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Thermodynamic Activity Measurements with Knudsen Cell Mass Spectrometry

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Introduction

Coupling the Knudsen effusion method with mass spectrometry has proven to be one of the most useful experimental techniques for studying the equilibrium between condensed phases and complex vapors (1). The Knudsen effusion method involves placing a condensed sample in a Knudsen cell, a small "enclosure", that is uniformly heated and held until equilibrium is attained between the condensed and vapor phases. The vapor is continuously sampled by effusion through a small orifice in the cell. A molecular beam is formed from the effusing vapor and directed into a mass spectrometer for identification and pressure measurement of the species in the vapor phase. Knudsen cell mass spectrometry (KCMS) has been used for nearly fifty years now and continues to be a leading technique for obtaining thermodynamic data. Indeed, much of the well-established vapor specie data in the JANAF tables (2) has been obtained from this technique. This is due to the extreme versatility of the technique. All classes of materials can be studied and all constituents of the vapor phase can be measured over a wide range of pressures ($\sim 10^{-4}$ to 10^{-11} bar) and temperatures (500-2800 K). The ability to selectively measure different vapor species makes KCMS a very powerful tool for the measurement of component activities in metallic and ceramic solutions.

Today several groups are applying KCMS to measure thermodynamic functions in multicomponent metallic and ceramic systems. Thermodynamic functions, especially component activities, are extremely important in the development of CALPHAD (Calculation of Phase Diagrams) type thermodynamic descriptions (3). These descriptions, in turn, are useful for modeling materials processing and predicting reactions such as oxide formation and fiber/matrix interactions. The leading experimental methods for measuring activities are the Galvanic cell or electro-motive force (EMF) technique and the KCMS technique. Each has specific advantages, depending on material and conditions. The EMF technique is

suitable for lower temperature measurements, provided a suitable cell can be constructed. KCMS is useful for higher temperature measurements in a system with volatile components.

In this paper, we briefly review the KCMS technique and identify the major experimental issues that must be addressed for precise measurements. These issues include temperature measurements, cell material and cell design and absolute pressure calibration. The resolution of these issues are discussed together with some recent examples of measured thermodynamic data.

Basic Technique

The unique feature of a Knudsen cell mass spectrometer is the vapor generation system. This has been discussed in several excellent reviews (1,4,5). Typically a Knudsen cell is 1 cm in diameter x 1 cm tall with an orifice of well-defined geometry. The orifice is small (typically 0.5-2 mm diameter) to ensure molecular flow is maintained as molecules pass through the orifice, $i.e.$, molecule-wall collisions dominate over molecule-molecule collisions. As a general rule, the orifice dimensions must be keep to less then one tenth of the mean free path of the vapor species, over all experimental conditions. This, in turn, leads to an upper pressure limit of $\sim 10^{-4}$ bar for a 1 mm orifice. The lower pressure limit is determined by the sensitivity of the instrument and is typically $\sim 10^{-11}$ bar. As we are dealing with high temperatures and low pressures the vapor can be assumed to behave according to the kinetic theory of ideal gases. On this basis, accurate predictions can be made for the effusion characteristics through the Knudsen cell orifice (5). This allows design of an optimum Knudsen cell geometry. A well-defined molecular beam is sampled from the effusate at angles close to the normal of the orifice, collimated by one or more apertures and directed into the ionization chamber of the mass spectrometer.

Figure 1 shows a portion of a typical Knudsen cell mass spectrometer*. The basic components—ionizer, accelerator, ion sorter, and detector—remain similar to the designs of the 1960s. However improved vacuum systems, electronics, and data acquisition systems have led to more reliable instruments. The

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* Modified Model 12-90-HT, Spectrumedix, State College, PA

major features of a mass spectrometer for analysis of high temperature vapor are summarized as follows. A small, representative, fraction of the molecular beam is ionized via impact with a focused beam of mono-energetic electrons. An adjustable electron energy permits precise determination of the particular energy at which an ion appears. This measurement is very useful in understanding the origin of the observed ions in the mass spectra. Once formed, the ions are directed into a high voltage accelerating region and then into a magnetic field for selection according to mass-to-charge ratio. Other common techniques for ion selection such as quadrupole filters and time-of-flight instruments have been used. However the magnetic field ion selector is most desirable due to its stability and lack of mass discrimination. Finally the ions are directed into an electron multiplier. Ion currents can be measured by measuring the voltage drop across a precision resistor or ions may be counted directly. The ion counting technique is preferred, again, due to its lack of mass discrimination and easy adaptation to data acquisition systems.

The output of the mass spectrometer is in ion intensity, I_i. For many thermodynamic measurements this must be converted to partial pressure, P_i, via the following equation:

$$P_i = \frac{k\,I_i\,T}{\sigma_i} \tag{1}$$

Here T is the absolute temperature of the vapor source, σ_i is the ionization cross section, and k is the machine constant. The machine constant is a combination of numerous factors involved in the formation of the molecular beam, the ionization process, ion collection efficiency, transmission efficiency of the analyzer, and collection efficiency of the detector. To calculate absolute vapor pressures the values of both k and σ_i must be known. In order to determine the machine constant, a number of experimental issues must be addressed.

Critical Experimental Issues

A number of requirements must be satisfied for precise measurements. The first requirement is an inert cell. A wide range of refractory-metal and ceramic materials have been used for Knudsen cells. Generally

metallic alloys are studied in refractory ceramic cells (Al_2O_3, ZrO_2, Y_2O_3, etc.) and ceramics are studied in refractory metal cells (W, Mo, Ir, etc.).

Provided a suitable cell material can be identified, cell design is the next issue. The size of the orifice is generally determined by the maximum vapor pressure over the sample in the temperature range of interest. The continuous effusion of the vapor from the cell means that a pressure gradient is present in the cell but cognizant design of the cell for a given orifice can limit the divergence of the measured pressure from the equilibrium value to well within the random error of the technique. Numerous studies have considered this issue (5). In general this is achieved by a cell with a larger diameter than height and a sample with a large surface area (generally the sample area should be at least one hundred times greater than the orifice area). This is readily done with a powder, but may require a larger cell area with a liquid.

Temperature control and measurement are major sources of error in this technique. The following requirements must be met: *1*) a constant temperature must be maintained, *2*) temperature gradients in the cell must be eliminated, and 3) the absolute temperature must be accurately measured. Temperatures can be measured by either a pyrometer or thermocouple. These measurements must be taken of the cell, either with of black body hole drilled into the cell or a thermocouple tightly coupled to the cell. A typical calibration may involve slowly varying the temperature through the melting point of a pure metal (e.g., Ag, Au, Cu, etc) and observing both the corresponding plateau in vapor pressure and thermal arrest. Temperature calibration must be done frequently for thermocouples as the vacuum and reactive vapor environment can result in rapid changes in wire composition.

It is also important that the neutral precursors for the observed ions be identified. For metallic vapors this identification is generally simple, e.g. the Ti vapor above Ti alloys forms Ti^+ ions. For ceramics this can be more involved as they generally form a more complex ionization pattern, e.g. ZrO_2 vaporizes to $ZrO(g)$ and $O(g)$. Typically low energy ionizing electrons are used to minimize fragmentation and simplify the mass spectrum, but this reduces sensitivity.

Another issue related to the ion intensity measurement is the separation of background peaks from the peak of molecules emerging from the Knudsen cell. There are several approaches to solving this problem. The ionizing electron energy can be chosen to limit fragmentation of background hydrocarbons and limit the number of background peaks. A magnetic sector instrument typically has a resolution of 1000 or greater, which allows separation of inorganic peaks from any hydrocarbons. Finally a shutter, as shown in Figure 1, can be used to interrupt the molecular beam emerging from the cell so the background can be identified and subtracted.

The best test for proper operation of a Knudsen cell instrument is a simple 'second law' heat of vaporization of a well-characterized vapor pressure standard. This is illustrated in Figure 2 for copper, where the slope of the line in a plot of ln (I_iT) vs $1/T$ gives a heat of vaporization. An acceptable heat is within 2 kJ/mol of the accepted value (2). This generally indicates the above issues of proper cell material and design, temperature control and measurement, and spectra interpretation are satisfied. It also indicates the vapor sampled is primarily from the cell and not condensation and re-evaporation from the heat shields.

A second law heat does not require the conversion of ion intensity to absolute pressure, however, many types of measurements do require this conversion via equation (1). In order to do this precisely a standard is needed. Reliable vapor pressure data are available for most pure metals and these are excellent standards. However care must be taken to measure the standard and sample vapor pressures under exactly the same conditions: the molecular beam must be directed to the same region in the ion source, and the cells used for the vapor pressure standard and the sample must have matched orifices to ensure the molecular beams are identical.

In theory, one can measure the vapor pressure of a standard to obtain the machine, change samples, and measure the ion intensities for the alloy. However, maintaining an identical machine constant from run to run involves using a rigidly mounted cell and an isolation valve between the Knudsen cell chamber and the ionizer. An isolation valve permits the ionizer to remain running when a sample is changed. Only a few instruments have these features for a reliable, constant value of k (1,6).

For most instruments, the machine constant changes from run to run. Three methods have been developed to circumvent this problem. The dimer/monomer approach developed by Berkowitz and Chupka (1,7). This requires a system where both species are readily measurable with a well-established dimer/monomer equilibrium and conditions:

$$2A(g) = A_2(g) \tag{2}$$

Thus the activity of component A in the alloy, a(A), becomes the ratio of this equilibrium for the alloy and pure materials:

$$a(A) = \frac{I^o(A) \, I(A_2)}{I^o(A_2) \, I(A)} \tag{3}$$

Here $I^o(A)$ and $I^o(A_2)$ are the ion intensities measured of A(g) measured over the pure element A and I(A) and $I(A_2)$ are the ion intensities of A(g) measured over the alloy containing A. Clearly this approach is limited to specific systems.

A second approach involves taking the ion intensity ratio in a binary alloy and manipulating the Gibbs-Duhem equation to cancel the calibration constant (1,8). The resultant equation for an alloy AB is:

$$ln \, \gamma_A = - \int_{x_A=1}^{x_A} x_A d[ln \, (I_A^+ / I_B^+) - ln(x_A / x_B)] \tag{4}$$

Here γ_A is the activity coefficient of A, x_A and x_B are the mole fractions of A and B respectively, and I_A and I_B are the measured ion intensities of A(g) and B(g) over the alloy. This technique has been widely used to obtain activities and partial molar quantities for a number of systems. It requires only measurements of the alloy—no standards are necessary. The drawback of this technique is the need for measurable vapor pressures over a range of compositions for both components. An example of some data for the Fe-Al system obtained in our laboratory is shown in Figure 3 (9). Note the negative deviations from ideality which are consistent with solution models of this systems (10).
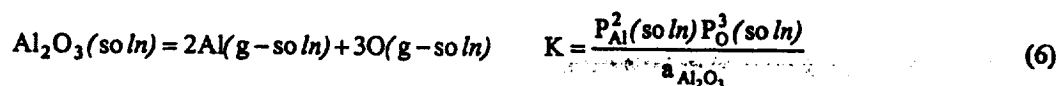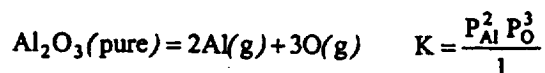
Finally, the third approach to this problem is the multiple cell technique, which we believe to be the most versatile. This method was first discussed in 1960 by Büchler and Stauffer (11); and further developed by several groups. Two or more cells are adjacent to each other as shown in Figure 1. Consider, for example, the measurement of Al activity in a Ti-Al alloy. Ideally one would have pure Al in one cell and Ti-Al in the other cell and the activity, a_{Al}, is simply:

$$a_{Al} = \frac{P_{Al}(soln)}{P_{Al}(pure)} = \frac{I_{Al}(soln)}{I_{Al}(pure)} \tag{5}$$

Here P and I are the partial pressure and ion intensity, respectively. The problem is that the molecular beams tend to mix. There is no easy solution to this problem. Chatillon (12) has developed the "restricted collimation" method in which a series of fixed collimating apertures physically limit the vapor entering the ion source to that which originated from within the cell orifice of interest. We overcome this problem of beam mixing by using a secondary *in-situ* standard, *i.e.*, instead of pure Al in the above example pure Cu or Au is used (13). This approach requires some additional corrections—so that an expected pure Al ion intensity is derived from the measured Cu or Au intensity. Such corrections are obtained from an additional run with pure Al in one cell and the Cu or Au standard in the other.

Figure 4 illustrates some recent data on Ti-45 a/o Al. Note that both a_{Al} and a_{Ti} are reported. The upper limit of measurement is determined by both the high vapor pressure and the melting point of the alloy. The lower limit is determined by the sensitivity of the instrument. The low vapor pressure of Ti gives only a narrow range for a_{Ti} measurement. However a_{Al} can be measured over a wide range. We found that these data extrapolated to some a_{Al} measurements taken with the EMF technique and a CaF_2 electrolyte at 1073 K (13). An important application of these data is the prediction of the stable surface oxide—TiO_2 or Al_2O_3 (13).

We have illustrated some of the above techniques with metallic alloy systems. It should be noted that these techniques are all applicable to ceramic systems as well. These systems produce mass spectra which are much more complex and the activities must be derived accordingly. Consider a solution with alumina as a constituent (12):

$$Al_2O_3 \text{(pure)} = 2Al(g) + 3O(g) \qquad K = \frac{P_{Al}^2 \, P_O^3}{1}$$

$$Al_2O_3 \text{(so ln)} = 2Al(g - so ln) + 3O(g - so ln) \qquad K = \frac{P_{Al}^2(so ln) \, P_O^3(so ln)}{a_{Al_2O_3}} \qquad (6)$$

$$a_{Al_2O_3} = \frac{P_{Al}^2(so ln) \, P_O^3(so ln)}{P_{Al}^2 \, P_O^3} = \frac{I_{Al}^2(so ln) \, I_O^3(so ln)}{I_{Al}^2 \, I_O^3}$$

Several groups are actively using the KCMS technique to measure the properties of complex oxide solutions (1,12,14). This type of data are used to develop oxide solution models.

Conclusions

One of the oldest and most useful techniques in fundamental high temperature science is Knudsen cell mass spectrometry. A large amount of well-established data on pure compounds has been determined from this technique. The extreme versatility of this technique continues to make it a leading experimental approach for fundamental thermodynamic data. Today, the emphasis is more on solutions and the KCMS technique is particular suited to measurement of activities in multi-component solutions. The primary experimental issues are discussed for these types of studies.
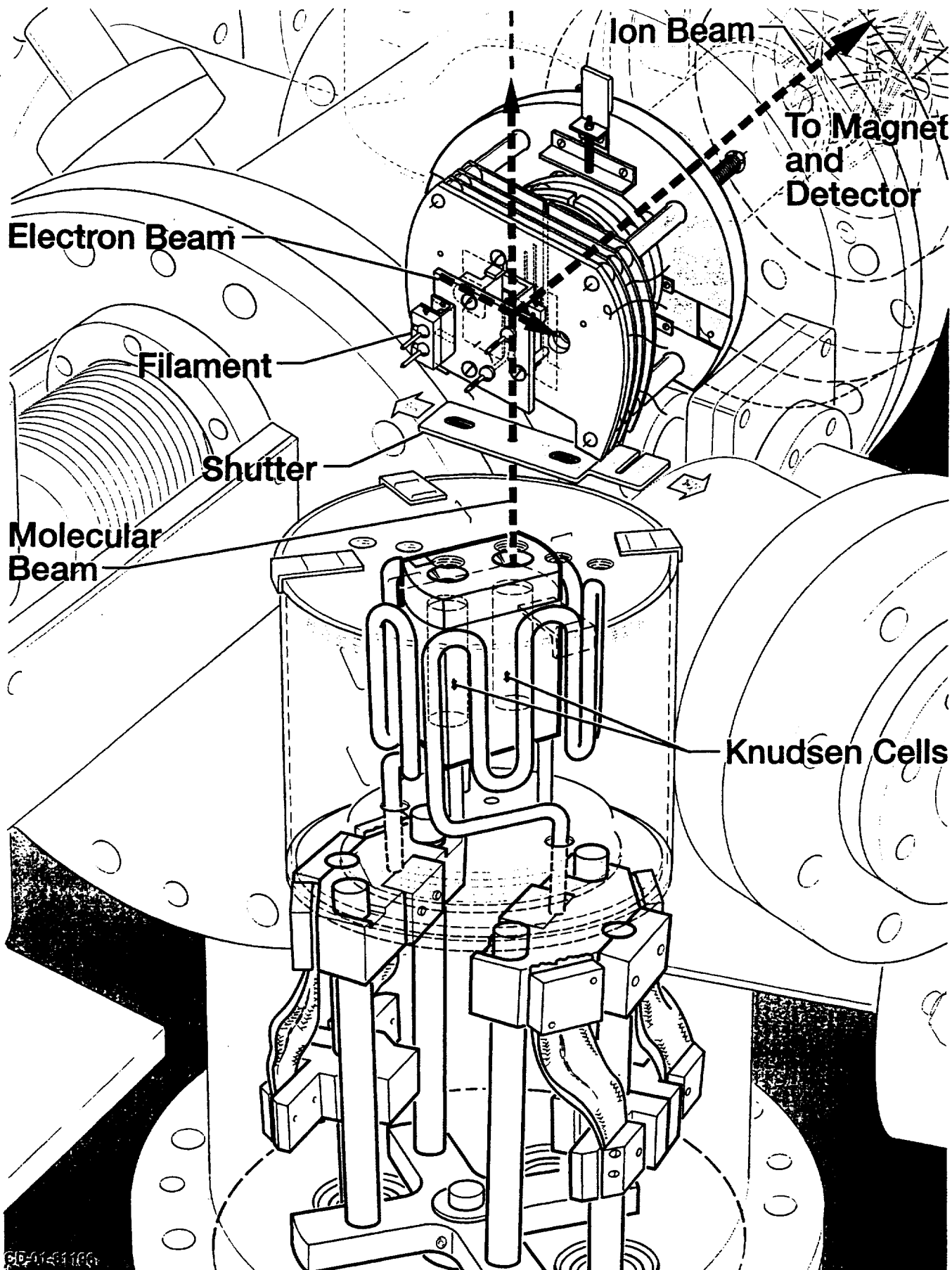
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Figure Captions

1. Partial schematic of a Knudsen cell mass spectrometer.

2. Second law heat of vaporization for copper. The tabulated value is 331.8 kJ/mol (2)

3. Data obtained for the Fe-Al system at 1573 K by the ion-current ratio technique (9).

4. Data for the Ti-45Al system obtained by the double cell technique (13).

Ion Beam

To Magnet and Detector

Electron Beam

Filament

Shutter

Molecular Beam

Knudsen Cells

Detail of Knudsen Cell Flange and Ionizer

Fig 1

$\Delta_v H(Cu) = 332.0 +/- 0.9$ kJ/mol

ln (IT-arbitrary units)

1/T(K)

Fig 2

Fig 3

Fig. 4