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# Thermodynamic Measurements Using the Knudsen Cell Technique

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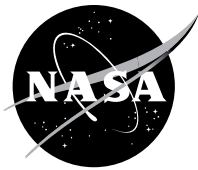
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# Thermodynamic Measurements Using the Knudsen Cell Technique

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## Abstract

The Knudsen cell technique has been used for over a century and is a valuable tool for measurement of vapor pressures and thermodynamic properties. It is based on a small enclosure (~1 cm long by 1 cm diameter) in which a condensed phase/vapor equilibria can be established. A small (<1 mm) orifice on the cell allows sampling of the vapor via a variety of techniques including weight loss, torsion effusion, target collection, and mass spectrometry. Many excellent measurements based on these methods have been reported. However in order to obtain reliable measurements, a variety of factors must be considered. They include proper cell material selection, accurate and uniform temperature control and measurement, and proper sampling of the vapor. Each of these factors are discussed in detail in this chapter. Typically these studies are conducted at high temperatures and it is a challenge to select an inert container material. Recommended materials are discussed and in some cases the container may be used as part of the system under study. Temperature control and measurement is perhaps the most important issue. In most systems, the furnace must be compact yet there can be no temperature gradient in the cell. Temperatures are measured with either a thermocouple or pyrometer and the relative advantages of each are discussed. Sampling method considerations depend on the particular technique. It is essential that all of the vapor or a representative portion of the vapor be sampled. The distribution of the effusate from a Knudsen cell is discussed and sampling positions discussed. Mass spectrometry is often used to study the effusing vapor and the relations between ion current and vapor pressure are discussed.

## 1.0 Introduction to Knudsen Cell Thermodynamic Measurements

The Knudsen cell methods is a classic technique for measuring vapor pressures. It was first discussed by M. Knudsen in his seminal paper on the vapor pressure of Hg in 1909 (Ref. 1). Most Knudsen cells are similar to Figure 1, measuring about 1 cm diameter and 1 cm high. Basically, a near equilibrium is established between the condensed phase and the gas. A small orifice of a well-defined geometry allows sampling of the vapor (effusate from the cell) to determine both the vapor composition and the vapor pressure. Since 1909, Knudsen cell methods have been used extensively to measure vapor pressures of a wide range of materials. The vapor pressure over a substance is a fundamental measurement which leads to basic information of the atomization energy of a condensed phase and solution parameters for multicomponent mixtures.

Design of a Knudsen cell involves many considerations: cell geometry (diameter, height), orifice geometry (diameter, length, knife edge vs. channel), and cell material. These issues have been discussed in various reviews (Refs. 2 and 3) and will not be covered in this report.

The vapor emerging from a Knudsen cell can be analyzed with a variety of methods. Most common are torsion effusion, thermogravimetry, target collection, and mass spectrometry. These have been reviewed in the widely referenced book compiled by Margrave (Ref. 2) and a similar volume compiled by Rapp (Ref. 3).

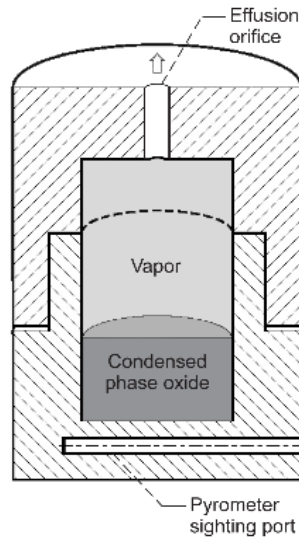


Figure 1.—Knudsen cell schematic.

## 1.1 Torsion Effusion

Torsion effusion is an elegant technique which directly measures the force exerted from a vaporizing substance (Refs. 2 and 3). The basic technique relates vapor pressure,  $P_T$ , to the force to twist a wire. A torsion cell is shown in Figure 2. This is given by:

$$P_T = \frac{2\tau\theta}{(A_1d_1f_1 + A_2d_2f_2)} \quad (1)$$

Here  $\tau$  is the torsion constant for the fiber;  $\theta$  is the angle of rotation,  $A_1$  and  $A_2$  are the areas of orifice 1 and 2 respectively,  $d_1$  and  $d_2$  are the distances of the orifices from the centerline, and  $f_1$  and  $f_2$  are the force factors for each cell.

## 1.2 Thermogravimetry

Thermogravimetry involves measuring cell and sample weight changes due to loss of vapor from the cell. This may be done by simply weighing the cell before/after heating for a period of time in a vacuum. Or it may be done more accurately by continuous weighing with a recording balance during heating. Such a thermogravimetric apparatus (TGA) is shown in Figure 3. The rate of weight loss,  $dm/dt$ , is simply related to vapor pressure,  $P$ , by the Hertz-Knudsen-Langmuir expression.

$$J = \frac{1}{A} \frac{dm}{dt} = \frac{WP}{\sqrt{2\pi MRT}} \quad (2)$$

Here  $J$  is the vapor flux [ $\text{kg}/\text{m}^2\text{-sec}$ ]  $A$  is the area of the orifice [ $\text{m}^2$ ],  $W$  is the transmission coefficient for the orifice [unitless],  $M$  is the molecular weight of the vaporizing species [ $\text{g}/\text{mol}$ ],  $R$  is the gas constant, and  $T$  is the absolute temperature [ $\text{K}$ ]. This technique can easily be used for a free surface (Langmuir) evaporation study as well, where in Equation (2) the  $A$  would be the exposed surface area [ $\text{m}^2$ ]. Such systems can also be combined with torsion effusion and the average molecular weight of the effusing species can be determined (Ref. 3).

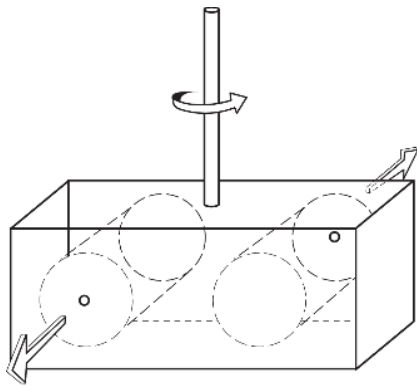


Figure 2.—Torsion effusion cell holder. Cell orifices on opposite sides cause a twist of the suspending fiber.

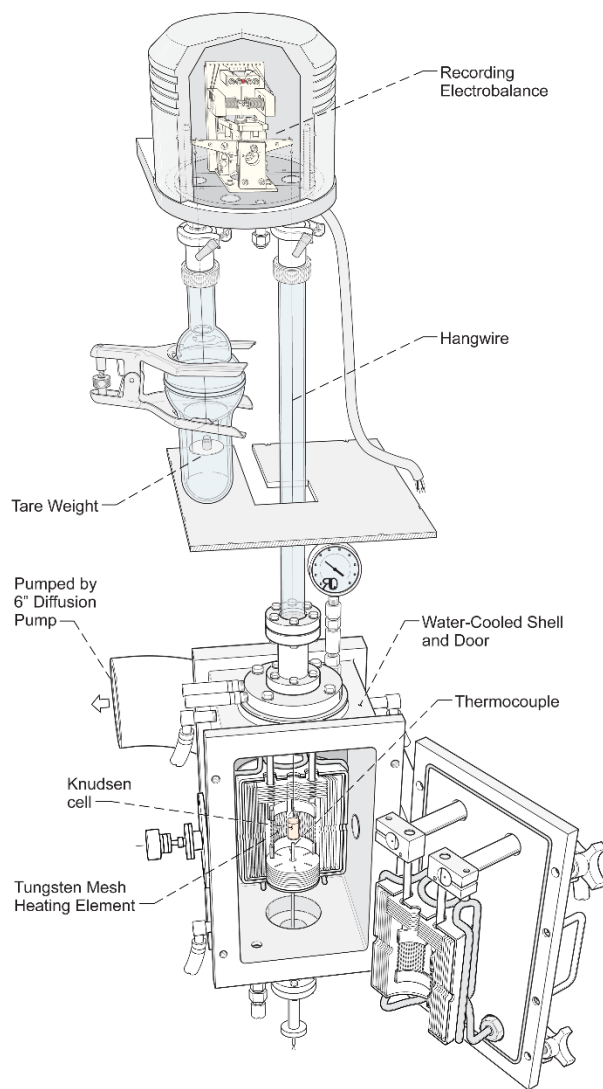


Figure 3.—Thermogravimetric system for Knudsen cell vaporization studies. A sensitive electrobalance records weight changes from the cell and sample due to vaporization.

### 1.3 Target Collection

Target collection is similar to thermogravimetry, however, in this case the effusate from a Knudsen cell is collected during an isothermal heat treatment, usually on a flat plate some distance from the orifice (Ref. 4). The collected deposit may then be analyzed with a variety of analytical techniques—inductively coupled plasma (ICP), electron microprobe, or even radioactive assay. The amount of deposit can be related to the rate of material effusing from the cell orifice by correcting for the fraction of total material collected and accounting for the attenuation of the beam as  $1/d^2$ , where  $d$  is the distance from the orifice to the target (Ref. 4).

### 1.4 Knudsen Effusion Mass Spectrometry (KEMS)

Perhaps the most commonly used method for measuring vapor pressures from a Knudsen cell is a Knudsen effusion mass spectrometer (KEMS) (Figure 4). Inghram and colleagues at the University of Chicago first coupled a mass spectrometer to a Knudsen cell (Ref. 5). Since then numerous investigators have used this technique to measure thermodynamic data on a variety of substances and these data are tabulated in the widely used compendia (Refs. 6 and 7). There are many excellent reviews on this method (Refs. 8 to 12). The key relationship in KEMS is that between vapor pressure,  $P_i$ , and ion intensity,  $I_i$ :

$$P_i = \frac{k I_i T}{\sigma_i(E) \gamma_i} \quad (3)$$

Here  $k$  is the instrument constant,  $T$  is the absolute temperature,  $\sigma_i(E)$  is the ionization cross section at the electron energy used, and  $\gamma_i$  is the multiplier gain.

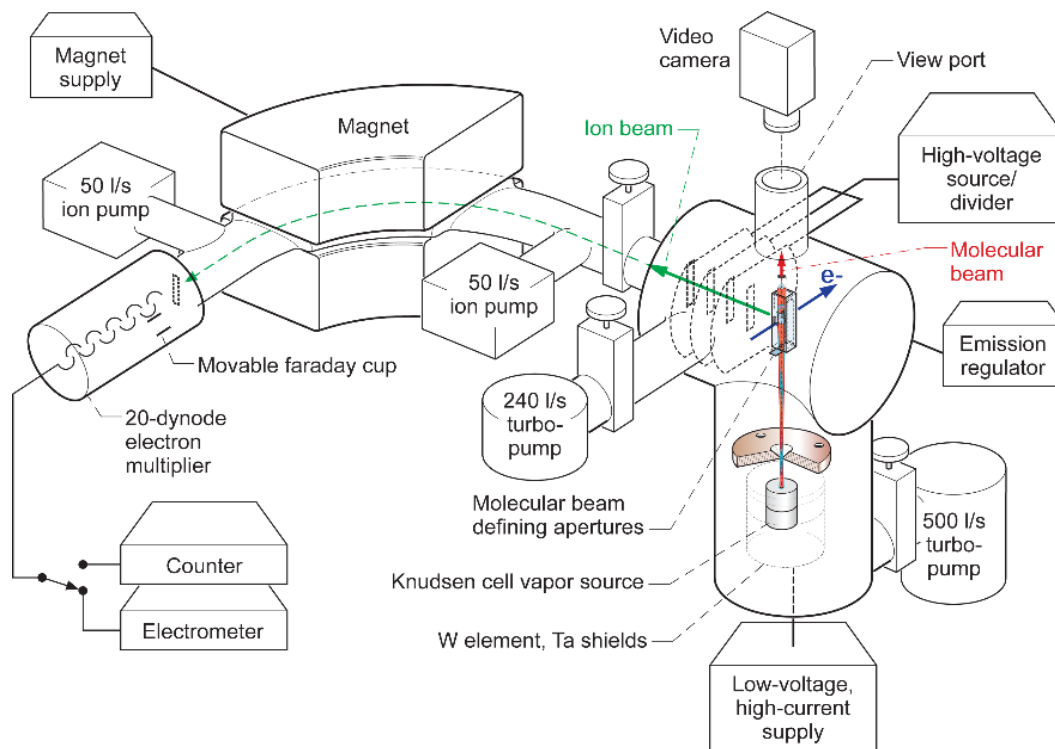


Figure 4.—Knudsen effusion mass spectrometer (KEMS) system. Note the four major sections: the Knudsen cell and furnace, ionizer, magnetic ion sorter, and detector. This is a modified Nuclide/MAAS/Patco HT-12-90 Instrument at NASA Glenn Research Center.



In this chapter we examine the critical experimental considerations for the effective use of Knudsen cells. Our emphasis is on KEMS, however for all the methods discussed, there are several important considerations for producing accurate thermodynamic data, such as: (1) selection of an adequate cell material, (2) well-controlled heating and temperature measurements, (3) proper sampling of the effusate/molecular beam, and (4) an attainment of equilibrium. Today, computer simulations of molecular beams assist with this. Finally, we conclude with some unique considerations for mass spectrometric analysis of effusates.

## 2.0 Vacuum System Considerations

Knudsen measurements must be done in a vacuum. This is primarily in order to meet the requirement for the Knudsen cell orifice that the mean free path be 10X the orifice diameter so that molecule/orifice wall collisions dominate over molecule/molecule collisions. The molecular beam emerging from the cell also should not be perturbed by a large background pressure.

In mass spectrometry a high vacuum is necessary, as many of the electronic parts are oxygen sensitive. The ionizing filament is typically composed of tungsten or thoriated iridium, which are both reactive with oxygen. The high voltage accelerating and focusing plates in the ionizer require a vacuum for proper operation. Finally the detector is made of oxygen sensitive materials, generally copper-beryllium. Typical vacuum levels are  $10^{-6}$  torr in the Knudsen cell furnace chamber,  $10^{-8}$  torr in the ionizer chamber, and  $10^{-9}$  or better in the ion filter/magnet region and detector. In this molecular flow region, large pumping ports are required for effective and uniform pumping. Today most instruments use turbo pumps; ion pumps may be used in the ion filter/magnet region and detector where the load is much less.

The most effective vacuum thermogravimetric system should have a large pumping port near the sample (e.g., Figure 3, whereas vacuum thermogravimetric systems with pumping at the end of a furnace tube may not have as effective pumping or a good vacuum in the vicinity of the cell.

## 3.0 Selection of Cell Materials

In principle, any solid material can be made into Knudsen cell (Figure 1). Of course, the first requirement is that the material be stable up at the temperature of interest (i.e., structurally sound, low vapor pressure, no phase transformation). The more challenging requirement is that the cell material be inert or at least react in a known way with the sample to be studied. Note also that for thermogravimetric measurements, the cell should not interact with the residual gases in the vacuum. For example, oxygen active metals such as Zr and Hf cannot generally be used. Table I presents a listing of some of the cell materials commonly used in our laboratory and the samples that have been studied with them. Also listed are special considerations.

TABLE I.—EXAMPLES OF CELL MATERIALS

Cell material	Test sample (reference)	Special issues
Graphite	Au (13), Cu(14)	C shows some solubility in Au
Al <sub>2</sub> O <sub>3</sub>	Ag (15), Au	Liquid metals get into grain boundaries and after repeated use weaken cell
Mo	SiC-SiO <sub>2</sub> (16)	-----
Mo	Y <sub>2</sub> SiO <sub>5</sub> + Y <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> + Mo (17)	For higher SiO <sub>2</sub> activities
Mo	Yb <sub>2</sub> SiO <sub>5</sub> + Yb <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> + Mo (18)	For higher SiO <sub>2</sub> activities
Ta	Y <sub>2</sub> O <sub>3</sub> + Y <sub>2</sub> SiO <sub>5</sub> + Ta (17)	For lower SiO <sub>2</sub> activities
Ta	Yb <sub>2</sub> O <sub>3</sub> + Yb <sub>2</sub> SiO <sub>5</sub> + Ta (18)	For lower SiO <sub>2</sub> activities
Y <sub>2</sub> O <sub>3</sub>	Ti-Al (19); Ni-Al (20)	-----
BN	B <sub>2</sub> O <sub>3</sub> (21)	-----
Re, Ir	Olivine (22)	-----

It is important to recognize that no two materials are truly inert. There is always some degree of interdiffusion or reaction. In some cases, the cell inner walls may react and form a more inert material. Furthermore, it may be advantageous that the cell be a part of the reaction, such as the Mo and Ta cases in concert with RE silicates shown in Table I (Refs. 17 and 18).

Many of the refractory materials are expensive and difficult to machine. In these cases a liner might be used, which minimizes the amount of exotic material needed. In the case of Ir, the Ir liner is placed in a graphite cell (Ref. 22). Ir is known not to form carbides, so reaction between the liner and the cell was minimal. Other groups have used an Ir liner in a tungsten cell (Ref. 23).

## 4.0 Sample Material

As noted, a wide range of materials are studied with Knudsen cells. There are some certain limitations which must be considered. First, as stated earlier, the Knudsen cell method requires that the mean free path of the vapor phase be 10X the orifice diameter. This sets an upper limit on vapor pressure measurements. However it should be noted that Wahlbeck (Ref. 24) developed corrections to extend the range of Knudsen cell measurements.

A second consideration is the surface interactions with the cell. While bulk chemical reactions may be minimal, problems such as surface diffusion and surface creeping must be avoided or minimized. At high temperatures, surface diffusion may be an issue, which will interfere with accurate measurements. Cater (Ref. 25) has pointed out that knife edge orifices tend to promote this whereas channel orifice may minimize it. Selection of different cell materials as discussed in the previous section may also help. A more extreme problem, which occurs with some glasses and liquids, is creep up the cell walls. This is difficult to avoid and renders Knudsen cell measurements invalid. Some solutions to this problem are the employment of large cells or different cell materials. Additionally, an alloy of Pt/5Au should help with this problem.

A third consideration is the amount of material in the cell. In theory, for an equilibrium situation, this should not matter. But there are clearly lower limits, as there must be sufficient vapor generated. For our cells, we use 200 to 400 mg, depending on the sample. Surface area of the sample may be an issue, particularly for multiple phase mixtures when particle contacts are important. Most discussions of Knudsen cell measurements comment that the ratio of the area of the effusion orifice to the surface area of the sample must be a very small number. But there is no set rule; ideally the vapor pressure measured should be independent of this area.

For thermodynamic measurements, proper assemblage of phases must be present (Ref. 4). Consider the phase rule:

$$F = C - P + 2 \quad (4)$$

Here F is degrees of freedom, C is the number of components, and P is the number of phases. Generally in Knudsen cell measurements, we fix temperature and measure pressure, which is a univariant system. With one component, we have two phases (e.g., solid and gas). Two components requires three phases (e.g., two solid phases and gas) (Ref. 3) and so on.

## 5.0 Temperature Control and Measurement

The importance of well-controlled and maintained heating and temperature measurement cannot be emphasized enough. First consider heating of the cell. The major requirements are constant temperature and uniform temperature through the cell. The challenge in heating is that generally (particularly in a

mass spectrometer), the furnace must be very compact. Many Knudsen cell measurement devices, particularly mass spectrometers, require rigid support. This is typically done by using metal rods to support the cell, as shown in Figure 5. These rods will pull heat from the cell, however this is minimized by making the rod diameter small as possible and including thermal shields below the cell as seen in Figure 5.

Heating methods include resistance heating, electron bombardment, laser heating, and induction heating. The most common methods in KEMS instruments are resistance heating and electron bombardment. Both have advantages and disadvantages. Resistance heating only requires a low voltage, high current power supply. Temperatures stabilize with just a constant voltage, a temperature sensing feed-back loop is not necessary. The high current requires water cooled electrical feed-throughs, but arcing is not an issue with the low voltages. The major problem is that resistance heating heats everything in the vicinity of the heating element and hence heat shields are required. Also the cell must be appropriately placed in the heating zone so that there are no thermal gradients. Figure 5 shows a helical heating element around a Knudsen cell. This is then surrounded by a tight heat shield pack of 6 to 10 layers of W, Mo, and/or Ta. Electron bombardment requires more complex electronics. Early systems had the problem of “thermal runaway” but modern electronics has protections against this problem. These systems run on high voltages and hence arcing is a potential problem. However current is much less so that larger, water cooled power feedthroughs are not necessary. In electron bombardment, temperatures up to 800 °C are achieved with resistance heating. Above 800 °C, electron bombardment is used. These systems typically have two zones and any gradient in temperature can be removed by appropriate adjustment of the zones.



Figure 5.—Tantalum helical elemental around an alumina Knudsen cell.

Temperature measurement devices include thermocouples and optical pyrometers. The general requirements are that the device measure the temperature in the cell as close as possible and the calibrations be conducted frequently. Calibrations are most commonly conducted against an International Temperature Standard (ITS) standard melting point (Ref. 26). Figure 6 shows the triple point for Au. Other methods of temperature calibration are complete vaporization of a known material (Ref. 9) and adjustment of temperature to obtain the accepted enthalpy of vaporization. Both thermocouple and pyrometers have advantages and disadvantages.

Thermocouples rapidly respond, have convenient placement, and readily feed their output to a data acquisition system. However they tend to degrade in vacuum and metal vapor containing atmospheres. Intimate coupling between the thermocouple and the cell is important. We have spot welded a Ta band around the cell bottom, which holds the thermocouple bead firmly to the cell side. Other investigators have welded or clamped the thermocouple to the cell.

Measuring cell temperatures with a pyrometer has many advantages. First there is no metal contact with the cell, so no route for heat loss from the cell. Pyrometers are useful to temperatures  $>2000\text{ }^{\circ}\text{C}$  and modern brightness pyrometers can easily be adapted to data acquisition systems. Typical measurements are made on a dead-end hole with a 1 mm diameter. Generally the length-to-diameter ratio for such a dead-end hole should be 10 or greater. This small hole means the optics of the pyrometer must be able to sight a 1 mm target at a distance of 20 cm, depending on the particular system. It is also important to shield against stray radiation. A major issue is keeping the sighting window clean. A dirty window can give temperature errors of  $50\text{ }^{\circ}\text{C}$  or greater! A shutter is used to protect the window when it is not in use. The window must be frequently inspected and cleaned and calibrations must be done frequently.

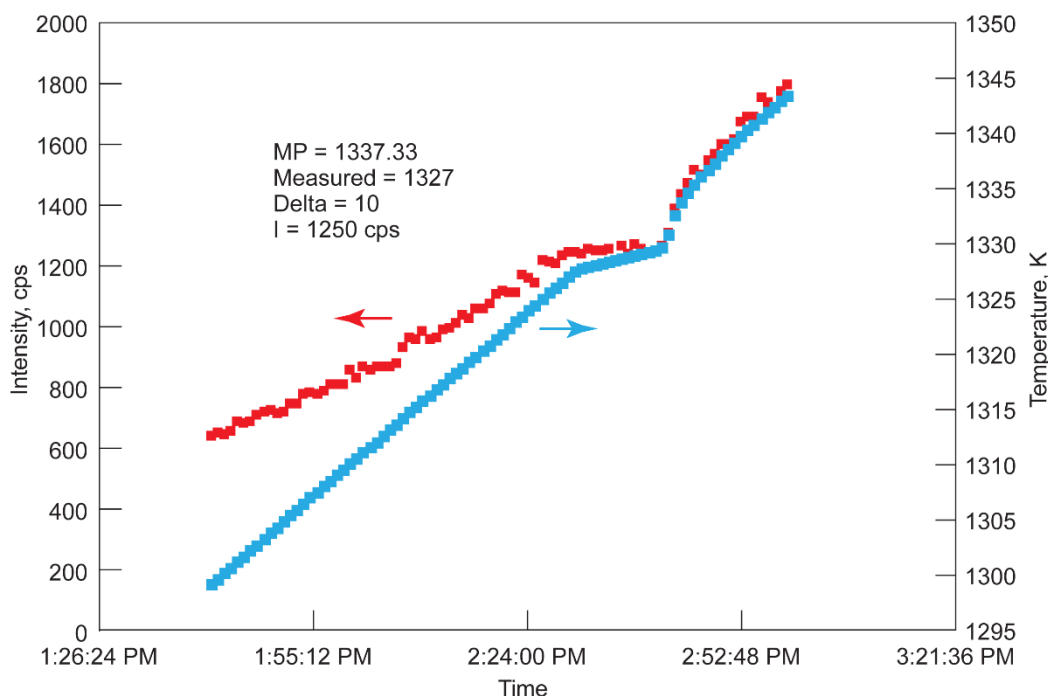
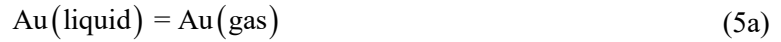


Figure 6.—Melting point calibrations with KEMS for Au.

A good check of temperature calibration and general mass spectrometer operation is a measurement of enthalpy of vaporization of a standard, typically Ag or Au in an Al<sub>2</sub>O<sub>3</sub> cell. The enthalpy of vaporization is given from the Van't Hoff relation. Consider the vaporization of Au:



$$\Delta_{\text{vap}}G^\circ(T) = \Delta H^\circ - T\Delta S^\circ = -RT\ln K_p = -RT\ln P_{\text{Au}} \quad (5b)$$

$$\frac{\partial \ln P_{\text{Au}}}{\partial (1/T)} = -\left(\frac{1}{R}\right)(\Delta_{\text{vap}}H^\circ(T)) \quad (5c)$$

Applying Equation (3) leads to:

$$\frac{\partial \ln(I_{\text{Au}}T)}{\partial (1/T)} = -\left(\frac{1}{R}\right)(\Delta_{\text{vap}}H^\circ(T)) \quad (5d)$$

Figure 7 shows an enthalpy of vaporization of Au. In such a measurement temperature is randomly varied to avoid systematic error and data points should be reproducible over several days. It is good practice to frequently take calibration measurements, such as those in Figure 6 and Figure 7, before proceeding to measurements on unknowns.

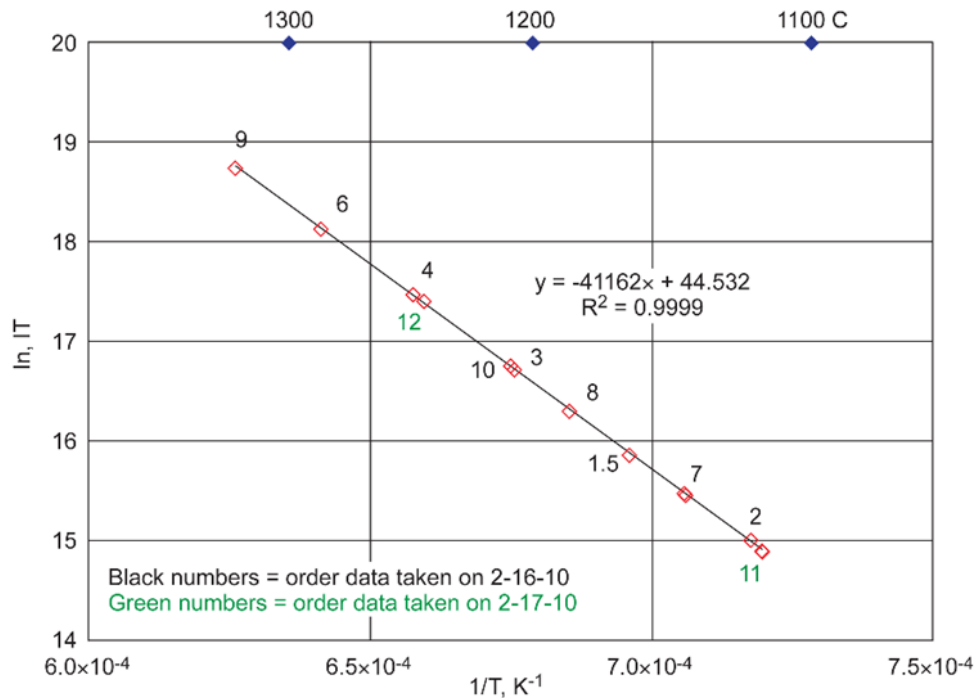


Figure 7.—Enthalpy of vaporization of Au. Note that data points are reproducible over several days.

## 6.0 Attainment of Equilibrium in the Knudsen Cell

Knudsen cell measurements are based on the assumption of equilibrium within the cell. First, the orifice on the Knudsen cell means the system is no longer a closed system and hence we can only attain “near equilibrium”. In order to compensate for the orifice, Whitman (Ref. 27) and Motzfeld (Ref. 28) have developed methods to extrapolate to zero orifice size. A thorough explanation of this method is discussed by Paule and Margrave (Ref. 29). The vapor fluxes in the cell and out of the orifice are considered and the following equation derived:

$$P_m \left[ 1 + f \left( \frac{1}{\alpha_c} + \frac{1}{W_A} - 2 \right) \right] = \frac{\alpha_L}{\alpha_c} P_{eq} \quad f = \frac{W_B B}{A} \quad (6)$$

Here  $P_m$  is the measured vapor pressure,  $W_A$  is the transmission factor (between 0 and 1) for the cell,  $W_B$  is the transmission factor (between 0 and 1) for the orifice,  $P_{eq}$  is the equilibrium pressure,  $\alpha_c$  is the condensation coefficient (fraction of molecules that stick to the sample surface on striking),  $\alpha_L$  is the evaporation coefficient (fraction of molecules on surface in equilibrium with the vapor). Generally the condensation coefficient is taken as equal to the vaporization coefficient, which is not strictly correct but a reasonable assumption. Thus a plot of  $P_m$  vs.  $P_m \left[ f \left( \frac{1}{\alpha_c} + \frac{1}{W_A} - 2 \right) \right]$  should yield a line with intercept of  $P_{eq}$ . Furthermore, the vaporization coefficient can be extracted from the slope of such a line which gives a measure of the kinetic barrier to equilibrium (Refs. 16 and 17). In general, metals have vaporization coefficients close to unity; whereas compounds, such as oxides, carbides, and nitrides, may have vaporization coefficients much less than unity. A Knudsen cell study of the reactions of SiC and SiO<sub>2</sub> indicated a strong dependence on orifice size (Ref. 16), as shown in Figure 8. Note also that Equation (6) can be used to design a cell geometry that is best for studying a system with a low vaporization coefficient (Ref. 29).

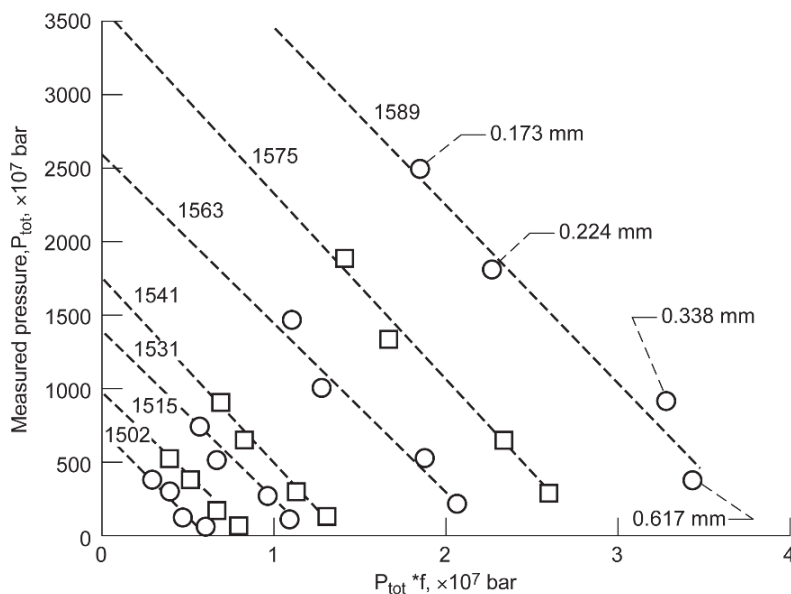


Figure 8.—Whitman-Motzfeld extrapolation to zero orifice size for SiC + SiO<sub>2</sub> (Ref. 16). The condensation coefficient is  $\sim 8.5 \times 10^{-4}$  for this reaction, indicating a kinetic barrier to equilibrium. Reprinted with permission from Wiley.

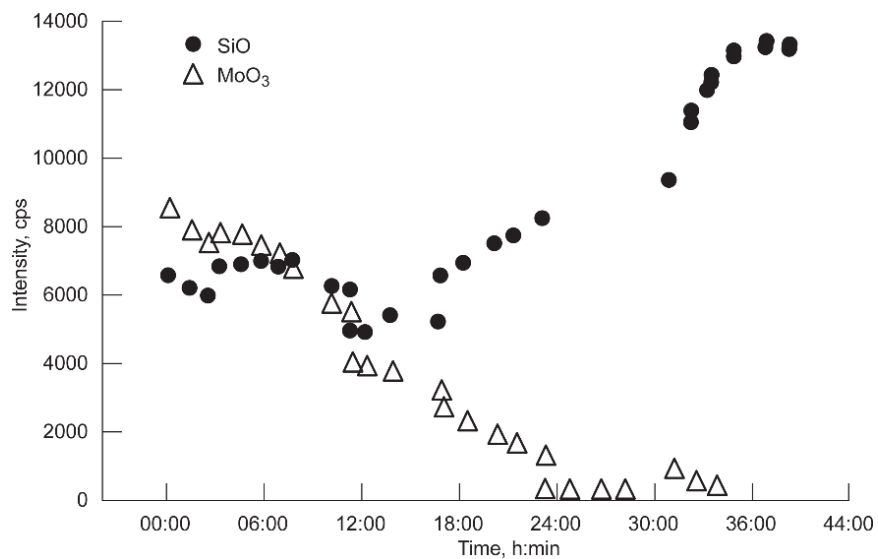


Figure 9.—Approach to equilibrium with a 3:1 molar ratio mixture of Mo and SiO<sub>2</sub> at 1695 K (Ref. 18). Reprinted with permission from Elsevier.

However in some instances the approach to true solid/vapor equilibria may be very slow or not even attainable in a reasonable amount of time. One condition for equilibrium is that the ion intensity (pressure) must be constant with time. Thus simply following a peak as a function of time is a first test for equilibrium. This may take a few minutes, hours, or even longer as observed in Figure 9 for a mixture of Mo and SiO<sub>2</sub>. Some systems may never reach equilibrium, in which case the Knudsen cell method is not suitable.

## 7.0 Sampling of the Effusate

The next issue is proper sampling of the effusate. It is possible to calculate the distribution of molecules emerging from a Knudsen cell orifice using analytical methods (Ref. 30) or a Monte Carlo (Ref. 31) simulation. Figure 10 shows calculated distributions for an orifice with a very limited wall length and a longer, more pipe-like orifice. The thin orifice gives a nearly spherical distribution; whereas the thicker orifice gives a more directed distribution.

It is important to understand this distribution for any measurement with Knudsen cells. Clearly for target collection studies, one must know the fraction of effusate collected for an accurate measurement of total vapor flux. For in-situ weight loss studies, one needs to direct the beam to avoid condensation on the weighing apparatus. Similarly the beam must be properly directed for torsion effusion studies. In the case of mass spectrometric studies, sampling should be done on the most intense portion of the effusate.

Note that these calculations are for ideal orifices and assume no molecule/wall interactions. There are a number of studies of actual distributions from orifices, which may differ from ideality due to molecule/wall interactions, surface diffusion, vapor reactions, etc. Such issues are important to understand and may influence thermodynamic measurements. Grimley (Refs. 30 and 32) has developed angular distribution measurements to interpret mass spectra.

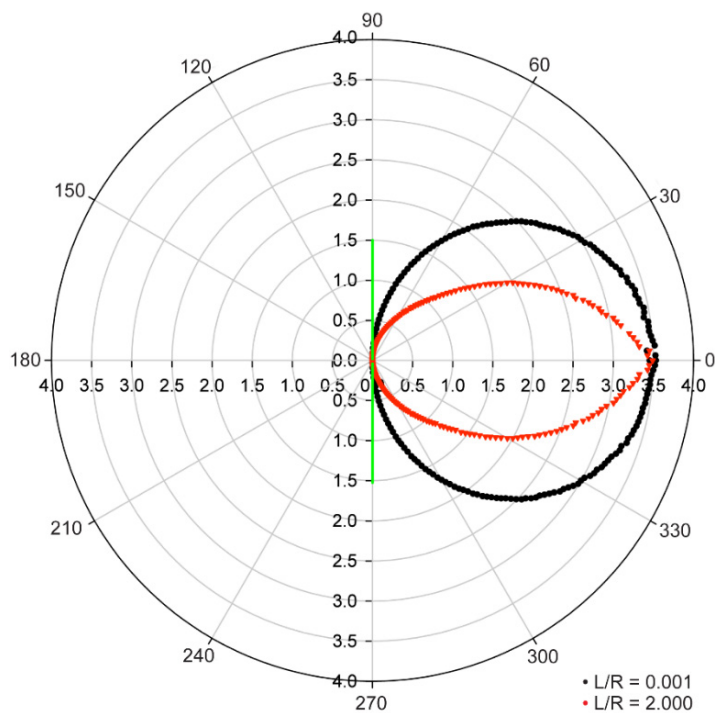


Figure 10.—Two dimension view of molecular distribution for a thin orifice (black circle) and channel orifice (red oval) (Ref. 11).

## 8.0 Mass Spectrometry Issues

As noted, the primary method of analyzing the effusate from a Knudsen cell is with a mass spectrometer. The mass spectrometer is a widely used analytical instrument in many disciplines; however its application to analysis of high temperature vapors requires some special considerations.

Identification of the parent molecule from the observed ion(s) is accomplished via a variety of methods, including mass-to-charge ratio, isotopic ‘finger print’, and ionization efficiency curves, which yield appearance potentials and any evidence of fragmentation (Ref. 9). It is important to note the reliable ionization efficiency curves require a carefully designed ionizer with mono-energetic electrons. Many commercial instrument have ionizers designed for maximum yield, but not necessarily well-defined electron energies.

Ideally one would like to convert the ion intensity (typically in millivolts or counts-per-second) to partial pressures (bar). This is done from Equation (3). In practice, obtaining the constants in Equation (3) can be quite difficult. Whenever possible, it is best to use ion intensity ratios, so that the constants in Equation (3) cancel and one is left with a partial pressure ratio.

Consider each of the constants in Equation (3). The first constant ‘k’ is known as the machine constant and this encompasses terms such as the ion-extraction efficiency, the transmission probability of the mass analyzer, and the detection coefficient (Ref. 33). These values are all gathered into this one constant, which is typically determined from the trip point or plateau for a known standard, such as Au, Ag, or Pt as shown in Figure 6 for Au. An important issue is the constancy of ‘k’, which often changes each time the vacuum is broken and the ionizer is turned off/on. One way around this is to use a multiple cell (Refs. 11, 33, and 34) instrument with a standard reference material in one cell. Another way is to put a valve in between the Knudsen cell chamber and the ionization chamber (Refs. 35 and 36). This valve must be specially designed to withstand the high temperatures of the Knudsen cell chamber and also keep



the Knudsen cell as close to the ionizer as possible. All such measurements require a stable ionizer and frequent calibration checks.

Another important issue is mass discrimination effects (i.e., sensitivity is a function of mass-to-charge ratio). This is a particular issue for older quadrupole systems. Modern quadrupole systems have circuitry that compensates for mass discrimination effects. Magnetic sector instruments generally have much less of a problem with this. In addition, a nonmagnetic ion source tends to minimize these effects. Traditional ion current measurement at the detector gives signals that are proportional to the square root of mass. However ion counting does not require this correction.

Separation of the signal from the background is also an important issue. There are a variety of methods that can be used. Of course, the best approach is to use high capacity, clean vacuum pumps. As noted, most systems today use turbo pumps. Some investigators have used cryo-pumps, but vibration isolation is necessary. A high resolution instrument is useful. Typically the hydrocarbon peak is 0.01 amu or less than the corresponding inorganic peak at the same mass number. Most instruments have a shutter, which allows an interruption of the molecular beam. Some investigators have used a chopper in conjunction with a lock-in amplifier so that only the modulated portion of the beam is detected. But the practical difficulties of putting a motorized toothed wheel near the hot cell make this approach challenging.

## 9.0 Summary and Conclusions

Vapor pressure measurements via Knudsen cells have long been a standard method for measuring low vapor pressures of materials as well as activities in solutions. Various methods of actual measurement of the vapor effusing from a cell have been discussed. Precise measurements require a number of considerations. These include vacuum system considerations, selection of proper sample/cell combinations, control and measurement of temperature, attainment of equilibrium in the cell, sampling of the vapor, and some consideration unique to mass spectrometry. Each of these issues has been discussed and recommendations made from our and others laboratory experience.

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