

Initial Measurements of the Vapor Pressures of Simple Refractory Materials: Cu and Fe.

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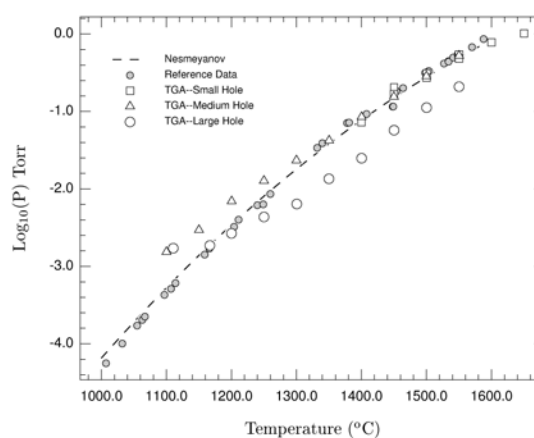
Introduction: It has become increasingly clear over the past decade that high temperature processes played important roles in the Primitive Solar Nebula. Unfortunately, basic data, such as the vapor pressures of iron or SiO have not been measured over the appropriate temperature range (near $T \sim 2000\text{K}$), but must be extrapolated from lower temperature measurements often made more than 50 years ago. The extrapolation of the available data to higher temperatures can be quite complex (e.g., see [1] for SiO vapor pressures) and can depend on other factors such as the oxygen fugacity or the presence of hydrogen gas. Moreover, modern technology has made possible more accurate measurements of such quantities over a wider temperature range. We recently acquired a commercial Thermo-Cahn Thermogravimetric system capable of vacuum operation to 1700°C and measurement of mass change with microgram accuracy in a 100g sample or smaller. In what follows we will report our progress in learning to make vapor pressure measurements using this system.

Initial Trials and Errors: We first attempted to measure the mass loss rate of pure iron metal in a vacuum from the crucibles supplied with our system from 1100K to 1975K and got reasonable, but not reproducible, results. We eventually discovered that the loss rate was subtly dependent on the depth of the iron sample within the crucible and on the previous use history of the sample under study, as well as on the actual diameter of the crucible. This was obviously unacceptable. In addition, as there is some significant controversy over the true vapor pressure of iron metal [2], we decided to measure the vapor pressure of copper [3] instead in order to ensure a reliable standard against which we could assess our measurement techniques.

We decided to design and construct a very simple effusion cell to replace the open topped crucibles that we had been using. Using closed-end alumina tubes as starting material, we bored a tiny hole ($\sim 2\text{mm}$) in the side of a small (6mm O.D., 25 mm in length) tube very near to the closed end. We then inserted this tube, open end first, into a 30 mm long, 10 mm O.D. closed end tube that acted as our new crucible. We cut a hole several millimeters in diameter into the outer tube at the location of the small hole in the inner tube to allow the metal vapor to escape. The pair of tubes used to

make the effusion cell were chosen to provide a relatively snug fit between the outer wall of the inner tube and the inner wall of the outer tube. This ensured that the small hole in the side of the cell was the primary avenue of escape for the hot vapor. The resultant data agreed quite well with the previously measured copper vapor pressure data [3] as shown in Figure 1, below.

Figure 1. Vapor Pressure of Copper



The effusion cell has the advantage that the vapor pressure within the cell is quite easy to calculate, provided that the diameter of the hole is known accurately. We do not need to calculate or estimate thermal accommodation coefficients or otherwise model the vapor-liquid interface. The mass loss rate from the cell is directly proportional to the vapor pressure in the tube provided that this vapor remains in equilibrium with the bulk metal. Although one might first assume that the smaller the effusion hole, the more accurate the measurement, this does not seem to be true. First, a very small diameter hole is difficult to measure accurately and results in a very small mass loss rate from the cell. Both of these factors increase the uncertainty in the measurement. Second, we recently realized that at low vapor pressures and using a small diameter hole, the leak rate from between the walls of the concentric alumina tubes could begin to be significant compared to the rate of effusion through the hole. This could explain the deviation between our values of the copper vapor pressure and the data in Nesmeyanov

[3] at temperatures between 1100 – 1300K as seen in Figure 1.

The obvious solutions are to either use a larger diameter hole or find a way to slow the leak rate between the concentric tubes. Unfortunately, if the hole in the effusion cell is made too large, then the vapor pressure within the cell drops below equilibrium as more vapor is lost than can be replaced from the metal surface. This is illustrated in Figure 1, where we used a hole roughly four times the area of the original 2 mm diameter hole to obtain the data shown as open circles. These measurements consistently yielded a vapor pressure lower than our previous measurements or those of the reference data. We are currently working on a method to better seal the annulus between the alumina tubes against vapor loss without introducing other problems such as higher-vapor-pressure contaminants.

Unfortunately, the major disadvantage of the effusion cell is that it is impossible to assess the effects of reactive gases on the vapor pressure of the material under study. Although relatively high pressures of hydrogen or of a CO/CO₂ mixture could certainly be made to flow into the cell, the mass loss measured would no longer be simply related to the equilibrium vapor pressure of the metal. In addition, we would have great difficulty in assuring ourselves that the additional gas came to equilibrium with the surface of the metal. For this reason we intend to use a second crucible with a much more open design to measure the vapor pressures of refractory species in the presence of reactive gases. We will first measure the vapor pressure using the effusion cell in a vacuum, then re-measure it in flowing helium or argon gas in order to enable correction for the effects of background gases. Finally, we will measure the mass loss rate in the presence of the gas of interest.

Preliminary Measurements of the Vapor Pressure of Iron: Given the caveats noted above, we chose a hole-diameter of roughly 1 mm for our first measurements of the vapor pressure of iron using the effusion cell. These measurements fall roughly a factor of five below the “best” available liquid or solid iron vapor pressure data [2], as can be seen in Figure 2 below.

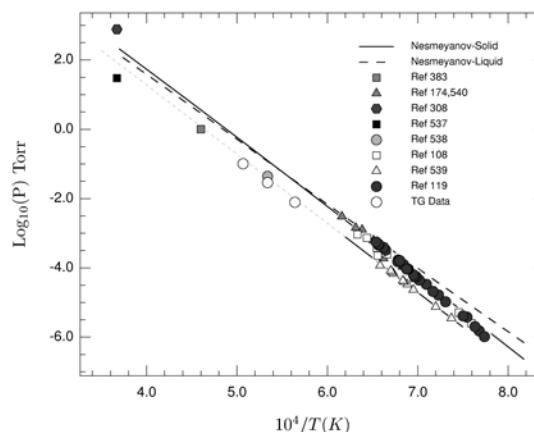


Figure 2. Preliminary measurements of the vapor pressure of iron (open circles) compared to data available in the literature.

Note that there are very few measurements of the vapor pressure of iron above about 1600K. Note as well that there is one set of data taken at lower temperatures that falls below the rest of the available data. This data set extrapolates quite nicely to higher temperatures, and goes cleanly through our data as well as three of the four older, higher temperature measurements available in Nesmeyanov [2]. In March, we will present iron vapor pressure data taken using a variety of hole sizes over the temperature range from 1975K down to approximately 1100K in vacuum.

References: [1] Schick H. L. (1960) *Chem. Rev.* 60, 331 - 362. [2] Nesmeyanov A. N. (1963) *Vapour Pressure of the Elements (translated by J. I. Carasso), (Academic Press, NY)* pp.149 - 157. [3] Nesmeyanov, A. N. *Ibid.* pp.380 - 385.