Novel Applications of Knudsen Effusion Mass Spectrometry

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Knudsen effusion mass spectrometry (KEMS) has been widely used for analysis of high temperature vapors and measurement of thermodynamic properties of both vapor and condensed phases. In this paper we discuss some recent novel applications of KEMS to rock and mineral dating, measurement of vaporization coefficients, and measurement of partial thermodynamic quantities.

The natural decay sequence of ^{40}K to ^{40}Ar has a half-life of 1.25 billion years. Despite being a noble gas, at low temperature the daughter ^{40}Ar is trapped in K-bearing minerals and provides a means of determining age. A technique developed at Caltech (1) involves adding a spike glass containing a known amount of isotopically enriched ^{41}K and ^{39}Ar to the sample in question. A lithium borate fluxing agent is also added to provide a lower melting and homogenisation temperature. The mineral age is determined from:

$$ t = \frac{1}{\lambda} \ln \left(\frac{^{40}Ar^*}{^{40}K} \left(\frac{\lambda}{\lambda_e} \right) + 1 \right) $$

Here λ is the total decay constant and λ_e is the decay constant for ^{40}K to ^{40}Ar. The critical measurement is the ratio of the decay product $^{40}Ar^*$ to ^{40}K. In this demonstration project (1), the Ar isotope is measured via noble gas mass spectrometry and the K isotope is measured via KEMS. A test specimen of basalt showed good agreement with published ages for a natural basaltic rock. Future plans are to build an instrument that combines analyses for both isotopes and should be suitable for a planetary probe.

The second application involves the application of our multi-cell KEMS instrument to measurement vaporization coefficients. Oxide materials have vaporization coefficients that vary from 0.5 to 10^{-6} (2) and it is very important to know these quantities for each component on any study of oxide thermodynamics. The method of Chatillon et al. (3) is adapted to our instrument using three Knudsen cells of varying orifice size. This is illustrated in Figure 1. It is critical that the entrance aperture to ionizer (field aperature (3)) have a diameter smaller than the orifice size, so the ionizer effectively 'sees' only inside the Knudsen cell.   Thus the differences in vapor flux from cell to cell are due to the vaporization coefficient alone. Using the Whitman-Motzfeld equation, the vaporization coefficient can be determined for different components of an oxide solution:

$$ \frac{1 - \left(\dfrac{I_i}{I_j} \right)}{f_j - f_i \left(\dfrac{I_i}{I_j} \right)} = - \left(\frac{1}{\alpha} - 0.51 \right) $$

Here f is the product of cell body cross section and the transmission factor for the orifice divided by the orifice cross section, I the ion intensity, and α is the vaporization coefficient. The subscripts i and j refer to the particular cell.
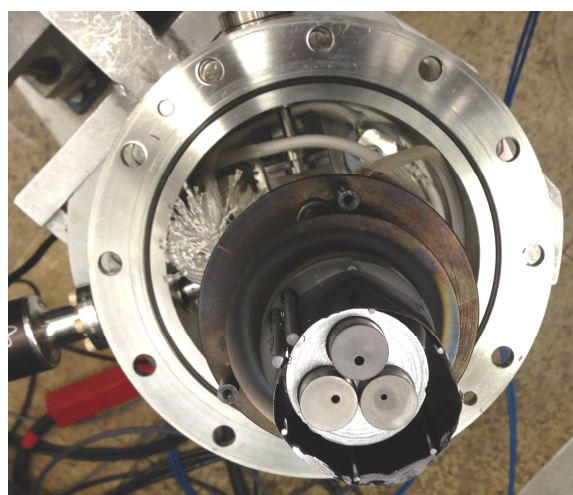

Figure 1. Knudsen cell flange with three cells having different orifice sizes for vaporization coefficient measurements.

The third area involves the use of a reducing agent for signal enhancement (4). The specific example of rare earth silicates is used. At temperatures near 1500 K, the signal from the SiO_2 component is not measureable. Careful choice of reducing agents (such as Mo and Ta) generate measureable $SiO(g)$ signals while not changing the solid state composition of the oxides.

References:

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