

ENERGY TRANSPORT AND THERMODYNAMIC BEHAVIOR

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VAPOR PRESSURE MEASUREMENT

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The usefulness of thermodynamics as a tool in materials engineering has been discussed in many standard texts on thermodynamics over the last century. More recently its utility both for predicting materials performance in various environments, as well as for materials synthesis, has been rather thoroughly treated by many outstanding figures such as Brewer, Margrave, and others. Its use however, has been severely restricted at the temperatures of current interest because of a lack of the fundamental data needed to carry out the calculations. These considerations in addition to those of elucidating the processes involved in vaporization constitute the main impetus to the measurement of vapor pressures.

Vapor pressure is that pressure exerted by a vapor when it coexists in equilibrium with its condensed phase. This simple statement is not at all indicative of the difficulties the modern experimenter encounters in examining systems of interest. To begin with he must find an inert vessel to contain his sample. At high temperatures he is bound to have a head-on encounter with what appears to be the first law of High Temperature Chemistry: namely that "At high temperatures all substances react with each other, with the measuring instruments, and on many occasions with forms of matter which the experimenter would swear were not even present in the room." A quick check of this law can be made by anyone attempting to measure any property of any material at temperatures of 2000°K or above. This in essence is the "container problem" which rules out the classical static and transpiration methods so familiar to many workers in other fields of chemistry

The second major problem centers around the fact that if a pressure can be measured by means of one of these methods, it represents a total pressure which in turn is made up of the sum of the individual partial pressures of the various species present in the vapor. The species in the vapor may bear little resemblance to what might be expected from a knowledge of the composition of the condensed phase. It is evident then that measuring vapor pressures at high temperatures is centered around that of construction of equipment made of suitable materials and the determination of vapor species. The most widely used techniques are based on the kinetic theory of gases, and are commonly referred to as the "Knudsen" effusion method and the "Langmuir" method.

The Knudsen Effusion Method

The Knudsen method is based on the consideration of molecular effusion of an ideal gas into a vacuum through a small orifice, from a vessel at a given pressure. With this in mind consider a closed, inert vessel of low vapor pressure which contains one or more condensed phases at constant temperature. If the contents of the vessel are in a state of equilibrium, the number of molecules leaving the surface of the condensed material are equal to the number of molecules condensing. Furthermore, the vapor pressure built up within the vessel is due to the number of gas molecules striking any unit surface area within the vessel. Now if the vessel is pierced with a hole whose dimensions are small compared to the mean free path, the molecules striking the area of the hole will effuse and can be counted and characterized. The effusion under such conditions will not affect the equilibrium in the vessel or change the pressure. With these conditions in mind, the

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relation derived from kinetic theory between the rate of effusion and the pressure in the cell is given by:

$$\frac{dn}{dt} = P (2 \pi MRT)^{-\frac{1}{2}} \quad (1)$$

where:

- $\frac{dn}{dt}$ = rate of collision of molecules/cm² of any wall surface = rate of effusion (mole/sec/cm²)
P = pressure in cell (dynes/cm²)
M = molecular weight of vapor molecules (g/mole)
R = gas constant (ergs/deg. mole)
T = absolute temperature (°K)

With some algebraic manipulation the equation can be written in a form more usable for the experimental determination of vapor pressures:

$$P = \frac{w}{a} \left(\frac{2 RT}{M} \right)^{\frac{1}{2}} \quad (2)$$

where:

- w = rate of effusion = rate of mass loss (grams/sec)
a = area of effusion hole = net vaporization area (cm²),

and the other symbols are the same as in equation 1.

This is the basic relation used in the Knudsen method, and it can readily be seen that the theoretical basis for it is quite sound. When the experiment can be conducted within reasonable temperatures, on a simple condensed phase which is in equilibrium with a known monomolecular vapor, a simple measurement of weight loss as a function of time can yield quite good results for the vapor pressure at a given temperature.

In practical application, especially at high temperatures, numerous compromises are frequently made whose effects may be known and corrected. But in some cases unaccountable errors may be introduced. The source of some of these errors will be illustrated in the discussion of the specific analysis techniques which are commonly used. The well known container problem which is crucial in high temperature applications will not be discussed, but the next measurement technique will show how it can be completely avoided.

The Langmuir Technique

In the Langmuir method, no container is used and the evaporation is carried out from the unconfined surface of the sample.

The treatment of this situation begins with the fact that the number of molecules leaving the surface of any enclosed, condensed phase at equilibrium equals the number recondensing. If it is assumed that every molecule which strikes this surface sticks, then the

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number condensing per unit area is the same $\frac{dn}{dt}$ previously presented by equation 1. And at equilibrium this $\frac{dn}{dt}$ must also equal the rate of evaporation.

In practice there is the possibility that not all of the molecules which strike the surface will find favorable sites for retention by the surface. For this reason a condensation coefficient α is defined as the ratio of the number of molecules condensing on a surface to the total number which strike it. Equation 1 must then be modified to read:

$$\frac{dn}{dt} = \alpha P (2 \pi MRT)^{-\frac{1}{2}}, \text{ (rate of condensation)} \quad (3)$$

all the symbols have been defined above. At equilibrium this expression must also describe the rate of evaporation. This basic equation is then utilized in the Langmuir method by modifying it to yield a vapor pressure at temperature from a measured weight loss rate. The modified version is:

$$P = \frac{w}{a \alpha} \left[\frac{2 \pi RT}{M} \right]^{\frac{1}{2}} \quad \text{(equilibrium evaporation rate assumed)} \quad (4)$$

All the symbols have been previously defined but it must be noted that since there is no orifice, \underline{a} is now the total sample surface area and not an orifice area.

There are however some disturbing inconsistencies about the coefficient α . It is difficult to see what a condensation coefficient described and defined in the above manner could possibly have to do with evaporation under the conditions of the typical Langmuir experiment on refractory materials. Here there are great pains taken to keep ambient pressures low enough to insure that a particle which leaves the surface will condense elsewhere and never return to the evaporating surface. The α deduced for equations 3 and 4 is clearly α condensation assumed equal to α vaporization. Yet the literature is full of confusing and misleading definitions of α . It has commonly been called a condensation (or sticking) coefficient, and evaporation (or vaporization) coefficient, and an accommodation coefficient. These quantities can all be validly defined but they all differ from each other. All of these names for α appear, frequently with the implication that this is the quantity one would use for the α in equations 3 and 4. Perhaps it would help to use α_c , α_v , and α_a for the respective quantities. The α in equations 3 and 4 is probably most nearly related to α_v . In practice an additional definition has been used and should probably be adopted as α_L :

$$\alpha_L = \frac{\text{vapor pressure determined by Langmuir technique}}{\text{true equilibrium vapor pressure}}$$

It is rather obvious that α_v and α_L especially are ill defined because they are correction factors used to accommodate rates of various surface phenomena to the kinetically determined collision number, α_c . The α 's usually discussed in the literature pertaining to vapor pressure work are actually either α_L or some ratio of α_c and α_v . These α 's could vary widely with experimental conditions. Still another α (perhaps α_c') is of interest where the vapor is being condensed on cold plates during an experiment. The α_a mentioned above relates gross energy transfer per collision with a wall.

It will become obvious that many experiments being conducted often really lie somewhere between the Knudsen and the Langmuir methods. This is especially true of much work claiming to use the Knudsen technique. If the various α 's involved are equal to 1, then useful information can be obtained. If one or more of the pertinent α 's are not at least close to one, the data is certainly going to be ambiguous. The variation of the α 's with temperature and pressure is not understood. Because of these "coefficient" problems and other problems inherent to these techniques it is not surprising that absolute vapor pressure data from various experimenters can vary over an order of magnitude. Fortunately the slopes of the vapor pressure vs $1/T$ curves are more reproducible among various experimenters and therefore the derived heats of vaporization are reasonably reproducible in spite of the great spread in the absolute pressure data. In this same vein a properly conducted Langmuir experiment can be relied upon to yield reliable rates of vaporization for materials heated in a vacuum. This in itself is a valuable piece of design data which does not require an understanding of the vaporization mechanisms.

Methods for Vapor Analysis

As has already been mentioned above that the simplest method for obtaining the rate of vaporization, and consequently the vapor pressure, is a measurement of the rate of weight loss during a reasonable time period at temperature. By this method a measurement at a single temperature could take many hours, in the case of some refractories of interest, and little if any information is obtained on the nature of the vapor. If the vapor composition is not that which is assumed, then only some unknown multiple of the true vapor pressure can be calculated. The weight loss method can be used with either the Knudsen or the Langmuir techniques. Normally the former is considered first with materials of relatively high vapor pressures and where an appropriate container can be found. Where the rates of weight loss are low at workable temperatures, or the container problem exists, the Langmuir method may be considered, to avoid the container problem and to utilize the higher rates of vaporization attendant with the higher temperatures and larger vaporizing surface areas available in this case. The αL must of course be known or estimable for a valid experiment.

To improve the sensitivity of either technique, the oldest device used is a collimator hole which forms a molecular beam from a calculable fraction of the total vapor effusing from the sample. This beam is then condensed on a collector plate for subsequent analysis. The formula used with a Knudsen cell and collimator has been derived from the kinetic theory of gases with the assumption that the molecules leaving any surface have a cosine distribution and are in the molecular flow regime:

$$f = \frac{D^2}{D^2 + 4L^2} \quad (5)$$

where f is the fraction of the molecules leaving a small (point) ideal orifice, located in a plane parallel to a collimator and on a line joining the centers of the two holes, which pass through the collimator hole for collection or detection. D is the collimator diameter and L is the distance between the orifice and the collimator. The amount of material condensed on the plate is then determined by some method of quantitative analysis such as direct weighing, chemical or instrumental analysis, or possibly by the highly sensitive methods made available by radioactive isotopes and activation analysis. The vapor pressure is calculated from the number of moles of vapor that have been collected through the collimator by multiplying equation 2 by $1/f$. The αc for simple vapors on the cold metal

plate is assumed to be 1. Notice that species information is obtainable in the methods described so far.

The collimated beam may also be analyzed by other methods to yield both qualitative and quantitative information on the vapor species composition, partial pressure, and rate of vaporization. The most widely used methods for more direct identification are momentum and velocity detection, and both absorption and mass spectroscopy. If separate experiments are set up, emission, absorption, mass, radio frequency, and microwave spectroscopy can yield much direct information on vapor species. Electron diffraction is becoming an extremely powerful tool for elucidating gas phase molecular structure at high temperature. The field emission microscope has been proposed for vapor studies but since gas sorption is involved, little direct information on equilibrium gas phase molecules can be expected.

Devices which may be termed momentum detectors are among the oldest means for directly obtaining a vapor pressure and/or, indirectly, an average molecular weight. If a Knudsen cell, with the orifice in the top, is suspended from a balance; then at any given temperature the force on the balance is the sum of the weight of the crucible plus contents, plus the change of momentum due to the effusing beam. The weight of the tared crucible and contents can be obtained at any time by quenching the furnace temperature. By using equation 1 the rate of mass loss yields only the product $P(M)^{-\frac{1}{2}}$. Combining this with the beam momentum, obtained by difference, will yield an average molecular weight.

A method closely resembling the above is the torsion effusion experiment in which the sample is contained in a cylindrical or box shaped container and suspended in a furnace by means of a fine wire. Two eccentric holes are drilled into the container on the extremities by a diagonal line perpendicular to the support wire. The vapor effusing through the holes exerts a twisting moment on the cell and support wire, causing it to rotate through an angle against the torsional force of the wire. By measuring the angular deflection, the area of the holes and their respective moment arms, and knowing the torsional constant of the wire, the momentum carried by the beam can be obtained. The cell can also be hung from a balance to obtain continuous mass loss data.

The advantages of the momentum detectors are that relatively high background pressures can be tolerated, vapor composition need not be known to obtain a total vapor pressure, an average molecular weight can be obtained if mass loss rate data is also measured, and total pressure data can be obtained rapidly without periodic removal of the sample for weighing. Disadvantages include inability to obtain detailed information on complex vapor species, induction heating techniques cannot be employed unless steps are taken to prevent the magnetic force fields from giving erroneous weights or deflections, and extraneous oscillations are usually present. Another method yielding beam momentum involves measuring the deflection imparted to a loaded plate of known area upon which the vapor beam impinges. This method has the same advantages of momentum detectors but can circumvent some of the disadvantages including the last two mentioned.

The collimated beam can be passed through a mechanically rotated velocity selector to yield an intensity distribution as a function of selector velocity. This intensity distribution is a function of the velocity which in turn is a function of the gas molecular weight. For complex vapors at high temperatures the resolving power is usually poor and the results usually ambiguous.

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Methods utilizing magnetic and electrical field interactions with the vapor particles have severe limitations and appear to have little advantage over mass spectroscopy; therefore, no further discussion will be given.

Emission and absorption spectroscopy have little application in the analysis of beams as such, but are valuable where separate experiments can be set up. Absorption spectroscopy appears to have some promise for vapor beam analysis if used in conjunction with the matrix isolation technique. An apparatus of this kind, built by General Electric will be discussed later.

One of the best techniques for obtaining both detailed species composition information together with partial pressure data is the mass spectrometer. Recently two excellent discussions on this kind of study have been given by Porter and Inghram. Inghram's recent treatment gives an excellent discussion of the limitations and techniques involved in the mass spectrometric study of vaporizing samples. A controversy has developed as to whether the Bendix time of flight mass spectrometer or the Nuclide Analysis Associates instrument is the more suitable for vapor pressure determinations. The Nuclide Analysis Associates model is based on a design developed by Inghram utilizing large radius magnetic deflection to separate the ions. The operating principles are basically the same as those magnetic types used in many laboratories over the years. Much improved resolution has been achieved primarily through the use of a 12-inch radius magnetic field instead of the usual 6-inch radius.

The time of flight instrument utilizes a pulsed ionization source in conjunction with properly pulsed extraction and accelerating grids together with a less familiar ion separation principle. The ionized species are all accelerated down a field-free drift tube with the same energy, and arrive at a detector in a time that is proportional to their (molecular weights)^{1/2}. This process is repeated every 100 micro-seconds and gas phase processes which are changing rapidly with time can be detected. The resolution is such that adjacent peaks at about mass 200 are just separated. Usable mass range is in the thousands of atomic mass units with less resolution. Sensitivity is in the parts/million range. The electronics of the time of flight instrument have proven to be somewhat unstable and a source of continuous calibration has been needed to obtain quantitative data. There are some who believe that, if properly used, the time of flight spectrometer can be employed to perform any of the measurements done by Inghram with comparable accuracy.

At this writing no one has been able to obtain experimental results from this instrument to compare in utility with those obtained by Inghram with his equipment. For example Inghram has reported appearance potential measurements down to 1 to 2 ev; the best that has been done with a modified time of flight is ~5 ev. The time of flight has not been used to identify an unknown compound by studying the isotopic distribution of its constituent atoms. Inghram reports that his instrument has sufficient resolution for this work.

It appears safe to say that the Bendix is certainly adequate for the study of the simpler vapor systems where there are perhaps a few relatively stable species with reasonably different molecular weights below 200 a.m.u. Partial pressure of 10⁻⁸ atm appear to be detectable.

The main advantage of the time of flight appears to be in the fact that the basic machine costs about $\frac{1}{3}$ that of the commercially available version of the Inghram machine and takes up much less space. Further, the time of flight's rapid analysis capability (10,000 individual spectra/sec. and $\frac{1}{3}$ micro second sampling time) allows its use for the study of

the kinetics of rapid gas reactions. The Inghram machine does not lend itself as well to this type of study where concentrations of many species must be followed simultaneously.

It appears that no mass spectrometer utilizing electron impact ionization is capable of directly detecting molecular species with very low dissociation energies. Except for some of Inghram's work, there have been almost no studies done with ionization electron energies below about 5 ev with his type of machine. Dr. White, at Ohio State University, has recently made the time of flight machine perform with this electron energy during his studies on some of the rare earth oxides. But even 1-2 ev appears to be enough energy to fragmentize some molecules and it appears that one must use some other ionization method or abandon mass spectrometry entirely for this type of molecule. Matrix isolation and electron diffraction appear to be good bets in this area.

In summary, it can be said that vapor pressures can be obtained only within a factor of 3 to 5 or more due to the problems associated with the detection and analysis techniques mentioned above. Derived heats of vaporization can be obtained with greater accuracy since the slopes of $\ln P$ vs $1/T$ are generally more reproducible than the absolute vapor pressures. Some of the serious problems and limitations responsible for this lack of reproducibility have been mentioned and it is apparent that a great amount of thought, care, and fortitude are required in these measurements.

In addition to the above, there appears to be many questions that remain to be answered in the fundamental assumptions underlying the Knudsen and Langmuir techniques themselves. Evidence is piling up against universal applicability of basic assumptions that are usually made in these types of studies. The question of α briefly discussed above is only one of these. The classically derived "Clausing" or transmission factors have been shown to have fundamental errors in their derivations. Indeed many questions concerning the validity of the cosine law itself have appeared. In the use of the Knudsen technique, a standard means of obtaining information on the vaporization coefficient is to repeat the experiment with successively smaller orifices and extrapolate the data to zero orifice conditions. In some cases this technique has yielded a pseudo-equilibrium value for vapor pressure which differs from the known equilibrium vapor pressure by orders of magnitude and yet is quite reproducible.

Work must be done on the techniques themselves before an understanding of many anomalies, including those mentioned above, will be gained. Some idea of the severe departures from the ideal conditions previously described will be indicated in the following discussions of contractor equipment.

Description of Some Current Equipment

The following description of equipment being used by Air Force contractors illustrates the kind of compromises usually made in practice. In the ensuing discussion figures describing apparatus being used by the AVCO Corporation and the General Electric Company will be discussed and departures from the ideal experimental conditions should be apparent.

Figure 1 shows the details of two Knudsen cells being used extensively by the AVCO Corp. The cell shown in figure 1a is used where a smaller orifice size than is afforded by that in figure 1b is needed or desirable. It should be noted that the circular orifice of either cell is rather large but still within the Knudsen condition of being smaller in diameter than the mean free path of the vapor molecules. Since the very low vapor pressures of highly refractory materials are being measured the large orifice size represents a compromise made in order to be able to obtain a measurable rate of effusion. The cell is

constructed in two halves to facilitate fabrication of these difficult to machine refractory materials. The possible consequences of this expedient is the fact that an alternate source of effusing molecules must be dealt with. This is, however, minimized by keeping close tolerances, by the use of liners, and the presence of water cooled baffles and collimators which condense out most of the vapor that originates anywhere else in the heated area except from the cell orifice. It should be noted that these cells are more in the nature of cylindrical channels rather than true Knudsen cells. That is, it is not really possible to even approach an equilibrium pressure if the equilibrium pressure is such that it will be significantly greater than the ambient pressure outside of the cell. The two cell halves are heated independently to avoid temperature gradients. As a result only processes which can be considered as having a vaporization coefficient of unity can be studied and a Clausing correction factor is appropriate here. In practice the factor would only amount to a 2 to 3 percent correction in the vapor pressures and is therefore ignored. A Clausing correction for the sloping portion of the channel does not exist though work on this problem is in progress at several universities. It can be seen that the conditions produced by vaporizing from these cells lie somewhere between non-ideal Knudsen conditions and the Langmuir experiment.

Figure 2 is a schematic diagram of the "Simple Effusion Apparatus" utilized by the AVCO Corp. in one phase of their studies. One of the previously described effusion cells is heated by electron bombardment. Temperature gradients are minimized by heating the upper and lower halves separately and by surrounding the whole assembly with a radiation shield. The temperature is measured by sighting on a black-body hole, drilled into the bottom of the cell, with a calibrated optical pyrometer. Using this arrangement it is possible to hold the cell temperature to within $\pm 5^{\circ}\text{C}$. The water cooled baffles condense most of the vapor molecules which leave the cell orifice at low angles as well as vapors which may originate at other points within the radiation shields such as the support members, electron source filaments, cell surface, or the joint between the cell halves. The targets or condensation plates for the vapor are stored within a cavity built into a liquid nitrogen cooled cold finger for efficient condensation of the vapor. The target and collimator are arranged so that only the vapor in approximately a 5-degree solid angle strikes the collector plate. The entire apparatus is pumped to pressures sufficiently low so that the target surface is within a mean free path of the cell orifice; therefore, once a molecule leaves the orifice it cannot reach the target if it has undergone a collision with another gas molecule or a surface other than the target. The cold finger aids the pumpdown by condensing almost any residual background gases. The magnetically operated shutter permits accurate (to $\pm \frac{1}{2}$ sec) timing of the period during which vapor is collected. It also permits a background determination by shutting off the vapor beam. A stack of 12 targets, a built-in magnetically operated target ejector, and a target storage area permit determinations to be made at a number of different temperatures without opening the apparatus. Each target is analyzed for the amount of condensate by direct weighing or, in the case of samples with extremely low vapor pressures, appropriate isotopes may be vaporized and radioactive counting methods can be used. In some cases a radioactive isotope is available for direct evaporation and counting, in other cases the condensate can be sent out for activation in a nuclear reactor and subsequently counted. All three methods have been used.

Figure 3 shows a schematic of the "Effusion-Mass Spectrometric" equipment. The method of producing the vapor beam is similar to that in figure 2. Here instead of condensing out the vapor within a mean free path of the orifice, the vapor beam passes through a collimator into the ionization region of a time-of-flight mass spectrometer. A portion of the molecules in the vapor beam is ionized by impacting with a high energy beam of electrons which passes through the vapor beam at right angles. The unionized portion of the

vapor beam continues in a straight line and is condensed on the liquid nitrogen cold finger whose function is to keep the background pressure in the instrument as low as possible. The ionized particles in the beam are extracted at right angles to both the electron and vapor beams and accelerated down a field free flight tube by means of appropriately pulsing the grids shown on the figure. The vapor beam must pass through the grids shown on the radiation shields before entering the mass spectrometer. These grids are impressed with opposite polarities in order to prevent most of the stray electrons from the cell heating source, and also any positive ions formed in the region around the effusion cell by any process, from entering the mass spectrometer. As a further precaution, a magnetically controlled shutter can be used to shut-off the vapor beam for the purpose of obtaining a background correction measurement at any time as in the simple effusion apparatus. In this program the apparatus is used primarily to obtain information about the nature of the species existing in the vapor. The simple effusion and the continuously monitored effusion methods are used to obtain absolute pressure data. However, this mass spectrometric equipment has been shown to yield quantitative vapor pressure and heat of vaporization data with large uncertainty in the former case, less uncertainty in the latter. As mentioned previously, the slope of vapor pressure vs $1/T$ is more reproducible than are absolute vapor pressures. To circumvent the problem of the unpredictable gain fluctuations produced in the electronics of the instrument, all peaks are continuously compared to a xenon or argon background peak whose absolute value is known because it is produced by a quantitatively controlled leak of the gas into the system.

Another calibration method is to continuously compare the unknown peak to one produced by an inert material, whose vapor pressure vs T is known, also present in the cell. The sensitivity of the "as received" instrument has been improved by a modification of the ionization region to permit placement of the cell closer to the ionization region and by widening the collimating slits of both the electron beam and the vapor beam. The sensitivity was thereby increased by a factor of 10 to 100 with some loss of resolution. The instrument could now detect silver isotopes at equilibrium pressures of about 10^{-7} to 10^{-8} atm and resolve adjacent mass peaks at about mass 200. High speed differential pumping has been added to the effusion cell and ionization regions in order to reduce background, pump-down time, and to permit the study of species arising from the interaction of materials with reactive gases being bled into the effusion cell. In practice, it has not been possible to obtain useful results with electron energies below about 12 ev in spite of the fact that the electron energy is continuously variable between 0 and 100 ev. Accurate appearance potentials down to low electron energy have not been seriously attempted for this reason.

Figure 4 shows a schematic diagram of the apparatus used for monitoring continuously the weight of a vaporizing sample and the force exerted by the vapor particles effusing from a cell orifice. The basic method is well known. The advantage of this device over its previous counterparts is the fact that data taking has been made highly automatic. The sample is hung from one arm of a highly sensitive analytical balance and radiantly heated by means of a resistance furnace. A magnet coaxial with a stationary solenoid is attached to the arm of the balance. The force exerted by the sample is determined by calibrating the force between the solenoid and the magnet in terms of the current flow in the solenoid. Thus the balance never leaves the null position and only the solenoid current is measured by the voltage drop it produces across a series resistor. The voltage is read by a suitable recording potentiometer thus producing a weight vs time trace. The solenoid current is controlled to hold the null position by virtue of the fact that any movement of the balance arm due to changing forces exerted by the evaporating sample is sensed by coils of a linear variable differential transformer. The displacement of its rigidly mounted core from the null position produces an error voltage and a phase change in the transformer secondaries

which are respectively related to the magnitude and direction of the displacement. As a result of this phase and voltage signal, a servo drives a potentiometer to vary the amount of current flowing through the solenoid windings. Thus, much of the tedious changing of weights and data recording are largely eliminated.

Figure 5 shows a schematic diagram of the null point torsion effusion apparatus developed under this program. Again the basic principles of operation are well known and the most attractive feature of the equipment is its automation. However, in this case a few more fundamental benefits have been obtained. In the past versions of this type of equipment the experimenter was plagued by frequent calibrations because of changes in the torsional constant of the wire from hysteresis, thermal cycling, and simple changes in the torsional constant with temperature because the wire extended into the furnace hot zone. Also the wire material and/or diameter had to be changed frequently in order to stay within a given angular displacement and a desired accuracy for various pressure ranges. Generally the pressures to be measured can vary over 2 or 3 orders of magnitude, so a wire must be selected with a torsional constant that will yield a measurable deflection at the lowest pressure yet remain on scale for the highest pressures measured. Only a fraction of the total possible rotation of the cell is normally measurable with most equipment. In the equipment under discussion these difficulties are virtually eliminated. The usual type of cell is attached to a rather long rigid bar which in turn is suspended from a fine wire which possesses as low a torsional constant as possible consistent with the strength necessary to carry the weight of the assembly. This wire is then attached to a micrometer head to facilitate positioning of the zero point. In this apparatus the wire is located at room temperature and acts only as a bearing. Its torsional constant sets the lower limit of sensitivity of the equipment. The effusion-torsion force is counterbalanced by the force produced between the solenoid, rigidly mounted to the suspended bar and effusion cell, and two fixed magnets. The latter force is proportional only to the measured current passing through the solenoid. A mirror, which is rigidly mounted to the suspension bar, reflects a beam of light coming through the sight to two photocells. As the mirror rotates it increases the amount of light falling on one of the photocells. This causes a motor to turn a potentiometer which alters the current flow in the solenoid in a manner which returns the suspension to the null point. The solenoid current can be monitored by a recorder to record vapor pressure vs time or temperature. The system is calibrated by utilizing materials of known vapor pressure. An added advantage of the magnets and solenoid is that they also act as a damping device to eliminate many of the random oscillations present in the usual torsion-effusion system.

Figure 6 is a schematic diagram of equipment utilized by the General Electric Company for Langmuir evaporation studies at extremely high temperatures. Vaporization data was obtained on some of the most refractory materials known at temperatures generally higher than attained in any previous measurement. The temperatures and materials of interest precluded the use of any known container material and therefore dictated the use of the Langmuir method. The measurements made are necessarily very time consuming and most basic in nature. The apparatus consists mainly of a water cooled quartz heating chamber. A ring shaped specimen is placed on the support wires and quickly brought to temperature by means of 25 KW induction heater. The complications entailed by the use of a radiation shield are avoided because of the large amount of power available. After the sample has vaporized at temperature for a reasonable length of time the heater is shut off and the cooled specimen is removed from the apparatus and weighed. The vapor pressure is then calculated from the Langmuir equation by simply dividing the weight loss by the time at temperature and assuming that $\alpha L = 1$. The method must be considered crude because of its simple but tedious nature. Only simple weight losses, physical dimensions, and time periods are measured and the sample has to be removed, weighed,

and reinstalled in the apparatus for each data point. This procedure thus entails considerable care and requires a large amount of pump-down time. Also for the materials of interest the sample has to remain at temperature for appreciable time periods in order to obtain reasonable weight losses especially at the lower temperature ranges. Temperatures are measured by sighting an optical pyrometer on 4 black-body holes drilled circumferentially around the ring and correcting for window transmission. The effective temperature for any run is taken as the arithmetic average of all measurements during the run. Gradients of $\pm 20^{\circ}\text{K}$ were typically encountered. It is readily seen that this method is capable of yielding the rate of weight loss in vacuum for a material as a minimum. Further, if $\alpha L = 1$ and the vapor species are known, the vapor pressure and other thermodynamic and kinetic data may be obtained. The vapor species generally are not obtainable by this method. This information was obtained by other means. The temperature ranges investigated (to 3400°K) are among the highest that have been attained in this type of work.

Figure 7 is a schematic diagram of the matrix isolation apparatus constructed by G.E. which is used to determine the identity and structure of high temperature vapor species. The species are allowed to effuse from a Knudsen cell and are condensed simultaneously with a stream of inert gas, introduced by the matrix line, on a liquid helium cooled window. The attempt here is to "freeze in" the high temperature molecule in its existing configuration for later study by infrared absorption techniques. In general a large number of molecules are needed for infrared studies and several hundred times this amount of inert gas is needed to form an effective matrix. The Knudsen cell is heated inductively and after a sufficient density of the matrix-molecule deposit has been built up, the gas flows are interrupted and the window is rotated parallel to the other two windows shown. The infrared absorption spectrum of the deposit is then obtained and examined. The method though promising is as yet not too well established and is plagued with numerous experimental difficulties. Aside from the problems associated with the use of a Knudsen cell itself there is the considerable difficulty and expense of working with liquid helium. The effusion cell must be extremely well shielded. There is some difficulty in the interpretation of the resulting data since the matrix has been found to interact with the trapped molecules and thereby shift its fundamental absorption frequencies. The shifts have been explained qualitatively in a few cases but much more work remains to be done. For example there is some evidence that migration and subsequent reaction in the matrix even at liquid helium temperature, may alter the nature of the original species formed in the high temperature vapor. The technique has promise in that a measurable number of molecules can be obtained at temperatures significantly lower than normally necessary in other methods and that the spectra obtained are generally less complex. The lower temperatures also make the container problems less acute. This method should prove to be a valuable supplement to the information currently being obtained by means of optical and microwave spectroscopy and also electron diffraction.

As indicated by the above description of the methods and currently used equipment, it is evident that much work remains to be done even before an understanding of many of the most basic elements of high temperature vapor pressure measurements will be obtained. In particular much ingenuity will be required in the future in devising experiments which will shed light on the nature of the various α 's of interest in vaporization studies, applicability of the cosine law, influence of orifice size and shape, sorption effects on equilibrium attainment at low vapor pressures in cells, electron impact cross-sections, photo and thermal ionization effects and pseudo-equilibrium situations. Methods for improving the accuracy and the ease of data taking should be developed. And last but not least, entirely new methods for the determination of vapor pressures and vapor species should be sought for, which do not have some of the disadvantages of methods presently in use.

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The following reference material contains excellent bibliographies and direct information on vapor pressure measurement as discussed in this paper.

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4. WADD TR 60-646, Part I, Contract AF 33(616)-6841
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6. Bulletin MS-6, Bendix Corporation, Cincinnati 8, Ohio.
7. Argonne National Laboratory Report, ANL-6156, 1960.

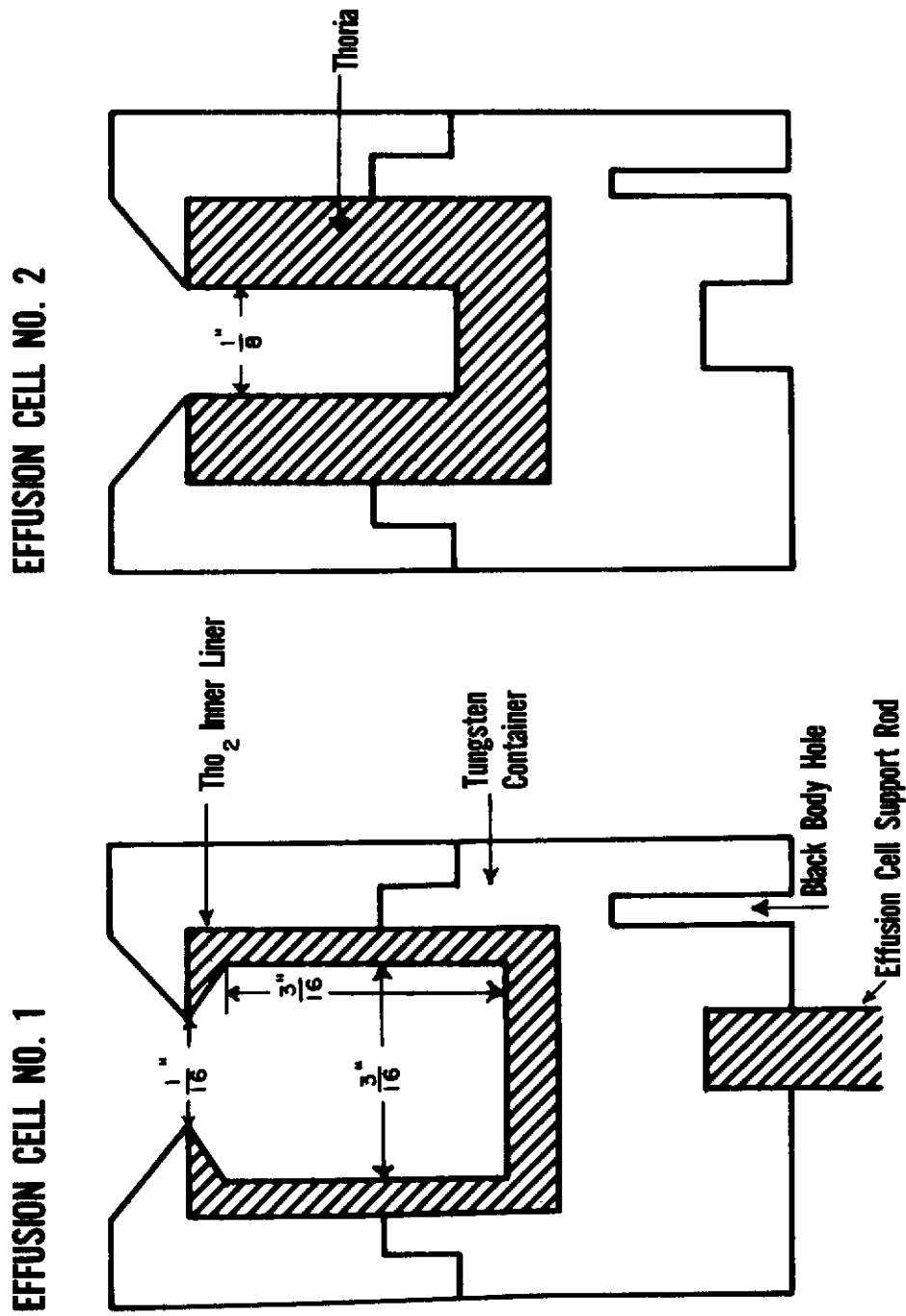


Figure 1.

SCHEMATIC DIAGRAM OF THE SIMPLE EFFUSION APPARATUS

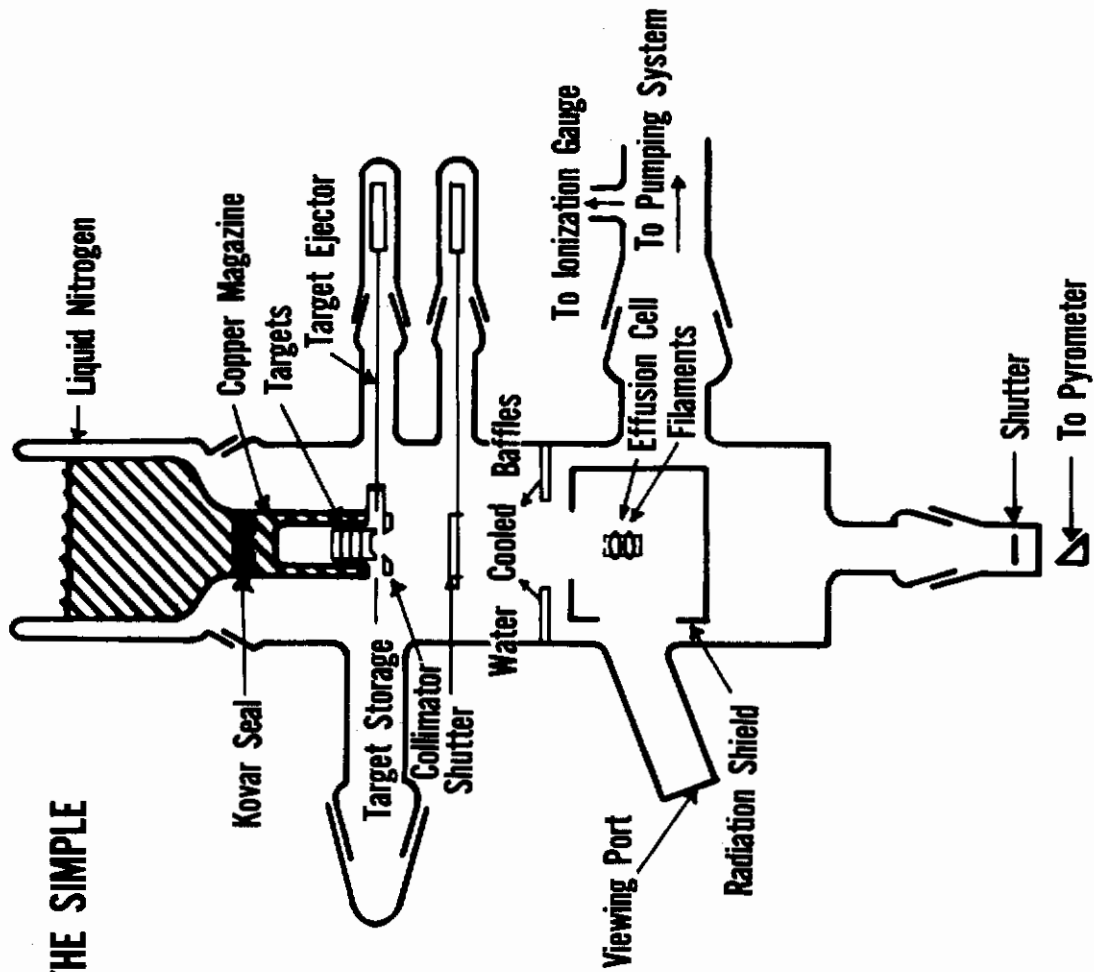


Figure 2.

THE EFFUSION - MASS SPECTROMETRIC SET-UP

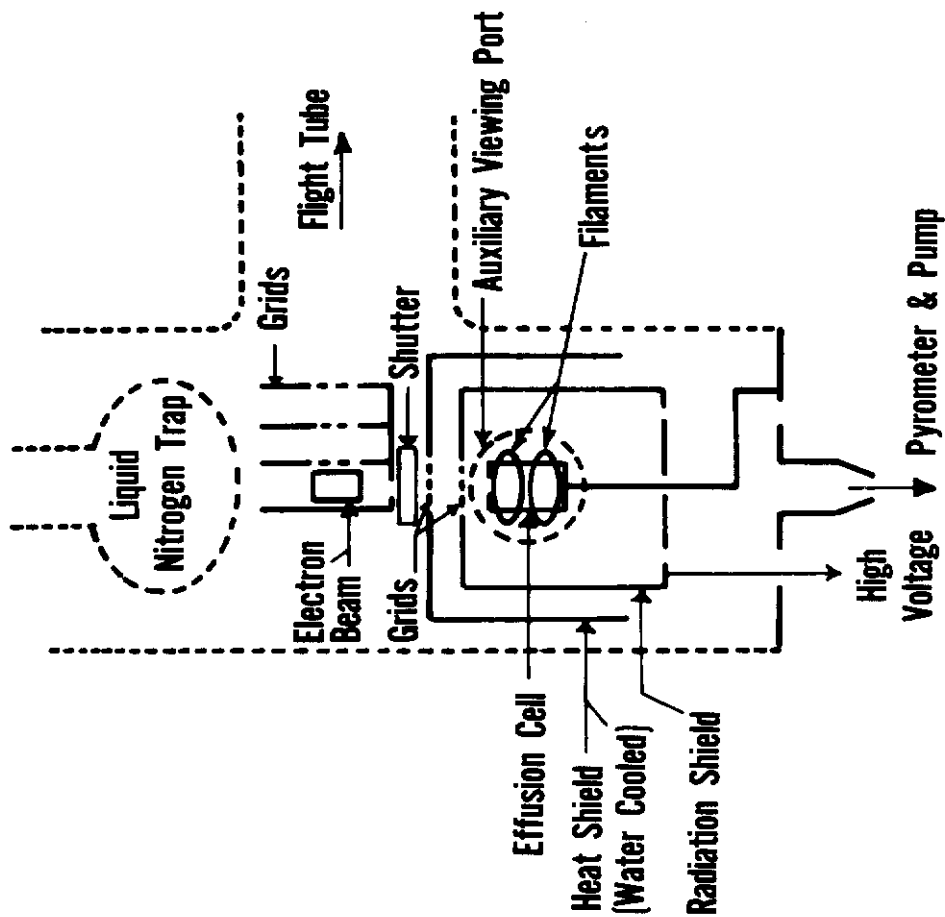


Figure 3.

CONTINUOUSLY MONITORED WEIGHING DEVICE

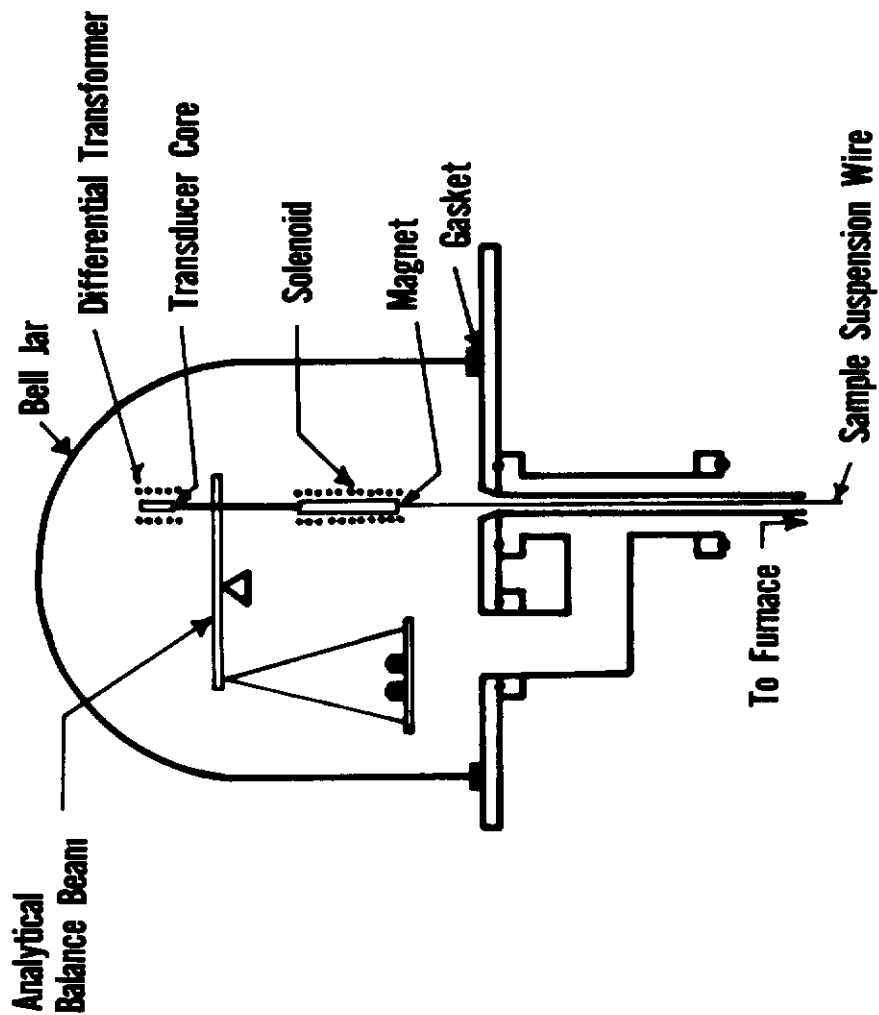


Figure 4.

NULL-POINT TORSION EFFUSION APPARATUS

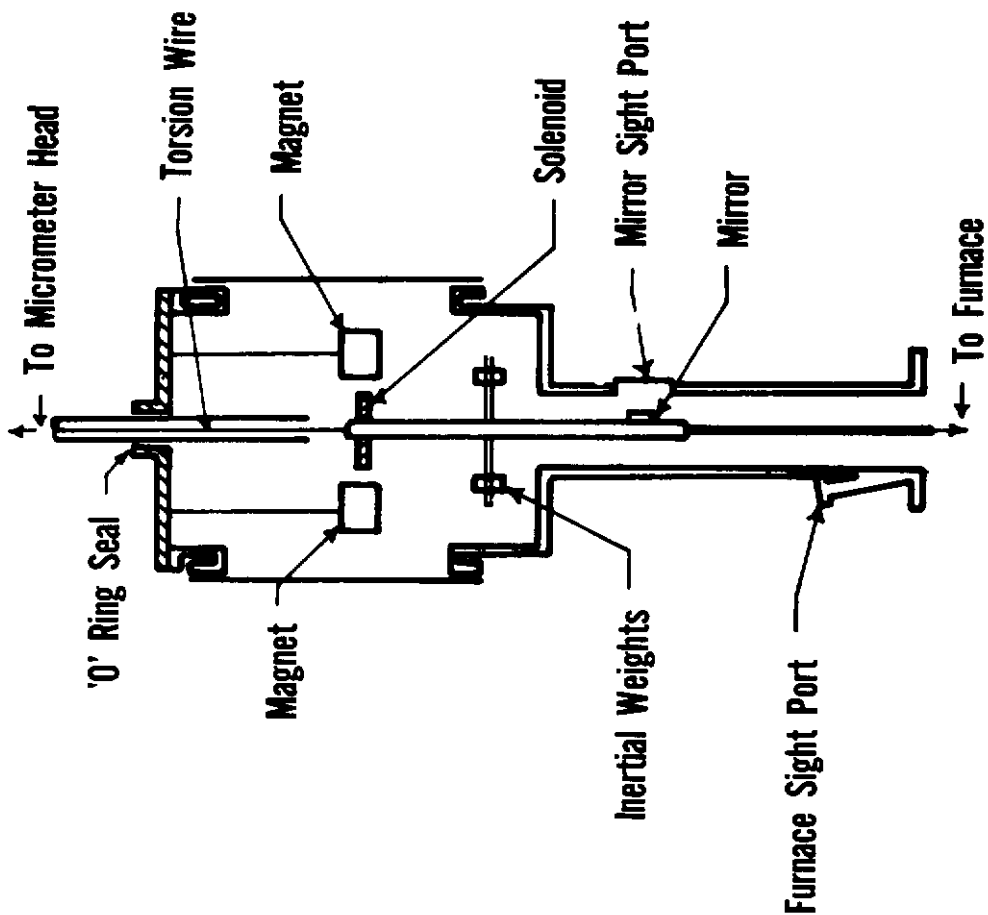


Figure 5.

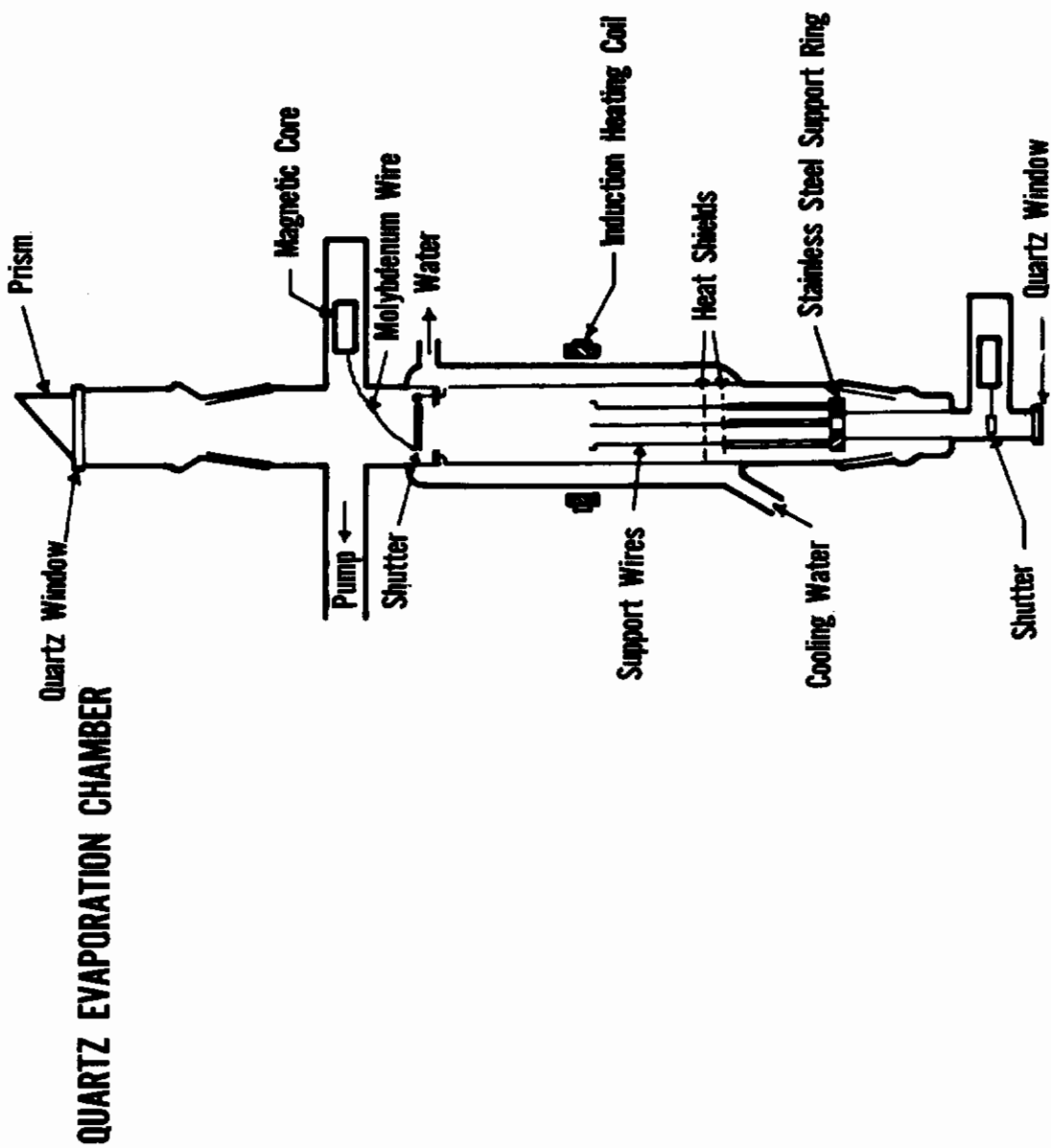


Figure 6.

EQUIPMENT FOR MATRIX ISOLATION STUDIES

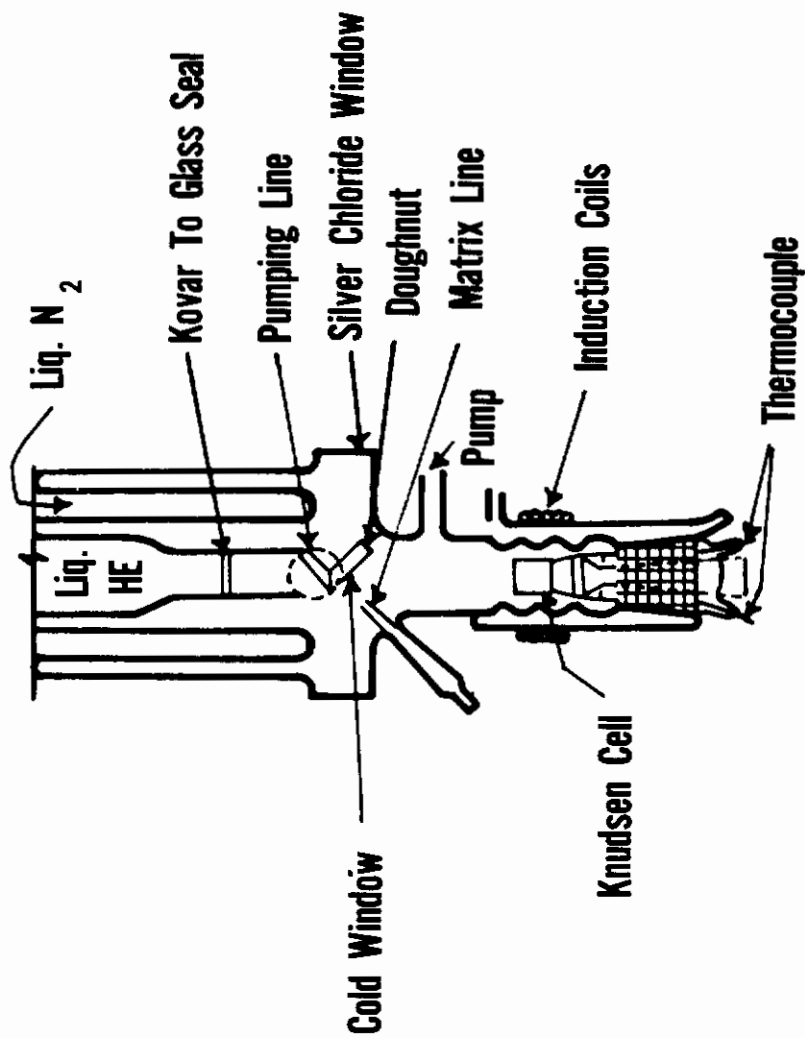


Figure 7.