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Vapor Pressure of Palladium from 1473 K to 1973 K

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The vapor pressure of palladium was studied using a Knudsen effusion cell and a commercial thermogravimetric balance. Vapor pressures were measured using four Knudsen cells of different effusion areas with consistent results. Most of the available vapor pressure data for palladium has been taken below the fusion temperature, and only a few experimental studies exist on the vapor pressure of liquid palladium. In this current study, vapor pressures were measured from 1473 K to 1973 K (from well above and well below the melting point). In addition, the range in temperature covered in the current study represents one of the largest continuous investigations of palladium vapor pressure to date. The standard enthalpy of sublimation calculated via a third-law analysis of the vapor pressure data is (377.7 ± 0.2) kJ·mol^{-1}, in excellent agreement with the recommended value of (377 ± 5) kJ·mol^{-1} from the most recent review of available palladium vapor pressure data.

Introduction

This laboratory has recently begun measuring the vapor pressures of various refractory materials using the well-established Knudsen effusion method and a commercial thermogravimetric (TG) balance. The goal in these studies is to provide vapor pressure data on high-temperature species that can be used to unravel the condensation histories of meteorites and dust grains in the universe. In a recent test to confirm the accuracy of the equipment and methods used in these studies, the vapor pressure of palladium was measured both above and below its melting point. Although there is reasonable agreement among the available vapor pressure data for palladium, most of these data have been taken below the fusion point and only a handful of vapor pressure studies have been made with liquid palladium. To our knowledge, the work reported herein represents the largest continuous span of vapor pressure data taken for both the solid and liquid condensed phases of palladium.

Again, the goal in performing these studies is to provide vapor pressure data on numerous, high-temperature species that can be utilized to help understand the formation histories of solid material in the universe. Palladium was studied because it has several attractive features that make it an ideal candidate to test the current experimental system. Namely, palladium is available in high purity; it has an appropriate vapor pressure for Knudsen cell studies in the desired temperature range (up to approximately 2000 K); the vapor is essentially monatomic;[1] and there is reasonable agreement among most of the available experimental vapor pressure data sets. Another important characteristic of palladium is that the condensed phases are resistant to oxidation at elevated temperatures. Between (350 and 790) °C, palladium can form a thin oxide coating, but above this temperature, this oxide layer decomposes by liberating oxygen, leaving behind the clean, shiny metal. Many of the platinum group metals form oxides in the gas phase under oxygen atmospheres that contribute to an apparent enhanced volatility. Of these platinum group metals, palladium shows the least enhanced volatility. For example, palladium evaporation is enhanced by 20 % in the presence of oxygen whereas the enhancement of platinum is a factor of approximately 10 000.[2] Because of these attractive physical properties, palladium was chosen as a test of the current system. Due to the wide temperature range of the current data and the excellent agreement with previous vapor pressure studies of palladium, the results of this study are reported in this paper.

Experimental Equipment

A detailed description of the experimental apparatus and procedure has been given in a previous work with iron, and the reader may refer to this for additional details.[3] The equipment and experimental procedure used in the current study are very similar to the iron investigation with the exception of three significant modifications in the experimental equipment that will be described later in detail.

A schematic diagram of the system used in this work is shown in Figure 1. The balance used in this work is a CAHN TG2171 that can be operated to a maximum temperature of 1973 K and is able to accept sample sizes as large as 0.1 kg with microgram sensitivity. Sample cells were suspended from a thin, alumina rod attached to one arm of the TG balance. During operation, the cell was placed within the 99.8 % alumina reactor tube of the balance. This tube has an approximately 3.5·10^{-4} m^3 volume and 2.54 cm inner diameter. Knudsen cells are therefore limited in diameter to approximately 1.27 cm.

The sample section of the reactor tube is heated within the cylindrical, insulated furnace section of approximately 30 cm height and 23 cm diameter. Within this insulated section are six, U-shaped, molybdenum disilicide resistive heating elements of approximately 20 cm length. These elements are equally spaced around the circumference of the reactor tube. Because these elements are heated in series and are equally spaced around the reactor tube, the possibility of radial temperature gradients within the sample area is very low. To minimize the possibility of axial temperature gradients, the lower part of the cell (containing the metal sample) is positioned in the middle of

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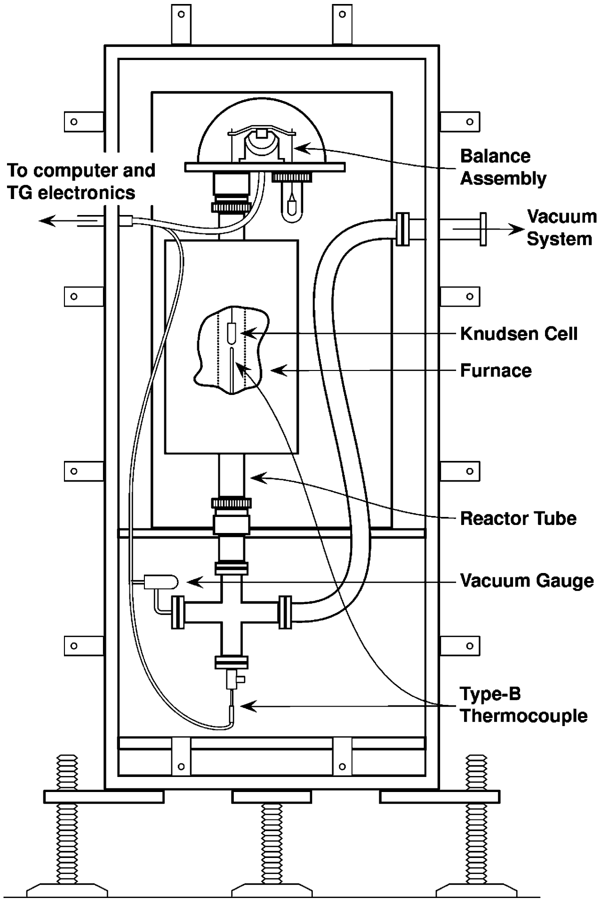

Figure 1. Schematic diagram of the thermogravimetric balance and furnace assembly. The entire furnace and balance assembly is within a metal enclosure that can be purged with nitrogen. Vacuum and electrical connections are made through sealed ports in the sides of the enclosure.

the heated zone and the cell height is much smaller than the total height of the furnace hot zone. During an experiment, the balance region and reactor tube volume were pumped using both mechanical and turbomolecular pumps and vacuum was maintained at a level of 10^{-3} Pa or lower throughout the measurements. The sample cell temperature was measured using an alumina-sheathed, type-B thermocouple which was positioned just under the bottom of the sample cell.

Mass measurements were recorded continuously throughout the experiment, and individual isothermal times were similar to those with iron and could range from (30 to 45) min at the highest temperatures to 4 h or more at the coolest temperatures. For iron, mass data were taken once per second. In the current work with palladium, this sampling frequency was doubled. This large amount of data was reduced and smoothed by taking averages over 2 min intervals. Rates of mass loss and temperature change were calculated from differences in these 2 min averages. To eliminate transient regions between isothermal periods or periods of time where the temperature was not sufficiently steady, periods of mass loss were only selected for further processing if the temperature fluctuation remained below 0.25 $K\cdot min^{-1}$. For each of these isothermal periods or temperature "plateaus," all of the associated 2 min mass loss rates were averaged to compute a mean mass loss rate for the isotherm. These values could also be calculated by simply taking the differences between the beginning and ending masses for the isotherm and dividing by the isothermal time. By taking several averages and calculating a mean mass loss rate, the standard deviation of the mean also provides an indication of the quality of the measurement. At low temperatures where the mass loss rate is small and the noise level of the balance is approached, deviations in the mean mass loss rate can become larger and contribute to larger error levels in the calculated vapor pressures. These raw data on the mass loss rates with time were then converted to vapor pressure data as outlined in the section on vapor pressure calculation. As noted earlier, there have been three modifications to the system over that used for iron, and each of these changes is described in the following subsections.

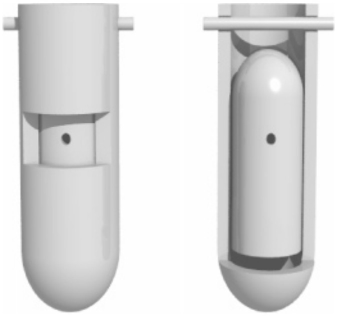

Figure 2. Alumina effusion cell constructed from closed-end tubes. A small amount of zirconia adhesive is used at the top of the smaller tube to seal the thin gap between the two tubes.

Cell Design. In the previous work with iron, the Knudsen cell was formed from two, closed-end, 99.8 % alumina tubes of differing diameters. The tube sizes were chosen such that the smaller tube (with a nominal inside diameter of 6.35 mm and outside diameter 9.53 mm) would fit snugly within the larger tube (with a nominal inside diameter of 9.53 mm and 12.7 mm outside diameter). The Knudsen cell orifice was drilled in the closed end of one of the tubes at a 45° angle to the tube centerline. A finite wall thickness (as opposed to an infinitely thin, knife-edged orifice) causes impedance to the flow of molecules from the cell. Corrections can be applied to account for this wall thickness impedance, but accurate measurement of this wall thickness is extremely crucial. Correction factors based on the experimental work of Clausing[4,5] are applied to the raw data, and these factors depend on the ratio of the cell wall thickness at the effusion orifice to the radius of the effusion orifice. Most alumina tubes vary slightly due to the casting process, but it was reasoned that the closed end could potentially be more susceptible to variations in wall thickness. Additionally, the wall thickness is much harder to measure at this location.

To lessen these potential errors, the cell has been modified to the one illustrated in Figure 2. The cell has a comparable height to the cells used with iron (approximately 5.5 cm overall length), but the Knudsen orifice has been placed at approximately $^{2}/_{3}$ of the height of the small tube and 90° to the tube centerline instead of the top. In addition, previous cells used a 1 mm molybdenum wire to attach to the hang down assembly of the TG balance. In some cases, after multiple runs lasting for several days, a slight thinning of this molybdenum wire was observed, possibly due to the gradual formation of the volatile molybdenum oxide. As a result, this metal loop was eliminated in the new cell design. The loop was replaced with a single thin rod of alumina placed through the top of the outer alumina cylinder. Nearly all of the components of the new cell and hang down assembly in the hot zone of the furnace have been replaced with 99.8 % alumina. The only exception is the zirconia adhesive (Resbond 904, Cotronics Corporation) used to additionally seal the thin gap between the two tubes. This adhesive is placed at the top of the smaller tube and at the edges of the window of the larger tube where the orifice is located. An effort is made to use the minimum amount of this adhesive as is necessary to still achieve a good seal. As in the case with the previous iron cells, once the tube is sealed, it cannot be reopened and recharged.

Measurement of Orifice Diameters. The accurate measurement of the Knudsen diameter is an important factor in processing the vapor pressure data. This measurement has been improved by measuring the diameters from digitized video images taken from an optical microscope. Sample cells are fixed in an X−Y traveling, micrometer-resolution stage under the microscope, and the orifice diameter is measured from the change in stage position as the edges of the effusion orifice pass a reference point on the video screen. This method allows for much better accuracy in the orifice measurement, and the estimated the error in the hole size measurement is now ±0.02 mm.

Nitrogen Purge. The alumina reactor tube which encompasses the cell within the furnace hot zone is sealed with an O-ring at the top/bottom collars. Because this alumina reactor tube is heated to nearly 2000 K, the lowest operating vacuum level set by the balance manufacturer is approximately 10^{-3} Pa and this was the level of vacuum used in the experiments reported here. The current apparatus will be used with metals or other materials, and it would be beneficial to reduce the possibility of oxidation by reducing this partial pressure of oxygen even further. To achieve this, the furnace and balance assembly are placed within an enclosure that may be purged with nitrogen from the vent of a liquid nitrogen dewar.

A schematic of this enclosure is shown in Figure 1. The entire balance and furnace assembly has been placed within this enclosure, and the front is sealed with a sheet of Plexiglas. This sheet of Plexiglas is compressed against the front frame of the cart using a number of metal fasteners, depicted in the diagram as the small rectangular sections around the perimeter of the front of the enclosure. Electrical and vacuum connections are made through ports on the side of this enclosure. During a run, the balance and reactor tube are evacuated and the nitrogen flow rate is increased until there is a slight positive pressure within the enclosure as measured with a very sensitive flow meter. Although oxidation is not expected to play a role with palladium, and purging with nitrogen should not be necessary, experiments were taken with both the previous setup (unpurged) and with the new nitrogen purge to verify that the two systems gave identical results.

Experimental Procedure

After the components of a cell were constructed, a sample of high-purity (99.95 %) palladium was placed within the tubes and the seam at the top of the cell was covered with a relatively thin layer of the zirconia adhesive. The cell was then allowed to dry at room-temperature overnight. Prior to placing the cell in the furnace, the diameter of the effusion orifice was measured using the microscope and digital camera system described previously. The cell was then placed on the sample side of the balance, and the reactor tube was sealed and evacuated. If the nitrogen purge system was used, the flow of nitrogen gas was also started at this time. The cell was then raised to a temperature of 200 °C and held at this temperature for an hour to remove any possible volatiles. Afterward, the cell temperature was raised to 800 °C and held at this temperature until the weight signal was steady, indicating no mass loss. The cell was then heated to high temperatures, and the mass of the effusion cell was constantly monitored over time. Experimental runs purged with nitrogen were limited by the capacity of the liquid nitrogen dewar and typically lasted 48 h while runs made without this purge could last somewhat longer.

Vapor Pressure Calculation

Vapor pressure data for palladium were calculated from the rate of mass loss measurements using the following equation[4−7]

$$P_{\mathrm{m}} = \left[\frac{\mathrm{d}m}{\mathrm{d}t}\right]\frac{1}{W_{\mathrm{B}}B}\sqrt{\frac{2\pi RT}{M_{\mathrm{w}}}} \tag{1}$$

In eq 1, P_{m} is the measured vapor pressure, ($\mathrm{d}m/\mathrm{d}t$) is the rate of mass loss, B is the cross sectional area of the effusion orifice, R is the ideal gas constant, T is the temperature, and M_{w} is the molecular weight of the evaporating material. If the Knudsen cell has some finite wall thickness at the orifice location instead of being an infinitely thin sheet, then there is the possibility of back-reflection of molecules through this short "pipe" rather than transmission through a knife-edged orifice. Correction factors for this reduction in transmission through a cylinder have been tabulated by Clausing,[4] and an empirical fit to the data has been given by Kennard.[5] For a hole depth (wall thickness) denoted by l and the radius of the hole denoted by a, the Clausing correction factor, W, is given by[5]

$$W = \frac{1 + 0.4(l/a)}{1 + 0.95(l/a) + 0.15(l/a)^2} \tag{2}$$

In eq 1, W_{B} denotes this Clausing factor for the Knudsen cell orifice.

As vapor effuses from the orifice, the loss of vapor must disturb the equilibrium between the vapor and the condensed phase within the cell. The relation between this true, equilibrium vapor pressure, P_{eq}, and the measured pressure, P_{m}, is given by the Whitman−Motzfeldt equation[6,7]

$$P_{\mathrm{eq}} = \left[1 + f\left(\frac{1}{\alpha} + \frac{1}{W_{\mathrm{A}}} - 2\right)\right]P_{\mathrm{m}} \tag{3}$$

The term α is the evaporation accommodation coefficient (assumed to be 1 for palladium), and W_{A} is the Clausing factor for the Knudsen cell. The factor f in eq 3 is given by

$$f = \frac{W_{\mathrm{B}}B}{A} \tag{4}$$

where A is the cross-sectional area of the Knudsen cell. In summary, for a particular Knudsen cell geometry, eqs 1 to 4 are used to calculate the vapor pressure of palladium from experimentally measured values of the cell temperature and the rate of mass loss.

In a previous work with iron, the equilibrium vapor pressure values were calculated using a slightly different set of equations. In particular, the cell Clausing factor was not included in the previous data treatment. The values for the palladium vapor pressures calculated by eqs 1 through 4 are approximately 3 % higher than the values that would be calculated using the same equations as given in the previous study with iron.[3]

Estimation of Uncertainties

In this work, vapor pressure data were calculated from the measured temperature, the measured mass loss rates, and from factors related to the cell geometry (effusion orifice diameter, wall thickness, etc.). The molecular weight of palladium used in the vapor pressure calculation was 106.421 taken from the IUPAC technical report published in 2003.[8] In a previous study with iron, the accuracy of the type-B thermocouple was checked by measuring the melting point of iron. In this test, a hole was drilled through a small sample of iron and a loop of molybdenum wire was threaded through this hole. The iron piece was then suspended from the hang down assembly in the same location as the sample cell is normally located. The temperature was then raised slowly near the fusion temperature of iron. As the iron sample melted and fell from the molybdenum loop, the balance indicated a quick drop in mass and the temperature of this drop was recorded. In this check, the fusion temperature was found to be within 1 K of the currently accepted iron fusion temperature 1811 K.[3] Therefore, estimated uncertainties in the thermocouple measurement are assumed to be similar to those associated with type-B thermocouples, approximately ±5 K.

In calculating the effusion area and the Clausing factor for the cell orifice, the orifice diameter and length are needed. As noted previously, the measurement of the orifice diameter has been improved and the estimated uncertainty in this quantity is ±0.02 mm. In all of the experimental runs with palladium, the wall thickness of the effusion cell was (1.27 ± 0.02) mm. In eq 3, the geometry of the cell interior must be known to calculate W_A and A for the cell. The inner diameter of the tube is (6.3 ± 0.2) mm while the height from the evaporating surface to the effusion orifice is estimated as (10 ± 2) mm.

Finally, as noted earlier, the mass loss rate for a given isothermal period is calculated from the series of 2 min averages for the sample period, and the mass loss rate is taken as the mean of these individual loss rates with an estimated error taken as the standard deviation of this mean value. With the improvement in the orifice measurement in this work, the largest source of error is typically in the mass loss rate. Nevertheless, the contribution from all of the estimated uncertainties as noted above are computed in the computer program used to process the raw data using the formulas listed in the previous section, and this total error is used to set uncertainty estimates on the final vapor pressure values.

Experimental Results

Data for palladium were taken using both the original TG system and the system modified to purge the furnace with nitrogen as described earlier. In both systems, runs with two different effusion orifices were made to ensure consistency of the results with changing effusion areas. Specifically, runs with 1.27 mm and 2.06 mm effusion diameters were made with the original, unmodified TG system and runs with 1.30 mm and 1.96 mm effusion diameters were made with the purged system. The collected vapor pressure results are presented in Table 1. Listed in Table 1 are the temperature of the isothermal period, the diameter of the effusion orifice, the calculated values for effusion orifice area, B, the Clausing factor for the effusion orifice, W_B, the cross-sectional area of the effusion cell, A, the Clausing factor for the Knudsen cell, W_A, the factor, f, as given in eq 4, the total mass lost during the isothermal period, the length of time of the isothermal period, the mass loss rate, the ratio of the equilibrium to measured vapor pressure, P_{eq}/P_m, and the calculated, equilibrium vapor pressure and estimated uncertainty in this value. The total mass loss and isothermal time are simple differences in these quantities at the beginning and end points of the isothermal period. These values were not used to compute the mass loss rate given in Table 1. As noted earlier, the mass loss rate was calculated from a series of mass loss rates taken over 2 min averages. The mean of these mass loss rates as well as the standard deviation of this mean value are listed in column 10 of Table 1. Values were calculated in this manner since the standard deviation of this mean value gave some indication of the error in these mass loss rates. In general, these deviations are small and the mass loss calculated by this averaging procedure is often identical to that calculated via dividing the total mass loss rate by the isothermal period. In cases where the mass signal is extremely small or if there is some initial lag in the change in the effusion rate as the temperature is changed, these values can exhibit large deviations and these values are rejected.

The data encompass the temperature range from (1473 to 1973) K and span approximately 3.5 orders of magnitude in vapor pressure. As a result, this current study represents one of the largest continuous experimental data sets on palladium vapor pressure ever collected. These data are also plotted in Figure 3, and much of the data have estimated error levels comparable to the size of the symbol used. In general, the higher temperature data exhibit less scatter and tend to have smaller error bars than the lower temperature points. Again, total mass loss rates at these lower temperatures are much smaller, and the measured mass loss rates are more susceptible to noise in the mass signal with time. To partially compensate for this diminished signal, the data points at these lower temperatures are collected over much longer times than at the higher temperature points, typically several hours. Also, at a given temperature, the total mass change is proportional to the effusion area so the very lowest points typically arise from cells with the larger effusion areas.

Weighted fits to the data above and below the fusion temperature have been calculated and are shown in Figure 3 as the solid, black lines. The code used to perform the weighted least-squares fit to the data was taken from ref 9, and weighting factors were constructed from the individual standard deviations of each point, $\sigma_{i.}$ Specifically, the weighting factor, w_i, for an individual point was taken as $w_i = (1/\sigma_i^2)$. One advantage in using this routine is that in addition to the fit parameters it also provides uncertainty estimates in these computed values based on the estimated uncertainty levels of the individual points.

Using the fusion temperature 1828 K reported by Arblaster gives[10]

(1473 to 1828) K:

$$\log_{10}(P(\mathrm{Pd_s})/\mathrm{Pa}) = (10.93 \pm 0.14) - \frac{18910 \pm 240}{T/\mathrm{K}} \tag{5}$$

(1828 to 1973) K:

$$\log_{10}(P(\mathrm{Pd_l})/\mathrm{Pa}) = (10.74 \pm 0.21) - \frac{18530 \pm 400}{T/\mathrm{K}} \tag{6}$$

Both fits have an $r^2 = 0.99$. Also shown in Figure 3 as the short, dashed line is the most recent compilation of palladium vapor pressure published by Arblaster in 1995.[10] As is seen in the plot, the agreement between the data reported by Arblaster and the current experimental study is extremely good.

Using thermodynamic data also compiled by Arblaster, the standard enthalpy of sublimation (1 bar standard state pressure), $\Delta_{sub}H°$ (298.15 K), of palladium was calculated for each data point in Table 1 using a third-law analysis. These enthalpies and their estimated uncertainties are given in the last column of Table 1. In these calculations, it is assumed there is negligible error in the thermodynamic data used and the reported uncertainty is due entirely to the uncertainty reported in the corresponding pressure value. The mean value for $\Delta_{sub}H°$ (298.15K) calculated from the data is (377.7 ± 0.2) kJ·mol^{-1} where the estimated uncertainty is taken as the standard deviation of this mean value. A second-law analysis of the data

Table 1. Experimental Data for Palladium Vapor Pressure Measurements

T K	d mm	B mm^2	W_B	A mm^2	W_A	f	mass loss mg	t s	loss rate $mg\cdot min^{-1}$	P_{eq}/P_m	P_{eq}/P_a	$\Delta_{sub}H°$ (298.15 K) $kJ\cdot mol^{-1}$
1473	1.96	3.01	0.611	31.7	0.412	0.0581	0.481	21480	0.001 ± 0.001	1.083	0.01 ± 0.01	380 ± 10
1498	1.96	3.01	0.611	31.7	0.412	0.0581	0.216	5280	0.002 ± 0.001	1.083	0.02 ± 0.01	377 ± 7
1523	1.96	3.01	0.611	31.7	0.412	0.0581	0.533	10320	0.003 ± 0.001	1.083	0.03 ± 0.01	380 ± 5
1548	1.96	3.01	0.611	31.7	0.412	0.0581	1.832	15240	0.007 ± 0.003	1.083	0.06 ± 0.02	375 ± 5
1573	1.96	3.01	0.611	31.7	0.412	0.0581	0.766	4440	0.010 ± 0.001	1.083	0.09 ± 0.01	377 ± 2
1576	2.06	3.32	0.622	31.7	0.412	0.0653	1.353	6960	0.012 ± 0.0010	1.093	0.09 ± 0.08	380 ± 10
1598	1.96	3.01	0.611	31.7	0.412	0.0581	0.653	2400	0.0162 ± 0.0009	1.083	0.141 ± 0.009	376.3 ± 0.9
1600	2.06	3.32	0.622	31.7	0.412	0.0653	0.782	3480	0.01 ± 0.01	1.093	0.11 ± 0.010	380 ± 10
1623	1.27	1.27	0.514	31.7	0.412	0.0206	0.567	3360	0.010 ± 0.004	1.029	0.2 ± 0.1	375 ± 6
1623	1.27	1.27	0.514	31.7	0.412	0.0206	0.682	2280	0.009 ± 0.008	1.029	0.2 ± 0.2	380 ± 10
1623	1.96	3.01	0.611	31.7	0.412	0.0581	0.532	1440	0.0221 ± 0.0008	1.083	0.193 ± 0.0010	377.7 ± 0.7
1626	2.06	3.32	0.622	31.7	0.412	0.0653	1.401	3360	0.025 ± 0.009	1.093	0.20 ± 0.07	378 ± 5
1648	1.96	3.01	0.611	31.7	0.412	0.0581	0.636	1200	0.0318 ± 0.0007	1.083	0.28 ± 0.01	378.3 ± 0.6
1650	2.06	3.32	0.622	31.7	0.412	0.0653	1.866	3360	0.03 ± 0.01	1.093	0.26 ± 0.09	380 ± 5
1660	1.27	1.27	0.514	31.7	0.412	0.0206	1.131	3360	0.020 ± 0.004	1.029	0.5 ± 0.1	374 ± 3
1673	1.27	1.27	0.514	31.7	0.412	0.0206	0.988	3480	0.017 ± 0.004	1.029	0.40 ± 0.09	379 ± 3
1673	1.27	1.27	0.514	31.7	0.412	0.0206	1.146	2520	0.019 ± 0.005	1.029	0.4 ± 0.1	377 ± 4
1673	1.96	3.01	0.611	31.7	0.412	0.0581	1.088	1440	0.045 ± 0.002	1.083	0.40 ± 0.02	378.9 ± 0.7
1676	2.06	3.32	0.622	31.7	0.412	0.0653	3.124	3360	0.06 ± 0.01	1.093	0.44 ± 0.09	378 ± 3
1685	1.27	1.27	0.514	31.7	0.412	0.0206	1.584	3360	0.028 ± 0.003	1.029	0.67 ± 0.09	374 ± 2
1698	1.27	1.27	0.514	31.7	0.412	0.0206	1.694	5280	0.02 ± 0.01	1.029	0.5 ± 0.3	382 ± 8
1698	1.30	1.32	0.519	31.7	0.412	0.0216	0.868	1560	0.033 ± 0.001	1.031	0.76 ± 0.06	375 ± 1
1698	1.96	3.01	0.611	31.7	0.412	0.0581	1.547	1440	0.065 ± 0.001	1.083	0.58 ± 0.02	379.3 ± 0.6
1700	2.06	3.32	0.622	31.7	0.412	0.0653	4.216	3360	0.075 ± 0.009	1.093	0.61 ± 0.07	379 ± 2
1706	1.27	1.27	0.514	31.7	0.412	0.0206	2.077	3360	0.037 ± 0.003	1.029	0.9 ± 0.1	375 ± 2
1723	1.27	1.27	0.514	31.7	0.412	0.0206	1.199	2400	0.030 ± 0.005	1.029	0.7 ± 0.1	381 ± 2
1723	1.27	1.27	0.514	31.7	0.412	0.0206	2.438	2400	0.051 ± 0.008	1.029	1.2 ± 0.2	374 ± 2
1723	1.30	1.32	0.519	31.7	0.412	0.0216	1.126	1440	0.047 ± 0.001	1.031	1.08 ± 0.08	376 ± 1
1723	1.96	3.01	0.611	31.7	0.412	0.0581	2.206	1440	0.092 ± 0.001	1.083	0.83 ± 0.03	379.5 ± 0.6
1726	2.06	3.32	0.622	31.7	0.412	0.0653	4.882	2520	0.116 ± 0.009	1.093	0.94 ± 0.08	378 ± 1
1740	1.27	1.27	0.514	31.7	0.412	0.0206	2.557	3240	0.047 ± 0.005	1.029	1.2 ± 0.1	378 ± 2
1748	1.27	1.27	0.514	31.7	0.412	0.0206	4.306	3960	0.065 ± 0.009	1.029	1.6 ± 0.2	375 ± 2
1748	1.30	1.32	0.519	31.7	0.412	0.0216	1.623	1440	0.068 ± 0.002	1.031	1.6 ± 0.1	376 ± 1
1748	1.96	3.01	0.611	31.7	0.412	0.0581	2.370	1080	0.1318 ± 0.0009	1.083	1.20 ± 0.04	379.5 ± 0.5
1750	2.06	3.32	0.622	31.7	0.412	0.0653	9.302	3480	0.16 ± 0.01	1.093	1.31 ± 0.09	379 ± 1
1773	1.27	1.27	0.514	31.7	0.412	0.0206	3.782	2520	0.081 ± 0.005	1.029	2.0 ± 0.2	377 ± 1
1773	1.30	1.32	0.519	31.7	0.412	0.0216	2.249	1440	0.094 ± 0.002	1.031	2.2 ± 0.2	376 ± 1
1776	2.06	3.32	0.622	31.7	0.412	0.0653	10.068	2520	0.24 ± 0.01	1.093	2.0 ± 0.1	378 ± 1
1798	1.27	1.27	0.514	31.7	0.412	0.0206	5.552	3480	0.10 ± 0.01	1.029	2.4 ± 0.4	380 ± 2
1798	1.30	1.32	0.519	31.7	0.412	0.0216	3.450	1680	0.123 ± 0.002	1.031	2.9 ± 0.2	377 ± 1
1800	2.06	3.32	0.622	31.7	0.412	0.0653	18.116	3360	0.32 ± 0.01	1.093	2.7 ± 0.1	378.4 ± 0.7
1802	1.27	1.27	0.514	31.7	0.412	0.0206	4.143	2520	0.10 ± 0.02	1.029	2.4 ± 0.4	380 ± 3
1806	1.27	1.27	0.514	31.7	0.412	0.0206	3.770	3240	0.07 ± 0.04	1.029	2 ± 1	387 ± 9
1823	1.27	1.27	0.514	31.7	0.412	0.0206	6.827	2400	0.162 ± 0.007	1.029	4.0 ± 0.3	377 ± 1
1825	2.06	3.32	0.622	31.7	0.412	0.0653	17.679	2400	0.442 ± 0.006	1.093	3.7 ± 0.1	378.7 ± 0.6
1840	1.27	1.27	0.514	31.7	0.412	0.0206	3.383	1080	0.189 ± 0.006	1.029	4.7 ± 0.4	378 ± 1
1840	1.27	1.27	0.514	31.7	0.412	0.0206	6.721	2160	0.186 ± 0.006	1.029	4.7 ± 0.4	378 ± 1
1848	1.27	1.27	0.514	31.7	0.412	0.0206	11.030	3480	0.191 ± 0.009	1.029	4.8 ± 0.4	379 ± 1
1850	2.06	3.32	0.622	31.7	0.412	0.0653	35.342	3360	0.63 ± 0.01	1.093	5.3 ± 0.2	378.0 ± 0.6
1860	1.27	1.27	0.514	31.7	0.412	0.0206	13.543	3360	0.242 ± 0.006	1.029	6.1 ± 0.5	378 ± 1
1873	1.27	1.27	0.514	31.7	0.412	0.0206	12.425	2400	0.3 ± 0.2	1.029	8 ± 4	377 ± 8
1873	1.27	1.27	0.514	31.7	0.412	0.0206	13.006	2520	0.301 ± 0.006	1.029	7.6 ± 0.6	377 ± 1
1883	1.27	1.27	0.514	31.7	0.412	0.0206	8.271	1920	0.26 ± 0.02	1.029	6.6 ± 0.7	381 ± 2
1885	1.27	1.27	0.514	31.7	0.412	0.0206	12.983	2400	0.324 ± 0.008	1.029	8.2 ± 0.6	378 ± 1
1898	1.27	1.27	0.514	31.7	0.412	0.0206	12.456	1920	0.4 ± 0.3	1.029	10 ± 7	380 ± 10
1898	1.27	1.27	0.514	31.7	0.412	0.0206	14.878	2400	0.372 ± 0.007	1.029	9.4 ± 0.7	378 ± 1
1900	2.06	3.32	0.622	31.7	0.412	0.0653	55.464	2880	1.16 ± 0.01	1.093	9.8 ± 0.3	377.7 ± 0.6
1910	1.27	1.27	0.514	31.7	0.412	0.0206	17.143	2400	0.429 ± 0.006	1.029	10.9 ± 0.8	378 ± 1
1912	2.06	3.32	0.622	31.7	0.412	0.0653	31.167	1440	1.30 ± 0.01	1.093	11.1 ± 0.4	377.9 ± 0.6
1923	1.27	1.27	0.514	31.7	0.412	0.0206	16.633	1920	0.5 ± 0.1	1.029	13 ± 3	377 ± 4
1923	1.27	1.27	0.514	31.7	0.412	0.0206	16.790	1800	0.551 ± 0.005	1.029	14 ± 1	376 ± 1
1925	2.06	3.32	0.622	31.7	0.412	0.0653	46.735	1920	1.46 ± 0.02	1.093	12.5 ± 0.4	378.4 ± 0.6
1940	1.27	1.27	0.514	31.7	0.412	0.0206	25.119	2520	0.598 ± 0.008	1.029	15 ± 1	378 ± 1
1942	2.06	3.32	0.622	31.7	0.412	0.0653	69.314	2280	1.82 ± 0.01	1.093	15.7 ± 0.5	377.8 ± 0.6
1948	1.27	1.27	0.514	31.7	0.412	0.0206	21.637	1800	0.7 ± 0.2	1.029	18 ± 5	376 ± 5
1948	1.27	1.27	0.514	31.7	0.412	0.0206	26.379	2400	0.659 ± 0.007	1.029	17 ± 1	378 ± 1
1948	1.27	1.27	0.514	31.7	0.412	0.0206	28.308	2040	0.824 ± 0.009	1.029	21 ± 2	374 ± 1
1950	2.06	3.32	0.622	31.7	0.412	0.0653	60.581	1800	2.02 ± 0.01	1.093	17.4 ± 0.6	377.6 ± 0.6
1950	2.06	3.32	0.622	31.7	0.412	0.0653	61.479	1920	1.92 ± 0.02	1.093	16.6 ± 0.6	378.4 ± 0.6
1954	1.27	1.27	0.514	31.7	0.412	0.0206	70.595	5040	0.83 ± 0.03	1.029	21 ± 2	375 ± 1
1963	1.27	1.27	0.514	31.7	0.412	0.0206	24.545	1920	0.768 ± 0.006	1.029	20 ± 1	378 ± 1
1963	2.06	3.32	0.622	31.7	0.412	0.0653	23.270	600	2.33 ± 0.02	1.093	20.1 ± 0.7	377.5 ± 0.6
1965	2.06	3.32	0.622	31.7	0.412	0.0653	37.429	960	2.34 ± 0.03	1.093	20.3 ± 0.7	377.7 ± 0.6
1965	2.06	3.32	0.622	31.7	0.412	0.0653	70.724	1800	2.36 ± 0.01	1.093	20.4 ± 0.7	377.7 ± 0.6
1970	1.27	1.27	0.514	31.7	0.412	0.0206	15.490	1080	0.9 ± 0.3	1.029	24 ± 9	376 ± 6
1972	1.27	1.27	0.514	31.7	0.412	0.0206	18.866	1320	0.86 ± 0.02	1.029	22 ± 2	378 ± 1
1973	1.27	1.27	0.514	31.7	0.412	0.0206	17.153	1200	0.859 ± 0.0010	1.029	22 ± 2	378 ± 1
1973	1.27	1.27	0.514	31.7	0.412	0.0206	24.020	1560	0.9 ± 0.1	1.029	24 ± 3	376 ± 2
1973	2.06	3.32	0.622	31.7	0.412	0.0653	75.160	1920	2.35 ± 0.09	1.093	20 ± 1	379.1 ± 0.8

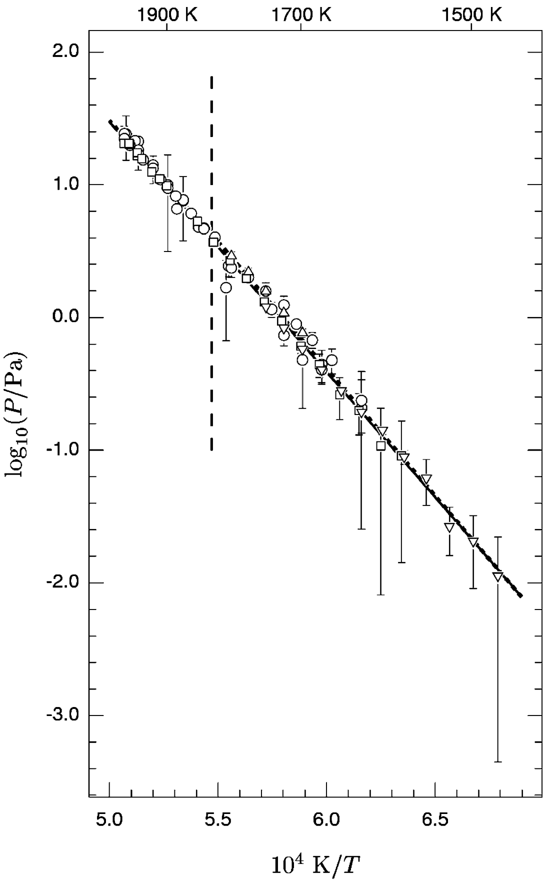

Figure 3. Measured vapor pressure for palladium for various effusion cell orifice diameters. Shown in the figure are data points for the following: ○, 1.27 mm orifice size; and □, 2.06 mm orifice size taken with the original thermogravimetric (TG) system. Data taken with the nitrogen-purged TG system are also shown for the following: △, 1.30 mm orifice; and ▽, 1.96 mm orifice. The fits to the current experimental data are shown as the solid line while the recommended values from Arblaster are shown as the dashed line. The fusion temperature of palladium is denoted by the vertical dashed line.

yields $\Delta_{\mathrm{sub}}H°$ (298.15 K) = (378 ± 8) kJ·mol^{-1} and (372 ± 5) kJ·mol^{-1} for the data above and below the fusion temperature, respectively, in reasonably close agreement with the third-law value.

As a further check on the consistency of the results, the fusion enthalpy of palladium was also calculated from the two fits given in eqs 5 and 6. In theory, it is possible to calculate the enthalpy of fusion from the difference in slopes of the data above and below the fusion temperature. In Arblaster's compilation, this value is reported as 16.1 kJ·mol^{-1} while the enthalpy of vaporization at this temperature is approximately 364 kJ·mol^{-1}. Therefore, there is an approximately 4 % change in the slope at the fusion point. This is a very small change and being able to accurately detect this small difference would seem to demand very high precision in the experimental data. In this work, the fusion enthalpy calculated from the difference in the vapor pressure slopes is 7.7 kJ·mol^{-1}, approximately half the value reported by Arblaster. Although both fits to the data reported in this work are very good, it should be noted that the estimated uncertainty in this calculated difference is comparable with the value itself. A similar problem exists with trying to calculate the fusion temperature. The fusion temperature is calculated as the intersection point of two, nearly parallel, lines, making it highly sensitive to any errors. The intersection point predicted by eqs 5 and 6 is 1951 K. Although this is well above the actual fusion temperature of palladium, it is similar to the findings of Bharadwaj et al. where they computed the fusion temperature from their fits to their palladium vapor pressure data to be 1925 K.[11] So, in summary, it appears there is a slight change in slope near the fusion temperature associated with the enthalpy of fusion, although making definitive assessments of this value appear to be beyond the scope of the precision of the current data.

Previous Experimental Works

The vapor pressure of palladium was first measured in 1958 using the Knudsen method by Haefling and Daane and the third law heat of sublimation was found to be $\Delta_{\mathrm{sub}}H°$ (298.15 K) = 352.9 kJ·mol^{-1}.[12] These early vapor pressure data were later found to be significantly higher than other experimental studies, and it is theorized that these higher values were likely due to cracks in the graphite/tantalum cell used by Haefling and Daane, thereby contributing to a higher apparent vapor pressure.[13] A subsequent Langmuir free evaporation study by Walker et al. gave a $\Delta_{\mathrm{sub}}H°$ (298.15 K) that was approximately 30 % higher than that of Haefling and Daane.[14] These authors noted that the $\Delta_{\mathrm{sub}}H°$ (298.15 K) calculated from their own data and also that of Haefling and Daane showed variations with temperature, indicating the likelihood of some type of systematic error in both works. Some time later it was discovered that the likely cause of the variation in the data of Walker et al. was a change in the calibration with temperature of the balance used.[15] In this later work, this drift was corrected and the palladium vapor pressure was again measured. Nevertheless, this large discrepancy between these two early data sets prompted Dreger and Margrave to perform another Langmuir study of palladium vapor pressure and the authors found $\Delta_{\mathrm{sub}}H°$ (298.15 K) to be between those reported by Walker et al. and Haefling and Daane.[13] In 1961, Alcock and Hooper studied the increased volatility of the platinum group metals under oxygen atmospheres and provided vapor pressure data for palladium from (1675 to 1775) K.[2] These data were also in rough agreement with the results of Dreger and Margrave. During the mid-1960s, several other palladium vapor pressure reports appeared that confirmed vapor pressure values consistent with Dreger and Margrave's results. In 1964, Zavitsanos reported results from a Knudsen cell study[16] while both Norman et al.[17] and Trulson and Schissel[1] reported results from Knudsen cell, mass spectroscopic studies in 1965. In addition, Trulson and Schissel reported that a mass spectroscopic scan up to 1748 K showed that palladium vapor was essentially monatomic.[1]

In 1973, Hultgren et al. compiled and reviewed the available vapor pressure data taken to date.[18] On the basis of their review of the data they estimated $\Delta_{\mathrm{sub}}H°$ (298.15 K) = (376 ± 5) kJ·mol^{-1}. In 1995, this palladium data compilation was revised in the very comprehensive report by Arblaster.[10] This report included vapor pressure data taken by atomic absorption,[19] evaporation,[20] Langmuir free evaporation,[13−15,21] Knudsen effusion,[11,12,16] Knudsen effusion combined with mass spectrometry,[17,22−25] the transport method,[2] and finally by torsion effusion.[26−28] Using the additional vapor pressure and updated thermodynamic data taken since the Hultgren et al. report, Arblaster revised the value of $\Delta_{\mathrm{sub}}H°$ (298.15 K) up slightly to (377 ± 5) kJ·mol^{-1}. Many of the recent studies on palladium vapor pressure have been taken using the Knudsen effusion mass spectrometry method and have focused on this metal since noble metals are produced as fine metallic inclusions in fission reactors and these noble metals play an important role in the high-temperature chemistry occurring in the fuel and other fission products.[22−24] In addition, palladium has also been suggested as a calibration reference for mass spectroscopy.[25] The data from Kulkarni cover an extremely wide temperature range, 589 K, and 8 orders of magnitude in vapor pressure,[25] although the standard enthalpy of sublimation of 381.7 kJ·mol^{-1} calculated from their data is slightly higher than most of the other recent KEMS studies that range from (375.5 to 377.7) kJ·mol^{-1}.

Of the experimental works tabulated by Arblaster and used to calculate the recommended $\Delta_{\mathrm{sub}}H°$ (298.15 K) for palladium, only three works contain liquid palladium vapor pressures. These include the evaporative study of Taberko et al.,[20] the atomic absorption measurements by Bodrov et al.,[19] and the Knudsen effusion study by Bharadwaj et al.[11] In addition, all of the data of Taberko et al. was taken above the fusion temperature, ranging from (1828 to 2022) K. Bodrov et al. collected data for both the solid and liquid phases over a wide temperature range, (1511 to 2022) K, but there is a gap in their data for solid palladium from 1678 K to the melting point. In addition, the data taken by Bodrov et al. were collected via atomic absorption measurements and they depend on several factors that are not accurately known. In these studies, the effective absorption path length is typically not accurately known and, more seriously, the oscillator strengths for palladium vary widely. The calculated vapor pressure values are roughly proportional to the oscillator strength used, and Bodrov et al. report that this value ranges more than a factor of 10 in the literature from a low of 0.024 to a maximum value of 0.458. Bodrov et al. chose to use the published value of 0.036 for the oscillator strength since it gave the closest agreement between their vapor pressure results collected by atomic absorption and published palladium vapor pressure data.

Until now, the study by Bharadwaj et al. was the largest, continuous temperature span of vapor pressure data that was taken well above and below the palladium fusion point, from (1627 to 2040) K.[11] Both the work of Bharadwaj et al. and the data reported in this paper have been taken using the Knudsen effusion method over a nearly comparable temperature range, although the current span of data in this work is somewhat larger. It is interesting to note the close agreement between the third law enthalpy of sublimation values for these two works. Using the same thermodynamic data as reported by Arblaster, Bharadwaj et al. found $\Delta_{\mathrm{sub}}H°$ (298.15 K) = (377.2 ± 0.1) kJ·mol^{-1} for their data which is in excellent agreement with the value, (377.7 ± 0.2) kJ·mol^{-1}, reported in this work.

Summary

The vapor pressure of palladium has been measured using the Knudsen effusion method and a commercial, thermogravimetric balance. Experiments with other high-temperature species including pure metals are planned, many of which are susceptible to oxidation at these elevated temperatures. To circumvent this problem, the balance has been modified so that the entire furnace region may be continuously purged with nitrogen, thereby minimizing any oxidation of the sample. To test this modified system, these vapor pressure studies of palladium have been performed with the original and modified system. Palladium was chosen because the condensed phase is resistant to oxidation at elevated temperatures. Data for palladium vapor pressure were taken over an extensive temperature range and were in excellent agreement with other available vapor pressure data. In addition, data taken using both the original and nitrogen-purged systems gave identical results. The third-law standard heat of vaporization calculated from the current study was (377.7 ± 0.2) kJ·mol^{-1}, in excellent agreement with the current recommended value of (377 ± 5) kJ·mol^{-1}.

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