another on "The Homogeneity of Neon" (16) which definitely presented proof that substances could exist with identical or practically identical chemical and spectrographic properties but have different atomic weights. The need for a name for these substances became imperative and Soddy (15) suggested the word isotopes (θισοσ equal θώτης place) because they occupied equal places in the periodic table.

It was not until after the war in 1919, however, that definite proof of the existence of an isotope of mass twenty-two for neon was demonstrated by Aston (17). Earlier indication of the complexity of neon had been obtained by making careful density measurements on atmospheric neon after it had been subjected to fractional diffusion. Now the proof was presented with the first mass spectrograph.

Mass spectrographic analysis of the non-radioactive elements progressed so rapidly from this point that by 1935 (18) the last of the elements, Platinum, had been resolved into its commonest isotopes. While discoveries of rare isotopes of some elements are still being reported
all the main stable constituents of the elements had been found by 1935.

Progress in the analysis of non-radioactive isotopes appears in Table I.

Table I

Progress in Isotope Analyses in the Stable Elements Taken from Various Sources

<table>
<thead>
<tr>
<th>Year</th>
<th>Month Reported</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1919</td>
<td>Nov.</td>
<td>Ne, Ce, Hg</td>
</tr>
<tr>
<td></td>
<td>Dec.</td>
<td></td>
</tr>
<tr>
<td>1920</td>
<td>March</td>
<td>He, H(^4), N, Kr, Xe</td>
</tr>
<tr>
<td></td>
<td>July</td>
<td>B, F, Si, Bi, S, P, As, Xe, I, Mg</td>
</tr>
<tr>
<td></td>
<td>Dec.</td>
<td></td>
</tr>
<tr>
<td>1921</td>
<td>Feb.</td>
<td>Li</td>
</tr>
<tr>
<td></td>
<td>June</td>
<td>Na, K, Rb, Cs, Ni</td>
</tr>
<tr>
<td></td>
<td>Nov.</td>
<td>Be, Ca, Zn</td>
</tr>
<tr>
<td>1922</td>
<td>June</td>
<td>Sn, Xe</td>
</tr>
<tr>
<td></td>
<td>Sept.</td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td>Nov.</td>
<td>Se, Al, Xe</td>
</tr>
<tr>
<td></td>
<td>Dec.</td>
<td>Sb</td>
</tr>
<tr>
<td>1923</td>
<td>June</td>
<td>Ge</td>
</tr>
<tr>
<td></td>
<td>August</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>Sept.</td>
<td>Sc, Ti, V, Cr, Mn, Co, Ga, Sr, Y, Ag</td>
</tr>
<tr>
<td>1924</td>
<td></td>
<td>Ba, La, Pr, Nd, Zr, Ce, Cd, Te, Bi</td>
</tr>
<tr>
<td>1925-1928</td>
<td></td>
<td>More accurate masses-- H(_2), Pb, Se, S</td>
</tr>
<tr>
<td>1929</td>
<td></td>
<td>O, Pb</td>
</tr>
</tbody>
</table>

*Aston (19) confidentially announced the simplicity of hydrogen in 1920 only to be disproved in 1932 by Brickwedde and Urey (20).*
Table I (Continued)

<table>
<thead>
<tr>
<th>Year</th>
<th>Month Reported</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1930</td>
<td></td>
<td>Cr, Mo, W</td>
</tr>
<tr>
<td>1931</td>
<td></td>
<td>Os, Ru, Rh, Te, V</td>
</tr>
<tr>
<td>1932</td>
<td></td>
<td>Cb, Ta, H</td>
</tr>
<tr>
<td>1933</td>
<td></td>
<td>Nd, Sm, Eu, Gd, Tb</td>
</tr>
<tr>
<td>1934</td>
<td></td>
<td>Dy, Ho, Er, Tm, Yt, Lu, Rh, Ca, Ti, A</td>
</tr>
<tr>
<td>1935</td>
<td></td>
<td>Pt, Pd, Au, Ir</td>
</tr>
</tbody>
</table>

In recent years isotopes have assumed value for reasons other than those applicable to the testing of prevailing theories of the atom. By use of unnaturally concentrated isotopes, chemical reactions, inorganic, organic and biochemical have been subjected to "tracer" experiments. Especially has this "tracer" technique been of value to biochemists who have used concentrates of C\textsuperscript{13}, N\textsuperscript{15}, O\textsuperscript{18}, and D to act as "tags" for chemical compounds used in their work. These are the stable isotopes. The list of references wherein deuterium alone has been used in such experiments runs well over a thousand. While the element carbon has the radioactive isotope C\textsuperscript{14}, for some experiments C\textsuperscript{13} is still mandatory. No radioactive isotope of nitrogen is known that is of value for the "tracer" technique. Tritium, the unstable isotope of hydrogen, is
In very small supply; in addition it is so weakly radioactive as to make detection and assay difficult. Because of its large percentage mass difference its chemical behavior in some instances is significantly different from that of protium.

In order to assay these stable isotopes the technique most widely adaptable is the use of the mass spectrometer.

The literature contains numerous descriptions of machines and review articles (21) have been written discussing types of mass spectrometers. Several industrial firms are producing and selling mass spectrometers which are generally expensive. For this reason a program was initiated in these laboratories to construct mass spectrometers suitable for work with hydrogen, carbon, nitrogen, and oxygen. Because of difficulties inherent with the use of hydrogen tracers a separate machine was assembled for this element. Parts were obtained after the end of the war from excess properties of the Manhattan District of Army Engineers. The special hydrogen machines of the dual collector type were designed by Nier (22) during the war research program associated with the production of the atomic bomb; they used the 60° sector magnetic field. Thus experience was first gained in these laboratories with the 60° sector type
instrument which Nier (23, 24) has so ably designed and used. For this reason the machine constructed for carbon, nitrogen and oxygen assay was also a 60° sector type instrument following closely Nier's most recent design (24).

All single focusing mass spectrometers using electrostatic ion acceleration and a magnetic field to separate ions according to their m/e ratio depend upon the same basic theoretical principle. As far as construction is concerned each may be divided into four component parts: (1) the gas supply system, (2) the ion source, (3) the mass analyzer and (4) the collecting and recording system.

The gas supply or sample handling system offers no inherent construction difficulties and is probably the easiest to assemble. These systems generally are arranged so that the gas to be analyzed is introduced into the ion source through some kind of capillary leak at a slow uniform rate. The pressure of the gas behind the leak may be adjusted to give any desirable leak rate.

The ion source is the most temperamental part of the machine; it is difficult to construct and adjust. Simplicity of design, efficiency, steadiness of ion current, elimination of stray field effects are all problems which must be considered. In machines built in these laboratories ion sources designed by Nier have
been used.

The mass analyzer of the carbon, nitrogen and oxygen mass spectrometer consists of a copper tube bent to the proper radius for a 60° sector magnetic field while that of the hydrogen machine is of special design. The distinct feature is the magnet. Alnico V permanent magnets are used in the case of the hydrogen machine while the magnet is electrically powered for the larger machine. Power for the magnet coils is obtained in the latter case from an electronically controlled supply. Ion beams, after being separated into their components according to their m/e ratios are collected and measured electrically. A scheme is employed whereby two ion beams are simultaneously collected.

The first part of this thesis deals with a description of the building of the mass spectrometers. While no claim is made to completeness of presentation an attempt has been made to balance the stress laid upon the strictly theoretical aspects and the practical construction aspects of the subject. It is difficult to say where the line can be drawn between what should necessarily be described and what should be considered common laboratory technique. What may seem obvious to the author in this regard may be obscure to others and so a genuine attempt has been
made to include over and above what seems necessary, some items that may not at first seem essential to the presentation.

The second part of this thesis deals with an application of the use of mass spectrometers in physical chemical research. The kinetics of the reactions between uranium metal, H₂, HD and D₂ have been examined. Results of the investigation are reported.
II. CONSTRUCTION OF MASS SPECTROMETERS

A. General Theory

1. Ion path

The following discussion applies not only to the Nier type instruments built in these laboratories but to other types as well. The derivation of the fundamental equation governing the ion paths are based on the arrangement which is shown in Figure 1.

![Figure 1](image-url)
An ion* is allowed to enter through the slit in plate A into the electric field between plates A and B. Because of the potential difference \( V \) between A and B it acquires a velocity \( v \). When the ion passes through the slit in B it enters a region BC in which there is no field of any kind; hence this distance is traveled in a straight line with constant velocity. The kinetic energy acquired in moving from A to B is equal to the loss in potential energy over this distance. Hence from the definition of potential difference and the law of conservation of energy it follows that

\[ V_e = \frac{mv^2}{2} \]  

The region CD represents a trapezoidal-shaped magnetic field of constant field strength while DE represents a region in which there is no field. If the ion enters the magnetic field perpendicular to the lines of force in the field, the ion path will be circular. This is true since the force acting upon the ion is constant and always at right angles to the motion. The theory of electrodynamics gives for the force acting upon charge \( e \) moving with velocity \( v \) in a magnetic field of strength \( B \) as

*The term "ion" in this section is used to designate any charged particle.
\[ F = \frac{Hev}{c} \]  

(2)

in which \( c \) is the velocity of light in centimeters per second. Since the ion path is circular the centripetal force given by (2) must balance the centrifugal force hence it follows that

\[ \frac{Hev}{c} = \frac{mv^2}{R} \]  

(3)

in which \( R \) is the radius of the circle. Solving (1) for \( v^2 \) we obtain the relation

\[ v^2 = \frac{2Ve}{m} \]  

(4)

Solving (3) for \( m \)

\[ m = \frac{HeR}{vc} \]  

(5)

or

\[ m^2 = \frac{He^2R^2}{v^2c^2} \]  

(6)

Substituting \( v^2 \) from (4) into (6) gives:

\[ m^2 = \frac{He^2R^2m}{2Ve^2c^2} \]  

(7)

from which we obtain

\[ \frac{m}{c} = \frac{He^2R^2}{2Ve^2} \]  

(8)

By holding \( H \) constant, ions of different m/e ratios may be brought into focus by varying \( V \). The same result may be obtained by varying \( H \) and holding \( V \) constant.

The variable \( R \) is fixed by the geometrical design of the instrument.
Using more practical units such as

\[ m, \text{ in atomic weight units; } e, \text{ number of electronic } \]

charges on the ion; \( B \), in gauss; \( r \), in centimeters; and \( V \) in volts,

equation (9) becomes

\[
\frac{m}{e} = \frac{H^2 R^2}{V} \cdot \frac{300 V}{e\text{s.u.}} \cdot \frac{4.803 \times 10^{-10} \text{e.s.u.}}{\text{ionic charge}} \cdot \frac{1}{1.67 \times 10^{-24} \text{gm.}} \cdot \frac{1}{(2.998 \times 10^{10})^2 \text{cm}^2 \cdot \frac{1}{2}}
\]

or

\[
\frac{m}{e} = 4.82 \times 10^{-5} \frac{H^2 R^2}{V} \tag{10}
\]

This may be termed the practical working equation for all mass spectrometers using electrostatic ion acceleration and a homogeneous magnetic field to separate the ionic beam into its \( m \) components.

2. **Focusing of charged particles by magnetic field and determination of the resolving power**

It has been well known (25, 26) that when charged particles diverge from a point in a magnetic field they are brought to a first order focus when they have turned 180°. Generally this is true for small angle divergence in a homogeneous field. By making proper variation in
the intensity of the deflecting field second order focusing may be obtained (27). This is important for large angle diverging beams. However, for the case at hand it is sufficient to consider only first order focusing. It was soon realized that the 180° case is a particular case of a more general relation (28).

Barber (29) and Stephens (30) developed the general focusing criteria from a consideration of the geometry involved. From their findings not only was it established that refocusing takes place along a line drawn through the point source of the particles and the apex of the magnetic field but also deviation from perfect focusing could be determined. Furthermore resolving power for particles of different energy or mass could be calculated.

For the sake of completeness the development of Stephens is given in some detail. Let Figure 2 represent a homogeneous magnetic field \( \mathbf{H} \) perpendicular to the paper. The boundaries of the field are planes \( GP \) and \( JP \) also perpendicular to the paper, which make the arbitrary angles \( \Theta \) and \( \Gamma \) with the normal to the line \( AC \). Inside the region \( GEFFJ \) the paths of charged particles will be arcs of circles which are tangent at the edges of the field to the direction of entrance and exit. Outside this wedged shaped field the particle paths are straight.
Figure 2.
If a homogeneous beam of charged particles passes through the entrance slit at A making an angle $\Theta$ with the base line it will enter the field at E perpendicular to GP. If the field $H$ is set for radius of curvature $EP = R$ and

$$EP = a \sin \Theta = PF,$$

the center of curvature of arc $EF$ will be $F$ and the beam will leave the field at $F$ perpendicular to $PJ$ to enter the collecting slit at $B$. All other beams such as $AKL$ homogeneous with $AEF$ but making a slight angle $\alpha$ with $AE$ will be refocused so that they cross at a point very close to $B$. Hence for a given homogeneous beam of charged particles of slight divergence best refocusing will take place at a distance $b$ from the apex $P$ of the field and on a line through $A$ and $P$ where

$$a \sin \Theta = b \sin \gamma.$$  

(12)

Departure from perfect focusing is called the "spread" and indicated on Figure 2 by $S$; $UB$ or $s$ is called the "spread along the base line."

$$S = s \sin \gamma.$$  

(13)

Now if another beam which differs from the original in some property of the particle, i.e. $v + \Delta v$ for electrons or $m + \Delta m$ for ions, enters through the slit at $A$ and
continues along $AE$ its radius of curvature will be greater in the magnetic field and it will follow the line $AEVC$ intersecting the base line at $G$. The "dispersion" of the apparatus is defined as $D_1BC$ or $d$ is the "dispersion along the base line." Since practically $FB$ and $VC$ may be considered parallel (Fig. 2 is somewhat exaggerated.)

$$D \approx d \sin \gamma.$$ (14)

The ratio $D/S$ will hence represent the theoretical resolving power of the apparatus.

To find $S$ in terms of $\alpha$, $\Theta$ and $\gamma$ consider the following. Let the $x$ axis be $APG$ and the $y$ axis be perpendicular at $A$. Considering the path $AKLU$ the coordinate points are $x_1y_1$ at $K$; $x_2y_2$ at $T$; $x_3y_3$ at $L$ and $x_4y_4$ at $U$. Also $KT = EP = r = a \sin \Theta$. $KT$ is perpendicular to $AK$. By standard methods of analytical geometry

$$x_1 = \frac{a \cos \Theta}{\cos \alpha} \cos(\Theta + \alpha)$$ (15)

$$y_1 = \frac{a \cos \Theta}{\cos \alpha} \sin(\Theta + \alpha)$$ (16)

$$x_2 = a \left[ \cos\Theta \cos(\Theta + \alpha) + \sin \Theta \sin(\Theta + \alpha) \right]$$ (17)

$$y_2 = a \left[ \cos\Theta \sin(\Theta + \alpha) - \sin \Theta \cos(\Theta + \alpha) \right]$$ (18)

or substituting from (15) and (16)

$$x_2 = x_1 + a \sin \Theta \sin(\Theta + \alpha)$$ (19)
\[ y_2 = y_1 - a \sin \Theta \cos (\Theta + \alpha) \]  

(20)

Considering \(x_2y_2\) as the center of a circle of radius \(a \sin \Theta\), there results the equation of a circle

\[(x-x_2)^2 + (y-y_2)^2 = a^2 \sin^2 \Theta\]  

(21)

The equation of the line through \(P\) and \(L\) \((x_3y_3)\) is

\[ y = (x-a) \cot \gamma \]  

(22)

whence the intersection of the line \(PL\) and the circle

\[(x-x_2)^2 + [(x-a) \cot \gamma - y_2]^2 = a^2 \sin^2 \Theta\]  

(23)

Expanding and collecting terms followed by a solution gives

\[ x^2 \left[ 1 + \cot^2 \gamma \right] + x \left[ -2 (x_2+y_2 \cot \gamma + a \cot^2 \gamma) \right] + \left[ x_2^2 + y_2^2 + 2 ay_2 \cot \gamma + a^2 \cot^2 \gamma - a^2 \sin^2 \Theta \right] = 0 \]  

(24)

For brevity let

\[ m = 1 + \cot^2 \gamma = \csc^2 \gamma \]  

(25)

\[ n = -2 (x_2+y_2 \cot \gamma + a \cot^2 \gamma) \]  

(26)

\[ c = x_2^2 + y_2^2 + 2 ay_2 \cot \gamma + a^2 \cot^2 \gamma - a^2 \sin^2 \Theta \]  

(27)

\[ x_3 = \frac{-n + \sqrt{n^2 - 4mc}}{2m} \]  

(28)

\[ y_3 = (x_3-a) \cot \gamma \]  

(29)

\[ y_4 = 0 \]  

(30)

\[ x_4 = x_3 + s \]  

where \(s\) is the line \(QB\) in triangle \(LQB\).

Now \(\tan \gamma = \frac{y_3}{x_3-x_2} = \frac{y_3}{y_3-y_2}\)  

(31)
or
\[ E = y_3 \left[ \frac{y_3 - y_2}{x_3 - x_2} \right] \]  

(32)

Hence
\[ x_4 = x_3 + y_3 \left[ \frac{y_3 - y_2}{x_3 - x_2} \right] \]  

(33)

Now
\[ s = (a + b) - x_4 \]

from (13) we had
\[ S = s \sin \gamma = (a + b - x_4) \sin \delta \]
\[ S = a \left( \sin \gamma + \sin \Theta \right) - x_4 \sin \gamma \]
\[ S = a \left( \sin \gamma + \sin \Theta \right) - \frac{x_3(x_3 - x_2) + y_3(y_3 - y_2)}{x_3 - x_2} \sin \gamma \]  

(34)

Substituting, expanding functions of \( \alpha \) and then approximating by dropping all powers of \( \alpha \) greater than two
\[ S \approx a \alpha^2 \left[ \frac{\sin^2 \Theta}{\sin \gamma} + \frac{\sin^2 \gamma}{\sin \Theta} \right] . \]  

(35)

In the case where \( \delta = \Theta \)
\[ S \approx a \alpha^2 \sin \Theta . \]  

(36)

To find \( D \), the dispersion, consider first the case for electrons. An increase in velocity \( \Delta v \) causes an increase in the radius of curvature \( \Delta R \) such that
\[ \frac{\Delta R}{R} = \frac{\Delta v}{v} \]  

(37)
provided the field \( H \) is held constant. If the new radius \( R + \Delta R \) is drawn, and the new position and the new angle with which the beam leaves the field determined as above, the intercept will be on the line \( APC \). This distance can be obtained in terms of \( a, \Theta, \kappa \) and \( \Delta R \). All powers of \( \Delta R \) greater than one are dropped. Substituting for \( \Delta R \)

\[
D = a \left[ \sin \Theta \right] \left[ \frac{\Delta v}{v} \right] \left[ \sin \Theta + \sin \kappa \right]. \tag{38}
\]

For \( \Theta = \kappa \)

\[
D = 2a \frac{dv}{v} \sin \Theta \tag{39}
\]

For a constant magnetic field by equating the centrifugal and centripetal forces

\[
\frac{mv^2}{R} = \frac{Hev}{c} \tag{40}
\]

where \( m \) is the mass of the particle,

- \( R \) is the radius of curvature,
- \( v \) is the velocity,
- \( e \) is the charge on particle,
- \( H \) is the magnetic field strength,

and \( c \) is the velocity of light.

From (40)

\[
R = \frac{mv^2}{He} \tag{41}
\]

and
\[
\frac{dR}{R} = \frac{dv}{v} \quad \cdot 
\]

Solving for the theoretical resolving power in the general case from (35) and (38)

\[
\frac{D}{\lambda} = \frac{2}{\lambda^2} \frac{dv}{v} \left[ \frac{\sin \Theta + \sin \gamma}{\sin \Theta + \sin^2 \theta} \right] \tag{43}
\]

Applying this to one of the cases at hand using (41) (39) (36) where \( \Theta = \gamma \)

From (41)

\[
H = \frac{mve^2}{Re} \tag{44}
\]

Taking the logarithm and differentiating

\[
\frac{dH}{H} = \frac{dm}{m} + \frac{dv}{v} - \frac{dR}{R} \tag{45}
\]

or

\[
\frac{dm}{m} = \frac{dR}{R} + \frac{dH}{H} - \frac{dv}{v} \tag{46}
\]

Assuming the field \( H \) to be constant and \( R \) to be fixed in the apparatus

\[
\frac{dm}{m} = - \frac{dv}{v} \tag{47}
\]

Neglecting the sign of \( \frac{dv}{v} \) since we are dealing with positive quantities, from (39)

\[
D = 2a \frac{dm}{m} \sin \Theta \tag{48}
\]
Where $a = 30$ centimeters, from (36)

$$S = 15\alpha^2$$  \hfill (49)

and

$$D = 30 \frac{dm}{m}$$  \hfill (50)

As a criterion for the theoretical resolving power

$$D = S$$

and

$$\frac{dm}{m} = \frac{1}{2} \alpha^2$$

From the dimensions of the collimating slits of the source of the carbon, nitrogen and oxygen mass spectrometer built in these laboratories (See Figure 3)

$$d = \tan \alpha = \frac{0.5}{12} = 0.0357 \approx \alpha \quad \text{in radians}$$

Calculating the spread

$$S = 15 \times (0.0357)^2 = 0.019 \text{ cm.} \approx 0.2 \text{ mm.}$$

This would be the minimum width for the collecting slit which is placed perpendicular to the main beam on the
base line.

The actual dimensions of the copper analyzer tube in the case of the carbon, nitrogen and oxygen mass spectrometer will ultimately determine the maximum value of the dispersion of the apparatus. To find \( D \) we know that an increase in mass of a particle increases the radius of curvature such that

\[
\frac{\Delta R}{R} = \frac{\Delta m}{m}
\]

From the set dimensions of the apparatus

\( R = 15 \text{ cm.} \)
\( \Delta R = .75 \text{ cm.} \)

\[
\frac{\Delta R}{R} = \frac{0.75}{15} = 0.05 = \frac{\Delta m}{m}
\]

From (39)

\( D = 30 \times (0.05) = 1.5 \text{ cm.} \)

From the value for \( S \) obtained above

\[
\frac{D}{S} = \frac{15 \text{ mm.}}{0.2 \text{ mm.}} = 75
\]

The value of 1.0 mm. for the width of the outlet slit is chosen to give flat topped peaks. Since the spread \( S \) is 0.2 mm, there is good assurance that this will be so.
B. Hydrogen Mass Spectrometers

In order to gain experience in the construction and operation of mass spectrometers the assembly of special hydrogen machines was first undertaken. The design of these machines is due to Nier and co-workers (22). Several unique features not previously incorporated in mass spectrometers for measurement of the hydrogen isotopes are used. Generally these are employed in order to simplify the operation of the machines. The most important of these follow.

1. The magnetic field used for bending the ions in the analyzer is supplied by several small Alnico V horseshoe magnets. No large electromagnet is used with its expensive power supply. The magnets are housed within a glass envelope which also contains the other parts of the mass spectrometer.

2. Ions of masses 2 and 3 and masses 3 and 4, are collected simultaneously on appropriately placed collectors. Separate tubes are used for each of the ion pairs.

3. The ratio of the ion pairs is read directly on a decade divider. Thus the ratio measured is essentially independent of fluctuations in the apparatus. The method is actually a "null method" for determining the ion ratios.

4. All non-critical parts of the accompanying
electrical circuits are powered by simple alternating current power supplies. For the sake of simplicity the electrometer and feed-back amplifiers are powered by batteries.

5. The entire apparatus is contained in a compact angle iron frame. In the construction of the tube, Nichrome V (80% Ni, 20% Cr) is used throughout. Magnet pole pieces are made from cold-rolled, mild steel. All screws except those in the source and collector are steel.

1. Ion source

The ion source used in these machines is one designed by Nier and commonly spoken of as the Nier I type. Parts of the source are described in Figures 4 and 5. Twenty-five mil and ten mil Nichrome V sheet were used for construction of the parts. Generally those parts which were required to be more rigid were made of the 25 mil metal while those which have little or no rigidity requirements were made of 10 mil metal.

Insulating spacers were made from 2.7 mm glass capillary tubing. The length of those between the ground plate and focus plates were 10 millimeters. Those between the focus plates and shield were 4 mm. The spacers between trap and top shield plate and repeller and top were also 4 mm long. Five millimeter spacers were used on the
Figure 4. Parts of the ion source of the Hydrogen mass spectrometers
Figure 5. Parts of the ion source of the Hydrogen mass spectrometers.
top shield plate. Tolerances on the lengths of the spacers were ± 0.01 mm. Glass sleeving made from 2.5 mm. diameter pyrex tubing was used over the main posts and leads to trap and repeller. Figure 6 shows a photograph of the assembled source. Leads from the various electrodes are Nichrome V wire A.W.G. #30 fitted with slip connectors made from 40 mil I.D. nickel tubing. Those fit the re-entrant leads in the press seals of the glass envelope.

2. Mass analyzers

In Figure 7a is found a description of the tube which supports the source and also acts as a pathway for ions traversing the distance from source to magnet. The end plates are constructed of 25 mil Nichrome V; the body of the tube from 10 mil metal sheet. On the right side of Figure 10 is a photograph of this tube.

Also described in Figure 7a are the magnet parts; in Figure 7b the magnet support. Figure 8 shows the parts of the disassembled magnet. The five Alnico horseshoes lie in the middle of the photograph with the pole pieces on either side. In the upper left corner is the magnet support structure, while the upper right shows the means used to secure the magnet assembly in place. By threading Nichrome wire, A.W.G. 24, through the holes in this tension piece and then twisting the two ends of the wire until the ends
Figure 6. Assembled source and the collector plates
Figure 7a. Mass analyser tube and magnet parts
Figure 7b. Magnet support
Figure 8. Magnet parts
of the crescent begin moving toward each other the magnet assembly is secured within the glass envelope. This operation is accomplished by leading the wires out the pumping lead of the envelope and twisting using a hand drill brace to obtain an even twist. Figure 9 shows the magnet assembled. The distance between the pole pieces is $3/8$ inches. These are held apart by the top plate which is loosely riveted to the tension piece as shown in Figure 9. The bottom edges of the pole pieces are held apart by being fastened to the magnet support structure. The strength of the field for the 3-2 magnet is 765 gauss while that of the 3-4 magnet is 655 gauss.

3. Collectors

A tube fabricated from Nichrome V, rectangular in cross section, supports the collecting slits and also maintains their position relative to the magnet. A detailed description of this part is found in Figure 11. Spacing of the collectors was according to calculations which are discussed in another section of this thesis. In the case of the 2-3 tube the slits are placed 4.0 cm. apart; the slits are 2.9 cm. apart in the 3-4 tube. This distance is measured from center to center of the near and far slits. In order to assure large flat-topped peaks the exit slits are made purposely wide. The near
Figure 9. Assembled magnet
Figure 10. Source support and collector slit support with the secondary electron shield in place
slit is 10 x 14 mm. while the far slit is 14 x 14 mm. In the 2-3 tube \( H_2^+ \) ions are collected at the near slit and \( HD^+ \) ions collected at the far slit. In the 3-4 tube \( HD^+ \) ions are collected at the near slit while \( D_2^+ \) ions are collected at the far slit.

The actual arrangement of the both pairs of slits is amply shown in Figure 11. Aside from the different slit positions for the two pairs of ions the collector end of the mass spectrometers are identical.

A secondary electron shield is placed between the collector slits and the collector plates in order to minimize secondary electron currents due to ion bombardment of the edges of the slits and the collector plates. The detail of this part is shown in Figure 12. By means of 0-80 round headed screws fitted through sheet mica the secondary electron shield is fastened to the collector slit structure. Sheet mica serves to electrically insulate the two. The large holes in the shield end pieces give sufficient freedom for adjusting the distance from collector slits to shield. This distance is 3 millimeters. A photograph of the collector assembly appears on the left in Figure 10.

Figure 13 illustrates diagrammatically the manner in which the parts are assembled. While the ion tracks
Figure 11. Collector slit support
Figure 12. Secondary electron shield
Figure 13. Diagram of hydrogen mass spectrometer showing source, magnet and collectors.

1. Shield
2. Electron Trap (not shown)
3. Ion Repeller
4. Focus
5. Focus

Numbers refer to octal plug connections to high voltage supply and emission regulator.
shown therein as dashed lines are those for the 2-3 tube. They are similar in the 3-4 tube. In order to fulfill the focusing conditions for the sector type arrangement, the actual magnetic field is assumed to have a boundary in excess of the physical dimensions of the pole pieces equivalent to the air gap between the pole pieces. The above statement is based upon a calculation by Nier (23) which indicates that the integrated effect of the fringing flux carried to a first order approximation is equal to the air gap between the poles.

The collectors are two rectangular 25 mil Nichrome V plates to which is spot-welded 60 mil Nichrome V wires. These in turn are fitted with a heavy, slitted sleeve connector which is attached to the appropriate tungsten re-entrant lead sealed through the glass envelope.

Figure 14 pictures both the actual assembled pieces of the mass spectrometer and the collector plates. On the plate farthest to the right in the photograph is shown the means for electrically connecting the two plates together as required during calibration of the instrument. This consists of a piece of piano wire which is pulled in contact with the bar on the other collector plate when a small Alnico magnet is brought up to the glass envelope.

In the fabrication of all parts of the mass
Figure 14. Mass spectrometer assembly and the collector plates
spectrometer where Nichrome V sheet is used to form boxes, tubes or special structures, spot welding is employed to fasten the parts together. This is made feasible by using tabs, angle sheets and in general standard sheet metal techniques. All line up pins, main posts in the source, repeller supporting posts, and the trap support post are made from 0.057" Nichrome V rod. This size is convenient in that it represents the major diameter of a 0-80 N.F. thread. Where threaded parts are used this size thread is used throughout. Nuts used for holding the source together are made of clipped 40 mil Nichrome V sheet drilled and tapped for a 0-80 thread.

The glass envelope which encloses the entire mass spectrometer assembly is fashioned from Corning 774 glass (Pyrex). Two four lead press seals are used to introduce the various voltages to the source electrodes in addition to the -45 volts applied to the secondary electron shield. These are located above the source and opposite to each other. The lead from the secondary electron shield is by means of a quartz insulated Nichrome V wire, A.W.G. 30. Leads from the collector plates through the envelope to the amplifiers are made by means of single tungsten seals, specially skirted to cut down possible leakage. Figure 15
Figure 15. Diagram of the glass envelope for the hydrogen mass spectrometer.
shows diagrammatically the detail of the envelope while Figure 16 is a photograph of the envelope.

In order to place the spectrometer parts into the envelope it is necessary to cut off ends A, B and C. This is a simple operation if a hot wire tubing cutter is available. With the ends cut off the tube is ready for assembly. The magnet is first put in place by gently easing the magnet structure into the large tube that forms the stem of the Y-shaped envelope. The ends of the wire threaded through the holes in the tension piece are worked out through the pumping lead. Next the source support tube is put in place. A specially made long magnetized screwdriver facilitates fastening this tube to the magnet pole pieces. The source is then put in its proper place and fastened securely using the captive screws on the ground plate. Leads from the various electrodes to the press seals are arranged as shown in Figure 17. Colors referred to in the figure correspond to the insulation of the leads in the cable from the emission regulator and high voltage supply. Numbers refer to the pins of the male octal plug.

The collector end is next put in place. The long lead from the secondary electron shield is carefully introduced past the magnet and then connected to the
Figure 16. Mass spectrometer envelope
Figure 17. Source wiring arrangement for the hydrogen mass spectrometer.
appropriate lead of the press seal as indicated in Figure 17. In order to get the rectangular collector end in place it is necessary to first turn it on its side. It is then rotated to bring the line-up pins in juxtaposition with the line-up holes on the magnet pole pieces. Again use of the long magnetized screw driver facilitates fastening the collector assembly securely to the pole pieces.

The collector plates are next put in place. These should be placed symmetrically with respect to the sides of the secondary electron shield structure. Much of the success here depends upon patience since many trial and error adjustments are necessary. They consist of bending the support wires and trying over and over until proper alignment of the collector plates is achieved.

When all metal parts are assembled in the glass envelope the wire of the tension piece is twisted until the assembly no longer moves within the envelope. A re-check of the collector plate alignment may be necessary. Check should be made to be sure that the collector plates are not shorted to the secondary electron shield; the shorting wire should be working. Connection from the press seal above the source to the secondary electron shield should also be checked.
With all metal parts in place the ends of the glass envelope are sealed. The filament stem is blown in place and a gas inlet lead set into the tube. This enters by the separate arm at the collector end of the envelope and introduces the gas through the large hole in the top shield plate of the source. Figure 18 shows the assembled mass spectrometer within the glass envelope; the sheet metal can of galvanized steel which serves to shield the pre-amplifier stage of the feed-back amplifier and close examination will also show the filament leads and gas inlet tube.

Figure 19 is a photograph of the collector end of the 3-2 mass spectrometer. The upper re-entrant lead goes to the first stage of the feed-back amplifier which is housed within the 45/50 ¥ ground glass joint. The lower lead goes to the FP-54 amplifier. The figure shows the shorting wire between the two collectors and the manner in which the collectors are aligned. HD$^+$ ions are collected on the bottom plate while H$_2$$^+$ ions are collected on the upper plate. The arrangement in the 3-4 tube is essentially the same as the above, however, since the heavier D$_2$$^+$ ions are predominant in numbers their current is amplified using the feed-back amplifier. Since they are collected on what would correspond to the
Figure 18. Mass spectrometer assembly in the glass envelope
Figure 19. Collector end of the 3-2 mass spectrometer
bottom plate of Figure 16 the lead from this plate in the 3-4 tube goes to the tungsten re-entrant lead at the top of the picture. Since HD\(^+\) ions in the 3-4 tube are least in number their current is measured by the FP-54 amplifier. The grid lead from this amplifier is shown in Figure 19 as the bottom re-entrant lead; hence the connection from the upper collector plate is brought to this lead. Thus the leads from the collector plates in the 3-4 tube are actually crossed. This is shown diagrammatically in Figure 20.

![Figure 20.](image)

4. **Spacing of collector slits in hydrogen mass spectrometers**

In the construction of the collector end of the hydrogen
mass spectrometers exact placement of the two exit slits presented a problem. Since the percentage difference between the masses of the ions being collected is great the distance between the slits is relatively great. In order to maintain some kind of symmetry the collector was designed with the slits spaced on either side of the point where an ion of mass half way between the masses of the ions actually collected would come to focus. Thus in one tube this arrangement represents a hypothetical ion of mass 2.5; in the other tube an ion of mass 3.5.

In the diagram in Figure 21 the lines OBM and OCN represent the boundaries of the magnetic field arranged symmetrically to line OP. Point A is the source of ions and line AOF the line upon which refocusing of the ions occurs. All ions leaving A possess the same energy.

From the figure

\[ AO = OE \quad (51) \]
\[ BO = OD = r_1 = \text{radius of } M_1 \quad (52) \]
where \( M_1 \) represents an ion of intermediate mass to those being collected.
\[ GC = r_2 = \text{radius } M_2 \quad (53) \]
where \( M_2 \) represents the ion of heaviest mass being collected.
\( HK = r_3 = \text{radius of Mg, where M}_3 \text{ represents the ion of lightest mass being collected.} \) (54)

\[ OG = r_2 - r_1 \] (55)
\[ HO = r_1 - r_3 \] (56)
\[ EF = OF - OE \] (57)
\[ JE = OE - OJ \] (58)

According to the Law of Sines, for the triangle OGC,

\[ \frac{\sin 2\alpha}{r_2} = \frac{\sin \Phi}{r_2 - r_1} \] (59)
\[ \sin \Phi = \frac{r_2 - r_1}{r_2} \sin 2\alpha \] (60)

Similarly

\[ \frac{\sin \beta}{OC} = \frac{\sin 2\alpha}{r_2} \] (61)

or

\[ \frac{\sin (180^\circ - 2\alpha - \Phi)}{OC} = \frac{\sin 2\alpha}{r_2} \] (62)
\[ OC = r_2 \frac{\sin (180^\circ - 2\alpha - \Phi)}{\sin 2\alpha} \] (63)

In the triangle OCF

Angle OCF = \( 90^\circ + \phi \)

Angle COF = \( \alpha \)

Angle OFC = \( 180^\circ - 90^\circ - \alpha - \phi \)

Again according to the Law of Sines

\[ \frac{\sin (180^\circ - 90^\circ - \alpha - \phi)}{OC} = \frac{\sin (90^\circ + \phi)}{OF} \] (64)
From (63) and (64)

$$OF = r_2 \sin (180^\circ - \phi - 2\alpha) \sin (90^\circ + \phi) \over \sin 2\alpha \sin (180^\circ - 90^\circ - \alpha - \phi)$$  \hspace{1cm} (65)$$

For the triangle ODE

$$\frac{\sin \Theta}{r_1} = \frac{\sin 90^\circ}{OE}$$  \hspace{1cm} (66)$$

$$OE = \frac{r_1}{\sin \Theta}$$  \hspace{1cm} (67)$$

From (57) (65) and (67)

$$EF = r_2 \sin (180 - \phi - 2\alpha) \sin (90 + \phi) = \frac{r_1}{\sin \Theta}$$ \hspace{1cm} (68)$$

Now consider triangle OHK

$$\frac{\sin \psi}{r_1-r_3} = \frac{\sin 2\theta}{r_3}$$  \hspace{1cm} (69)$$

$$\sin \psi = \frac{r_1-r_3}{r_3} \sin 2\theta$$  \hspace{1cm} (70)$$

Similarly

$$\frac{\sin \gamma}{OK} = \frac{\sin 2\theta}{r_3}$$  \hspace{1cm} (71)$$

or

$$\sin (180 - 2\theta - \gamma) = \frac{\sin 2\theta}{r_3}$$ \hspace{1cm} (72)$$

$$OK = \frac{r_3 \sin (180 - 2\theta - \gamma)}{\sin 2\theta}$$ \hspace{1cm} (73)$$

In the triangle OKJ

Angle KOJ = \alpha

Angle OKJ = 90^\circ - \psi

Angle OJK = (180 - 90 + \psi - \alpha)
As before

\[
\sin \left( 90 - \psi \right) = \frac{\sin (180 - 90 + \psi - \alpha)}{OJ} \tag{74}
\]

From (73) and (74)

\[
OJ = r_j \sin (180 - 2 \theta - \psi) \sin (90 - \psi) \sin 2 \theta \sin (180 - 90 + \psi - \alpha) \tag{75}
\]

From (58), (67), and (75)

\[
JE = \frac{r_1 - r_3 \sin (180 - 2 \theta - \psi) \sin (90 - \psi)}{\sin \theta \sin 2 \theta \sin (180 - 90 + \psi - \alpha)} \tag{76}
\]

Equations (68) and (76) thus give the distances from point E at which the two ion species will come to focus on line AOF.

It may be well to emphasize at this point that while the above development was done for the symmetrically placed magnetic field where angles MOP and PON are equal to 30° it is a simple matter to do the same for the general case by following closely the same reasoning as employed above.

In the case of the mass spectrometer tubes constructed for measurement of the hydrogen isotope ratios the following parameters were used.

- \( r_1 = 5.00 \text{ cm.} \), set in the design for ion of mass 2.5 in the 3-2 tube or mass 3.5 ion in the 3-4 tube
- \( \theta = 30° \)
- \( \alpha = 60° \)
For the $\text{H}_2^+$, $\text{HD}^+$ tube

\[ r_2 = 5.48 \text{ cm.}, \text{ the radius of the } \text{HD}^+ \text{ in the magnetic field} \]

\[ r_3 = 4.47 \text{ cm.}, \text{ the radius of the } \text{H}_2^+ \text{ in the magnetic field} \]

These values are calculated from the relation

\[ \frac{m}{e} = 4.82 \times 10^{-5} \frac{r^2 H^2}{V} \]

the working equation of single focusing mass spectrometers using electrical acceleration and magnetic fields as arranged in the described machines.

For the $\text{HD}^+$, $\text{D}_2^+$ tube

\[ r_2 = 5.35 \text{ cm.}, \text{ the radius of the } \text{D}_2^+ \text{ in the magnetic field} \]

\[ r_3 = 4.63 \text{ cm.}, \text{ the radius of the } \text{HD}^+ \text{ in the magnetic field} \]

In both mass spectrometer tubes values for $r_2$ and $r_3$ are given for simultaneous collection of the respective ions.

By calculation the distances JE and EF for the HD, $\text{H}_2$ mass spectrometer are 2.01 and 1.99 centimeters respectively. Similarly for the HD, $\text{D}_2$ mass spectrometer these distances are 1.38 and 1.46 centimeters respectively. The sums of these two sets of distances are actually used in the design of the collector end of the tube. In the case of the 3-2
tube from center to center the distance between the two slits are 4 centimeters while for the 3-4 tube this distance is 2.9 centimeters as seen in Figure II.

5. Main vacuum system

The envelopes of both hydrogen mass spectrometers are evacuated by means of a two stage mercury diffusion pump (H. S. Martin, M40050, 30 mm. pump lead) backed by a mechanical pump (Welch Duo Seal 1400B). Dry ice-trichlorethylene slush is used to cool the cold finger. Four hundred milliliters of mercury are used to fill the diffusion pump boiler which is heated by an 18 ohm (A.W.G. 22 Chromel A) finger type heater. The heater is operated using an auto transformer. About 250 watts (approximately 65 volts applied to heater) are necessary to operate the diffusion pump at optimum speed. The vapor tube from the boiler to the jets is insulated using a layer of aluminum foil covered by two layers of asbestos paper around which is wrapped a double layer of 1 inch x 1/16 inch woven asbestos tape. Aluminum foil is wrapped around the outside of the asbestos insulation. By insulating in this manner lower heater temperature is required; this has the advantage of longer heater life which becomes quite important when the unit is to run constantly for long periods of time.
An ion gauge is used as a vacuum indicator. The ion gauge tube is a Type 507 (National Research Corporation). The circuit employed with this tube is an adaptation of the N.R.C. circuit published in an instruction booklet for their Ion Gauge Control Unit, N.R.C. Type 706. No vacuum indicator is used for pressures above 5 microns (0.005 millimeters of mercury). Experience has shown that the sound of the backing pump and satisfactory operation of the diffusion pump indicate when a pressure less than 5 microns is being obtained.

6. Gas sample handling system

Since the mass spectrometers are designed to handle only samples already in gaseous form, a means of handling gases (31) has been devised. Essentially the apparatus includes a gas burette and manifold with facilities for evacuation of the burette and manifold; for lowering the mercury column and for raising the column. The same gas handling system is used for both the 3-2 and 3-4 hydrogen mass spectrometer tubes. Provisions are made for introducing samples into either of the two tubes by capillary leaks. Figure 22 is a diagrammatic sketch of the system while Figure 23 is a photograph of the actual apparatus.

The manifold is set up to take four separate sample bulbs. Standard taper ground glass joints, size designated
Figure 22. Diagrammatic representation of the gas sample handling system.
Figure 23. Gas sample system
as 7/25, make interchanging the bulbs a simple matter.
The types of sample bulbs used is amply shown in Figure 23.
In order to limit space, two millimeter capillary glass
tubing was used in the fabrication of the manifold.

The burette itself consists of a 25 millimeter glass
tube to which is attached at the upper end a closed end
manometer with a range of 0-15 centimeters of mercury
pressure. The burette may be evacuated by means of a
mercury diffusion pump which in turn is backed by a
mechanical pump (Welch Duo Seal 1400 series). In addition
to the manometer, a thermocouple vacuum gauge (R.C.A. Type
1946) is used to indicate pressure in the burette. This
set up indicates when a satisfactory vacuum is obtained
when samples are pumped from the burette and manifold after
completion of an analysis. When the filament current of
the gauge is 70 milliamperes a reading of 158 microamperes
on the thermocouple output meter indicates that the
pressure in the system has fallen below one micron of
mercury. The control circuit for the gauge is described
in a later section.

To lower the mercury level in the burette a means has
been furnished whereby the space above the mercury in the
burette reservoir may be evacuated. Connection with the
five liter vacuum reservoir may be made by opening appropriate
stopcocks. This vacuum reservoir need only be evacuated occasionally during the time analyses are being made. To raise the mercury level, the pressure in the space above the mercury in the burette reservoir may be increased by means of a rubber pressure bulb.

The capillary leaks consist of 20 inch lengths of capillary copper tubing, inside diameter 0.006 inches, constricted at the end near the mass spectrometer by means of a clamp (24). With gas pressure of several centimeters of mercury in the sample manifold the pressure in the mass spectrometer pump lead will rise about 0.001 micron and in the ion source to several times this figure. The purpose of the 20 inch length of capillary tubing is to prevent back diffusion of gas fractionated at the constriction where a combination of both viscous and molecular flow takes place. The choice of the proper capillary diameter and length insures that the mass flow velocity will be greater than the back diffusion velocity. Hence the gas entering the mass spectrometer will be representative of the gas in the sample manifold. While this precaution is not too important in the case of isotope analyses where the percentage difference of the adjacent masses is small, it is important in gas analysis where a complex gas mixture consisting of constituents of different viscosity
and widely varying molecular weight is introduced into the mass spectrometer. The composition of the gas stream entering the machine will depend upon the pressure behind the leak and the amount of any one constituent will bear no simple relation to the actual amount of this constituent in the sample manifold unless a capillary as described above is used. In the case of the hydrogen isotopes where the percentage mass difference is large this effect is also important.

The length of capillary tubing is coiled and housed under a protective cover. The two leaks may be observed in Figure 23 to the left of the gas burette. Connections are made from the capillary to the glass sample system and gas inlet tubes of the mass spectrometers by Kovar to pyrex graded seals.

To operate the sample system a bulb containing the gas sample is connected to the manifold by means of a standard taper joint. A light coating of Apiezon N grease is first applied to the inner joint of the sample bulb. By opening the manifold stopcock the space up to the bulb stopcock is evacuated. If the sample is to be introduced into the 3-2 machine the stopcock leading to the capillary leak should be open while that leading to the leak of the 3-4 machine be closed. The manifold is
evacuated to less than one micron (0.001 millimeters of mercury). Then the capillary leak stopcock and the stopcock leading to the vacuum train are closed. The stopcock of the sample bulb is then carefully opened to allow the sample to enter the manifold and burette. A sample pressure of about 5 to 10 centimeters is sufficient for analysis in both the 3-2 and the 3-4 mass spectrometers. The sample bulb stopcock is then closed and as a precaution against a leaky seal at the standard taper joint the manifold stopcock is also closed. The stopcock to the capillary leak is then opened and the analysis of the sample may be made.

During the introduction of the sample into the manifold and burette the two-way stopcock on the burette mercury reservoir should be opened to the atmosphere. If it is desired to decrease the pressure of the sample in the burette the gas may be expanded by lowering the mercury level. This is accomplished by opening the two-way stopcock to the vacuum reservoir. Should it be desired that the sample pressure be increased the two-way stopcock should be first opened to the atmosphere and then closed. The pressure bulb stopcock should then be opened and the bulb pumped so as to raise the Hg level in the burette until the desired sample pressure is
obtained. This is very useful when the sample volume is small.

After an analysis has been completed the sample may be pumped from the manifold and burette. A word of caution is however timely. If the sample pressure had to be increased by raising the mercury level in the burette it is absolutely necessary that the two-way stopcock of the burette reservoir be opened to the atmosphere before evacuation of the manifold. If this precaution is not taken the manifold, manometer and capillary leak will fill up with mercury necessitating extensive dismantling of the apparatus in order to clean out the mercury. Since mercury amalgamates with copper it may necessitate replacement of the capillary.

7. Electrical Circuits

7a. Accelerating voltage supply and emission regulator

The ion accelerating voltage supply and the electron emission regulator (22) for the electron gun in the source are mounted on the same chassis. For the former a conventional vacuum tube rectifier and filter is employed. The output voltage is stabilized at 450 volts by means of three VR150 gas discharge tubes. Because of the wide collecting slits and the manner in which ion ratios are determined it is not necessary to resort to more elaborate
voltage regulation. The upper part of Figure 24 shows diagrammatically the circuit in use. The voltage dividing system used to supply potentials to the various source electrodes appears in the upper right corner; it is evident that the focus plates both carry a variable potential with respect to the shield. Grounding one of the focus plates by throwing switch $S_4$ sweeps the ion beam aside in the source. Potential for the repeller plate in the source which is variable from shield to 12 volts above the shield potential is obtained from potentiometer $R_{11}$ in the power supply of the emission regulator. A dummy plug connects the power supply to the voltage divider to serve in case of failure of the power supply in which case batteries may be used.

Transformer $T_3$ of the emission regulator (See bottom Figure 24) is employed as a conventional power transformer complete with rectifier and filter as well as four VR-75 gas discharge tubes to obtain stable voltages for the various electrodes of $V_{12}$. Transformer $T_2$, however, is used in an unconventional manner. Tubes $V_2$ and $V_3$, type 45, are connected across the high voltage winding as half wave rectifiers. The five volt winding is used to supply current to the filament of the mass spectrometer. A resistance is placed in series with the primary of the
Figure 24. High voltage supply and emission regulator
List of Parts for the High Voltage and Emission Regulator

R₁, 2  5000 ohms, 10 watt
R₃  1000 ohms, adjustable, 10 watt
R₄  5000 ohms, adjustable, 10 watt
R₅  200,000 ohms, 1 watt
R₆, 7  50 ohms, 5 watt
R₈  25000 ohms carbon potentiometer
R₉, 10  10000 ohms, 1 watt
R₁₁  2000 ohms carbon potentiometer
R₁₂  3 ohms, special shunt to make M₂ a 0-10 milliammeter
R₁₃, 15  0.1 megohms carbon potentiometer
R₁₄  0.3 megohms, 1 watt
R₁₆-25  Ten steps 10000 ohms each
R₂₆  10000 ohms, General Radio, 314A
R₂₇  150 ohms, 50 watt potentiometer
R₂₈  50 ohms, 50 watt adjustable
V₁  83
V₂, 3  45
V₄  80
V₅  6SJ7
V₆-9  VR-75
V₁₀-₁₂  VR-150
M₁  0-10 milliammeter, A.C.
M₂  0-1 milliammeter, D.C.
$T_1$  Thordarson, T74R28
$T_2$  Thordarson, T13R04
$T_3$  Thordarson, T13K13

$S_1, 2, 3$  SPST
$S_4$  SPDT
$S_5$  SPDT
$S_6$  TPDT
transformer. Thus, whenever tubes $V_2$ and $V_3$ are drawing
a large current due to their grids being more positive
than normal, the drop in the resistance in series with
the primary will be larger than normal and hence the
filament current of the spectrometer will be less than
normal. By means of $V_5$, type 6SJ7, any slight change
in the total emission of the filament of the mass
spectrometer will be amplified and appear as a large
change in the grid potential of $V_2$ and $V_3$. The circuit
thus acts in such a way as to make the electron emission
of the mass spectrometer filament remain at any pre-
determined value; this value may be adjusted by varying
resistor $R_8$. Under normal conditions total emission
is held at 5 milliamperes. Trap current will be about
500 microamperes. To operate the emission regulator
$R_{28}$ is varied until the operating range for the circuit
is reached. This will be approximately 50 ohms for a
tungsten filament, 25 mils wide and one mil thick such
as is used here. With $R_{28}$ properly set $R_{27}$ may be
varied over a range without appreciably effecting the
emission. For total emission of 5 milliamperes the
filament current is about 4.5 amperes.

The middle left panel of Figure 25 shows the panel
arrangement for the ion accelerating voltage supply and
Figure 25. Front panel of the hydrogen mass spectrometer
emission regulator. In the upper left corner of the panel from left to right are placed the two focus controls R₁₃ and R₁₅ and the repeller control R₁₁; below them is the fine and coarse adjustment of the shield potentiometer followed by the switch S₄ whereby ions are swept aside in the source. In the lower left corner is shown the off-on switch S₃ for the power supply with a red pilot bulb above it. On the right side of the panel are contained the controls for the emission regulator. The two meters at the top are the filament and emission current respectively. Below the filament current meter is the filament current control R₂₇. To the right is the emission control R₂ and the meter switch S₆ whereby either total emission or trap current may be read on the 0-10 milliammeter, M₂. A filament selector switch S₅ which switches on either the 3-2 or 3-4 tube filament followed by S₁ and S₂ to the right makes up the bottom row. In the lower right corner are two fuse holders.

The above circuits are used with both 3-2 and 3-4 tubes as has been already indicated in the case of the filaments. Two octal plugs on the back of the chassis connected in parallel using the pin numbers appearing in Figure 24 are used to supply source potentials to the both tubes simultaneously. For the sake of simplicity
only the filaments are selectively controlled.

7b. FP-54 amplifier

Before discussing the circuit itself it is well to consider some of the elementary principles upon which operation of the circuit and electrometer tube depend. The circuit employed for this amplifier is that of Dubridge and Brown (32), using an FP-54 Pliotron. Other single tube circuits are described in the literature (33, 34, 35) but this one was chosen for simplicity and reliability.

The essential feature of this circuit is the connection of the space charge grid. Since this grid operates at a positive potential it collects electrons and its current may be four to five times the plate current. If the filament emission changes for any reason the currents to the plate and space charge grid will change in about the same ratio. Hence one may be balanced out against the other so that the galvanometer is unaffected by filament emission instability.

Upon reference to Figure 26 it is evident that the voltage drop, e, across the galvanometer is given by

$$ e = R_bI_s - R_oI_p $$

(77)

provided the current through the galvanometer is small compared to $I_p$ and $I_s$. ($R_o$ is small and is merely for
Figure 26. Diagrammatic simplification of the FP-54 electrometer amplifier.

Since for operation the galvanometer current should be zero, \( e = 0 \) and

\[
\frac{R_b}{R_o} = \frac{I_p}{I_s}
\]  
(78)

This is the first condition to be satisfied. Obviously once it is satisfied the galvanometer current will remain zero in spite of emission fluctuations which change \( I_p \) and \( I_s \).

In addition it is also desirable that \( e \) be independent of battery voltage changes and hence \( I_f \). If it is assumed that

\[
\frac{de}{dI_f} = 0
\]  
(79)
it follows that

\[ \frac{dI_p}{dI_f} = \frac{R_b}{R_o} \cdot \frac{dI_s}{dI_f} \]  

(80)

as the second condition to be satisfied for neutralization.

In order for both conditions to hold for a fixed value of \( \frac{R_b}{R_o} \) it is necessary that curves \( I_p \) vs. \( I_f \) and \( I_s \) vs. \( I_f \) be straight lines which intersect on the \( I_f \) axis; Dubridge and Brown (32) found this to be the case for a typical PP-54 Pliotron. While the actual curves were not straight lines there are fairly flat sections in both. Neutralization was achieved by operating the filament at a current where both curves are essentially flat.

While equations (78) and (80) give conditions for balance in terms of tube characteristics it is not necessary to determine these to balance the circuit.

Actually to balance the circuit \( R_5 \) is adjusted to give a filament current of 90 milliamperes, the rated value for the tube. Then \( R_o \) is adjusted to bring the galvanometer to approximately zero. Connections should be so made that as \( R_o \) decreases the galvanometer deflection also decreases. With the Ayrton shunt set for low sensitivity, slowly vary \( I_f \) by changing \( R_5 \) in such direction that the galvanometer deflection is decreased. The galvanometer tends to go through a fairly flat minimum; if it goes off scale it
should be brought back by adjusting $R_0$. If the value of $I_f$ at the minimum is more than 3 or 4 per cent from the rated value for the tube shift the tap on $R_2$ to a new position and repeat until this criterion is satisfied.

Then with the shunt at full galvanometer sensitivity make the final adjustment for minimum by adjusting $R_5$ and finally bring the galvanometer to zero by adjusting $R_0$. The circuit is then ready for operation. It may show a drift for 20 to 30 minutes until thermal equilibrium of all the components is established.

In the actual circuit used in these laboratories values for the several resistors are different from those of Dubridge and Brown. The changes were made in order to make best use of the materials on hand. All electrode potentials are maintained at the same relative values within themselves and do not exceed the manufacturers' maximum recommended ratings.

The upper portion of Figure 27 shows in diagrammatic form the FP-54 amplifier circuit. Resistors $R_1$ and $R_2$ are 40000 and 2000 megohms respectively. Two sensitivity ranges are made possible by closing or leaving open the switch $S_4$. A grounding switch is also incorporated in the control grid circuit in order to be able to check the inherent amplifier stability should this be desired. The
Figure 27. FP-54 and feedback amplifiers
List of Parts of the FP-54 and Feed-Back Amplifiers

| R<sub>1</sub> | 40,000 megohms, Victoreen Hi-Meg |
| R<sub>2</sub> | 2,000 megohms, I.R.C., FH-1 |
| R<sub>3</sub> | 20,000 megohms, Victoreen, Hi-Meg |
| R<sub>4</sub> | 44.4 ohms special wire wound |
| R<sub>5</sub> | 55.5 ohms special wire wound |
| R<sub>6</sub> | 6000 ohms precision wire wound |
| R<sub>7</sub> | 3000 ohms precision wire wound |
| R<sub>8</sub> | 1000 ohms micropot |
| R<sub>9</sub> | 20000 ohms micropot |
| R<sub>10</sub> | 10000 ohms precision wire wound |
| R<sub>11</sub> | 7000 ohms precision wire wound |
| R<sub>12</sub> | 2000 ohms precision wire wound |
| R<sub>13</sub> | 1000 ohms precision wire wound |
| R<sub>14</sub> | 500 ohms precision wire wound |
| R<sub>15</sub> | 250 ohms precision wire wound |
| R<sub>16</sub> | 200 ohms precision wire wound |
| R<sub>17</sub> | 50 ohms precision wire wound |
| R<sub>18</sub> | 5000 ohms 1 watt |
| R<sub>19</sub> | 10000 ohms 1 watt |
| R<sub>20</sub> | 22000 ohms 1 watt |
| R<sub>21</sub> | 50000 ohms 1 watt |
| R<sub>22</sub> | 120000 ohms 1 watt |
| R<sub>23</sub> | 50 ohms, General Radio, 214A |
$R_{24}$ 100000 ohms micropot
$R_{25}$ 10000 ohms micropot
$R_{26}$ 500000 ohms, carbon potentiometer
$R_{27}$ 20 ohms, 5 watt
$R_{28}$ 150 ohms, 5 watt
$R_{29}$, $R_{31}$ 1 megohm, 1 watt
$R_{30}$ 3 megohms, 1 watt
$R_{32}$ 15000 ohms, precision wire wound
$R_{33}$ 1 ohm decade resistor, General Radio 510A
$R_{34}$ 10 ohms decade resistor, General Radio 510B
$R_{35}$ 100 ohms decade resistor, General Radio 510C
$R_{36}$ 1000 ohms decade resistor, General Radio 510D
$R_{37}$ 10000 ohms decade resistor, General Radio 510E
$R_{38}$ 40000 ohms precision wire wound
$V_1$ FF-54, General Electric Plotron
$V_2$ 959
$V_3$, 4 185
$V_5$ 6J5
$T_1$ 110 v. to 6.3 v. 1 amp. filament transformer
$T_{2,3}$ 80 mh. radio frequency chokes
$C_{1-4}$ 0.1 microfarad 450 volts
$C_5$ 0.01 microfarad 450 V.D.C.
$M_1$ 0-100 milliamperes, D.C.
$M_2$ 0-1 milliamperes, D.C.
Leeds and Northrup type 2500B galvanometer, sensitivity 0.0005 microamperes/millimeter, resistance 480 ohms, C.D.R.X. 8000 ohms

$S_1$ 6 contact, double wafer, non shorting

$S_2$ SPTT

$S_3$ SPTT

$S_4$ Special switch in FP-54 housing

$S_5$ Special switch in FP-54 housing

$S_6$ SPDT

$S_7$ SPST

$S_8$ 11 contact single wafer
FP-54 tube is mounted in a special housing which may be evacuated. A five terminal press seal by means of a graded glass seal to Kovar metal which is in turn soft soldered to the housing as shown in Figure 28b allows entry of the filament, plate, screen grid and sensitivity switch leads. The control grid lead into the housing is a 1/8 inch brass rod insulated from the brass side tube of the housing (see Figure 28a) by polystyrene or hard rubber insulators. Figure 28b shows the arrangement of the grounding switch while Figure 28a shows the arrangement of the sensitivity switch. Flexibility and vacuum tightness of the switches is afforded by Sylphon bellows.

A hard rubber plate 3/8 of an inch thick is used to mount the base supporting structures and to insulate them from the grounded housing. The FP-54 tube is mounted on springs soldered to the tube base pins. In order to shield the tube from stray magnetic fields as well as from electrostatic fields the main body of the housing is constructed from mild steel. Figure 28c shows a top view of the housing with the cover removed. Connection from the tops of the two grid resistors to the control grid is made with Litz wire.

The entire grid lead from the collecting plate of the mass spectrometer to the FP-54 tube is in an evacuated space.
Figure 28. Special housing for the FP-54 electrometer
FF-54 Housing

Side View Partially Sectioned

Radiator

Vac. Ports in Insulator

Sylphon

Grounding Switch

Spring

5 Terminal Press

Silver Solder

Kovar Metal Soft Solder

1 Housing for the FF-54 electrometer tube
Figure 28c. Special housing for the FP-54 electrometer tube
Connection of the amplifier housing to the glass tube, by which entry is made into the mass spectrometer envelope, is by means of a Sylphon bellows fitted with adjustment screws which prevent collapse of the bellows when it is evacuated. Seals between bellows and housing and bellows and envelope are made vacuum tight by first taping with Scotch electrical insulating tape and then painting with Glyptal varnish. The section of the grid lead not shielded by the bellows or amplifier housing side arm is carefully shielded using aluminum foil. The glass surfaces are first washed with 95% Ethyl alcohol and then wrapped with the foil. Care is taken to be sure the foil shield is grounded.

The galvanometer used in the FP-54 amplifier has a sensitivity of 0.0005 microamperes per millimeter on a scale placed one meter from the mirror. However in practice the scale is mounted 1.5 meters from the mirror thus increasing the galvanometer sensitivity to 0.00033 microamperes per millimeter on the scale. The scale which is one meter long and graduated in millimeters is shown in Figure 25.

A special mounting is used for the galvanometer in order to overcome difficulties due to vibrations transmitted throughout the building. In order to correct for horizontal
vibrations a simplified version of Mueller's modification
of the Julius suspension is employed; the essentials of
which are described by Strong (37). A new method for damping
the oscillations of the suspension was devised in these
laboratories in which four vanes moving in an oil bath
damp oscillations more quickly. The suspension made
of brass, is set on a copper sheet over sponge rubber
one inch thick which absorbs vertical vibrations. Figures
23, 29 and 30 show different views of the mounting while
Figure 31 is a dimensioned drawing of the same.
Figure 29. Galvanometer mounting
Figure 30. Arrangement for mounting the 3-4 hydrogen mass spectrometer tube showing the mounting for the galvanometer of the FP-54 amplifier in the background.
Figure 31. Galvanometer mounting
7c. **Feed-back amplifier**

The feed-back amplifier follows the design of Roberts (38). Essentially there are three stages of amplification with a cathode follower for the output. In order to make the amplifier as nearly battery operated as possible miniature tubes are used in the amplification stages. Filament current is supplied from a twelve volt storage battery which also supplies power for the FP-54 amplifier. Plate potentials are all supplied from a 90 volt B-battery.

![Diagram](image.png)

**Figure 32. 959 electrometer tube housing**

The first stage of the amplifier (see bottom of Figure 27) makes use of a 959 tube connected as an electrometer. Grid number three of this acorn type is well insulated with a grid current of $10^{-12}$ to $10^{-13}$ amperes which makes it suitable for use as an electrometer.
The tube is mounted in a regular doughnut shaped acorn tube socket which is in turn fitted to a male 45/50 standard taper ground glass joint. A five terminal press seal allows for entry of leads to the tube. Grid resistor $R_3$ is contained in this special tube housing which is illustrated in Figure 32. Leads made of heavy wire from the press seal to the filament and screen grid terminals support the socket. Other connections within the housing are made with flexible wire. A shielded cable serves to connect the electrometer tube to the remainder of the amplifier which is housed in a chassis along with the FP-54 controls and the decade slide wire. The second and third stages of amplification of the feedback amplifier make use of the miniature tubes type 135. A 6J5 tube is employed for the cathode follower; a separate transformer supplies its heater current.

The feedback amplifier is operated as follows.

With no ions falling on the collector plate, which is connected to the third grid of the electrometer tube, resistors $R_{24}$, $R_{25}$ and $R_{26}$ are adjusted until the drop in $R_{32}$, the cathode resistor of the 6J5 is precisely equal to the potential of the 45 volt battery $E_4$. This may be easily determined by observing meter $M_2$, the output meter in the slide wire circuit. For a more sensitive means of
balancing the amplifier $S_2$ may be switched to the 3 position with the grid of the FP-54 ungrounded. Under these conditions the FP-54 amplifier is used merely as a zero balancing device. After this preliminary adjustment has been made the amplifier is ready for current measurement purposes.

Controls for both FP-54 and feed-back amplifiers along with those of the decade slide wire are located in the same chassis. The lower right panel of Figure 25 shows the positions of the various controls indicated diagrammatically in Figure 27.

Across the top of the panel are the controls of the FP-54 amplifier. From right to left they are the Ayrton shunt, coarse zero adjustment, on-off switch, coarse balance, $R_g$, the filament current meter $M_1$, fine balance, $R_g$, the FP-54 selector and the filament current control $R_{23}$.

The feed-back amplifier controls are in the middle row along with switches $S_2$ and $S_3$. From left to right they are $S_2$, the off-on switch, coarse balance $R_{24}$, output meter $M_2$, fine balance $R_{25}$ and $S_3$. $R_{26}$ is adjusted internally within the chassis. Below the off-on switch of the feed-back amplifier is a 2-3; 3-4 amplifier selector. Since the amplifiers for both the 3-2 and 3-4 hydrogen tubes use a common control chassis it is
necessary to have some means of switching from one set to the other. The bottom row on the panel indicates the controls of the decade slide wire.

Ion current ratios are determined by a null method (39) which in principle depends upon introducing a portion of the output of one amplifier into the grid circuit of the other in order to balance out the effect of an ion current falling on the collector of the second amplifier. Actually, the output of the amplifier measuring the greater ion current is applied to a decade slide wire in exactly the same manner as the potential is supplied across the slide wire of a potentiometer. Then by tapping off a portion of this potential and introducing it in opposite polarity into the grid circuit of the amplifier used to amplify the least ion current the effect of this current may be balanced out. The second amplifier is used only as a device for determining the null point.

As an illustration using the circuit in Figure 27 assume $S_2$ is turned to the 2 position and a current due to $H_2$ ions of $2 \times 10^{-10}$ amperes is hitting the mass 2 collector of the 3-2 tube. Since $R_3$ is $2 \times 10^{10}$ ohms the drop across the resistor is four volts. Meter $M_2$ would indicate four volts because the output of the feed-back amplifier is almost precisely equal to input,
a fact which will be shown to be true in subsequent sections of this thesis. However, the above four volt output is opposite in polarity to the input voltage; it follows that by setting $S_2$ in the 2 position any fraction of this voltage may be fed into the grid circuit of the FP-54 amplifier. The fraction may be such as to be exactly equal to the potential drop across $R_1$ or the $R_1$, $R_2$ combination if it is to be used. This is a true null method. For example if the intensity of the ion currents should both double the output of both the feed-back amplifier and the FP-54 electrometer amplifier would double. As a consequence of the increase of the feed-back amplifier output a signal twice as great would be fed into the FP-54 grid circuit as before the ion current intensities changed. This would balance out the output of the FP-54 amplifier due to the doubly great signal being received. Thus the system not only serves as a null method but also automatically compensates for changes in ion intensities which may occur during an analysis.

The validity of the null principle may be proved by examination of Figure 33 which is a schematic diagram of Figure 27. Consider first the lower part of the figure. An ion current falling on the mass 2 collector gives rise to a voltage drop across $R_3$. 
Figure 33. Schematic diagram of the FP-54 and feedback amplifiers
\[ V_{DC} = I_{R3} R_3 \]  

where \( I_{R3} \) represents the ion current.

If \( G \) is the voltage amplification of the feedback amplifier

\[ V_{DA} = V_{DC} - GV_{DA} \] (82)

Solving

\[ V_{DA} = \frac{V_{DC}}{1 + G} \] (83)

and

\[ V_{AC} = GV_{DA} = V_{DC} \left( \frac{G}{1 + G} \right) \] (84)

As \( G \) is very large, approximately 1000 for the amplifier employed,

\[ V_{AC} \approx V_{DC} \] (85)

It should also be noted that the signal which on input was positive with respect to ground has been inverted to one which is negative. Since the internal resistance of the amplifier as seen by the output terminals is very low one may connect a conventional voltmeter across these terminals to measure the output voltage; a 0-1 milliammeter in series with approximately 50000 ohms constitutes such a meter. If a current of \( 10^{-9} \) amperes flows through \( R_3 \)

\[ V_{DC} \approx V_{AC} = 20 \text{ volts} \]

The meter would indicate 0.4 milliamperes. The current
amplification for this particular arrangement would be

\[
\frac{4 \times 10^{-4}}{1 \times 10^{-9}} = 4 \times 10^5
\]

Observation of the upper part of Figure 33 will show that if point B is made coincidental with A the FP-54 amplifier will function on the usually "straight deflection" method. However if B is moved the proper distance up from A the voltage drop \( V_{AB} \) can be made precisely equal to \( I_{R_1} R_1 \), where \( I_{R_1} \) is the ion current to mass 3 collector. That is, the FP-54 acts as a null instrument to indicate when

\[ V_{AB} = I_{R_1} R_1 \]  

(86)

The feedback amplifier provides the potential for the potentiometer ABC as a dry cell would in a conventional potentiometer. However, there is the important distinction that the voltage \( V_{AC} \) is automatically proportional to the current falling on mass 2 collector. Thus the balance point B is independent of variations in the ion current intensities provided both currents vary in the same way at the same time.

To find the ratio of \( I_{R_1} \) and \( I_{R_3} \)

\[
\frac{I_{R_1}}{I_{R_3}} = \frac{V_{AB}}{V_{AC}} \cdot \frac{R_3}{R_1}
\]  

(87)
Since $V_{AB} = R_{AB}I$ and $V_{AC} = R_{AC}I$, in which $I$ is the current in the slide wire it follows that

$$\frac{I_{R_1}}{I_{R_3}} = \frac{R_{AB}}{R_{AC}} \cdot \frac{R_3}{R_1}$$

(88)

which in the case of the 3-2 tube would be the $HD^+/H_2^+$ ratio; in the 3-4 tube it would be the $HD^+/D_2^+$ ratio. Where $R_3/R_1 = 1/2$, the nominal value for the resistor ratio, $(R_3 = 20000$ megohms; $R_1 = 40000$ megohms) since $R_{AC} = 50000$ ohms the ratio would be given directly in parts per hundred thousand.

However, by way of precaution, it should be noted that in the actual potentiometer used, $AC$ is made up of five decade units and a fixed resistor $R_4$ plus the meter resistance (about 30 ohms). All units below a thousand ohms are plain resistors hence the total resistance in series with the meter will depend upon the particular setting of the dials. If $R_3/R_1 = 1/2$ and $R_4 = 40000$ ohms a dial setting of $9753.1$ would indicate the $3/2$ ratio to be $9753$ parts per hundred thousand. However a simple computation shows that this should be

$$\frac{9753.1}{50753.1} \cdot \frac{1}{2} \approx 9600 \text{ parts per hundred thousand}$$

Since the additional $753.1$ ohms in the circuit resulted in a reading $1.6\%$ too high it is apparent that a correction
can be made which is about 1% for each 500 ohms in the
hundred position. However, in the case of hydrogen
where measurements are affected by the "pressure effect,
"memory" and apparatus discriminations due to the large
percentage mass differences it would be good if 1%
accuracy can be obtained.

At this point it is well to examine whether it is
necessary that the feed-back amplifier be balanced during
analyses. From Figure 27 it is apparent that the output
voltage, $AC$, is the difference between 45 volts and the
drop across $R_{32}$. Thus, when no ion current is falling on
the collector one ordinarily adjusts the resistors in the
959 plate circuit so that $V_{AC} = 0$. However, since the
FP-54 is used only as a null instrument and the zero point
is determined by sweeping both ion beams aside in the ion
source it is not necessary that the feed-back amplifier be
balanced even approximately. To demonstrate this first
assume the feed-back amplifier to be in perfect balance,
i.e. with no ions falling on the collector, $V_{AC} = 0$.
Next allow ions to strike the two collectors and adjust
point $B$ until the FP-54 amplifier indicates a balance,
that is, $V_{FA} = 0$. The true ratio of ion currents is then
given by reading the position of point $B$. Let $x = \frac{R_{AB}}{R_{AC}}$
for this condition. Thus $I_{R_1} R_1 = X V_{AC}$. 
Next assume that prior to measuring the ion current ratio the feed-back amplifier was not precisely balanced, that is, there exists an output voltage \( V_{AC}^{0} \) even before ions strike the collectors. Again allow ions to strike the collectors and adjust point B until shutting the ions off or on results in no change in the FF-54 galvanometer reading. Let \( y = \frac{R_{AB}}{R_{AC}} \) for this case. The potential at point F may then be written.

For ions striking collectors
\[
V_{F} = I_{R_{1}} R_{1} = y (V_{AC} + V_{AC}^{0})
\]  
(99)

For ions off
\[
V_{F} = y V_{AC}^{0}
\]  
(90)

But these two quantities are equal under the conditions of balance

\[
I_{R_{1}} R_{1} = y V_{AC}
\]  
(91)

However, it was shown that
\[
I_{R_{1}} R_{1} = x V_{AC}
\]  
(92)

Thus
\[
x = y
\]

From the above discussion it is evident that the ion current ratio determination is independent of the feed-back amplifier balance although it is necessary to point out that should the
degree of unbalance be too great it will be impossible to operate the circuits because the light spot reflected from the galvanometer will not remain on the scale.

7d. Ionization gauge circuit

To determine the pressure in the main mass spectrometer tube a hot cathode type ionization gauge is used. Tube designation of the gauge is type 507.* With a plate potential at -20 volts and a grid potential at 150 volts with respect to the cathode this tube has an ion current with dry air of 100 microamperes at one micron of mercury pressure. In the published data (40) on the tube the calibration curve obtained by plotting plate current against pressure is a straight line between 1 and 0.001 microns. From data on other ionization gauges (41) there is little reason to doubt that this linearity is extendable to even lower pressures.

A vacuum tube voltmeter is used to determine the magnitude of the ion current in the gauge. In the voltmeter circuit the two sides of a dual triode, type 7F7, serve as two arms of a balanced bridge. The degree of unbalance caused by a signal from the ionization gauge plate to the grid of one side of the 7F7 is measured by a 0-100 microammeter which is in turn calibrated in terms

*Sold by the National Research Corp., 70 Memorial Drive, Cambridge, Massachusetts.
of pressure. A range switch is provided that covers the entire pressure range from 5 microns to 0.0001 microns.

Reference to Figure 34 will indicate that regardless of what ion current is being received by the plate in the ionization gauge, the grid potential of the half of the 7P7 tube which receives the signal will vary over the same voltage range. When the current becomes so small for one grid resistor as to make the voltmeter insensitive, switching to the next highest step increases the value of the resistor by a factor of ten; a consequent increase in sensitivity occurs.

One minor change has been made in the circuit as shown on Figure 34. A DPDT switch is inserted into the grid and filament circuits of two ionization gauges in such a manner that the one control circuit serves gauges for both 2-3 and 3-4 mass spectrometer tubes. Other electrode potentials in both gauges are supplied simultaneously.

In the upper right corner of Figure 25 is shown the panel for the ionization gauge circuit. The two meters measure the grid current and degree of bridge unbalance respectively. To the left of the grid current meter is the grid current control. Below this is the control switch for normal operation or for outgassing the grid;
Figure 34. Ionization gauge control circuit
the line switch is at the bottom. From left to right along the bottom of the panel, after the line switch, is the line pilot light, zero set, zero control, range switch and the switch already mentioned above that enables either the 2-3 or 3-4 ion gauges to be operated. Below each meter is a fuse of appropriate size which is connected in series with the meter.

Procedures are given below for operating the circuit after the type 507 has been installed and all connections made. Since both ends of the grid are connected to terminals in the base of the ionization tube it may be heated electrically for purposes of outgassing. With the range switch in X5 position and the control switch in the outgas position turn the grid current control counterclockwise until the control relay is energized; then slowly turn it clockwise until the grid of the gauge shows a dull red glow. Allow the outgassing to take at least 5 minutes. A longer time may be required in some cases in which it may be necessary to outgas the plate along with the grid.

After the grid has been outgassed, switch the control to normal; the range switch should still be in the X5 position. Adjust the plate meter to zero using the zero control. Again turn the grid current control counterclockwise until the relay is engaged, then clockwise until
the *grid* current meter indicates 5 milliamperes. When switching from *outgas* to *normal* operations the control relay drops out; this is a safety feature to prevent damage to meters, ionization gauge filament or both.

Pressure is read on the *plate* meter which has been calibrated according to the following formulae.

\[
P_{\text{mm. Hg}} = \text{Range setting} \times \text{microamperes} \times 10^{-5}
\]

\[
P_{\text{micron Hg}} = \text{Range setting} \times \text{microamperes} \times 10^{-2}
\]

Maintenance of this circuit in general involves only changing tubes. Tube types 5W4 and VR150 may be changed without altering the amplifier characteristics of the vacuum tube voltmeter. Changing tube type 7F7 will generally require re-balancing the circuit. This may be done by switching the range switch \( S_4 \) of Figure 34 to the number 1 or *adjust* position. The ionization gauge cord should be removed. Resistor \( R_y \), which is found on the back of the chassis is then adjusted to give full scale reading on the *plate* meter. The range switch is switched to the 2 or X5 position and the *zero* balance control adjusted to give a zero reading on the *plate* meter. Then the above adjustments are repeated. Generally two such cycles of adjustments are required to balance the vacuum tube voltmeter.

Should trouble arise and all tubes check "good" on
the tube tester, and/or if changing tubes does not remedy
the trouble check the ionization gauge cord for continuity.
If all leads within the cord are continuous repeat the
balancing as indicated above and then plug the cord into
its socket. With the sensitivity switch in the X5 or
X 0.01 position if a plate meter reading greater than 2
per cent of full scale deflection is obtained the cord
is faulty and should be replaced. For other trouble the
circuit should be checked in the electronics shop.

7e. Thermocouple gage circuit

In order to indicate when a sample is evacuated from
the gas sample system a thermocouple vacuum gauge is in­
corporated into the vacuum train. Although it is of
little interest to know the exact pressure in the sample
manifold it is of considerable interest to know when the
pressure has fallen below some maximum value. The
thermocouple gauge used in this application is tube type
1946 manufactured by the Radio Corporation of America.
The control circuit for this gauge is illustrated
diagrammatically in Figure 35.
The upper left panel of Figure 25 illustrates the arrangement of the controls. The two meters are the 0-200 microampere and 0-100 milliampere meters respectively. Below the former is the line switch with the 20 ohm filament control to the right. To operate the gauge a filament current of 70 milliamperes is required. A vacuum corresponding to one micron or less is indicated by a reading greater than 158 microamperes on the thermocouple output meter.

7f. Battery charger

A Mallory, Type 12AC-5, battery charger has been dismantled from its case and built up on a panel which is
located behind and below the main panel of the instrument. The panel may be seen in Figure 39 attached to the center support of the iron frame which contains the entire instrument.

As indicated in Figure 36 the a.c. line voltage is reduced to 18 volts by means of a transformer. This 18 volts is then rectified using a CuO rectifier. Meter M is merely an indicating meter to show the relative charging rate. The line switch is mounted on the pump control panel in the 5 position. A red pilot light distinguishes it from the pump switches. Switch S is a current limiting device which protects the batteries from damage due to too great charging rates.

7g. General wiring

All electronic circuits receive their line power from convenient receptacles placed on the back of the main frame. Both unregulated and regulated line voltage receptacles are found there. The latter obtain their power from a 2 K.V.A. Sorensen alternating current regulator with the output voltage set at 112 volts. Both lines are fused with plug-in type fuses.

The vacuum pumps of the 3-2 tube, the pumps for gas sample system and the battery charger are all permanently wired in place. Switches and pilot lamps for the various
Rectifier

Battery Charger
Mallory Type 12AC-5

Figure 36
pumps and charger are shown on the pump control panel in the lower left corner of the photograph in Figure 25; from left to right the controls are those for (1) the sample diffusion pump, (2) sample backing pump, (3) the 3-2 tube backing pump, (4) the 3-2 tube diffusion pump, and (5) the battery charger. The controls for the grounding switch of the 3-2 FP-54 grid and for switching the 2000 megohm resistor in parallel with the 40000 megohm grid resistor of the 3-2 FP-54 amplifier are shown to the right of the battery charger switch. Controls for similar switches in the 3-4 FP-54 amplifier are not on the panel because of lack of space. These must be operated by going behind the instrument. For a similar reason the switches controlling power to the 3-4 mass spectrometer tube backing and diffusion pumps are operated from behind the instrument.

8. General arrangement of apparatus

The arrangement of the circuit control panels has already been shown in Figure 25 which is a front view of the instrument. Other views of the instrument are found in Figures 29, 30, 37, 38, 39.

How the 3-2 mass tube is mounted in the angle iron frame in relationship to other parts of the instrument is illustrated by Figure 37. In this figure is also seen the
Figure 57. Rear view of the hydrogen mass spectrometer
5 liter glass bulb, surrounded by a wire safety screen, which serves as the vacuum reservoir for operating the gas sample burette.

Figure 30 illustrates the mounting of the 3-4 mass tube which is separate from the main frame and shows its position relative to the main frame. Above the 3-4 mass tube frame can be seen the special galvanometer mounting. A closer view of the mounting which is constructed from brass is shown in Figure 29. While this figure is a photograph of the galvanometer mounting used in conjunction with the larger mass spectrometer to be described in a later section of this thesis, the mount is identical to that used with the hydrogen mass spectrometers. The can below the movable table upon which the galvanometer sets, contains oil in which are suspended four fins at right angles to each other; their purpose being to damp oscillations of the movable table. The entire mounting is electrically grounded to eliminate the effects of static charge.

The positions of the backing pumps and the sample system diffusion pump are shown in Figure 38. A rear view of the battery charger is indicated just to the right of the diffusion pump. Still another view of the instrument is presented in Figure 39. It is felt that careful study
Figure 38. The left side of the hydrogen mass spectrometer
Figure 39. Lower front view of the hydrogen mass spectrometer
of the photographs alluded to in this section of the thesis will indicate more clearly the relative positions of parts of the hydrogen mass spectrometers than several pages of text. For this reason no more attempt will be made to further describe the machine.

9. **Operation**

9a. **Vacuum systems**

Before turning on either the backing pumps or the diffusion pumps several points should be checked. The oil level in the backing pumps should be correct. In the Welch pumps (Type 1400) employed in these laboratories this corresponds to a point midway between the center lines of the oil level gauge which is found on the side of the pump case.

The mercury level in the diffusion pumps should be such that the top of the re-entrant tube which constitutes the inner part of the boiler is covered. Water should be running through the diffusion pump condenser in a steady stream.

When the foregoing points have been checked the mechanical backing pumps of both the gas sample system and the 3-2 mass spectrometer tube can be started by throwing the number 2 and 3 switches on the pump control panel. Starting the backing pump for the 3-4 mass
spectrometer tube requires throwing a switch located directly in the line cord to the motor of the pump. After about fifteen minutes if the system being evacuated is clean and tight a good rough vacuum will have been obtained. Before turning on the diffusion pumps the pressure may be checked by applying one or both of two simple methods of determining relatively low pressures.

Since no pressure gauges are contained in the mass spectrometer tube systems which give readings for pressures above five microns (0.005 millimeters of mercury) the methods just alluded to are at best only crude approximations. When the Welch backing pumps are operating on a tight system, except for a characteristic clicking sound, they run quietly. A bubbling sound indicates either a leak in the system being evacuated or a low oil level in the pump case. If addition of 50-100 milliliters of oil to the latter does not remedy the noisy condition then a leak may be suspected. Further check on the pressure can be made however by observing the color of the gas discharge when a high frequency spark is brought up to any part of the exposed glass envelope or pump leads. Soon after the backing pump has been turned on the characteristic pink glow of nitrogen should appear between the sparking electrode and ground inside the vacuum system.
As evacuation proceeds and the pressure continues to drop in a tight system, the pink glow gradually disappears until only a slight greenish-blue fluorescence on the glass walls can be observed. Should the pink glow continue along with a noisy backing pump there is definite cause for suspecting a leak which should be found and remedied before proceeding further. If no leak is suspected the diffusion pump may be turned on by throwing switches 1 for the sample system and 4 for the 3-2 mass tube diffusion pump. The 3-4 mass tube diffusion pump may be turned on by throwing the switch on the autotransformer which supplies power to its heater. For best operation the mass tube diffusion pumps require power dissipation of about 250 watts (65 volts across the heater terminals) by the heaters while the gas sample system diffusion pump only requires about 125 watts (43 volts across the heater terminals). These values may vary a little for individual pumps and especially when new heaters are installed; however, they do present a reference point from which to work when trials are made at various autotransformer settings to determine optimum pump operating conditions.

After the diffusion pump heater has been on at optimum voltage for approximately one hour the pump should be operating and the vacuum low enough so that the ion gauges
can be turned on.

In order to include operating details peculiar to the evacuation of the gas sample system it is necessary to depart from the foregoing general discussion which applies more directly to evacuation of the mass tube envelopes.

Since an ordinary mercury manometer is attached to the gas burette it may be used to observe the initial stages of the evacuation of the sample system. Included in the vacuum line however is a thermocouple type vacuum gauge (RCA 1948) which is used to indicate more precisely the degree to which the manifold and burette have been evacuated between gas analyses. The thermocouple gauge is operated by applying a d.c. current of 70 milliamperes to the filament of the gauge. Observation of the pressure is made by reading the thermocouple output meter which has been calibrated in terms of gas pressure. A reading of more than 158 microamperes indicates that the pressure has dropped below one micron (0.001 millimeter of mercury) which is the maximum tolerable residual manifold pressure. When the gas sample system is being evacuated for the first time after having been open to the atmosphere for more than a few hours or even a few minutes on a very humid day it is well to pump on the system with both backing and diffusion pumps operating for at least 3 to 5 hours before cooling.
the cold trap with dry-ice-trichlorethylene slush. Because of the many stopcocks in the system a "bake out" period is impossible. However no real difficulty seems to arise due to exchange between the hydrogen of water held on the glass surfaces of the sample system and the gas sample provided the differences in isotope concentrations of consecutively analyzed hydrogen samples is not too great. It is difficult to prove this statement because of the many additional factors which may complicate the matter. Perhaps it is more correct to say that the whole apparatus behaves all right as long as the isotope concentrations of the samples do not differ greatly. However since the sample handling system does contribute to the possible difficulty it is well to at least call it to attention here. In order to obtain lowest possible pressures in the mass tube the space between the stopcock leading to the capillary leak and the leak must be opened to the sample vacuum system.

Returning to the general discussion concerning evacuation of the mass spectrometer tube envelopes both backing and diffusion pumps were operating. It is not possible to obtain low pressures in the envelope unless the whole apparatus is "baked out." The baking process is necessary in order to break down the silica gel-like-water combination which forms on glass surfaces. For purposes of
baking the envelopes of the mass spectrometers, resistance furnaces have been wound about the tubes so that when the furnace is dissipating four watts of power per square inch of surface a temperature of 350-400° C. is produced which is suitable for decomposition of the water-silica gel combination. A 220 volt autotransformer mounted in a portable cart (see figure 39, lower right) fitted with a voltmeter and an ammeter facilitates getting power to the "bake out" furnace. To avoid severe electrical shock the furnace connections should be made before the line plug of the autotransformer is connected to the 220 volt line. When all electrical connections have been made the autotransformer should be adjusted so that a total of about 800 watts (4 amperes at 200 volts) are being dissipated by the furnace. After the furnace has been up to temperature and has been operating for three to four hours (a longer period may be necessary when the mass tube envelope is being evacuated for the first time after being open to the atmosphere for an extended time.) the pressure as determined on the ionization gauge should drop below four microns. If this value is not obtained the baking time should be extended. If the pressure is below four microns, the ionization gauge, the exposed parts of the mass tube envelope and the pump leads should be carefully torched.
using the brush flame of the glass blowing torch or the clear blue flame of a large bunsen burner. When the hot glass just begins to produce the yellow sodium color in the flame the temperature of the glass is in the proper range. Care must be taken at this point not to overheat the glass so as to cause strains to develop. It is necessary that special care be exercised in torching the ionization gauge since it is made of Nonex glass which has lower strain and softening points than does pyrex glass. Also care should be exercised when torching the pump leads near the ring seal into the cold trap. As a precautionary measure it is better to stay completely away from this ring seal.

After the torching of the exposed parts of the system the ionization gauge control is turned to the outgas position and while the grid is hot, dry-ice-trichlorethylene slush is placed about the cold trap. The grid may be normally "outgassed" for 5 to 15 minutes although sometimes a longer period is required. Proper outgassing of the grid has been obtained when further heating causes no change in the pressure as indicated by the ionization gauge. When this has been achieved the ionization gauge control is turned to normal operation and the grid current control adjusted until a 5 milliampere grid current is
obtained. Baking is continued until the pressure drops to 0.003 to 0.004 microns (3 to 4 x 10^-6 millimeters of mercury); when this pressure is reached the baking furnace power dissipation is reduced to about 400 watts and baking proceeds at this lower temperature until the pressure drops to about 0.001 microns (1 x 10^-6 millimeters of mercury); the bake-out furnace is turned completely off and the 220 volt autotransformer disconnected first from the line and then from the furnace terminals in order to avoid possible serious electrical shock. When the mass tube envelopes cool to room temperature the pressure will drop below 0.001 microns. Pressures as low as 0.00002 microns (2 x 10^-8 millimeters of mercury) as measured by the ionization gauge have been observed in the mass spectrometer tube envelopes.

9b. Amplifiers

During the time required for evacuation of the mass tube envelopes (which may take 24 to 48 hours) and the gas sample system, the storage batteries which supply the electrode potentials in the FP-54 amplifier along with the filament current of the tubes in both amplifiers should be checked to determine whether or not they are fully charged. The amplifiers operate with minimum drift when these batteries are in the relatively linear part of their
discharge curve. Practically speaking, this is from 95% to 70% of full charge. The batteries may be re-charged should they be found discharged too much, by throwing switch number 5 of the pump control panel. A red pilot light distinguishes the battery charger switch from the pump switches.

In the feed-back amplifier, the radio "B" batteries which supply electrode potentials to the various tubes should have at least 90% of their rated potentials. Similarly the battery which supplies the -45 volts to the secondary electron shield should not be below 90% of its rated potential. Best results have been obtained using Burgess "Super B Batteries" (No. 20308) which give long life under constant use.

The FP-54 and feed-back amplifiers are turned on after the bake-out furnace on the mass spectrometer tube has been turned off; otherwise instability of the amplifiers results and it has been found that no time is saved by the longer warm up period of the amplifiers. The feed-back amplifier is balanced by adjusting the coarse adjustment so that the output meter in both high and low sensitivity positions reads zero. The FP-54 amplifier is adjusted using the coarse balance control so that the galvanometer light spot is on the scale; it is necessary
to turn on the high voltage power supply in order to light
the galvanometer lamp. The lamp is focused until a thin
line appears on the translucent galvanometer scale. Both
amplifiers are then allowed to come to thermal equilibrium.
When the drift of the FP-54 amplifier has been reduced to
less than 1 millimeter per minute with the galvanometer
shunt in #1 position, it is ready for use. While drift in
the feed-back amplifier is not so readily observed on its
output meter it may be observed by switching the FP-54
output switch to "full." In case the light spot of the
galvanometer moves off the scale it can be brought back
by first adjusting the coarse feed-back amplifier balance
and then the fine balance. Generally the feed-back
amplifier drifts more rapidly than does the FP-54 amplifier;
however, this drift usually settles down to less than one
millimeter per minute with the galvanometer shunt on #1
position in about eight hours. In terms of ion current
this rate of drift would correspond to an ion current of
$10^{-16}$ amperes.

When the amplifiers have reached a steady state, the
power supply to the emission regulator is turned on using
filament switch 1. The supply is allowed to warm up for
about one minute and then the mass spectrometer tube
filament turned on using Switch 2. The emission control
is then adjusted so that the emission current reads 0.5 milliamperes when the meter switch is turned to emission. Actually the total emission is 5 milliamperes since this meter is shunted in such a way that the current is ten times that observed on the dial. Trap current should be 200 microamperes to one milliamper; adjustment of the small source magnet to give a maximum trap current is made by trial and error movement of the magnet in the region of the source.

The mass spectrometer tubes after evacuation to pressures of less than $1 \times 10^{-6}$ millimeters of mercury are now ready for operation. With the appropriate amplifiers warmed up to steady operation the filament selector is switched to whatever tube is to be used and the filament turned on by throwing Switch 2. The emission is adjusted as indicated above and a search is made for the particular ion currents to be measured in each tube. To illustrate this procedure assume that a sample of ordinary chemically prepared hydrogen is allowed to pass through the capillary leak into the 3-2 mass tube and the ions switch turned to on. The ion accelerating voltage is varied until the current due to $H_2^+$ ions falls on the near collector plate to be amplified by the feed-back amplifier. Since the magnet field strength for the 3-2 machine is about 765 gauss the
ion accelerating voltage is about 280 volts, this being obtained by setting step 8 on the course and 2.8 on the fine ion voltage controls. The focus and repeller electrodes are adjusted to give maximum ion current intensities to the collectors. For the 3-2 tube these are left-focus 32, right-focus 29 and repeller 43. A maximum reading due to HD$^+$ ions will also be observed on the galvanometer of the FP-54 amplifier when the ion acceleration voltage is 280 volts. To balance the effects of one ion current against the other the FP-54 output switch is turned to the tap position and the decade divider adjusted until the galvanometer gives the zero reading. Since the zero reading may drift a little during the determination it is well to switch the ion currents on and off during the final balancing operation in order to precisely determine the zero reading. With ions off the galvanometer will seek the true zero position on the scale; approaching this zero from both sides during a determination gives a better value for the ion ratio.

The ratio of the values of the grid resistors in the electrometer tubes in both the feed-back and FP-54 amplifiers must be known in order to calculate the ratio of the ion currents. Nominally the value of $R_1/R_3$ (see Figure 27) is two but since it varies slightly from day to day it is
well to determine its value daily. The ratio may be determined experimentally by allowing the same ion current to first fall on one collector and then on the other. By a suitable switching arrangement it is possible to have the current as collected by each collector be amplified by the same amplifier. In the apparatus in these laboratories the FP-54 amplifier is employed for this purpose. The ion current due to \( \text{H}_2^+ \) formed from the residual \( \text{H}_2 \) molecules left in the mass spectrometer after a sample has been evacuated from the gas sample manifold is used. In the 3-2 tube for example this ion current is made to fall on the number 3 collector plate by increasing the ion accelerating potential to 408 volts which is obtained by a setting of 11 on the coarse and 2.8 on the fine ion voltage controls. A series of observations is made of the deflections of the galvanometer when the ion current is alternately turned on and off in the source. The magnitude of these deflections is proportional to \( R_1 \). In the apparatus in these laboratories these deflections will be from left to right from the zero point on the galvanometer scale. The same ion current is then made to fall on the number two collector by decreasing the ion accelerating voltage to 280 volts. However the FP-54 output switch is turned to the full position by means of which the signal
being collected by the number two collector is fed through $R_3$ directly into the grid circuit of the PP-54 amplifier. However because this signal is now opposite in sign to that normally received by the PP-54 amplifier the galvanometer deflections will be from right to left. Since the incoming signal is directly proportional to the magnitude of $R_3$ the ratio of the average values of the two series of galvanometer deflections gives the grid resistor ratio. To get a good statistical value for the magnitude of deflections due to the manner in which the ion current was collected at least ten observations are generally required in each series. How the grid resistor ratio enters into the calculation of the ratio of two ion species from the reading of the decade is illustrated in an example on page 100.

It is significant to point out that the above method for determining the resistor ratio is subject to an error due to the effect of the different ion acceleration potentials upon ion current intensity. Generally the ion current intensity falls off as the accelerating potential decreases thus a resistor ratio as determined according to the above method will be high. For tracer work where interest centers only about changes in isotope abundance ratios knowledge of the absolute value of the ratio of the
size of the grid resistors is not important. However where absolute grid resistor ratios are desirable it is probably easier to calibrate the machines by analyzing hydrogen of known deuterium content and to calculate the factor (which is the grid resistor ratio) by which the reading from the decade must be multiplied to give an absolute HD⁺/H₂⁺ ion ratio for a gas sample being analyzed. However since the grid resistor ratio changes slightly from day to day it is necessary to know what the magnitude of the changes are. For this reason a check on the resistor ratio must be made on every day the machine is used for making analyses.

Table II gives the source electrode settings for maximum ion intensity in both the 3-2 and the 3-4 mass spectrometer tubes.

Table II

<table>
<thead>
<tr>
<th>Tube</th>
<th>Left Focus</th>
<th>Right Focus</th>
<th>Repeller</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-2</td>
<td>32</td>
<td>29</td>
<td>43</td>
</tr>
<tr>
<td>3-4</td>
<td>53</td>
<td>46</td>
<td>57</td>
</tr>
</tbody>
</table>

Table III summarizes the data necessary to determine the resistor ratio in both 3-2 and 3-4 mass spectrometer tubes.
Table III

Ion Voltages for Resistor Ratio Determination

<table>
<thead>
<tr>
<th>Tube</th>
<th>Ion to Near Collector</th>
<th>Ion to Far Collector</th>
<th>Voltage</th>
<th>Coarse</th>
<th>Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-2</td>
<td>$H_2^+$</td>
<td>$H_2^+$</td>
<td>280</td>
<td>8</td>
<td>2.8</td>
</tr>
<tr>
<td>3-2</td>
<td>$H_2^+$</td>
<td>$H_2^+$</td>
<td>408</td>
<td>11</td>
<td>2.8</td>
</tr>
<tr>
<td>3-4</td>
<td>$H_2^+$</td>
<td>$H_2^+$</td>
<td>289</td>
<td>8</td>
<td>5.0</td>
</tr>
<tr>
<td>3-4</td>
<td>$H_2^+$</td>
<td>$H_2^+$</td>
<td>400</td>
<td>11</td>
<td>1.1</td>
</tr>
<tr>
<td>3-4</td>
<td>$D_2^+$</td>
<td>$D_2^+$</td>
<td>148</td>
<td>5</td>
<td>0.0</td>
</tr>
<tr>
<td>3-4</td>
<td>$D_2^+$</td>
<td>$D_2^+$</td>
<td>208</td>
<td>6</td>
<td>5.2</td>
</tr>
</tbody>
</table>

In the case of the 3-4 tube usually residual $D_2^+$ ions are used in the determination of the resistor ratio. However, data for $H_2^+$ ions are included since the occasion may arise where residual gas high in $H_2$ molecule concentration may have been lately analyzed in the tube.

Table IV summarizes the data necessary to collect appropriate pairs of ion species in both the 3-2 and the 3-4 mass spectrometers.

Table IV

Ion Voltage Required for Simultaneous Collection of Ions in the 3-2 and 3-4 Tubes

<table>
<thead>
<tr>
<th>Tube</th>
<th>Ion Voltage</th>
<th>Coarse</th>
<th>Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-2</td>
<td>280</td>
<td>8</td>
<td>2.8</td>
</tr>
<tr>
<td>3-4</td>
<td>208</td>
<td>6</td>
<td>5.2</td>
</tr>
</tbody>
</table>
10. **Hydrogen analyses**

When hydrogen gas at low pressures is bombarded with electrons a certain number of $\text{H}_3^+$ ions are formed (42, 43). The process is a secondary one presumably taking place through a collision of an ion with a neutral molecule. Thus the number of $\text{H}_3^+$ ions formed should vary as the square of the gas pressure in the apparatus while the number of $\text{HD}^+$ ions should vary linearly with the pressure in analyses of samples with high protium content. Since both types of ions appear at the 3 position in the mass spectrometer, which cannot resolve the slight mass differences between the two ions, a distinction between the two types of ions can be made only if the ratio of the $3/2$ ion intensities is plotted as a function of pressure. In the 3-2 mass tube the $\text{H}_2^+$ ion intensity is very nearly proportional to the pressure. According to Bleakney and Gould (43), if a plot of the $3/2$ ratio as the ordinate is made against the output of the feed-back amplifier as the abscissa, a straight line relation should be observed the intercept on the ordinate being the $\text{HD}/\text{H}_2^+$ ratio. The problem does not arise in the 3-4 mass tube since the $\text{D}_3^+$ ions, which would appear in the mass six position, are not collected. In samples of high deuterium content the probability of $\text{H}_3^+$ ions being formed is so small that their presence has a
negligible effect upon the ion intensity in the mass three position.

In his original work Bleakney (42) found the D/H ratio in a sample of commercial electrolytically prepared hydrogen to be $1/30,000$. Another report by Nier and co-workers (22) on the analysis of a sample of electrolytically prepared hydrogen gave the value $1/20,000$ for this ratio. Separation of the isotopes occurring during preparation by electrolysis accounted for the apparent discrepancy. The value $1/20,000$ for the D/H ratio in ordinary laboratory tank hydrogen has been also reported by other workers (44).

Figure 40 shows a plot of the $3/2$ ratio against pressure ($H_2^+$ ion intensity) as obtained for a sample of commercial tank hydrogen using the 3-2 mass spectrometer constructed in these laboratories. The HD/H$_2$ ratio is $9.8/100,000$ from which a D/H ratio of approximately $1/20,000$ is obtained which is in good agreement with results of similar determinations previously reported. Also shown in Figure 40 is the effect of 20 per cent air impurity in the sample. Although the intercepts are in good agreement it is clear that if all samples are analyzed at only one pressure for purposes of merely comparing the relative results, it is necessary that the samples be pure. The effect when only nitrogen is the impurity is similar to
Output of the feedback amplifier in m.a.

Figure 40. Analysis of tank hydrogen.

- Pure hydrogen
- 80% hydrogen, 20% air
that when air is the impurity.

The mass spectrometer has a "memory" for previous samples when different samples are analyzed. The effect of the "memory" is that the spectrometer will not immediately give the correct HD abundances. When the concentrations of isotopes in a series of samples do not change over a wide range the "memory" effect is not significant. Figure 41 shows that the introduction into the machine for a short time of a sample with an HD concentration 40 times that of tank hydrogen does not have any noticeable effect upon the normal HD/H\textsubscript{2} ratio.

An appreciable "memory" exists in the machine for greatly enriched gas samples. A sample whose HD/H\textsubscript{2} ratio as determined by the machine was 0.0331 was allowed to run into the machine for about 30 minutes. The sample manifold was evacuated and a series of analyses made on commercial tank hydrogen; each analysis was made on a fresh portion of the tank hydrogen. Several determinations were made during one afternoon and evening and then tank hydrogen was allowed to run into the machine overnight. The following morning tank hydrogen was again analyzed using the same procedure as above. The results of this experiment are shown in Figure 42. It is clearly indicated that the machine has an appreciable "memory" when samples
Before high sample

x. Immediately after

o Ten minutes after

Output of the feedback amplifier in ma.a.

Figure 41. 3/2 ratio versus H sub o ion intensity for the analysis of tank hydrogen after a sample with 40 times the HD content ran into the machine for ten minutes.
Figure 42. Analyses of tank hydrogen after a sample whose HD/H$_2$ ratio was 0.03306 was allowed to run into the machine for thirty minutes.
are analyzed that differ widely in their isotopic concentrations. However for experiments in which small changes in isotope concentrations take place the memory does not have an appreciable effect upon analytical results obtained from the machine.

It should be emphasized that the machine, when operating properly, will give consistent results for the same samples provided the "memory" effect is minimized. Table V summarizes the data obtained on three different samples analyzed over extended periods of time.

The data in the table clearly show that the mass spectrometer may be relied upon to yield reproducible results, an indication that changes taking place in the apparatus from day to day are too great.
Table V

Results of Analyses over an Extended Period of Time on Three Hydrogen Samples

<table>
<thead>
<tr>
<th>Sample DG-1-31</th>
<th>Sample HS-6-111</th>
<th>Sample HS-6-152</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>HD/H₂</td>
<td>Date</td>
</tr>
<tr>
<td>7-20-49</td>
<td>0.03290</td>
<td>8-22-49</td>
</tr>
<tr>
<td>7-20-49</td>
<td>0.03270</td>
<td>10-5-49</td>
</tr>
<tr>
<td>7-20-49</td>
<td>0.03330</td>
<td>10-6-49</td>
</tr>
<tr>
<td>7-21-49</td>
<td>0.03280</td>
<td>10-8-49</td>
</tr>
<tr>
<td>7-21-49</td>
<td>0.03350</td>
<td>10-14-49</td>
</tr>
<tr>
<td>7-26-49</td>
<td>0.03240</td>
<td>10-15-49</td>
</tr>
<tr>
<td>7-27-49</td>
<td>0.03290</td>
<td>10-18-49</td>
</tr>
<tr>
<td>7-27-49</td>
<td>0.03320</td>
<td></td>
</tr>
<tr>
<td>8-1-49</td>
<td>0.03240</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.03295</td>
<td>Average</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average</td>
</tr>
</tbody>
</table>

Results obtained from operation of the 3-4 mass spectrometer tube have not been as extensive as those obtained with the 3-2 mass tube. With the same sample manifold being used for both tubes it is necessary that the deuterium content of the water held on the glass surfaces be in equilibrium with that of hydrogen gas held in the manifold, otherwise analytical results are in error. Since the main experiments described in this thesis were
made with gases of relatively low deuterium content, no extensive use was made of the 3-4 mass tube. However, a series of analyses were made when the tube was set up using a sample of tank deuterium gas as obtained from Mr. R. Reuchle of these laboratories. Five different analyses on this sample indicated the deuterium content of the gas to be $99.6 \pm 0.2$ atoms per cent deuterium. Since this result did not indicate any serious difficulties with the 3-4 tube further trials were put off until the time would present the necessity of making them. Since operating details and difficulties encountered with the 3-4 mass spectrometers are completely reported by Nier and Stevens (44) and by Dean and Thode (45), it was not felt necessary to make extensive tests on the 3-4 mass tube set up in these laboratories except for determining local idiosyncrasies which are usually only of minor importance.

10a. **Errors in ion current intensity measurements**

One of the greatest causes of error is the improper adjustment of the focus and repeller electrodes in the sources of the mass spectrometers which may cause discrimination against ions of different masses. The possible extent of this error may be demonstrated by electrically connecting the two collector plates by placing
a small permanent magnet in the vicinity of the collectors so that the steel shorting wire connected to the near collector plate makes contact with the bar on the far collector plate. The ion-accelerating voltage is then changed so that $\text{H}_2^+$ ions first fall on one collector and then the other. The ratio of the collected currents as a function of the potentials of the focus and repeller electrodes is shown in Figure 43. It is observed that the ion-repelling voltage is not as critical as far as discrimination is concerned; however, if the focusing electrodes are improperly adjusted very large errors may arise. This is not surprising since an ion beam will not pass symmetrically through the defining slits if the focusing electrodes are not properly adjusted. Since the mass two and mass three ions have a slightly different trajectory (46) in the source which will act as a spectrometer itself so that there will be a selection before ions enter the analyzer. Optimum settings for the focus and repeller electrodes have been tabulated in Table II of this thesis. It is interesting to point out that these are also the settings for maximum ion current intensities besides those for least discrimination in the source.

The effect of ion-repelling voltage on the "pressure effect" is also of some interest. A sample was analyzed
Figure 43. Discrimination versus voltage of source electrode in the 3-2 mass spectrometer tube.

- Repeller  o Right focus  x Left focus

- Ion repelling voltage, 0-100 dial reading corresponds to 0-10 volts

- Right focusing electrode, 0-100 dial reading corresponds to about 1/7 of ion accelerating voltage

- Left focusing electrode, 0-100 dial reading corresponds to about 1/7 of ion accelerating voltage

Best dial settings for 3-2 mass tube, ion repeller 43, left focus 32, right focus 29
using different ion-repelling voltages. From the data plotted in Figure 44 it is evident that a low ion-repeller electrode voltage favors the formation of $\text{H}_3^+$ ions; increasing the voltage decreases the number of $\text{H}_3^+$ ions formed. However, as is indicated in the figure there is a voltage range in which this effect is at a minimum; further increase in the electrode voltage causes the effect to increase. In practice it is best to operate the mass spectrometer tubes with the repeller voltages at about 5 volts.

C. Mass Spectrometer of Range 1-75 Mass Units

The growing interest in the use of isotopes as tracers in chemical and biochemical problems at Iowa State College introduced the problem of assaying isotopic mixtures. Although radioactive isotopes are available for most elements some important ones, such as nitrogen or oxygen, do not have radioactive isotopes with decay periods long enough to make them suitable as tracers.

In order to assay these stable elements a mass spectrometer of greater mass range than the hydrogen machines, whose construction and operation have been already described in this thesis, was needed. Considerable experience had been gained with the 60° sector type mass
Output of the feedback amplifier in m.a.

Figure 44. $3/2$ ratio versus Hg ion intensity for several values of ion repelling voltages.

- x 1.5 volts
- o 8.0 volts
- . 3.7 volts
spectrometer in the work with the hydrogen machines so it was decided that the larger machine would also be a 60° sector type. In 1940 Nier (23) described a simple mass spectrometer of 15 centimeter radius; an example of which is set up in the Bacteriology Department of Iowa State College. This machine has a single collector and is battery operated. However during recent years there have been many improvements in the mass spectrometric art and a number of new instruments have been described (47-50). In 1947 (24) Nier described another machine which incorporated the two-collector design, previously discussed in the description of the hydrogen machines, applying it to the elements nitrogen, oxygen and carbon. The instrument could also be used for other elements found in the range of 1-75 mass units or for making gas analyses in general.

The mass spectrometer built in these laboratories was patterned after the 1947 Nier design; several changes were made to make better use of materials and equipment on hand. While the Nier design described an all-metal mass spectrometer tube the tube employed here is part metal and part glass. A different magnet was used and several changes were made in the electronic circuits. The entire instrument is mounted in a compact angle iron frame. The
only utilities required for operation are water for the diffusion pump condensers and 110 volt alternating current for the electronic circuits.

The outline of the description of the construction of this machine is similar to that for the hydrogen machines. Since general theoretical considerations have already been taken up in the beginning of this thesis there is no need to repeat them.

The mass spectrometer tube is part metal and part glass. The deviation from the all metal design of Nier (24) was made in order to make use of what materials were already on hand in these laboratories. An old style mass spectrometer tube had been obtained from a war excess properties list. This tube had a six-inch radius copper analyzer with both collector and source ends enclosed in glass envelopes. Evacuation of the mass spectrometer tube was effected through the collector end; the collector end of the analyzer tube was perforated to facilitate pumping. Hence, evacuation of the source end was by way of the analyzer.

One serious difficulty with mass spectrometer tubes in which the collector end is enclosed in a glass envelope is the problem of shielding. Various devices have been employed to overcome this difficulty; coating with Aquadag
being by far the most satisfactory. However ideal shielding for the collector end of a mass spectrometer tube would be to have the envelope made of metal; this was done in the tube built in these laboratories. The glass envelopes were removed in order to make use of the analyzer of the old style mass spectrometer tube. One end of the analyzer happened to be perforated, the other end was not. The perforated end was used to support the mass spectrometer source which was surrounded by a new glass envelope. To the unperforated end of the analyzer tube was soldered a length of two-inch stainless steel tubing. The collectors of the mass spectrometer were then set into this stainless steel tube as shown in Figure 45 which is a schematic drawing showing the mass spectrometer tube. Evacuation took place from the source end. Connection of the cold trap and two-stage mercury pump was by means of a glass pipe blown into the wall of the glass envelope surrounding the source. Figure 46 is a photograph of the assembled tube. Parts of the resistance furnace used to bake out the tube are seen in place on the analyzer.

1. Ion source

The general source construction is similar to that of the hydrogen mass spectrometers. The principal difference

*Type 304 which is non-magnetic.
Figure 45. Mass spectrometer tube
Figure 46. Mass spectrometer tube
is that the ion accelerating system has been made more complex. Two views of the assembled source appear in Figure 47, while Figure 48 indicates how electrical connections are made to the source components. As in the case of the hydrogen machines, electrons emitted from a hot tungsten ribbon pass through the ionizing region and are caught on a trap. A magnetic field of about 150 gauss produced by two Alnico poles fitted to an iron yoke collimates the electron beam.

An ion repeller plate was omitted in the source of the mass spectrometer since it was learned (51) that its absence did not greatly affect its operation. In experimental design of sources the repeller is included in order to have one more degree of control over the ion beam. It was omitted in the design in these laboratories for the sake of simplicity.

As was the case in the hydrogen mass spectrometers alignment of the ion beam in the source is achieved by the inclusion of two half plates $J_1$ and $J_2$, to which different variable voltages may be applied. The system acts as an ion-focusing lens. Three slits are employed to better collimate the ion beam. These are found on plate $S$ which is the lower plate of the shield and plates $G_1$ and $G_3$, both of which are grounded. The slit in plate $G_3$ is the
Figure 47. Assembled ion source
Figure 48. Source wiring arrangement
exit slit of the source from which the ribbon of ions passes into the copper analyzer tube.

Two more elements are added to the source in order to sweep the ions aside in the source so as to determine the galvanometer zero when analyzing a gas sample. These additions are the deflect plates $G_2$ and $D$; $G_2$ is always grounded. When $D$ is also grounded the ion beam will pass through the exit slit. However, the ion beam will be swept aside in the source by applying a potential to $D$ about one-fourth the magnitude of the shield potential. Figures 49 and 50 give detailed descriptions of the elements of the ion source, while Figure 51 is a photograph of the component parts.

To seal the glass envelope which surrounds the source to the copper analyzer a copper collar was first made from one-fourth inch copper plate and bored with a hole such that the collar slipped tightly over the analyzer. The collar was soldered in place just beyond the perforations in the source end of the analyzer using high melting (m.p. $\approx 1300^\circ$ F.) silver solder. To this collar was then soldered a Kovar metal cylinder, $1 7/8$ inches in diameter to which a length of 48 millimeter pyrex tubing had already been sealed, by means of a graded seal. The joint from copper collar to Kovar cylinder was made using low melting
Figure 49. Parts of the ion source
Figure 50. Parts of the ion source
Figure 51. Parts of the ion source
(m.p. = 1175° F.) silver solder. Two different types of silver solder were employed in order not to unsolder one joint while making another.

2. Mass analyzer

The mass analyzer tube is a one-inch copper tube 57.2 centimeters long which is bent in the middle along a 15 centimeter radius. One end of the tube is perforated with many one-eighth inch diameter holes. The bent portion of the tube is flattened to about 5/8 inch.

While the analyzer used in these laboratories was not constructed locally, for the sake of completeness a brief description of how it may have been done is included. A length of hard-drawn copper tubing several inches longer than the length mentioned above is annealed for about 8 to 10 inches in the center. The tube is filled with dry sand, capped at both ends, and bent empirically about a form with a 15 centimeter radius. A special bending tool similar to those used for tubing bends of smaller radius could be constructed but unless several tubes are to be made the extra expense would not be warranted. The bent tube is compared to an accurately made scale-drawing of the mass analyzer. After the bending operation has been satisfactorily accomplished the bent section is pressed between two trapezoidal shaped plates which closely resemble the
shape of magnet pole pieces. Several readjustments of the bend in the tube may have to be made after the flattening operation as the tube has a tendency to straighten. The finished tube should precisely follow the outlines of the scale drawing previously prepared.

The copper tube should then be cut off squarely, exactly 28.6 centimeters from the center of the arc of the bend to form the source end of the tube. A copper button, into which are drilled the line-up holes for the source, is silver soldered onto this end. The button also is slotted in order to allow the ion beam to pass and contains threaded holes into which the captive screws, which hold the source to the analyzer, are screwed. For about four inches the end of the analyzer tube is perforated with many holes in order to facilitate evacuation of the analyzer and collector.

The collector end of the mass analyzer tube is cut off squarely 23.0 centimeters from the center of the arc of the bend and a closely fitting copper collar soldered in place using high melting silver solder. To this is next soldered, using low melting silver solder, a length of non-magnetic stainless steel tubing the exact dimension of which should be such as to allow 12.7 centimeters between collars A and B of Figure 52 which shows the arrangement
Figure 52. Collectors
of the elements of the mass spectrometer collectors.

3. **Collectors**

A serious difficulty (51) arose with the collector system as originally designed by Nier (24). For some unknown reason after extended periods of operating the mass spectrometers the number one collector no longer would function properly. An apparent gradual change in the collector surface due to constant ion bombardment seemed to have been the reason. Also considerable rebounding of ions striking the flatplates was experienced. For this reason the design of the ion collectors in the mass spectrometer built in these laboratories went back to the old Faraday cup type collector (51). The use of grounded rings placed on either side of the number one collector has been obviated by the cup type design.

The collector assembly is supported by two 1/4 inch Inconel posts fastened to bottom plate B. Spacing between the various elements is maintained by accurately ground pyrex glass spacers. In general, the scheme is similar to that employed in the construction of the source. Nichrome V sheet is used throughout except where already noted. Twenty-five mil sheet is used for all plates while the collectors are made of ten mil material. All connections are made by spot welding.
Electrical leads enter the collector envelope by means of glass reentrant seals which are in turn sealed to Kovar metal. Silver solder is employed to make Kovar to monel metal seals. Monel metal used to shield the collector leads does not affect the collection of ion currents despite the fact that it is magnetic.

To the end of the monel metal tube, through which the ion collector leads pass, is silver soldered a sylphon bellows which allows direct connection to the iron container which houses the first stages of the ion current amplifiers. The entire path of the ion collector leads are thus well shielded.

4. Vacuum system of the mass spectrometer tube

The mass spectrometer tube is evacuated employing the same pumps used with the hydrogen mass spectrometers. A Type 507 ionization gauge is used to determine pressure. The control circuit for the gauge is identical to the one used in the case of the hydrogen machines except for the manner in which the circuit components are mounted on the chassis.

To aid in outgassing the mass spectrometer tube an electric resistance furnace has been wound around all the parts of the tube except that part of the analyzer passing between the poles of the magnet. Dissipation of about
4 watts per square inch (5 amperes flowing in the resistance wire) gives a satisfactory baking temperature. Since the portion of the copper analyzer between the pole faces is heated by conduction a small section of the furnace at each end of the "bare" part dissipates about 6 watts per square inch. A few hours of baking followed by an hour or two of operation with the filament turned on reduces the residual peaks to a level satisfactory for analysis. The pressure as measured by the ionization gauge will be about $2 \times 10^{-7}$ millimeters of mercury.

5. **Electro-magnet**

The mass spectrometer tube in the instrument was mounted so that a line drawn between source exit slit and collector slit is vertical; this necessitated having the magnet in a horizontal position. Figure 53a shows how the magnet was mounted to fulfill the above requirement. The yoke of the magnet was welded to two half-inch steel plates which were in turn welded to an angle iron frame. This frame was set into another frame to which were attached four wheels that run on two tracks which make it possible to wheel the magnet to and from the mass spectrometer tube. Leveling and side adjustment screws make it possible to precisely adjust the position of the magnet with respect to the analyzer. Figure 53b shows the magnet in place.
Figure 53a. Electromagnet
Figure 53b. Lower front view of the mass spectrometer
Ordinary mild steel, SAE 1020, was used to construct the yoke, cylindrical poles and pole pieces. None of the dimensions are critical. The choice of 3 15/16 inch stock for the cylindrical poles was made merely because 4 inch inside diameter brass tubing was used for the spools on which the coils were wound.

Each coil was wound with 14370 turns of number 24, Formvar* insulated copper wire. Connected in series they have a resistance of 1085 ohms at room temperature. A current of 145 milliamperes produces a field of 2300 gauss which is sufficient to collect nitrogen molecule ions having an energy of 2000 volts, while a current of 160 milliamperes produces a field of 2800 gauss sufficient to collect 2000 volt CO$_2^+$ ions. Power for the magnet is obtained from an electronically regulated supply, details of which are described in a later section of this thesis.

6. Gas sample system

The gas sample handling system for the mass spectrometer is the same as that used with the hydrogen machines. Some minor changes have been made but they concern only the manner of mounting or convenience of operation. An all metal vacuum reservoir, used in conjunction with the lowering of the

*Formvar is a special synthetic varnish used by the Anaconda Wire and Cable Company.
burette mercury level, has replaced the five liter glass bulb used in the earlier design. The entire apparatus: burette, manifold, pump leads, manometer, and vacuum reservoir, is mounted in an angle iron frame which is situated at the right end of the mass spectrometer writing desk. All stopcocks and burette operating controls are conveniently placed so that the instrument operator need not move from his place to make any adjustments on the sample system. The general location of the sample system is illustrated in Figure 54 while Figure 55 is a close-up view of the complete sample system.

Two different types of capillary leaks are employed with the mass spectrometer. One of the leaks is a molecular flow leak designed according to the suggestions of Honig (52). A known volume of gas at a pressure measured on the manometer of the gas sample system is allowed to expand into a larger volume. The gas is then allowed to pass from the large volume container through a small orifice into the mass spectrometer. A 5.05 cubic centimeter volume of gas at 10.0 centimeters of mercury is allowed to expand into a 10500 cubic centimeter container where the pressure will be 0.048 millimeters of mercury. At this pressure the mean free path of a CO₂ molecule, for example, is about 2 millimeters. To insure molecular flow according to the laws
Figure 54. Front panel of the mass spectrometer showing also the position of the gas sample system.
Figure 55. Gas sample system
discovered by Knudsen (53, 54) the orifice diameter should be smaller than 0.1 millimeter. It turns out that in order to limit the rate of gas flow from the reservoir so that the rise in pressure in the region of the source is not greater than 10\(^{-5}\) millimeters of mercury and to keep the pressure drop in the reservoir during a ten minute period\(^*\) to less than one per cent, an orifice 0.025 millimeter in diameter satisfies all requirements.

Honig demonstrated that with such a gas inlet scheme the intensity of ion currents in the mass spectrometer was proportional to the pressure in the reservoir as long as molecular flow conditions prevailed. However the fact remains that the composition of a gas mixture in the reservoir will change slowly due to the different flow rates of its components. This follows from the laws of Knudsen that state that the rate of molecular flow of a gas depends inversely upon the square root of its molecular weight. To illustrate this effect take the extreme case of a mixture of equal parts of butane (\(M = 58\)) and hydrogen (\(M = 2\)). After a period of time during which a change of one per cent occurs in the reservoir pressure the new composition of the mixture in the reservoir will be 51.1 per cent butane and 48.9 per cent hydrogen. Thus it is apparent that

\(^*\)Ten minutes is the average maximum time required for an analysis.
gas analyses over wide mass ranges must be performed as quickly as possible and with the gas reservoir being as large as possible.

The second leak into the mass spectrometer is the viscous flow leak already described in the section of this thesis dealing with the gas sample system of the hydrogen machines. Appropriate stopcocks make it possible to use either type of leak.

For isotope analyses the viscous flow leak is satisfactory since the ion species concerned ordinarily occupy adjacent positions in the mass scale. When many samples are encountered this type of leak also has the advantage of being rapidly pumped out between samples.

The molecular flow leak is most advantageously used for general gas analysis. Its main disadvantage for isotope work is the fact that the large reservoir may require as long as 20 minutes to evacuate after an analysis is completed. The ten liter reservoir is pictured in Figure 56. A thermocouple vacuum gauge, R.C.A. 1946, is used to indicate when the reservoir has been evacuated to less than $10^{-3}$ millimeters of mercury pressure. The control circuit employed for this gauge has already been described in the discussion of the hydrogen mass spectrometer gas sample system.
Figure 56. Sample reservoir for the molecular leak
7. **Electrical circuits**

The mass spectrometer employs vacuum tube circuits to perform all electrical operations where direct current is involved. Except for two batteries in the feed-back amplifiers and a battery used to supply a negative potential for the secondary electron shields in the collector end of the mass tube, the machine is line operated. Because of the nature and use of each electronic component of the machine it is best to describe the design, function and operation separately.

7a. **High voltage supply and voltage divider**

With the exception of several minor changes made in these laboratories the circuit for the high voltage supply follows closely that described by Mier (24), which in turn is an adaptation of the design of Hunt and Hickman (55). The essential feature of the design is the use of a triode as part of the load resistor in a conventional rectifier-filter power supply. Varying the potential applied to the grid of this triode varies the voltage drop across the tube. The varying grid potential is obtained by amplifying changes in the output voltage of the high voltage supply and feeding the output of the amplifier directly into the grid of the triode in such a manner that when the high voltage supply output becomes more positive than some
predetermined value, the grid of the load triode also becomes more positive, thus the voltage drop across the triode decreases. Should the high voltage output decrease in value the circuit operates in such a manner as to increase the voltage drop across the triode. With an amplifier of high enough gain very good voltage stabilization is possible. In the circuit as it appears in Figure 57 the output voltage is stabilized to better than one part in 10,000. With 155 volts applied from the magnet supply to the grid of \( V_{4} \), the maximum voltage applicable to the shield of the mass spectrometer is 2150 volts.

Changes made in the original Nier circuit involve the use of a 35T type tube in place of the 100TH as the load tube and the use of a 6SN7 type tube instead of a 6SL7 in the amplifier circuit. Also, since in these laboratories an ionization gauge was used instead of the Philips gauge for determining mass spectrometer tube pressure, the control circuit for the Philips gauge was omitted.

The voltage divider employed with the high voltage supply is essentially the same as in the original Nier circuit. Tap switch \( S_{1} \) gives 500 volt steps, \( S_{2} \) gives 50 volt steps and \( R_{25} \) continuous subdivisions of 50 volts. In order to better cover the entire voltage range from 0-2150 volts an additional step was added to \( S_{2} \) so that a
Figure 57. High voltage supply and voltage divider
List of Parts for the High Voltage Supply and Potential Divider

R1: 4 megohms (four 1 megohm, 1 watt in series)
R2: 50,000 ohms, 50 watts
R3, R4: 7 megohms (four 2.2 megohm, 1 watt in series)
R5: 330,000 ohms, 1 watt
R6: 4 megohms (four 1 megohm, precision wire wound in series)
R7: 300,000 ohms, precision wire wound
R8-R13: 500,000 ohms, precision wire wound
R14-R24: 50,000 ohms, precision wire wound
R25: 100,000 ohm potentiometer, General Radio Type 314A
R26-R35: 500,000 ohms, 1 watt
R36, 37: 1 megohm, 2 watts
R38: 1 megohm carbon potentiometer
C1: 0.5 microfarad, 3000 volts
C2,3: 1.0 microfarad, 600 volts
C4: 2.0 microfarads, 2000 volts
C5: 0.1 microfarad, 2000 volts
C6: 0.1 microfarad, 600 volts
C7: 2.0 microfarads, 2000 volts
C8: 0.1 microfarad, 2000 volts
C9: 24 microfarads, 2000 volts (six 4 microfarads in parallel)
H: Relay, thermal time delay, SPST, (50 seconds)
$S_1$ 4 contact, 2 wafer non-shorting tap switch

$S_2$ 11 contact, 2 wafer tap switch

$S_3$ 11 contact, 3 wafer tap switch

$S_4$ SPDT toggle switch

$S_5$ General Electric SP4T special high voltage switch converted to give required switching arrangement

$V_1$ 6SN7

$V_2$ 1616

$V_3$ 35T (Eitel and McCullough)

$V_4$ 6SN7

$V_5$, 6 VR 150

$T_1$ Type 13336 Kenyon Transformer Co., New York, N. Y. (2500 volts, 50 m.a.)

$T_2$ P 6133 Stancor

$T_3$ P 6135 Stancor
50 volt overlap could be had when changing from one 500 volt step to another.

The source electrodes of the mass spectrometer other than the shield obtain their potentials from the voltage divider controlled by switch $S_3$. Both fine and coarse focus adjustments are derived from this divider. Four-tenths the value of the shield potential is applied to the deflect electrode from a point between $R_{36}$ and $R_{37}$; switch $S_4$ provides a means for grounding this electrode.

Meter $M$, a 0-100 microammeter in series with resistors $R_{26}$ through $R_{37}$, constitutes a 1000 ohms per volt voltmeter. While nominally the sum of resistances is 25 megohms actually the value is about 26.5 megohms. Thus a reading on the meter of 81 microamperes indicates 2150 volts.

Provisions are made in the voltage dividing circuit which enables the mass spectrum of a particular sample to be scanned automatically by continually varying the potential applied to the shield. This is accomplished by charging a 24 microfarad condenser, $C_9$ to 2150 volts and then allowing it to discharge through the high voltage voltmeter. Since the actual resistance of the voltmeter is 26.6 megohms the RC time constant is 638 seconds. This rate of discharge is slow enough so that a 2.0 second recording potentiometer has ample time to get to the top of
any current peaks when the source exit and collector slits are as wide as those employed in the mass spectrometer. Switch $S_5$ of Figure 57 provides a means of charging condenser $C_9$ and then discharging it through the 26.6 megohm resistor.

The panel of the high voltage supply is pictured in Figure 54. In the upper right corner is the condenser scan switch $S_5$. Along the center of the panel is the high voltage meter $M$, the fine shield control $R_{25}$ and the line switch. Along the bottom is the coarse focus control $S_3$; the medium shield control $S_2$; the coarse shield control $S_1$; the fine focus control $R_{38}$; pilot light and the deflect switch $S_4$.

On the back of the chassis are connections for shield, focus, deflect and ground electrodes in the source; a plug for connection to $C_9$ which is not contained in the chassis; a plug for making the shield connection to the emission regulator, fuse holders for both line and high voltage secondary of the transformer $T_1$ and the 112 volt alternating current line plug. All connections and plugs are plainly labeled.

7b. **Electron emission regulator**

The emission regulator is both a source of power for the mass spectrometer filament and a controller for the
electron emission from the filament. The circuit of the regulator is similar in principal to that used to control electron emission in the hydrogen machines. The actual circuit employed was adapted from one published by Nier (24) which was based upon the design of Ridenour and Lampson (56). Total emission from the filament is regulated. The circuit adjusts itself so that the voltage drop across \( R_7 + R_8 \) of Figure 58 produced by the emission current equals the drop across the voltage regulator tube \( V_6 \). The emission can be varied by changing \( R_8 \). Resistors \( R_1 \) and \( R_2 \) are adjusted to put the regulator in the operating range. When \( R_2 \) is properly set small changes in \( R_1 \) do not affect the emission. Potentiometers \( R_6 \) and \( R_{10} \) are "ganged" together in a "put and take" manner and enable the electron accelerating potential to be adjusted between 7 and 75 volts. This feature is convenient in special applications such as the study of appearance potentials or for separating ions of the same mass but having different efficiency of ionization curves.

The entire circuit must be well insulated since it operates at potentials up to 2150 volts above ground. Regulation of the circuit is such that a line voltage change of 5 volts on either side of 112 volts does not change the electron emission by more than one part in 200.
Figure 58. Emission regulator
List of Parts for Emission Regulator

R₁  150 ohm, 50 watt, potentiometer
R₂  250 ohm, 50 watt, potentiometer
R₃  5000 ohm, 25 watt, adjustable
R₄  500000 ohm, 1 watt
R₅, R₉  500 ohm, precision
R₆, R₁₀  5000 ohm potentiometer, General Radio 214A
R₇  150,000 ohm, 1 watt
R₈  0.5 megohm carbon potentiometer
R₁₁, R₁₂  Wire wound shunts for meter M of such size as to convert M to 500 and 200 microamperes respectively
R₁₃  2000 ohm precision
R₁₄  20,000 ohm, 1 watt
C₁  8-8 microfarad, 600 v.
C₂, C₃  0.1 microfarad, 600 v.
T₁  P6013 Stancor, mass spectrometer filament supplied from 6.3 volt winding
T₂  1:1 isolation transformer, P6161 Stancor, 115 v.; 60 cycle to 115 v.; secondary insulated to 5000 v., 200 volt-ampere capacity
T₃  T19F98 Thordarson
T₄  P6013 Stancor
L  T20C54 Thordarson, 15 henry, 60 milliamperes
V₁  6AS7
V₂  5U4G
$V_3$ \hspace{1cm} 6SJ7

$V_4 - V_8$ \hspace{1cm} VR-75

$V_9$ \hspace{1cm} VR-150

A \hspace{1cm} 0-10 amperes, a.c.

M \hspace{1cm} 0-100 microamperes, d.c.

$S_1$ \hspace{1cm} SPST toggle switch

$S_2$ \hspace{1cm} DPST toggle switch, heavy duty connected in parallel

$S_3$ \hspace{1cm} DPDT toggle switch
The panel for the circuit appears on the right just above the galvanometer scale in Figure 54. Across the top is the filament current meter \( A \); the filament control, \( R_1 \); the electron acceleration potential control and the emission current meter, \( M \). Along the bottom of the panel is the line switch, the emission-trap switch \( S_3 \); the filament switch \( S_2 \); the emission control \( R_q \) and the line pilot light. On the rear of the chassis are the filament, shield, trap and line connections along with the 5 ampere line fuse and the \( 1/4 \) ampere fuse in the cathode circuit of the 6AS7. Control \( R_2 \) and the 5 ampere fuse in the mass spectrometer filament circuit are located within the chassis.

7c. Amplifiers and power supply

Two inverse feed-back amplifiers are employed for measuring ion currents falling on collectors 1 and 2 of the mass spectrometer. The design of these amplifiers is basically due to Nier (24). Incorporated in the design is the VX41A electrometer tube used as the input stage, followed by three additional stages of amplification plus a cathode follower for the output stage. Over-all gain of the amplifiers, which appear diagrammatically in Figure 59, is about 5,000.

Several modifications on the original design (24)
were made in these laboratories. One of the changes involved the manner in which the filament current and the plate and screen potentials were applied in the VX41A tubes. Another involved the way in which the cathode heater current was applied in subsequent stages of amplification in the amplifiers while yet others involved shielding the voltage regulator tubes and applying a capacitance across the pair of voltage regulator tubes employed in each amplifier. It was found that these last two changes helped to further reduce random oscillations in the amplifiers.

In the original Nier amplifiers the filaments of the VX41A tubes were heated by direct current obtained from the electronically regulated power supply which supplies all electrode potentials for the various tubes employed. However, in the laboratories instead of using special shunting resistors a series of voltage-dropping resistors were used. Inclusion of a variable resistor in the series made the current in the VX41A tube filament readily adjustable. To supply plate and screen grid potentials a part of the series of resistors was employed as a potentiometer. Examination of Figure 59 will indicate exactly how these changes were made. Comparison with the circuit diagrams of the amplifiers in Nier's article will
Figure 59. Feedback amplifiers
List of Parts for the Amplifiers

R₁ 40000 meg. Victoreen
R₂ 41000 meg. Victoreen
R₃-R₈ 1 meg. 1 watt
R₉, R₁₀ 7.5 K, 10 watt
R₁₁, R₁₂ 5K, W.W. Precision
R₁₃, R₁₄ 20K, Precision, W.W.
R₁₅, R₁₆ 100K Precision, W.W.
R₁₇, R₁₈ 35K Precision W.W.
R₁₉, R₂₀ 10K Precision, W.W.
R₂₁, R₂₂ 15K Precision W.W.
R₂₃, R₂₄ 1K Micropot
R₂₅, R₂₆ 1K GR214A
R₂₇, R₂₈, R₃₃, R₃₄ 300 W.W.
R₂₉, R₃₀ 3K carbon pot. linear taper
R₃₁, R₃₂ 20K W.W.
V₁, V₂ VX-41A (Victoreen Instrument Co.)
V₃-V₈ 6SJ7
V₉, V₁₀ 6J5
V₁₁-V₁₄ VR-75
C₁, C₂ 100 fd variable condenser
C₃, C₄ .02 fd
C₇ 0.15 fd
C₅, C₆ 0.1 fd
$T_1, T_3 \quad 6.3$ v., 1 a.
$T_2 \quad 6.5$ v., 3 a.
$S_1, S_2 \quad SPST$ (Ganged)
$S_3 \quad SPST$
show the obvious advantages of the scheme employed in these laboratories. The advantages are more apparent when it is recognized that each individual VX41A tube varies in characteristics enough to make replacement and readjustment in case of tube failure a real problem.

Cathode heater current in the second, third, and fourth stages of amplification along with the cathode follower output stage were supplied from line operated transformers. Instead of twelve volt tubes six volt tubes were used which made it possible to use readily available 6.3 volt transformers. To eliminate possible interaction between stages due to transformer coupling, the heaters in the second and third stages of amplification in each of the two amplifiers employ separate transformers, while the heaters in the remaining tubes in both amplifiers were supplied from a third transformer. Detail of the scheme appears in Figure 59. Since the alternating current lines are regulated at 112 volts using a Sorensen electronic regulator no trouble due to line fluctuations was experienced.

The amplifiers receive all direct current potentials from an electronically regulated power supply which will deliver 250 volts at 250 milliamperes with an a.c. ripple of less than 0.002 volts. Stability of the supply is such
that a change in line voltage of 5 volts on either side of 112 volts produces a change in the output voltage of about 0.01 per cent.

A distinct feature of the power supply, which is shown diagrammatically in Figure 60, is the way in which two separately variable output voltages are available, one for each of the amplifiers, without any observable impairment of the regulation. To accomplish this two cathode follower output stages are employed in which the control grid potential is obtained from the cathode resistor used as a potentiometer. By changing the position of the movable tap on the cathode resistor a range of output voltages from 150 to 250 volts may be obtained.

Operation of the amplifiers may best be described in a series of steps which should be carried out in the order in which they are presented. All connections from the power supply to the amplifiers are made along with connections to the line voltage mains. The batteries in the amplifiers should be connected as indicated on the terminals of the battery cable. Since the VX41A electrometer tubes are housed in a separated shielded container situated at the collector end of the mass spectrometer, the cables connecting the electrometer stages to the remainder of the amplifiers are plugged into the proper receptacles on
Figure 60. Amplifier power supply
List of Parts for the Amplifier Power Supply

R\textsubscript{1-4} 100 ohms, 10 watt
R\textsubscript{5} 220 K, 1 watt
R\textsubscript{6-7} 5 K, 10 watt
R\textsubscript{8, 10} 330 K, 1 watt
R\textsubscript{9} 500, 10 watt
R\textsubscript{11} 100 K, 1 watt
R\textsubscript{12-13} 35 K, carbon potentiometer
R\textsubscript{14} 15 K, 1 watt
R\textsubscript{15} 82 K, 1 watt
R\textsubscript{16, 17} 68 K, 1 watt
S SPST
T U.T.C. Special Series S-42
L Thor\textsubscript{\textae}arson, T20G56
V\textsubscript{1, 2} 5R4
V\textsubscript{3-6} 6B4
V\textsubscript{7, 8} 6SL7
V\textsubscript{9} VR-75
V\textsubscript{10, 11} 6Y6
C\textsubscript{1, 2} 2 mfd. paper
C\textsubscript{3} 0.15 mfd., 600 V.D.C.
C\textsubscript{4, 5} 40 mfd., 450 V.D.C.
the back of the amplifier chassis. The amplifier output leads should be connected to the appropriate receptacles on the back of the main panel.

The power supply is next turned on and the output voltages adjusted to about 225 volts. The heater current switch which controls the transformers used to heat the cathodes in the second, third, fourth and output stages of the amplifiers is then turned on. The filament current in the VX41A tubes is adjusted to between 7 and 8 milliamperes. After the power supply has warmed up enough so that this filament current is steady the electrometer plates switch should be turned on.

After a period of several minutes the output meter sensitivity switch should be snapped to the 2 position. If a positive voltage is observed with no ions falling on the collector of the mass spectrometer the coarse and fine balance controls are adjusted in an effort to zero the amplifier. Should this not be possible with these controls, the appropriate output control of the power supply is adjusted so as to bring the amplifier output to approximately zero. Finer adjustment then follows using the amplifier fine balance control. The output meter sensitivity switch is then snapped to the 11 position and a re-examination of the balance of the amplifier made.
To achieve final balancing, the fine balance control should be adjusted so that further turning no longer causes an increase in reading on the output meter. The power supply control is then adjusted so that the amplifier output meter reads just below zero. Exact balancing to zero follows using the fine balance control. With this zero adjustment made for both amplifiers they are ready to receive ion currents.

Generally it takes about eight to ten hours for the amplifiers and power supply to reach a steady state after they have been turned on. It will be necessary to repeat the zero adjustment of the amplifiers from time to time until they reach equilibrium. When the steady state is obtained the stability of the amplifiers is ± 0.2 millivolts for number one and ± 0.1 millivolts for number two. Short time fluctuation for both amplifiers as recorded with the 2-second Brown recording potentiometer are of the order of 0.01 millivolts. Drift from the zero over a period of about 8 hours is less than 3 millivolts.

The second panel from the bottom in Figure 54 pictures the amplifier panel. In the top row are the number one VX41A filament meter, the heater switch, and the number two VX41A filament meter. Along the middle line are the fine and coarse balance controls for number one.
amplifier and the coarse and fine balance controls for number two amplifier. At the bottom in the center of the panel is the electrometer plate switch.

On the back of the amplifier chassis are connector plugs for the cables to the electrometer stages; to the 90 volt batteries; to the power supply; for the two amplifier outputs; and the alternating current line which supplies the heater's transformers.

The amplifier power supply panel is pictured in the upper right of Figure 54. On the panel appear the line switch, pilot light, number two and number one output controls. On the back of the chassis are plugs for cables to the amplifiers and the alternating current supply.

7d. Magnet power supply

An electronically regulated power supply is used to supply power for the magnet coils and as a variable but well regulated source of potential for the bias of one of the grids of the 6SN7 control tube of the high voltage supply. The circuit for the power supply appears in Figure 61.

The supply delivers two separately regulated outputs. Regulation of the potential supply for grid bias of the high voltage supply is such that a change of line voltage 5 volts on either side of 112 volts will affect the output
Figure 61. Magnet power supply
List of Parts for the Magnet Power Supply

<table>
<thead>
<tr>
<th>Part</th>
<th>Resistance</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁  - R₄</td>
<td>10 ohms</td>
<td>10 watts</td>
</tr>
<tr>
<td>R₅  - R₈</td>
<td>20 ohms</td>
<td>10 watts</td>
</tr>
<tr>
<td>R₉  - R₁₀</td>
<td>20 ohms</td>
<td>10 watts</td>
</tr>
<tr>
<td>R₁₁  - R₁₂</td>
<td>1 megohm</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₁₃</td>
<td>470000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₁₄</td>
<td>12000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₁₅</td>
<td>22000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₁₆</td>
<td>15000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₁₇</td>
<td>100000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₁₈</td>
<td>47000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₁₉  - R₂₀</td>
<td>82000 ohms</td>
<td>1 watt, 1/2 watt</td>
</tr>
<tr>
<td>R₂₁</td>
<td>39000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₂₂</td>
<td>20000 ohm carbon potentiometer</td>
<td></td>
</tr>
<tr>
<td>R₂₃</td>
<td>240000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₂₄</td>
<td>27000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₂₅</td>
<td>10000 ohm carbon potentiometer</td>
<td></td>
</tr>
<tr>
<td>R₂₆</td>
<td>20000 ohms</td>
<td>2 watts</td>
</tr>
<tr>
<td>R₂₇</td>
<td>3900 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₂₈</td>
<td>2000 ohm carbon potentiometer</td>
<td></td>
</tr>
<tr>
<td>R₂₉</td>
<td>12000 ohms</td>
<td>1 watt</td>
</tr>
<tr>
<td>R₃₀</td>
<td>1000 ohms</td>
<td>100 watts</td>
</tr>
<tr>
<td>R₃₁</td>
<td>1000 ohms</td>
<td>100 watts, potentiometer</td>
</tr>
</tbody>
</table>
$C_1, C_2, C_3$ 2 fd, 600 V.D.C. paper

$C_4$ 0.075 fd, 600 V.D.C.

$C_5$ 0.1 fd, 600 V.D.C.

$C_6$ 12 fd, 450 V.D.C. electrolytic

$C_7$ 16 fd, 450 V.D.C. electrolytic

$T_1, T_2$ TR1024a, Red Arrow Electric Corp., Irvington, New Jersey

$T_3$ T-19F98, Thordarson

$T_4$ T-21F10, Thordarson

M Meter, 0-300 milliamperes
voltage by less than one part in 10,000. This output voltage is variable from 130 to 165 volts without effect on the regulation.

The output of that part of the power supply which is applied to the magnet coils is so regulated that, for the same line voltage change already mentioned, the output voltage is affected by about one part in 10,000. The supply will deliver up to 400 volts at about 400 milliamperes. In practice $R_{22}$ is adjusted so that the maximum current that can be applied to the magnet coils is 300 milliamperes. It is expedient to do this since meter $M$ is only a 0-300 milliameter. Switch $S_3$ allows for two ranges of magnet coil currents, a high range from 150 to 300 milliamperes and a low range from 0-165 milliamperes.

The panel for the magnet supply circuit is pictured on the upper left in Figure 54. Across the top is the magnet coil current meter $M$; the plate voltage switch $S_2$ and the high-low switch $S_3$. Along the mid line of the panel is the pilot light, the line switch, the line fuse and the magnet power control $R_{31}$. On the back of the chassis are the line, magnet and grid voltage for the high voltage supply connections along with the control $R_{25}$. The magnet voltage control $R_{22}$ and the high voltage supply grid potential control $R_{28}$ are within the chassis.
7e. Main panel

The output of amplifiers 1 and 2 is led to the main balancing panel shown diagrammatically in Figure 62. The components of the panel are arranged so that both ion currents may be measured on ordinary panel milliammeters in case rapid readings are required. For more accurate work either output may be measured on a galvanometer having a one meter scale. For precise determinations of the ratios of ion currents, a fraction of the output of one amplifier may be balanced against that of the other and a null measurement achieved; or the output of each amplifier may be balanced against an accurately measured fraction of the voltage of a battery.

This balancing system differs from that employed with the hydrogen machines. The slide wire is composed of "put and take" units thus assuring a constant resistance regardless of the setting of the movable tap. To explain how the balancing system functions consider Figure 63 which is a simplification of the circuit in Figure 62.

Resistor $R_1$ represents the put and take decade units while $R_2$ represents the resistor $R_{24}$ of Figure 62. $R_1$ and $R_2$ have values of 1111111 and 100,000 ohms respectively. $R_1$ is broken up into two parts $R_a$ and $R_b$ by the moving tap. Because $R_1$ and $R_2$ are approximately the same magnitude
Figure 62. Main panel
List of Parts for Main Panel Circuit

<table>
<thead>
<tr>
<th>Part</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$, $R_2$</td>
<td>50 ohm precision wire wound</td>
<td></td>
</tr>
<tr>
<td>$R_3$, $R_4$</td>
<td>150 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_5$, $R_6$</td>
<td>250 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_7$, $R_8$</td>
<td>500 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_9$, $R_{10}$</td>
<td>1500 ohm &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{11}$, $R_{12}$</td>
<td>2500 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{13}$, $R_{14}$</td>
<td>5000 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{15}$, $R_{16}$</td>
<td>15000 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{17}$, $R_{18}$</td>
<td>25000 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{19}$</td>
<td>80 ohm special wound</td>
<td></td>
</tr>
<tr>
<td>$R_{20}$</td>
<td>100 &quot; precision wire wound</td>
<td></td>
</tr>
<tr>
<td>$R_{21}$</td>
<td>500000 ohm &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{22}$</td>
<td>50000 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>5000 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{24}$</td>
<td>500 &quot; &quot; &quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>$R_{25}$</td>
<td>1 ohm decade resistance unit (Shallcross)</td>
<td></td>
</tr>
<tr>
<td>$R_{26}$, $R_{27}$</td>
<td>10 &quot; &quot; &quot; &quot; ( &quot; &quot; )</td>
<td></td>
</tr>
<tr>
<td>$R_{28}$, $R_{29}$</td>
<td>100 &quot; &quot; &quot; &quot; ( &quot; &quot; )</td>
<td></td>
</tr>
<tr>
<td>$R_{30}$, $R_{31}$</td>
<td>1000 ohm &quot; &quot; &quot; ( &quot; &quot; )</td>
<td></td>
</tr>
<tr>
<td>$R_{32}$, $R_{33}$</td>
<td>10000 &quot; &quot; &quot; ( &quot; &quot; )</td>
<td></td>
</tr>
<tr>
<td>$R_{34}$, $R_{35}$</td>
<td>100000 ohm decade &quot; &quot; ( &quot; &quot; )</td>
<td></td>
</tr>
<tr>
<td>$M_1$, $M_2$</td>
<td>Meter 0-1 milliamperes d.c. adjusted resistance to 50 ohms 1 per cent</td>
<td></td>
</tr>
</tbody>
</table>
$S_1, S_2$ 5 position, 2 circuit, non-shorting tap switch

$S_3$ 6 position tap switch

$S_4, S_5$ 11 position, 1 wafer shorting tap switch

G High sensitivity galvanometer, General Electric Catalog No. 32G321GR9, sensitivity 0.015 microamperes per mm, resistance 20 ohms, external critical damping resistance 186 ohms, period 2.6 seconds. Instrument is set on vibrationless mounting the same as with the galvanometer of the hydrogen mass spectrometers. The mirror is 1.5 meters from the translucent scale, thus the effective full galvanometer sensitivity is 0.010 microampere per millimeter on the scale.
Figure 63. Schematic diagram of the balancing circuit.
each amplifier has a similar resistive load across its output. The voltage drop across $R_2$ will be

$$E_2 = i_2 R_2$$

(93)

Across $R_1$ the drop will be

$$E_1 = i_1 R_1$$

(94)

At the state of balance no current will be flowing in the galvanometer circuit, thus the voltages at points A and B will be the same hence

$$E_2 = i_1 R_a$$

(95)

However, the ratio of the two voltages $E_1$ and $E_2$ is equal to the ratio of ion currents falling on the collector plates in the mass spectrometer so that

$$\frac{E_2}{E_1} = \frac{i_1 R_a}{i_1 (R_a + R_b)}$$

(96)

or

$$\frac{E_2}{E_1} = \frac{R_a}{R_a + R_b} = \frac{R_a}{R_1}$$

(97)

The actual voltages obtained as output from the amplifiers would be the same for a given ion current if the two amplifier input resistors were the same. However, since these resistors are very large and subject to manufacturing difficulties the ratio of the two must be determined experimentally. This is done simply by
allowing the same ion current to fall first on the number 1 collector and then on the number 2 collector. The ratio of actual output voltages of the amplifiers gives the grid resistor ratio. Thus if the two output voltages were \( E_1 = 5.0 \) volts and \( E_2 = 5.1 \) volts the amplifier grid resistor ratio would be

\[
\frac{E_1}{E_2} \sim \frac{R_1}{R_2} = \frac{5.0}{5.1} = 0.98
\]

For example if a sample of nitrogen was being assayed for the \( ^{29}N_2 / ^{28}N_2 \) ratio and a value for \( R_a \) of 1580 ohms was necessary to bring the galvanometer back to the zero reading, the ratio of the two nitrogen molecule species would be

\[
\frac{N_2^{29}}{N_2^{28}} = \frac{1580}{11111.1} \times 0.98 = 0.01394
\]

Because of the possible errors which may be introduced the correction for the discrepancy in amplifier input grid resistors must be applied. Since the ratio of the two grid resistors varies from day to day it is best to determine it daily before making any isotope analyses.

The main panel is pictured on the lower left of Figure 54. Across the top of the panel from left to right are the units, tens, hundreds, thousands and ten thousands decade unit controls. Below these are the number
one output meter, the tenth decade unit and the number
two output meter. Along the bottom is the galvanometer
selector switch \( S_2 \); the balance selector switch \( S_1 \); the
number one output meter sensitivity switch \( S_5 \); the number
two output meter sensitivity switch \( S_4 \) and the galvanometer
multiplier switch \( S_3 \). In the center of Figure 54 is
the galvanometer scale. The galvanometer is mounted on a
special mounting similar to the one already described in
the discussion of the hydrogen mass spectrometers. On
the back of the chassis are located the connector plugs
for the output cables of each amplifier; the galvanometer
cable; the 22.5 volt battery cable and the ground con­
nection.

7f. Ionization gauge control

The circuit used to control the type 507 ionization
gauge used as a vacuum indicator on the mass spectrometer
is identical to the one used in conjunction with the
hydrogen mass spectrometers. Operation of the circuit
has already been adequately covered under a previous
heading in this thesis. In order to conserve space, how­
ever, the components of the circuit were all included on
a five inch panel. This panel appears below the amplifier
panel in Figure 54. On the left side is the grid current
meter while on the right is the plate current meter.
Between the two meters are the zero adjustment for the vacuum tube voltmeter; the zero set switch; the grid current control; the outgas and normal operations switch; the line switch, pilot lamp, fuse holders and the range switch. Connections for the line cable and the ionization gauge cord are on the back of the chassis.

7g. Thermocouple gauge

When the molecular leak is used for gas analyses it is essential to know when the 10 liter sample reservoir has been evacuated to a pressure less than one micron (0.001 mm. of Hg). A thermocouple vacuum gauge fulfills the required sensitivity and so one (Type 1946 R.C.A.) was incorporated into the molecular leak system. The control circuit used with the type 1946 thermocouple gauge is exactly like that already described in the discussion of the hydrogen mass spectrometer gas sample system. The only change made for the larger mass spectrometer circuit is the separation of the filament current and thermocouple output meters. Only the latter is on the front panel of the machine. Its location is indicated in Figure 54 just to the left of the gas sample manifold.

7h. General wiring

Both regulated and unregulated 110 volt line voltages are used to power the electrical components of the mass
spectrometer. Duplex outlets carrying the regulated line current are located on the frame of the machine at points convenient for attaching line cables to the various electronic circuits.

Both backing and diffusion pumps are operated from the unregulated line. An entry receptacle on the frame makes it easy to connect the cable from the 110 volt mains to the machine. The various pumps receive their power from a distribution panel provided with switches and pilot lights. No fuses are used but rather circuit breaking switches (Heineman Circuit Breaker Co., Trenton, New Jersey, Catalogue No. 0131, 5 amperes, 110 volts a.c.) are employed on the distribution panel. The panel with switches labeled according to the pump it controls is found on the left side of the mass spectrometer frame.

8. General arrangement of the components of the mass spectrometer

It is not necessary to make an extensive description of the manner in which the different parts of the mass spectrometer are arranged. The many photographs already presented in this thesis give a much better description than could be presented in several pages of manuscript. In constructing the machine the author has made every effort to keep the entire unit as compact as possible. Design of the many components always had compactness
as a goal whenever it did not interfere with the general utility and ease with which the machine might be maintained. Figures 64 and 65 are two additional views which show the left side of the mass spectrometer.

9. Operation

9a. Vacuum system of the mass spectrometer tube and sample system

Before turning on either the backing pumps or the diffusion pumps several points should be checked.

1. The level of oil in the backing pump should be correct.

2. The level of mercury in the diffusion pump should be above the top of the inner tube of the boiler. This is readily checked by removing the boiler heater and observing the height of mercury in the boiler. A mirror facilitates making this observation.

3. Water should be flowing through the diffusion pump condenser.

After the above points have been checked the backing pump for the mass spectrometer tube can be started by throwing the switch marked M.S. BACKING PUMP on the side of the frame. After about 15 minutes
Figure 64. Left side of the mass spectrometer
Figure 65. Rear-left view of the mass spectrometer
of pumping, if the system is clean and tight a good enough vacuum should be obtained so that the diffusion pump may be turned on. However two checks on the vacuum obtained using only the backing pump are applied before turning on the diffusion pump. Usually Welch Duo-Seal mechanical pumps run quietly when a good vacuum is being obtained. If the pump used on this machine makes a bubbling sound either the oil level is low or there is a leak somewhere in the system. The former is simply tested by adding oil. Usually not more than 100 milliliters is necessary to quiet the pump. If noise persists then a leak may be suspected which should be found and remedied.

A second check on the vacuum being obtained is to use a high frequency spark discharge. The Tesla "leak hunter" is applied to any part of the glass system so that a gas discharge may be observed. Soon after the backing pump is turned on the characteristic glow of nitrogen should appear. As the pressure within the system falls the pink glow will gradually disappear until only a slight greenish-blue fluorescence on the glass walls will be observed. This indicates that the system is tight and the
diffusion pump should be turned on by throwing the switch marked M.S. DIFFUSION PUMP located on the side of the frame. The diffusion pump heater should be dissipating about 250 watts of energy for best operation of the pump. As a safety measure a thermostatic switch is attached to the copper cooling water exit tube from the diffusion pump condenser. This is set so that a rise in temperature of about $10^\circ F.$ causes the current to the heater to be cut off. If enough water is going through the condenser this will not happen. However since the water pressure in the laboratory fluctuates through quite a range a constant check must be made on the flow of water through the condenser in order to keep the diffusion pump operating.

After the diffusion pump has been turned on for about an hour it is safe to operate the ionization gauge. The ionization gauge control circuit is turned on and about five minutes allowed for the tubes to warm up. Zereting of the plate current meter is then accomplished by adjusting the zero adjust control. By turning the grid current control counterclockwise as far as it will go the relay is closed. (The range switch should be in the $X5$
position.) Turning the grid current control clockwise until the grid current meter reads 5 milliamperes puts the circuit in operation. The reading obtained from the plate current meter is then converted to pressure using the formula:

\[ P_{\text{mmHg}} = \text{RANGE} \times \text{microamperes} \times 10^{-5} \]

With no refrigerant around the cold trap the pressure in the system should be about \( 4 \times 10^{-3} \) millimeters of mercury or better.

In order to obtain the lowest pressures possible in the mass spectrometer tube the sample system should also be pumped out so that the pressure behind the capillary leaks is low. It is generally good policy to start the evacuation of the sample system at the same time that evacuation of the mass spectrometer tube is started following a procedure similar to that which has been already described in detail in connection with the discussion on the hydrogen mass spectrometers.

To further aid in obtaining pressures of less than \( 1 \times 10^{-6} \) millimeters of mercury in the mass spectrometer tube all gases both adsorbed and chemically bound to parts of the system must be removed. Heating the mass spectrometer tube, the pumping leads
and the ionization gauge tube to about 125° C., removes most adsorbed gases and water from the metal parts of the system. However water is known to react with glass (57) to form a layer of silica gel on its surface. The glass must be heated to over 350° C. under vacuum to remove the water from this surface layer. A furnace wrapped around the mass spectrometer tube which dissipates 4 watts per square inch of surface will maintain the temperature between 350° C. and 400° C. The portable autotransformer used in these laboratories for mass spectrometer tube baking is connected to the terminals of the furnace, the line switch turned on and the current in the furnace coils adjusted to 5 amperes. This gives the power dissipation requisite for adequate baking.

When an evacuation of the mass spectrometer is being made after the tube has been opened to the atmosphere for an extended period of time the length of baking time may be about 4 to 5 hours without refrigerant around the cold trap. Refrigeration is omitted during the initial bake-out in order not to freeze water in the trap. Before refrigerating the cold trap all exposed surfaces of the mass spectrometer
tube and the pumping system which are not heated by the furnace must be carefully torched. The ionization gauge control circuit should be switched to the outgas position. After the torching, the cold trap is refrigerated using either liquid nitrogen or dry-ice-trichlorethylene slush. For most work use of the latter is sufficient. Baking continues with the cold trap refrigerated until the pressure in the tube falls below $5 \times 10^{-6}$ millimeters of mercury. When this pressure is obtained which is usually 3 to 8 hours after the cold trap has been refrigerated, the current in the furnace coils around the mass spectrometer tube is reduced to about 3.5 amperes which reduces the power dissipation to about 2 watts per square inch. Baking continues at the new furnace temperature until the pressure falls below $2 \times 10^{-6}$ millimeter of mercury. Then the baking is stopped. The pressure in the mass spectrometer tube will fall below $1 \times 10^{-6}$ millimeters of mercury when all parts are cooled to room temperature if the baking has been done properly.

It is essential that the sample system be evacuated as well as possible in order to attain lowest pressures within the mass spectrometer. This
is accomplished by allowing both sample backing and diffusion pumps to run without the cold trap being refrigerated for several hours. It is not possible to bake the sample system because of the many greased stopcocks. However, the vacuum requirements are not as stringent as with the mass spectrometer tube, experience indicating that it is sufficient to merely refrigerate the sample system cold trap after 3 or 4 hours of pumping after which time the pressure usually falls below $1 \times 10^{-3}$ millimeters of mercury.

9b. **Electronic circuits**

1. The amplifiers

Operation of the amplifiers has already been described in the section of this thesis dealing with a description of the amplifiers and amplifier power supply. It is sufficient to re-mention here the order in which events take place in order that the circuits be placed in operation.

For quickest stabilization of the amplifier-power supply combination it is best to turn on first the heaters of the amplifier tubes. This is done to minimize the effect of the momentary high voltage surge that accompanies the warm-up
period of the power supply. After both power supply and heaters have been turned on for about 10 minutes the electrometer plates switch is thrown to the ON position. Balancing of the amplifiers then proceeds as has already been described in a previous section of this thesis.

2. Magnet supply

In order to minimize the effects of high voltage surges during the warm-up period of the magnet supply before throwing the line switch to the ON position check should be made that the plate voltage switch is in the OFF position. One minute after the line switch has been turned on the plate voltage switch may be turned on.

Current to the coils of the electromagnet is controlled by adjusting the magnet power control. A 0-300 milliammeter indicates the magnet current. Two ranges of control are possible a low range of 0-165 milliamperes and a high range of 150-300 milliamperes. The magnet supply circuit after being turned on requires a period of about one hour to come to thermal equilibrium. A slight drift in the output voltage
is observed during this time.

3. Emission regulator

The emission regulator controls the current supplied to the filament of the mass spectrometer. After the mass spectrometer tube has been evacuated so that the residual pressure due to air is less than $1 \times 10^{-6}$ mm. Hg the filament may be turned on. The line switch of the emission regulator is thrown and the circuit allowed to warm up for at least one minute and then the filament switch is turned on. Resistor $R_2$ which is situated on the chassis should be at its maximum value. With the filament turned on, $R_2$ should be adjusted until the total emission current is about 190 to 200 microamperes. This may be determined by turning the emission current meter control switch to emission. The value of the reading observed on the 0-100 microameter emission current meter times five gives the total emission current. Further adjustment of the current applied to the filament may be made using the filament current control $R_1$. If $R_2$ is adjusted properly $R_1$ may be varied through a relatively large range without affecting too
greatly the total emission current.

The magnitude of the electron current to the trap may be determined by turning the emission current meter control switch to the trap position and then observing the value of the reading on the emission current meter. Trap current is two times the actual value of the reading obtained from the meter. When the source magnet which is used to collimate the electron beam in the source is properly adjusted the trap current should be from 60 to 70 microamperes.

4. High voltage supply

The high voltage supply is the source of ion accelerating potential. After both magnet supply and emission regulator have warmed up the line switch of the high voltage supply should be turned on. This energizes all of the tube filaments in the supply along with the heater of the thermal delay switch which after about 50 seconds turns on the current applied to the primary of the high voltage transformer. If all the shield controls are turned to their highest positions the high voltage output meter should register 81 microamperes which corresponds to a potential of
2150 volts being applied to the shield in the source of the mass spectrometer.

To obtain maximum ion currents from the exit slits of the source, proper adjustment of the focus electrodes is necessary. In the machine in these laboratories this may be had with the coarse focus control in the 11 position and the fine focus control set at 63.

During mass spectrometric analyses it is often necessary to precisely determine the position of the zero of the ion current measuring devices. This may best be done by preventing the passage of ion currents through the mass spectrometer tube. Under this condition the measuring devices used to estimate the output of the amplifiers should return to some mark of reference or zero position. That the zero position must be measured from time to time is necessary due to the inherent tendency of all direct current amplifiers to drift. In order to prevent the ion current from passing through the mass spectrometer tube the simplest expediency is to unfocus the beam in the source. This is simply done by applying an unsymmetrical potential between the
deflect electrodes in the source which sweeps the ion beam aside thus preventing it from passing through the source exit slit. By throwing the deflect switch to the ions off position this is accomplished.

5. Main panel

After all the foregoing requirements have been fulfilled the mass spectrometer is ready for use as an analytical tool. To determine the ratio of isotope abundances in a sample of nitrogen used in a tracer experiment for example, a portion of the sample should be introduced into the manifold of the sample system in a manner similar to that already described in conjunction with the gas sample system of the hydrogen mass spectrometers. The stopcock to the capillary leak should be opened and the sample pressure adjusted to 5.0 centimeters of Hg. Under the electron emission conditions already described with the electron accelerating potential set at 75 volts the ion current due to N₂ ions will be represented by a an output of about 10 volts on the number one amplifier output meter. By properly adjusting the shield potential the ion current due to
$^{29+}_2N_2$ will pass through the slit in collector 1 and be received by collector 2. Output of the amplifier will be from about 20 to 250 millivolts depending upon the degree of enrichment or depletion of the $^{29+}_2N_2$ concentration used in the tracer experiments. The exact setting of the fine shield control for the peak current to collector is best observed by turning the sensitivity switch to the 1 position and the galvanometer selector to the 2 position. Using a galvanometer shunt value of appropriate sensitivity the ion current peak may be observed by the deflection of the galvanometer light spot on the scale to a maximum point. When the current due to $^{29+}_2N_2$ ions is falling on the 2 collector the current due to $^{28+}_2N_2$ ions will be falling upon the 1 collector. Both currents will be amplified by the appropriate amplifiers.

To make use of the null principle which has already been discussed in an earlier section of this thesis the galvanometer selector switch is turned to the 3 balance position. Because the main panel is symmetrically arranged any one of the four different balancing procedures may be
followed. With the **balance selector** in the 1 position the output of number one amplifier may be balanced against a portion of the potential of a 22.5 volt battery. The 2 position allows the same thing to be accomplished using the output of the number two amplifier. Position 3 allows the output of number two amplifier to be balanced against a portion of the output of the number one amplifier while position 4 reverses the situation with regards the two amplifiers.

For isotopic mixtures in which the relative abundance of the lighter isotope is greater than that of the heavier isotope which is generally the case in tracer experiments involving oxygen, nitrogen or carbon, position 3 of the **balance selector** is employed. Thus when the null principle is being employed to determine the ratio of abundances of two isotopic species of nitrogen, oxygen or carbon the ion accelerating potential is set so that the ion current due to the less abundant isotope falls on the number two collector. Then with the **galvanometer selector** set at **balance** and the **balance selector** in the 3 position the decade resistors on the output
circuit are varied until a balance is achieved. The zero or balance point is readily found by turning the ion beam off and on by means of the deflect switch in the high voltage supply.

The values of the null point on the decade resistors and the ratio of the two grid resistors in the first stages of the amplifiers are the necessary data needed to calculate the ratio of isotopic abundances. An example of how to calculate this ratio was discussed in the section of this thesis devoted to the main panel.

10. Performance of the mass spectrometer

Isotope abundance analyses have been made for the elements nitrogen and carbon with the mass spectrometer. For the former, nitrogen gas and for the latter, carbon dioxide, was employed for introducing the isotopic mixtures into the machine. Generally speaking the performance of the machine in these laboratories follows closely that of the mass spectrometer described in 1947 by Nier (24). Since many of the design parameters are identical, results obtained closely resemble those described by him.

A series of analyses have been made on tank nitrogen in conjunction with some $^{15}N/^{14}N$ abundance ratio determinations made for Mr. Ralph Barclay and Mr. Richard Sweet of
the Biochemistry Division of the Chemistry Department at Iowa State College. Results of the tank nitrogen analysis are expressed in Table VI.

Table VI
Tank Nitrogen Analyses

<table>
<thead>
<tr>
<th>Date</th>
<th>Decade Heading</th>
<th>Decade Reading</th>
<th>$R_1/R_2$</th>
<th>$N_2^{29}/N_2^{28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-20-49</td>
<td>4:40 p.m.</td>
<td>850</td>
<td>0.963</td>
<td>0.00753</td>
</tr>
<tr>
<td>7-20-49</td>
<td>4:55 p.m.</td>
<td>850</td>
<td>0.963</td>
<td>0.00753</td>
</tr>
<tr>
<td>7-20-49</td>
<td>5:30 p.m.</td>
<td>850</td>
<td>0.963</td>
<td>0.00753</td>
</tr>
<tr>
<td>7-21-49</td>
<td></td>
<td>850</td>
<td>0.963</td>
<td>0.00753</td>
</tr>
<tr>
<td>8-2-49</td>
<td></td>
<td>890</td>
<td>0.94</td>
<td>0.00748</td>
</tr>
<tr>
<td>8-2-49</td>
<td></td>
<td>880</td>
<td>0.94</td>
<td>0.00745</td>
</tr>
<tr>
<td>8-3-49</td>
<td></td>
<td>870</td>
<td>0.95</td>
<td>0.00745</td>
</tr>
<tr>
<td>11-1-49</td>
<td></td>
<td>861</td>
<td>0.98</td>
<td>0.00760</td>
</tr>
<tr>
<td>11-2-49</td>
<td></td>
<td>867</td>
<td>0.96</td>
<td>0.00750</td>
</tr>
<tr>
<td>11-4-49</td>
<td></td>
<td>885</td>
<td>0.95</td>
<td>0.00757</td>
</tr>
<tr>
<td>11-13-49</td>
<td></td>
<td>862</td>
<td>0.99</td>
<td>0.00760</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>0.00753</td>
</tr>
</tbody>
</table>

It is clearly indicated from the data in the table, that during a day's operation the machine may be relied upon to produce consistent results. The case indicated for the day 8-2-49 is probably an extreme case since on this occasion a slight adjustment of the position of the source
magnet was made between the two analyses listed. Even in this case however the difference between the two values obtained would not introduce significant errors into most tracer experiments. It is also significant that analytical results obtained with the machine over a period of five months do not deviate from the average of all observations listed in the table by more than about one per cent.

Normal carbon dioxide was assayed for its $^{13}/^{12}$ abundance ratio. During two days on which determinations were made no significant difference in the analytical results were observed as may be seen in Table VII.

Table VII
Decade Divider Readings Showing Analytical Reproducibility for Tank Carbon Dioxide on Two Different Days

<table>
<thead>
<tr>
<th>Decade</th>
<th>$^{13}/^{12}$</th>
<th>Decade</th>
<th>$^{13}/^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-25-49</td>
<td>0.0112</td>
<td>7-26-49</td>
<td>0.0112</td>
</tr>
<tr>
<td>1375</td>
<td>0.0112</td>
<td>1377</td>
<td>0.0112</td>
</tr>
<tr>
<td>1374</td>
<td>0.0112</td>
<td>1378</td>
<td>0.0112</td>
</tr>
<tr>
<td>1375</td>
<td>0.0112</td>
<td>1376</td>
<td>0.0112</td>
</tr>
<tr>
<td>1375</td>
<td>0.0112</td>
<td>1379</td>
<td>0.0112</td>
</tr>
<tr>
<td>1375</td>
<td>0.0112</td>
<td>1374</td>
<td>0.0112</td>
</tr>
</tbody>
</table>

*This ratio was calculated using a resistor ratio $R_1/R_2 = 0.983$. The apparent $^{13}/^{12}$ ratio thus obtained was
corrected for $^{12}O^{17}O^{16}$ and for the amount of 44 peak under the 45 peak by 0.0008 (58) and 0.0002 (24) respectively.

In order to check whether or not the mass spectrometer had a "memory" for samples of abnormally high N$^{15}$ content, a sample of nitrogen gas was obtained from Mr. Barclay containing 7 atoms per cent excess N$^{15}$. This was allowed to run into the machine for thirty minutes and then was evacuated from the sample manifold until the intensity of the ion current due to N$_2^{28+}$ ions formed from the residual nitrogen in the mass spectrometer tube was observed as an output of about 30 millivolts from the number two amplifier. (Under conditions during analysis of nitrogen samples the peak due to N$_2^{28+}$ ions would cause an output of about 10 volts from the number two amplifier.) A sample of tank nitrogen was analyzed as soon as the background fell to this value which was about five minutes after the start of evacuation of the gas from the sample manifold. No "memory" effect was observed.

To determine the sensitivity of the mass spectrometer to small changes in isotopic concentrations in gases, two nitrogen samples were analyzed whose N$^{15}$ concentrations differed slightly. To accomplish the determination one sample was admitted into the manifold at a pressure of 5.0 centimeters and a balance was made in the manner
previously discussed in this thesis. For this sample a decade reading of 1220 was obtained from which the $^{15}N/^{14}N$ ratio ($R_1/R_2 = 1.04$) was calculated and found to be 0.00573. Tank nitrogen was then added to the sample until the pressure doubled. The manifold pressure was adjusted to 5.0 centimeters; a new balance was made and a decade value of 1170 was obtained. From this value an $^{15}N/^{14}N$ ratio of 0.00555 was calculated. Thus for a 3.1 per cent change in the $^{15}N/^{14}N$ ratio the difference between the two decade values was 50 ohms. A five ohm change on the decade caused a change in position of the light spot on the galvanometer scale of one millimeter during the balancing procedure. Thus when achieving a balance on the machine, assuming the balance point can be adjusted to within ± one millimeter of the true balance point on the galvanometer scale, a change in isotope abundance ratio of ± 0.3 per cent should be detectable.
III. STUDY OF THE KINETICS OF THE REACTION BETWEEN URANIUM, $\text{H}_2$, HD AND $\text{D}_2$

A. Introduction and Historical Review

To test whether or not the hydrogen mass spectrometers could be applied in physical chemical research it was decided to examine the reaction between uranium metal and the three different isotopic constituents of hydrogen gas; namely $\text{H}_2$, HD and $\text{D}_2$. For purposes of clarity from now on only mixtures of these constituents will be referred to as hydrogen. When the opportunity arises to refer to a particular molecular species the symbols will be used. Should it be necessary to refer to the individual isotopic atoms the names protium and deuterium or the symbols H and D will be used.

It has been reported (56) that equilibrium in the reaction between uranium and hydrogen is attained very slowly. Thus under suitable reaction conditions it should be possible to determine the reaction rate of only the forward process in the reaction between metal and gas. Such an experiment may be performed if it is possible to observe the changes in concentrations of the constituents in hydrogen after the gas has been allowed to react with uranium for a short period of time. An apparatus in
which the experiment could be performed may conceivably be a large thermostated vessel containing hydrogen gas a section of which contains uranium metal. Some kind of shutter interposed between the metal and gas that prevents reaction between the two would make it possible for the reaction to be allowed to proceed only at the discretion of the experimenter. Such a device presents insurmountable experimental difficulties in addition to the errors that would invariably be introduced due to insufficient opportunity of all the hydrogen molecules in the vessel to react with or even come in contact with uranium metal during the course of the experiment.

A more feasible method, one which lends itself readily to experiment, for carrying out the reactions would be to allow hydrogen to pass over uranium metal in such a way that the gas molecules have a chance to react with the metal for a short time and then are transported from the point of reaction to a place in the apparatus where no reaction can occur. Such an apparatus would consist merely of a gas reservoir connected to a tube in which the reaction takes place to which is connected another reservoir into which gas molecules, which had an opportunity to react but did not, pass. Thus if a gas molecule did not react with the metal
it lacked the necessary energy required to take part in the reaction. From an observation of the rates at which the reactions took place at various temperatures the activation energy for the processes could be calculated.

To insure that each molecule of gas had a chance to react with metal the metal surface should be very large. This requirement is best met by subdividing the metal in order to get a high specific surface. Uranium metal is easily converted into a fine powder by first forming and then decomposing the hydride. By having a great excess of powdered metal available for reaction the processes would be best described as reactions of first order. Thus in the experiments described in this section of the thesis an attempt is made to keep the metal to hydrogen ratio in terms of moles on the order of 1000 to one.

A difference in the reactivities of the H₂, HD and D₂ with uranium observed in the course of the experiments may be expected to be due essentially to the difference of their zero-point energies (57). Since the zero-point energies differ for each molecular species of hydrogen as the square root of their reduced masses the ratios of the reaction constants, k₁ for H₂, k₂ for HD and k₃ for D₂ may be expected to vary inversely as the square roots of the reduced masses. Hence k₁/k₂ will be
\[ 2 \sqrt{\frac{3}{2}} \text{ or } 1.15; \frac{k_1}{k_3} \text{ will be } \sqrt{2} \text{ or } 1.414 \text{ and } \frac{k_2}{k_3} \text{ will be } \sqrt{3/2} \text{ or } 1.22. \] Experimental difficulties may be expected to introduce slight differences in these ratios. Should the differences be great it becomes necessary to determine the extent of other effects such as adsorption upon the rate constants. There is one brief mention in the literature (56) of a study of the kinetics involved in the reaction between uranium and hydrogen. The reaction rate was observed at 357° centigrade by following the decrease of the hydrogen pressure as the gas reacted with uranium. A rate constant was calculated for the initial rate of decrease of hydrogen pressure. A comparison of the reaction rate of D₂ with H₂ indicated the H₂ rate to be about four times that of D₂. A description of the experiments performed by the author follow in subsequent sections of this thesis. The results obtained are indicated and discussed.

B. Materials

Materials used in the construction of the apparatus are discussed in a later section of this thesis. The chemicals used in the experiments consisted of uranium, ordinary tank hydrogen and deuterium gas labeled
99.5+ per cent deuterium.

Uranium

The metal was obtained in the form of turnings which were cut from uranium produced by the Ames group working under the Manhattan Project. While no actual analyses were available or were made upon the material its probable constitution is that given by Spedding, et. al. in their report (56) on the formula of uranium hydride. For use in subsequent experiments the turnings were cut into fine chips, washed with dilute nitric acid, rinsed with distilled water and acetone and dried under vacuum. These chips were then mixed with 10-mesh fused silica powder, which had been carefully washed with boiling concentrated hydrochloric acid, rinsed with distilled water and acetone; and introduced into the reaction tube under an atmosphere of argon which was kept in the reaction tube at all times until it was possible to evacuate the tube.

Powdered uranium was formed by first allowing the metal chips, heated to 250° C., to be completely converted to uranium hydride and then decomposing the hydride by heating to 450° C. while constantly evacuating the gas being evolved. After about two hours of such treatment, isolation of the reaction tube from the vacuum system and heating to 600° C. produced no observable pressure change
in the tube. From this fact it was assumed that no unde-
composed hydride remained in the reaction tube.

**Hydrogen**

Ordinary tank hydrogen, which had been prepared
electrolytically, was used as a source of $\text{H}_2$ in the ex-
periments under discussion. This material had been
assayed many times using the 3-2 mass spectrometer
with the HD/$\text{H}_2$ ratio determined to be $0.000116 \pm 0.000020$
which gives a $\text{D}/\text{H}$ ratio of 1.2 parts in 20,000, a value
not in variance with other reports (22, 42) on this
ratio. Since the material is purified before being
mixed with deuterium no other attempts were made to
purify it before it was introduced into the apparatus.

**Deuterium**

This material as supplied by the Stuart Oxygen Company,
San Francisco, California, consisted of 99.5+ per cent
deuterium gas. No further assay was attempted since it
was used in mixtures with $\text{H}_2$ which were equilibrated and
assayed for their $\text{H}_2$, HD and $\text{D}_2$ content.

C. Apparatus

In order to study the interactions of $\text{H}_2$, HD and $\text{D}_2$
molecules with uranium metal it was necessary to have a
means of (1) making up and storing mixtures of the gaseous
molecules, (2) a reaction tube containing uranium and (3) a means of collecting samples of the gas mixture after it had been allowed to react with uranium. These are the essential components of the apparatus. In addition, other auxiliary components were necessary in order that the reaction between the gaseous molecules and metal could be carried out in a manner so that the data collected from the apparatus could be intelligently interpreted. A gas flow-rate limiter along with manometers for measuring pressure drops in the system were included. A purification system was added since the gases were required at the highest possible purity. The entire apparatus had to be thoroughly evacuated at various times during the experiments so a high vacuum train with its auxiliary pressure measuring devices was also included. Description of the apparatus in its entirety, which is depicted diagrammatically in Figure 65 and pictured in Figure 66, might be given better by considering the individual components in detail.

1. Reaction tube

The reaction tube consists of 19 millimeter outside diameter thin-walled Vycor made by sealing two Vycor-to-pyrex graded seals together. It is best to make this seal in an oxy-hydrogen flame. However, because minute
Figure 65. Kinetics apparatus
Figure 66. Kinetics apparatus
bubbles invariably form at the point where Vycor is fused to Vycor, to get the seal vacuum tight it was found necessary to run a bead around the point of seal using Vycor rod about one-sixteenth of an inch in diameter. The Vycor section of the tube is about 30 centimeters long.

Because the uranium metal used in the experiments is in a finely divided state having been prepared by decomposition of the hydride, it was necessary to devise some means of keeping the powdered metal in place. Glass wool, asbestos fiber and powdered fused silica were tried for this purpose. Powdered fused silica, that would pass a 10 mesh screen but which would remain on a 20 mesh screen, proved most satisfactory for both confining the powdered metal within a limited region of the tube and allowing the hydrogen gas to pass readily through the tube. A detailed description of the filling of the tube is found in Figure 67.
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Figure 67. Diagram of the reaction tube indicating the manner in which the filling was arranged.

2. Hydrogen gas reservoir

The reservoir in which pure $D_2$ and $H_2$ gases were mixed and stored consists of a two liter bulb into which was introduced a palladium filament for the purpose of equilibrating the $D_2$ and $H_2$ mixture to produce the equilibrium concentrations of $H_2$, $HD$ and $D_2$ molecular species. It was first assumed that heating the filament to above $600^\circ C$ would cause the reaction between $H_2$ and $D_2$ molecules on the palladium metal to proceed in such a manner that the equilibrium concentrations of $H_2$, $HD$ and $D_2$...
would be quickly produced. However, final equilibrium was very slow with this device as shown in Figure 68. After four hours the value of the HD/H₂ ratio gave no indication of becoming constant. Because another means of equilibrating the gaseous mixture offered better possibilities the use of the hot palladium filament was abandoned. Conditions more favorable for establishing the equilibrium in the gas mixture may have been found using the filament but no study was made to establish them. While knowledge of these would be desirable it was felt that whatever information could be gained would apply to the particular apparatus employed in these laboratories.

3. Gas-flow limiter

The gas-flow limiter consists of four fine bore capillary tubes of different lengths arranged in the manner illustrated in Figure 69. This arrangement allows several possible gas flow rates if the gas is allowed to flow through each individual capillary or combinations of two or more.
Figure 68. Equilibration of a H₂ - D₂ mixture using a palladium filament at 650° centigrade.
4. **Gas purification and equilibration of H₂, HD and D₂ concentrations in gaseous mixtures**

A fused silica tube, 28 millimeters in diameter and 35 centimeters long, filled with 137 grams of uranium and heated to 600° C. serves to purify the gases as they are first introduced into the two liter reservoir. Glass wool plugs in each end of the tube keep fine particles from being carried mechanically from the purification tube. The tube is connected to the rest of the apparatus by means of graded seals to pyrex glass. The uranium metal filling consists of turnings cut into pieces about 3/4 inches long.
After the reservoir is filled to about 760 millimeters pressure the temperature of the purification tube is allowed to cool to about 250-260° C. Reaction between the metal and hydrogen mixture takes place rapidly until all of the gas is consumed except that accounted for by the hydrogen in equilibrium with uranium in the above temperature range. In practice it is sufficient to allow the temperature of the purification tube to remain in this range for about one hour. Heating to 600° decomposes the hydride-deuteride formed at the lower temperature. It has been found that it is only necessary to allow the gas and metal to react once to insure equilibrium concentrations of H₂, HD and D₂. Repetition of the reaction-decomposition cycle causes no changes in these concentrations unaccountable for by experimental errors.

5. Sampling methods

Provision was made for collecting samples from the gas reservoir and from the gas stream which was passed over the uranium metal. A stopcock fitted with an outer 7/25 standard taper ground joint was attached to the wall of the gas reservoir; a similar device was attached to the reaction tube in a position immediately after the filling. Samples from the reservoir are collected in bulbs whose volume is about one cubic centimeter while
samples from the gas stream are collected in bulbs of about 50 cubic centimeters volume. Each sample bulb was fitted with a stopcock on each side of the bulb with the inner part of a 7/25 ground glass joint connected to one of the remaining tubes leading from the stopcocks. Thus a sample bulb may be connected to either the reservoir or the reaction tube by using the mating ground glass joints. Before collecting a sample in either of the two types of sample bulbs it is necessary that all the space that may contain gases other than those of particular value in the experiments, including the actual space of the bulb, be evacuated. A connection to the vacuum train manifold by means of a length of rubber tubing which serves either the reservoir or the gas stream sampling devices facilitates this operation.

6. Furnaces

A split-tube furnace (Hevi-Duty Electric Company, Type 70, 750 watts) was employed to heat the gas purification tube. An 18 ampere, 115 volt autotransformer (General Radio Company, Type 100 Q Variac) was used to power the furnace. With a reading of about 95 on the Variac dial the furnace temperature is about 600-650° C. A dial reading of about 25 will maintain the furnace temperature at about 250°-260° C, which is necessary for
the reaction between uranium and hydrogen to proceed at the optimum rate.

The furnace used to heat the reaction tube was of special design and built locally. The thermal element consists of 19 feet of #22 chromel wire wrapped on a fused silica tube 22 millimeters inside diameter for a length of 8 inches in such a way that the temperature variation over about 7 inches of the length is constant to less than 0.5° C. at a mean furnace temperature of 475° C. The temperature at the center four inches of the furnace tube is constant to less than 0.3° C. at 475° C. Dicalite insulation surrounds the furnace tube which is contained in a galvanized tin cylinder the ends of which are made from 1/2 inch transite. Overall length of the unit is 27 centimeters with a diameter of 7 inches. Two iron rods connected to the transite ends facilitate mounting on a rack using ordinary universal clamps. Power for the furnace is derived from two autotransformers (General Radio Corp., Type V5 Variac) the operation of which is described in the next section of this thesis.

7. Temperature control of furnaces

No attempt is made to control the temperature of the purification tube furnace other than setting the potential
applied across the furnace terminals and letting it come to thermal equilibrium with its surroundings; the temperatures obtained in this manner lie well within ranges suitable for the experiments. Temperature indication is by means of a chromel-alumel thermocouple whose thermal junction is placed at the center of the furnace.

The reaction tube furnace temperature is controlled to $\pm 1^\circ\text{C}$, using a Taco West Veritron indicator-controller. A chromel-alumel thermocouple serves as the thermo-sensitive element for the controller. In principle the controller is a simple on-off device; however, better temperature control is obtained by using the controller to operate a double pole double throw relay which switches one of two voltages derived from two separate autotransformers to the furnace element. One of the potentials is adjusted so that it is just low enough so that the temperature of the furnace slowly decreases while the other potential is adjusted so that the temperature of the furnace slowly increases. Thus the heating-cooling cycles of the furnace are spread out in such a manner that the furnace temperature varies at a slow rate over a range of 2 degrees centigrade. Since any particular observations being made take place during a maximum time of about 20 seconds, it is not essential that the temperature be absolutely constant.
By observing the slowly varying temperature and choosing the right moment, an experiment can be run at any predetermined reaction tube temperature with a precision conservatively estimated at ± 0.1° C. at a mean temperature of 75° C.

8. **Manometers**

A full-scale mercury manometer is used to determine the pressure of the gas in the reservoir during the experiments and to serve as a means of determining the amounts of hydrogen and deuterium gas being introduced into the reservoir when making up the gaseous mixtures. The pressure changes during the time hydrogen gas is being passed over powdered uranium metal are followed by a 24 centimeter closed-end manometer located at the end of the reaction tube.

9. **High vacuum system**

A vacuum system similar to that used to evacuate the mass spectrometer tubes in these laboratories serves to evacuate the reaction kinetics apparatus. This consists of a mechanical backing pump (Welch Duo-Seal, 1400 series) in series with a two stage mercury diffusion pump (H. S. Martin Company, Type M40050 Standard). A short length of 30 millimeter pyrex tubing serves as the manifold from which any part of the apparatus may be evacuated. An
ionization gage (Type 507, National Research Corporation, Cambridge, Mass.) was employed to record the pressure within the system. While it is not necessary that the very lowest possible pressures be maintained in the apparatus it is noteworthy that no trouble was experienced keeping residual pressures in the manifold below 0.01 microns \((1 \times 10^{-4} \text{ mm of Hg})\). Some instances were observed when the manifold pressure was of the order of 0.002 microns.

D. Experimental Procedure

It is perhaps best to discuss the experimental procedure as a series of operations in which they are performed during an experiment. Mixtures of deuterium and hydrogen gases are made up by introducing into the 2-liter reservoir what are essentially \(\text{H}_2\) and \(\text{D}_2\) gases of known partial pressures. The gases pass, prior to being introduced into the reservoir, through a purification tube containing uranium metal heated to 600° C. To minimize contamination of the \(\text{H}_2\) and \(\text{D}_2\) gases due to air in the lines leading from the gas tanks to the purification tube, the space in the lines is evacuated before opening the tank valves. A predetermined amount of each gas, as indicated by the pressure observed
with the manometer, is then purified and allowed to enter the reservoir. After the mixture has been made, the gas is equilibrated by cooling the uranium metal in the purification tube to 250 to 260° C, and allowing hydride formation to take place; subsequent decomposition of the hydride by heating the purification tube to 600° C, produces a gaseous mixture whose H₂, HD and D₂ concentrations remain constant.

By opening one or a combination of stopcocks in the gas-flow limiter, a portion of the gas mixture is then allowed to pass over the powdered metal, which has been heated to a predetermined temperature. Experience has indicated that the experiments with uranium are best controlled using stopcock number 4 which at room temperature allows enough gas to pass through the reaction tube so that a 50 cubic centimeter gas sample at 100 millimeters of mercury pressure can be collected in about 15 to 20 seconds. Prior to passing the gas mixture through the reaction tube and into the sample bulb the entire space that may be involved is evacuated to less than 0.1 micron.

When enough gas has passed into the sample bulb to yield a pressure of 100 millimeters of mercury on the short manometer, the sample bulb stopcocks are closed along with the stopcock of the gas-flow limiter. Closing of the
stopcocks is done as nearly simultaneously as possible. After the sample bulb is removed from the apparatus its contents are analyzed using the hydrogen mass spectrometer. For samples containing up to about 20 atoms per cent deuterium the 3-2 tube can be used by making a comparison of the intensity of the HD$^+$ and D$_2^+$ ion currents as amplified by the FP-54 amplifier in addition to the normally obtained HD$^+$/H$_2$$_2^+$ ion ratio. D$_2^+$ ions are focused upon the number 3 collector plate in the 3-2 tube using an ion accelerating potential of 210 volts. From the ratios HD/H$_2$ and D$_2$/HD the D$_2$:HD:H$_2$ ratio can be computed.

To prepare the uranium metal so that it may be used to make further observations of the hydrogen-uranium reaction rate it is necessary to decompose any hydride which may have formed during the time of reaction. Decomposition is accomplished by heating the reaction tube to 450° C. and simultaneously evacuating the liberated gas (58). When the pressure in the vacuum system manifold drops to less than 0.1 of a micron the reaction tube is allowed to cool to room temperature or to the predetermined temperature at which the next experiment is to be performed.
E. Experimental Results

1. Analytical data

A mixture of tank hydrogen and deuterium was made by first allowing H\textsubscript{2} to pass into the reservoir until the pressure was 684 millimeters of mercury and then adding D\textsubscript{2} gas until the pressure in the reservoir was 768 millimeters. The mixture of gas was equilibrated by forming and decomposing the uranium compound. A drop in pressure to 764 millimeters occurred due to the equilibration process. According to the make-up data the partial pressures in the mixture due to H\textsubscript{2} and D\textsubscript{2} were 684 and 84 millimeters of mercury respectively. This would correspond to a deuterium content of 10.92 atoms per cent. The average of twelve different analyses on this mixture performed on different days was 10.65 ± 0.11 atoms per cent deuterium. The discrepancy between this figure and that obtained from the make-up data which amounts to about -2.5 per cent may be accounted for by the small error introduced into the make-up figure by assuming the deuterium tank gas to be 100 per cent D\textsubscript{2}; by the probable decrease in D\textsubscript{2}\textsuperscript{+} ion current during the analyses due to the "voltage effect" and by the hold-up of a proportionally greater amount of deuterium than hydrogen by the metal in the purification tube. In each of these corrections the
trend is in the right direction. However, no attempt was made to apply any corrections to the ensuing analytical data since the over-all experimental errors in the experiments probably do not warrant it.

The equilibrated gas mixture was passed over the powdered metal at 27.5°, 35°, 45°, 50°, 60°, 75° and 100° C. In cases where it was possible, a 52.68 cubic centimeter sample at 100 millimeters pressure was collected. This was the case except for the 50°, 60°, 75° and 100° C. experiments in which the pressure of gas in the sample bulb rose to a maximum which was less than 100 millimeters of mercury and then decreased with varying degrees of rapidity, depending upon the temperature of the uranium metal. However, the gas samples were collected at as nearly as possible the maximum obtainable pressure for each experiment. Each sample was analyzed using the 3-2 mass spectrometer expressing the analytical results both as atoms per cent deuterium and the D₂:HD:H₂ ratio. Duplicate experiments were made at all reaction temperatures except 35° and 60° C. in which cases only single experiments were performed. However, these were done after data were collected from experiments run at the other temperatures. The good agreement of the single 35° and 60° C. experiments with
the others indicated that duplicates were probably not necessary. Details of the experiments are summarized in Table VIII.
## Table VII

**Experimental Data for Kinetics Experiments**

<table>
<thead>
<tr>
<th>Reaction Temp. °C</th>
<th>Reservoir Temp. °C</th>
<th>Atoms % D in Reservoir Gas</th>
<th>Δp of Gas in Res. During Experiment in mm. of Mercury</th>
<th>Millimoles Hydrogen Used in Exp.</th>
<th>Final Pressure in mm. of Mercury</th>
<th>Atoms % Time to Collect D in Sample in Secs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.5</td>
<td>27.5</td>
<td>10.62</td>
<td>8</td>
<td>0.908</td>
<td>100</td>
<td>10.36</td>
</tr>
<tr>
<td>35.0</td>
<td>27.0</td>
<td>10.55</td>
<td>9.5</td>
<td>1.078</td>
<td>100</td>
<td>11.17</td>
</tr>
<tr>
<td>45.0</td>
<td>29.0</td>
<td>10.70</td>
<td>11.5</td>
<td>1.297</td>
<td>100</td>
<td>11.50</td>
</tr>
<tr>
<td>50.0</td>
<td>27.5</td>
<td>10.67</td>
<td>12.5</td>
<td>1.353</td>
<td>88</td>
<td>11.62</td>
</tr>
<tr>
<td>60.0</td>
<td>27.0</td>
<td>10.65</td>
<td>14</td>
<td>1.593</td>
<td>80</td>
<td>12.21</td>
</tr>
<tr>
<td>75.0</td>
<td>27.0</td>
<td>10.60</td>
<td>16</td>
<td>1.616</td>
<td>62</td>
<td>12.90</td>
</tr>
<tr>
<td>100.0</td>
<td>27.0</td>
<td>10.65</td>
<td>18</td>
<td>--</td>
<td>&lt;5**</td>
<td>--</td>
</tr>
</tbody>
</table>

*Volume of all samples was 52.68 cubic centimeters.

**Not enough material was collected to make an analysis. Due to the reaction between the uranium and hydrogen the value 5 millimeters represents a maximum which decreased very rapidly. No further experiments were performed at temperatures higher than 100° C.*
As indicated in the table it was impossible to perform any reliable experiments at 100° C, because the reaction between metal and gas proceeded so rapidly that a maximum pressure of about 5 millimeters of mercury was observed in the sample bulb. Data from the reservoir gas and sample analyses appear broken down into essential categories in Table IX.
<table>
<thead>
<tr>
<th>Gas Sample Analyzed</th>
<th>HD/H₂</th>
<th>D₂/HD</th>
<th>Ratio D₂: HD: H₂</th>
<th>Moles Per Cent D₂</th>
<th>Moles Per Cent HD</th>
<th>Moles Per Cent H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir</td>
<td>0.244</td>
<td>0.0457</td>
<td>1:21.9:89.7</td>
<td>0.89</td>
<td>19.45</td>
<td>79.66</td>
</tr>
<tr>
<td>27.5°C</td>
<td>0.252</td>
<td>0.0461</td>
<td>1:21.7:86.2</td>
<td>0.92</td>
<td>19.92</td>
<td>79.15</td>
</tr>
<tr>
<td>35.0°C</td>
<td>0.257</td>
<td>0.0523</td>
<td>1:19.1:74.3</td>
<td>1.06</td>
<td>20.25</td>
<td>78.69</td>
</tr>
<tr>
<td>45.0°C</td>
<td>0.262</td>
<td>0.0567</td>
<td>1:17.7:67.4</td>
<td>1.16</td>
<td>20.58</td>
<td>78.28</td>
</tr>
<tr>
<td>50.0°C</td>
<td>0.287</td>
<td>0.0573</td>
<td>1:17.4:65.4</td>
<td>1.19</td>
<td>20.76</td>
<td>78.04</td>
</tr>
<tr>
<td>60.0°C</td>
<td>0.282</td>
<td>0.0607</td>
<td>1:16.5:58.5</td>
<td>1.32</td>
<td>21.72</td>
<td>76.96</td>
</tr>
<tr>
<td>75.0°C</td>
<td>0.300</td>
<td>0.0676</td>
<td>1:14.8:49.3</td>
<td>1.54</td>
<td>22.73</td>
<td>75.73</td>
</tr>
</tbody>
</table>
From a consideration of Figure 70 which is a diagrammatic representation of the reservoir, gas-flow limiter, reaction tube and sample collecting device, further information, which is necessary to evaluate the experimental data, is obtained.

![Figure 70](image)

The volumes of space in which gas may be held in the apparatus may be divided into AD, the region in which the gas never has had a chance to react with uranium; DE the region in which reaction occurs and EB the region in which the gas which has had an opportunity to react no longer can react with uranium. The volumes of the free space in each of these regions is A to D, 41.4 cc.; D to E, 12.2 cc.; E to C, 47.4 cc. and C to B 52.6 cc. The total volume
between points A and C was determined by allowing argon gas at a known pressure to expand from the space AC into the space CB. Since the volume BC was accurately determined at 27.0°C, the volume in space AC could be calculated using the perfect gas law. The average of several such determinations, designed to produce a final pressure after expansion of about 100 millimeters of mercury in order to obviate volume corrections in the manometer, was 101.0 cubic centimeters ± 0.2 per cent. The free volumes in regions A to D, D to E, and E to C were estimated from the dimensions of the reaction tube and from liquid displacement measurements made on a replica which was nearly the same as the reaction tube as possible except for the omission of powdered uranium in the filling. The estimated volumes in these regions are probably accurate to ± 0.5 cubic centimeters.

By considering the apparatus broken down into various regions and with their respective volumes determined it is possible to separate the amount of hydrogen used in the experiments into (1) the amount that never had a chance to react with uranium, (2) the amount that had a chance to react and then passed beyond what is given as point E in Figure 70, (3) the amount held in the free space of region D to E and (4) the amount which reacted with uranium to
form the hydride. The sample taken for analysis represents about 53 per cent of (2) and so it is assumed that its composition represents that of all the gas which has passed the point beyond the uranium in the reaction tube. In calculations concerning the actual number of millimoles of hydrogen held in the space of each region of the apparatus account must be made of the fact that temperature differences are present within a particular region. In both regions AD and BC 5.4 cubic centimeters of the total volume are at the reaction tube temperature while in 5.7 cubic centimeters of the volume the temperature varies from that of the reaction tube to room temperature. The remainder of the volume of each region is at room temperature. Table X summarizes the data obtained from calculations regarding the number of millimoles hydrogen contained in each region of the apparatus at the time the sample is collected in each of the experiments.
Table X
Hydrogen Held in Various Regions of the Apparatus

<table>
<thead>
<tr>
<th>Reaction Temp. in °C</th>
<th>Millimoles Hydrogen Which Have Passed Point E</th>
<th>Millimoles Hydrogen in Interstices of DE</th>
<th>Millimoles Hydrogen Not Passing Point D</th>
<th>Millimoles Hydrogen Reacted With Uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.5</td>
<td>0.535</td>
<td>0.065</td>
<td>0.222</td>
<td>0.086</td>
</tr>
<tr>
<td>35.0</td>
<td>0.529</td>
<td>0.064</td>
<td>0.220</td>
<td>0.265</td>
</tr>
<tr>
<td>45.0</td>
<td>0.503</td>
<td>0.062</td>
<td>0.217</td>
<td>0.515</td>
</tr>
<tr>
<td>50.0</td>
<td>0.467</td>
<td>0.053</td>
<td>0.192</td>
<td>0.641</td>
</tr>
<tr>
<td>60.0</td>
<td>0.420</td>
<td>0.047</td>
<td>0.173</td>
<td>0.953</td>
</tr>
<tr>
<td>75.0</td>
<td>0.328</td>
<td>0.035</td>
<td>0.133</td>
<td>1.320</td>
</tr>
</tbody>
</table>

It might be well to call attention to the data presented in column four of the table. While the volume of gas held in the region AD is essentially constant (volume corrections due to the expansion of the Vycor are negligible), the number of moles contained in the space of this region diminishes due to an increase in temperature of a part of the region.

From the data presented in Table X it is possible to calculate the ratios of the rate constants for the reactions between uranium, H₂, HD and D₂. In any of the experimental data observed the ratio of moles uranium available for reaction to the total moles of hydrogen used in the
experiments is about $1250/1.0$ to $1.8$. Thus it is expected that the rate of disappearance of any molecular species of hydrogen would conform to a first order expression. Hence it may be stated that

\[
- \frac{dP_{H_2}}{dt} = k_1 P_{H_2} \quad (98)
\]

\[
- \frac{dP_{HD}}{dt} = k_2 P_{HD} \quad (99)
\]

\[
- \frac{dP_{D_2}}{dt} = k_3 P_{D_2} \quad (100)
\]

From (98) and (99)

\[
\ln P_{H_2} = \frac{k_1}{k_2} \ln P_{HD} \quad (101)
\]

From (93) and (100)

\[
\ln P_{H_2} = \frac{k_1}{k_3} \ln P_{D_2} \quad (102)
\]

and from (99) and (100)

\[
\ln P_{HD} = \frac{k_2}{k_3} \ln P_{D_2} \quad (103)
\]

Integration of (101) leads to the expression

\[
\ln P_{H_2}^{\infty} = \frac{k_1}{k_2} \frac{\ln P_{HD}^{\infty}}{P_{HD}} \quad (104)
\]

Equations (102) and (103) lead to similar results.
To determine $p^0$, the initial pressure for the reactions it is necessary to determine what the pressure would have been in the reaction tube assuming that no hydrogen reacted with uranium. Column five of Table X gives the millimoles of hydrogen which reacted at each experimental temperature. From a consideration of the perfect gas law and the volume of the apparatus from a point half way between points D and E and point B of Figure 70, this being a reasonable estimation of the space which the gas would occupy, it is possible to calculate the apparent initial pressure. However, except in the case where the reaction was run at room temperature a complication arises. Part of the volume in which the gas would be contained is at the reaction temperature while the remainder is at room temperature. From a consideration of the dimensions of the apparatus 15.3 cubic centimeters of the total volume is at the reaction temperature. The total volume of the space which extends from point B to the point half way between D and E in the apparatus is 106.2 cubic centimeters. Thus 90.9 cubic centimeters of the total volume of gas will be at room temperature.

To determine the pressure at which the gas would be if no reaction with uranium had taken place consider first that the hydrogen that reacted with uranium occupies
volume $V_2$ (which is 15.5 cubic centimeters) at temperature $T_2$. Since $n$ moles of hydrogen reacted it is possible to calculate the pressure this amount of gas would exert upon the walls of $V_2$ at $T_2$. Then after allowing this gas to expand into volume $V_1$ (90.9 cubic centimeters) at temperature $T_1$ the problem is to determine the resultant pressure. Figure 71 indicates what the situation is diagrammatically.

The gas is first held in the left vessel where

$$n = \frac{P_2 V_2}{RT_2} \quad (105)$$

Then the stopcock is opened and the pressure decreases to $P_r$ in both left and right vessels.

$$n_2 = \frac{P_r V_2}{RT_2} = \text{number of moles of gas in the left vessel.} \quad (106)$$
and

\[ n_1 = \frac{P_1 V_1}{RT_1} = \text{number of moles of gas in the right vessel}. \]  \hspace{1cm} (107)

However, since \( n = n_1 + n_2 \)

\[ n = \frac{P_r}{R} \left[ \frac{V_1}{T_1} + \frac{V_2}{T_2} \right] \]  \hspace{1cm} (108)

or

\[ P_r = \frac{nRT_1 T_2}{V_1 T_2 + V_2 T_1} \]  \hspace{1cm} (109)

For the experiment at room temperature when \( T_2 = T_1 \)

\[ P_r = \frac{0.086 \times 10^{-3} \times 82.05 \times 300.5 \times 760}{106.2} \]

or

\[ P_r = 15.15 \text{ millimeters of mercury} \]

However the actual pressure observed (see Table VIII) when the sample was collected was 100 millimeters, thus \( P^0 \) for this experiment is the sum of the resultant pressure plus the sample pressure or 115.2 millimeters of mercury which represents the total initial hydrogen pressure. To find the initial partial pressures for each of the molecular species of hydrogen it is necessary to multiply this total \( P^0 \) by the mole fraction of each molecular species which is found in columns 5, 6 and 7 of Table IX considering the values of the mole fractions for the unreacted
reservoir gas.

The final total pressure \( p \) of equation (104) is that pressure at which the sample was collected. Thus to determine the final partial pressures of each molecular species of hydrogen, it is necessary to multiply the sample pressure which is found in Table VIII for each of the experiments by the mole fraction of each molecular species considering the values of the mole fractions for the sample obtained in the experiment under examination. Table XI summarizes the calculated initial and final partial pressures for the experiments.

**Table XI**

Initial and Final Partial Pressures for \( H_2, HD \) and \( D_2 \) in Hydrogen

<table>
<thead>
<tr>
<th>Exp' in °C</th>
<th>Total ( p^0 )</th>
<th>( p_{H_2}^0 )</th>
<th>( p_{HD}^0 )</th>
<th>( p_{D_2}^0 )</th>
<th>Total ( p )</th>
<th>( p_{H_2} )</th>
<th>( p_{HD} )</th>
<th>( p_{D_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.5</td>
<td>115.2</td>
<td>91.8</td>
<td>22.4</td>
<td>1.03</td>
<td>100</td>
<td>79.2</td>
<td>19.9</td>
<td>0.92</td>
</tr>
<tr>
<td>35.0</td>
<td>146.7</td>
<td>116.8</td>
<td>28.6</td>
<td>1.31</td>
<td>100</td>
<td>78.7</td>
<td>20.3</td>
<td>1.06</td>
</tr>
<tr>
<td>45.0</td>
<td>192.0</td>
<td>153.0</td>
<td>37.4</td>
<td>1.71</td>
<td>100</td>
<td>78.3</td>
<td>20.6</td>
<td>1.16</td>
</tr>
<tr>
<td>50.0</td>
<td>202.0</td>
<td>161.0</td>
<td>39.3</td>
<td>1.60</td>
<td>88</td>
<td>68.7</td>
<td>18.3</td>
<td>1.05</td>
</tr>
<tr>
<td>60.0</td>
<td>250.0</td>
<td>199.3</td>
<td>48.6</td>
<td>2.21</td>
<td>80</td>
<td>61.6</td>
<td>17.4</td>
<td>1.06</td>
</tr>
<tr>
<td>75.0</td>
<td>299.0</td>
<td>238.0</td>
<td>58.2</td>
<td>2.66</td>
<td>62</td>
<td>46.9</td>
<td>14.1</td>
<td>0.95</td>
</tr>
</tbody>
</table>

All pressures indicated in this table are in millimeters of mercury.
Substitution of the proper values from Table XI into formulae (102), (103) and (104) gives the ratios of the rate constants $k_1$, $k_2$ and $k_3$. As an example these ratios are calculated for the experiment at 27.5°C.

$$\log \frac{79.2}{91.8} = \frac{k_1}{k_2} \log \frac{19.9}{22.4}$$

$$\frac{k_1}{k_2} = -0.065 \div -0.052 = 1.25$$

$$\log \frac{79.2}{91.8} = \frac{k_1}{k_3} \log \frac{0.92}{1.03}$$

$$\frac{k_1}{k_3} = -0.065 \div -0.049 = 1.33$$

$$\log \frac{19.9}{22.4} = \frac{k_2}{k_3} \log \frac{0.92}{1.03}$$

$$\frac{k_2}{k_3} = -0.052 \div -0.049 = 1.06$$

In a similar manner these ratios are calculated from the data of experiments at other temperatures and the results are tabulated in Table XII.
Table XII

Ratios of Rate Constants for Reaction Between Uranium, H₂, HD and D₂

<table>
<thead>
<tr>
<th>Exp'1</th>
<th>k₁/k₂</th>
<th>k₁/k₃</th>
<th>k₂/k₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. in °C.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.5</td>
<td>1.25</td>
<td>1.33</td>
<td>1.06</td>
</tr>
<tr>
<td>35.0</td>
<td>1.15</td>
<td>1.83</td>
<td>1.60</td>
</tr>
<tr>
<td>45.0</td>
<td>1.13</td>
<td>1.71</td>
<td>1.44</td>
</tr>
<tr>
<td>50.0</td>
<td>1.11</td>
<td>1.58</td>
<td>1.42</td>
</tr>
<tr>
<td>60.0</td>
<td>1.14</td>
<td>1.60</td>
<td>1.40</td>
</tr>
<tr>
<td>75.0</td>
<td>1.14</td>
<td>1.58</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Using equations (98), (99) and (100), the data in Table XI and column eight of Table VIII, the rate constants for each reaction over the range of temperatures used in the experiments may be calculated. Such a calculation is included here for the experiment at 27.5°C.

From (98) upon integration there results

\[-\ln p_{H₂} = k₁ t + C \]  \hspace{1cm} (110)

where C is the constant of integration.

Integrating between initial and final conditions for the experiments

\[-\ln \frac{p_{H₂}}{p_{H₂}^0} = k₁ (t₂ - t₁) \]  \hspace{1cm} (111)
or

\[ \ln \frac{p_{H_2}}{p_{H_2}^0} = k_1 (t_2 - t_1) \]  

Converting to base ten logarithms

\[ \log \frac{p_{H_2}}{p_{H_2}^0} = \frac{1}{2.303} k_1 (t_2 - t_1) \]  

Similarly, expressions may be derived from equations (99) and (100) to give

\[ \log \frac{p_{HD}}{p_{HD}^0} = \frac{1}{2.303} k_2 (t_2 - t_1) \]  

and

\[ \log \frac{p_{D_2}}{p_{D_2}^0} = \frac{1}{2.303} k_3 (t_2 - t_1) \]

Using the data from Tables VIII and XI for the 27.5° C experiment

\[ \log \frac{91.8}{79.2} = \frac{15.6}{2.303} k_1 \]

\[ k_1 = \frac{2.303 \times 0.064}{15.6} = 0.00945 \text{ sec}^{-1} \]

Calculated in a similar manner

\[ k_2 = 0.00752 \text{ sec}^{-1} \]

and
$k_3 = 0.00707 \text{ sec}^{-1}$

Results of similar calculations for the experiments at other temperatures are listed in Table XIII.
Table XII
Rate Constants for the Reaction Between Uranium, $H_2$, HD and $D_2$

<table>
<thead>
<tr>
<th>Exp'1 temp. in °K.</th>
<th>$1/T \times 10^{-2}$</th>
<th>$k_1$ in sec.$^{-1}$</th>
<th>$\log k_1$</th>
<th>$k_2$ in sec.$^{-1}$</th>
<th>$\log k_2$</th>
<th>$k_3$ in sec.$^{-1}$</th>
<th>$\log k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.5</td>
<td>3.53</td>
<td>0.00945</td>
<td>-2.025</td>
<td>0.00752</td>
<td>-2.124</td>
<td>0.00707</td>
<td>-2.152</td>
</tr>
<tr>
<td>308.0</td>
<td>3.25</td>
<td>0.0243</td>
<td>-1.615</td>
<td>0.0212</td>
<td>-1.674</td>
<td>0.0150</td>
<td>-1.886</td>
</tr>
<tr>
<td>318.0</td>
<td>3.15</td>
<td>0.0398</td>
<td>-1.401</td>
<td>0.0352</td>
<td>-1.454</td>
<td>0.0229</td>
<td>-1.641</td>
</tr>
<tr>
<td>323.0</td>
<td>3.10</td>
<td>0.0455</td>
<td>-1.342</td>
<td>0.0408</td>
<td>-1.389</td>
<td>0.0301</td>
<td>-1.522</td>
</tr>
<tr>
<td>333.0</td>
<td>3.00</td>
<td>0.0798</td>
<td>-1.098</td>
<td>0.0697</td>
<td>-1.156</td>
<td>0.0500</td>
<td>-1.301</td>
</tr>
<tr>
<td>348.0</td>
<td>2.79</td>
<td>0.1843</td>
<td>-0.7351</td>
<td>0.1605</td>
<td>-0.795</td>
<td>0.1168</td>
<td>-0.953</td>
</tr>
</tbody>
</table>
From the data of Table XIII the energy of activation for the reactions may be calculated by making use of the Arrhenius relationship

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

(116)

whose integrated form is

\[ \ln k = -\frac{E}{RT} + \text{const}. \]  

(117)

in which it is seen that the relationship between \( \ln k \) and \( 1/T \) is linear. Plotting the data listed in Table XIII should result in a straight line the slope of which is \(-E/R\) from which the activation energy may be calculated. Such a plot is made in Figure 72 from which it is evident that all the data except those obtained for the 27.5° Centigrade experiment have a linear relationship when the Arrhenius equation is applied.

The energies of activation of the processes are 8,200 ± 200 calories for that involving \( \text{H}_2 \) molecules, 8,500 ± 200 calories for that involving HD molecules and 10,200 ± 200 calories involving \( \text{D}_2 \) molecules. Following reasoning similar to that previously cited in the literature based upon a consideration of the zero point energies of \( \text{D}_2 \), HD and \( \text{H}_2 \) molecules, the energy required for activation in the uranium -\( \text{D}_2 \) reaction should be greater than that for the uranium -\( \text{H}_2 \) reaction. The magnitudes of the observed
\[ \log k = - \frac{1}{2.303} \frac{E}{RT} \]

- \( k_1 \) slope = - 1800
- \( k_2 \) slope = - 1850
- \( k_3 \) slope = - 2230

Figure 72. Plot of \( \log k \) versus \( 1/T \) for the data presented in Table XIII.
activation energies are what may reasonably be expected for such reactions.

F. Discussion

It was stated earlier in this thesis that the reaction rates of uranium with H₂, HD and D₂ might be expected to vary inversely as the square root of the reduced masses of the hydrogen molecules. Thus the ratio \( \frac{k_1}{k_2} \) should be \( 2/\sqrt{3/2} \) or 1.15; \( \frac{k_1}{k_3} \) should be \( \sqrt{2}/1 \) or 1.415 and \( \frac{k_2}{k_3} \sqrt{3/2} / 1 \) or 1.22. The data listed in Table XII indicate good agreement at room temperature but relatively poor agreement for all other temperatures. However, from Figure 72 it is clear that the room temperature experiment did not fall in line with the other experiments when the Arrhenius equation was applied to the experimental data. Thus it becomes necessary to offer a plausible explanation for the general deviation of the experimental results from the principle mentioned above.

The experiments were designed to present as great a uranium surface as possible with which hydrogen molecules could come in contact. However, the use of finely powdered metal introduced an additional factor into the processes, that of adsorption. While the rates of reaction between uranium metal and hydrogen molecules might follow the
inverse square root rule, the rates at which the different molecular species of hydrogen are initially adsorbed may constitute the over-all rate determining step in the processes. Complications due to adsorption may be sufficient to account for the observed variations from the inverse square root rule.

The over-all process is probably best considered as taking place in three steps: (1) The gas molecule approaches the metal surface and is adsorbed forming an adsorption complex. (2) The adsorption complex either has sufficient energy to become an activated adsorption complex or it lacks the requisite energy and breaks down, which is equivalent to stating that the gas molecules evaporate from the surface. (3) Those adsorption complexes which are activated are then converted to a compound. Thus only molecules which are adsorbed have an opportunity to react and only those which possess sufficient energy to form an activated adsorption complex take part in the reaction between gas and metal.

The uranium-hydrogen reactions must then be considered as taking place in a heterogeneous system and the activation energies observed are only apparent activation energies. If it is assumed that the product of the reaction does not have a retarding influence upon the rate of reaction, then
where $\lambda$ is the heat of adsorption of a mole of hydrogen by uranium and $E$ is the true activation energy. The validity of this assumption is indicated by the fact that when hydrogen reacts with massive uranium the hydride formed continually sloughs off the metal surface allowing new surface to be exposed for reaction. A similar action is to be expected even in the case where finely powdered metal is employed since the crystalline forms of hydride and metal are different. Even if the hydride should have some retarding influence upon the reaction rate, the fact that less than one-thousandth of the uranium metal would take part in compound formation if all the hydrogen used in any of the experiments was converted to hydride indicates that the extent of the retarding action would certainly be small and probably negligible. In order to determine the true activation energy for the reaction between uranium, $H_2$, HD and $D_2$, it becomes necessary to know the heat of adsorption for these molecular species being adsorbed on uranium. Unfortunately, determination of the heats of adsorption is impossible since under none of the experimental conditions could the reaction between gas and metal be prohibited. An alternative is to consider other instances in which comparative studies on the heats
of adsorption of $H_2$ and $D_2$ have been reported. Maxsted and Moon (59) determined the relative rates of adsorption of $H_2$ and $D_2$ from -21 to 50° C. on finely divided platinum and found the rate of adsorption of $H_2$ to be 1.4 to 1.5 times that of $D_2$. They reported the energy of activation of the adsorption of the two gases to be 2500 calories mol$^{-1}$ and 2400 calories mol$^{-1}$. Soller, Goldwasser and Beebe reported (60) that the relative rates of adsorption of $D_2$ and $H_2$ on finely divided copper and indicate $H_2$ to be adsorbed 5.5 times as rapidly as $D_2$ at 0° centigrade. A difference of 750 calories in the activation energies for the two kinds of hydrogen in the range of about 10,000 calories is indicated. Beebe and Dowden (61) reported the heats of adsorption for $H_2$ and $D_2$ on chromic oxide to be 4600 and 4950 calories respectively while values of 1000 and 1700 calories are listed for the adsorption on nickel (62) in the temperature range 0-25° centigrade. Maidanovskii and Bruns (63) indicated a value of 17,000 calories for the initial heat of adsorption of $H_2$ on platinum at 100-120° C.

The range over which the heats of adsorption of $H_2$ and $D_2$ are distributed on metals other than uranium makes it impossible to attempt any analogies in the estimation of a reasonable value for the true activation energy of the
hydrogen-uranium reaction. Since it is not possible to actually measure the heats of adsorption of hydrogen on uranium the true activation energy for the reaction cannot be known. If the entire surface of uranium metal was covered with hydrogen molecules the amount adsorbed would not change with temperature and $A$ would be zero, and $E_a$ would be the true activation energy. However, this is unlikely under the conditions of the experiments and so the conclusion must be made that the true activation energies for the hydrogen-uranium reactions are less than the observed apparent activation energies but no actual values can be cited.

The report of Soller, Goldwasser and Beebe (60), in which it was indicated that the rate at which copper adsorbed $H_2$ was 5.5 times as rapid as the rate at which $D_2$ was adsorbed, indicates that the step in which hydrogen molecules are adsorbed on the uranium may be the controlling fact in the observed variations from the inverse square root rule. The above discussion shows that the heterogeneous nature of the reaction system makes it difficult to accurately determine the relative rates of these processes.

An alternate viewpoint should be examined by which the phenomena observed in the experiments described in the third section of this thesis may be explained. If the
rate of interaction between hydrogen and uranium does not depend upon the difference in zero point energies of the different molecular species it might involve diffusion of the molecules into the metal. Since the diffusion rates of gases depend inversely as the square root of their masses, the ratios of the reaction rate constants would be $k_1/k_3 = \sqrt{4}/\sqrt{2}$ or 1.415; $k_1/k_2 = \sqrt{3}/\sqrt{2}$ or 1.225 and $k_2/k_3 = \sqrt{4}/\sqrt{3}$ or 1.155. Comparison of these values with those cited in Table XII gives as good agreement as the ratios based upon the zero point energies and no choice can be made between the alternate viewpoints. It is therefore necessary to consider other factors involved in the experiments before a choice can be made between the zero point energy and diffusion interpretations of the experimental data. McBain (67), in studies on the sorption of hydrogen by charcoal, observed that there was an initial rapid adsorption of the gas followed by a slower process. The rate of adsorption of the slow process was in agreement with the laws of diffusion. In the experiments described in this thesis the extremely short times during which observations were made necessarily exclude any diffusion into the metal. Brunauer (68) stated that it is generally safe to conclude that in a purely physical adsorption, gas molecules are adsorbed as rapidly as they reach the surface. The slow effects are
due to chemisorption, chemical reaction, solution or to the inability of gas molecules to contact the surface of the metal.

Durau and Teckentrup (69) studied the purely physical adsorption of different gases, including hydrogen, on finely divided iron. They found that equilibrium was established very rapidly and the isotherms were completely reversible at 100°C and for a pressure range 50-750 millimeter of mercury. Benton and White (70) observed the sorption of hydrogen by nickel and copper and Taylor and McKinney (71) studied the sorption of carbon monoxide by palladium; they found a very rapid initial stage which indicated purely physical adsorption followed by a slow stage in which the rate of sorption was very slow. This second stage was designated by Taylor (72) as activated adsorption.

Consideration of the observations made on the hydrogen-uranium reaction and the three steps by which the over-all process is assumed to proceed (see page 276 of this thesis) indicate that the first step is most likely purely physical adsorption and proceeds very rapidly. The second or activating step is the slow step while the third step is very rapid. Thus the over-all rate of interaction between uranium and hydrogen is
controlled by the rate at which the activated complexes are formed. Since it has been shown in a previous discussion in this thesis that the rate of diffusion of the different hydrogen molecular species into the metal has little influence upon the rates at which reactions occur, the observed differences in the rates are probably due mainly to the difference in the zero point energies of the hydrogen molecules.
IV. SUMMARY

A. Construction of Mass Spectrometers

1. Hydrogen mass spectrometers

A special, dual-collector type mass spectrometer has been constructed in these laboratories by which hydrogen gas samples may be assayed for the abundances of their stable isotopic constituents. In addition to a description of the construction details, directions for operating the machine have been presented in this thesis. Sources of possible errors in the analytical procedures have been pointed out and suggestions have been made for overcoming them.

Some problems concerning operation of the mass spectrometer remain. The day to day reproducibility of the machine should be improved upon; the extent of discriminations that take place in the machine should be more precisely determined and a more satisfactory way of determining resistor ratios should be found.

Better utilization of the mass spectrometer for use as a tool in "tracer" experiments would result if a reliable method of determining the isotopic constitution of small amounts of water was developed. One approach to this problem is the possible adaptation of the water-
hydrogen equilibration method to small samples of water while another is the complete decomposition of the water to produce oxygen free hydrogen gas.

2. Mass spectrometer of range 1-75 mass units

Construction details and operating instructions have been presented in this thesis for a dual-collector type mass spectrometer of range 1-75 mass units. It has been demonstrated that the machine will give satisfactory results in assays of nitrogen and carbon dioxide sample for N\textsubscript{15} and C\textsubscript{13} respectively.

Further developments should follow along lines that will make the machine more useful for all types of gas analyses. These would necessarily include perfecting automatic scanning devices for recording the complete mass spectra of gas samples.

B. Kinetics of the Reaction Between Uranium, H\textsubscript{2}, HD and D\textsubscript{2}

The kinetics of the reactions between uranium metal, H\textsubscript{2}, HD and D\textsubscript{2} have been examined. There is strong evidence that the reaction involves several steps of which activated adsorption of the gas by the metal is the rate governing process. Rate constants have been determined for the over-all processes in the temperature range 27.5\degree C to 75\degree C centigrade. Energies of activation which are of reasonable magnitude have been calculated being 10,200 calories for
for the process involving D₂, 8,500 calories for the process involving HD and 8,200 calories for the process involving H₂. From a consideration of the zero point energies for these three molecular species of hydrogen, these results follow in the right order. However because of the adsorption step and since it is not possible to determine the heat of adsorption it is impossible to state that the observed activation energies are the true activation energies. Since the heat of adsorption during the process must be considered in the final interpretation of the results, the true activation energies are probably less positive than those observed. The adsorption step in the processes also accounts for the fact that the ratios of the rates of the reactions, which may be expected to differ inversely as the square roots of the reduced masses of the gas molecules, deviate somewhat from the theoretical values.

Heterogeneous reactions such as those reported in this thesis do not lend themselves readily to kinetics experiments. Because of the reactivity of the uranium-hydrogen system it was not possible to determine to what extent the heat of adsorption enters into the values obtained for the observed activation energies. However other metal-hydrogen systems which do not interact so rapidly should
better lend themselves to studies of this nature. It should then be possible to separate the adsorption-step from the reaction-step and thereby obtain the true activation energies.
V. ACKNOWLEDGMENTS

The author wishes to acknowledge his appreciation to Dr. F. H. Spedding who suggested that the work be undertaken and whose patient interest saw its completion; to Dr. A. O. Nier of the University of Minnesota for his willingness to give advice during the construction of the mass spectrometers even to the extent of giving unpublished advanced information; to Dr. E. I. Fulmer who helped raise the spirit when it had sunken low at various times and who along with Dr. Wallace Caldwell critically read part of the manuscript; to Dr. Fredrick Duke who aided with the kinetics problem and critically read the manuscript dealing with this part of the thesis; to Mr. Stanley Ball who aided in building and adjusting the electronic circuits; to Mr. Lael Smith who helped construct some of the mass spectrometer parts; to Mr. R. B. Thorness of the University of Minnesota Physics Instrument Shop for his help on the construction of the large mass spectrometer tube; to Mrs. Evelyn Kirkpatrick for her help in typing the manuscript and to the author's wife who helped proofread and arrange the final copy.
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