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Silicon Tetrafluoride Vapor Pressure Study

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September 2022

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Nuclear Nonproliferation Division

SILICON TETRAFLUORIDE VAPOR PRESSURE STUDY

D. E. Hanson
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September 2022

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ABBREVIATIONS

LAr	liquid argon
LN_2	liquid nitrogen
ORNL	Oak Ridge National Laboratory
psig	pounds per square inch gauge
PT	pressure transducer
RTD	resistance temperature detector
VP	vapor pressure

ABSTRACT

The vapor pressure (VP) of silicon tetrafluoride (SiF_4) was evaluated using three different cryogenic cold baths and multiple pressure transducers (PTs). Through this experiment, the known range of VP has been extended to a low temperature of 122 K. A functional relationship for the VP has been developed for the range between 122 and 159.6 K. This relationship was also used to estimate a VP value at 88 K, which was below observable levels with a 0.1 torr gauge.

1. INTRODUCTION

VP is the pressure exerted by a vapor in equilibrium with its condensed phase. SiF_4 exists in the solid phase at low temperatures. Previous experiments have been performed to measure the VP of solid SiF_4 at temperatures as low as 129 K [1]. However, no current data exists for VPs of solid SiF_4 at temperatures as low as liquid argon (LAr) or liquid nitrogen (LN_2) temperatures (88 K or 77 K, respectively). For use in practical applications, the VP at these low temperatures must be determined to verify if either coolant is a suitable mechanism for cold trapping SiF_4. For background, cold trapping is where gas is condensed and collected in a vessel via the use of some coolant. Cold trapping for this specific experiment is discussed further below, but a general objective of this method is to capture the gas and prevent vapors from being evacuated via a vacuum pump. Depending on the application, cold baths may be backed by a roughing pump (typically capable of creating vacuum in the 1×10^{-3} torr range) during operation. Thus, this experiment was performed to verify that the VP of SiF_4 is below the capabilities of a vacuum pump when cold trapped with various baths by determining VP values below the historical literature range and developing a new function for estimating the VP of SiF_4 at temperatures below the measurable range.

Experimental VP data for SiF_4 exists within published literature between 129 and 197.5 K [1], [2], [3]. The data from these experiments can be found in Figure 1. The agreement between the three data sets provides confidence in the reproducibility of the VP. This historical data serves as the basis of comparison for this work.

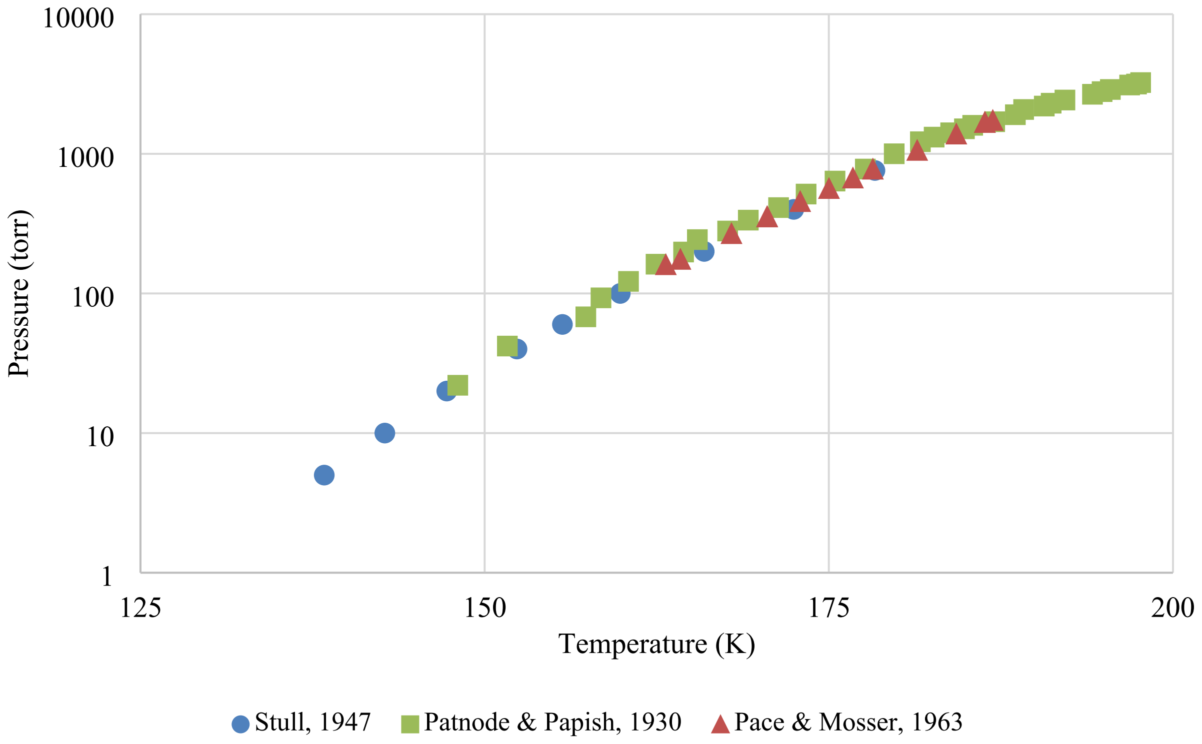

Figure 1. Historical SiF_4 VP data.

2. EXPERIMENTAL SETUP

A schematic of the experimental setup is shown in Figure 2. The SiF_4 was supplied from a compressed gas cylinder, which was fitted with a pressure regulator and housed in a gas cabinet for the duration of the experiment. The SiF_4 was transferred from the cylinder through stainless steel tubing into a dried and emptied test vessel, which was housed inside a laboratory hood. Due to the available lab space, existing tubing from the cabinet to the inside of the hood was used to connect the feed bottle and the test set-up. New tubing was used to connect from the existing piping inside the hood to the test vessel.

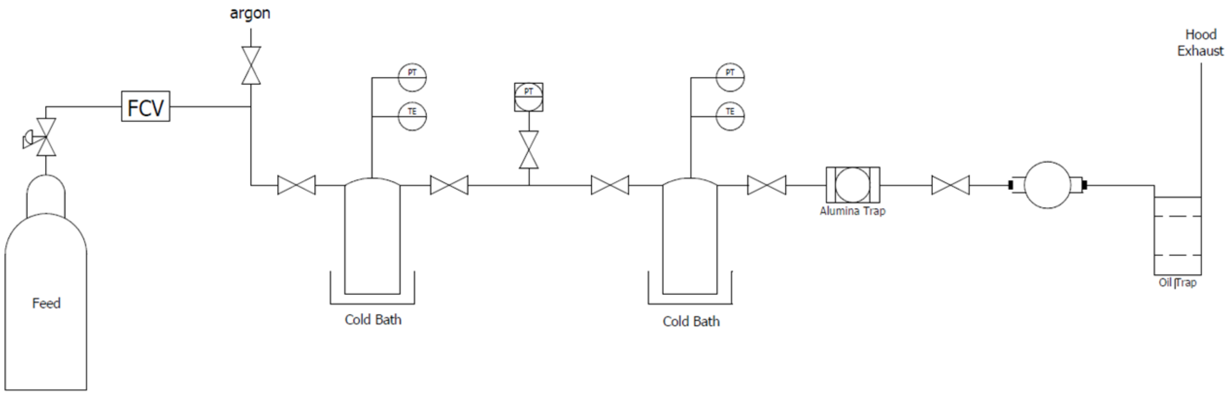

Figure 2. Process schematic for the VP experiments.

The test vessel was a small cylinder (approximately 9 in^3) with available ports for instrumentation and process connections. Exterior and interior views of the test vessel and its connections are shown in Figure 3. The test vessel was placed in the cold baths included in Table 1 to reduce the temperature of the SiF_4 to the desired points.

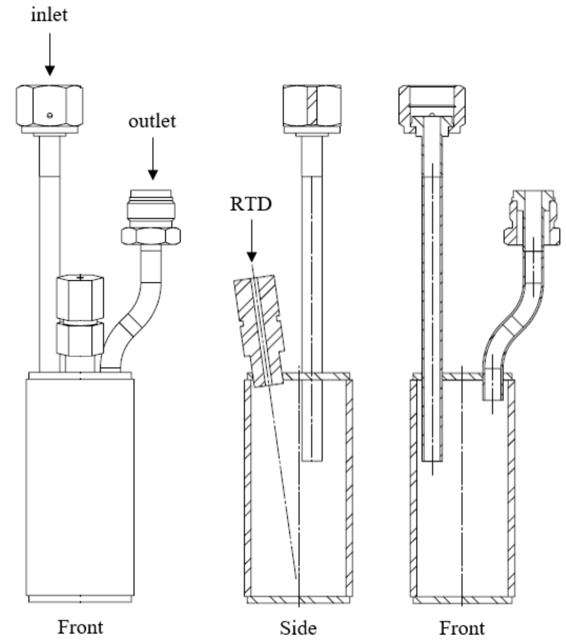

Figure 3. Test vessels used for the VP experiments.

Table 1. Cold bath composition

Cooling Agent	Solvent	Temperature (K)
LN_2	Isopentane	113
LAr	None	88
LN_2	None	77

Two test vessels connected in series were used in this experimental set up. The original intent was to use the first vessel to take VP measurements at various temperatures, and to use the second vessel as a cold trap to capture any excess process gas. The original intent of the system setup was disregarded after vacuum levels during testing indicated the secondary trap was not necessary to limit the amount of process gas released and the chemical trap was effective. This enabled either pressure vessel to be used for VP measurements. Throughout the experiment, the PTs were changed out several times to achieve better accuracy at different ranges. To minimize the amount of connection/disconnection from the process and exposure of the test equipment to atmosphere, the PTs were changed on the most convenient test vessel while keeping the other vessel under vacuum. This meant that throughout the experiment, both the first and second vessel were used to capture process gas for VP measurements. Downstream of the test vessels was a chemical trap filled with alumina media to capture process gas before it could reach the pump. Downstream of the chemical trap was a turbo pump, which was used to dry and evacuate the system throughout the test. Downstream of the pump was an oil trap to capture any excess material which may have passed through the chemical trap. The outlet of the oil trap was connected to the hood exhaust.

Four PTs were used throughout the experiment. The three PTs used to measure the pressure inside the test vessels at different stages throughout the experiment were a 100 torr (MKS AA02A Baratron) gauge, a 10 torr (MKS E27F Baratron), and a 0.1 torr (MKS E27F Baratron) gauge. The accuracies of these MKS PTs were ±0.10%, ±0.12%, and ±0.15% of the readings, respectively. The impact of these accuracies on the collected data proved to be insignificant, which will be discussed further in Section 4. A 925 Pirani vacuum gauge, with an accuracy of ±5% of the reading, was also used during the experiment, in-line between the two test vessels to verify vacuum throughout the system. The accuracy of this Pirani gauge was much lower than the gauges used in the vessels; however, since the purpose of this gauge was to verify system vacuum rather than collect process data, the accuracy of the gauge had no influence on the experiment. An analog pressure gauge upstream of the test vessels was used to measure the amount of gas added to the system. Three Class A PT100 resistance temperature detectors (RTDs), with a measurement accuracy of ± 0.55 °C, were used to measure temperature: one inside each vessel and one in the cold bath. The three RTDs were not changed during the experiment, but the position of the third was moved when a bath was changed to a different vessel. The RTDs indicated temperatures in degrees Celsius, and temperatures were then converted to Kelvin for analysis. Therefore, temperature measurement error is discussed in degrees Celsius throughout this document, while actual measured values are converted to Kelvin.

3. EXPERIMENTAL PROCEDURE

3.1 TEST VESSEL PREPARATION

The system was initially placed under vacuum following its assembly. Initially a roughing pump and (later) a turbomolecular pump were used to create the vacuum. Two different gauges were used to verify the level of the vacuum. Initially, a KJL-6000SS thermocouple gauge tube read by a KJL615TC-K digital display was used at the inlet of the roughing pump. This gauge was selected because it was already available in the lab and was meant to be a cost saver. The gauge was less accurate than desired, ±15% of the reading, and the indication was suspected to be high based on the capabilities of the pump. However, since the purpose of this gauge was simply to confirm system vacuum and not to collect process data, this was accepted. After several weeks of being connected to the operating pump, a system pressure of approximately 0.028 ± 0.004 torr was indicated. The roughing pump was then replaced with a turbo pump to maintain the vacuum and ensure the system was as dry as possible. The lowest system vacuum measured by the KJL-6000SS at the pump was approximately 0.021 ± 0.003 torr. Based on the capability of the roughing pump versus the turbo pump, the further decrease in pressure was expected, but the indicated value was still suspected to be high. The Pirani gauge was used to verify the level of the vacuum between the two test vessels. The Pirani gauge indicated a vacuum level on the order of 1×10^{-5} while on turbo vacuum, which is below the range of the KJL-6000SS. The Pirani indication confirmed the suspicion that the KJL-6000SS indication was a high offset value of the actual system vacuum. The Pirani also confirmed the system was sufficiently evacuated for the test.

The vacuum integrity of the system was evaluated with a helium leak test at different stages of the experiment. Prior to the introduction of any process gas, the system was dried and purged with argon gas, then placed under vacuum and evacuated. Throughout the experiment, if a line break was made the system was flushed with argon gas and evacuated for a period before reintroducing any process gas. The system was passivated after an argon flush by introducing a small amount of process gas into the system and allowing it to sit in the lines for a short period (several minutes) before being evacuated.

3.2 COLD BATH PREPARATION

The LN_2 and LAr were both purchased as cryogenic refrigerated liquids at 77 and 88 K, respectively, so no bath preparation was necessary for the colder temperature tests. To prepare the isopentane bath, the LN_2 was slowly poured into a dewar containing the solvent. The mixture was continuously stirred until a partially frozen (slush) consistency was achieved at the desired initial temperature. The composition of the mixture needed to be precise enough to achieve both the desired bath consistency and constant temperature. The addition of too much LN_2 would result in a mixture too thick to stir or maintain, and the addition of too little LN_2 would not achieve the desired initial bath temperature.

3.3 TEST METHOD

The SiF_4 gas was introduced into the system at room temperature. Gas was added to the system by slowly opening valves in series from the feed bottle up to the test vessel. A mass flow controller was used to control the flow rate of the gas. Feed was stopped when approximately 3 psig of gas was added to the test vessel. The applicable cold bath was prepared, and the test vessel was submerged in the cryogenic bath. Once the vessel was cooled and pressure indicated the bulk of the material had desublimed and was in the solid phase, the vessel was opened to the alumina trap and turbomolecular pump to remove a portion of the SiF_4 vapor, reaction byproducts, and any trace non-condensable gases, thus ensuring the pressure measured in the vessel was attributed only to SiF_4.

Isopentane was used to form the first cryogenic bath. The test vessel was submerged in the isopentane bath and allowed to cool for at least 15 min until the internal temperature was stable and within 5 °C of the bath temperature. The bath was then manually stirred at a relatively slow, constant rate and allowed to warm until the VP exceeded the range of the PT. This process was repeated for five separate runs using the 100 torr PT and four separate runs using the 10 torr PT. Testing durations were between 40 and 47 min (with an outlier of 58 min) using the 100 torr PT, and between 30 and 36 min using the 10 torr PT. The variation in test duration did not affect the resultant data as the pressure change was only dependent on temperature.

Due to the difficulty with the bath preparation and maintenance described in Section 3.2, this method of allowing the isopentane bath to warm in a controlled manner was preferable to attempting to maintain a constant temperature. To maintain a constant temperature, regular additions of LN_2 would need to be made as the bath would start to warm and, as stated previously, the LN_2 addition would need to be more precise than what was achievable with the set-up used to ensure the temperature and consistency were as desired. These additions would have resulted in unstable conditions within the vessel as a response to the constant temperature variation from warm to cold, which would have caused fluctuations in the data that were not necessarily representative of the actual VP. Allowing the bath to continuously warm instead allowed the material to follow its natural VP curve uninterrupted. The consistency in the results between each run confirms the validity of the warming method versus a constant temperature measurement.

The LAr and LN_2 baths were maintained at constant bath temperatures. As the liquid evaporated, additional liquid was added to maintain a constant bath depth. A total of four runs were completed for the LAr and three runs for LN_2. For the LAr and LN_2 cryogenic baths, the experiment run durations were between 7 and 18 min for LAr and 4 and 10 min for LN_2.

Pressure and temperature data were collected using LabVIEW at 1 s intervals for all tests. Data collection began once bath temperature and vessel pressure were stable and continued until the VP exceeded the range of the PT (isopentane) or until the testing duration was met (LAr and LN_2).

4. RESULTS

The data for each run were aggregated into a single data set. The pressure and temperature data recorded by LabVIEW were precise to the millionths decimal place, but for this analysis, data were rounded and truncated to the tenths decimal place for temperature and to the thousandths decimal place for pressure. The number of significant figures selected for the temperature and pressure data points was to 1) aid in data management while still ensuring a sufficient number of data points were included in the engineering level analysis and 2) ensure the values used in the analysis were not significantly impacted by instrument error. Data were then sorted by increasing temperature. The pressure data for each 0.1 degree interval were averaged across all runs.

The vessel internal temperature was evaluated and compared to the cryogenic bath temperature for the five 100 torr experimental runs. The graphical analysis is shown in Figure 4. In each run, the cryogenic bath and vessel internal temperatures were different. Experimental runs 1 and 2 had lower starting internal vessel temperatures due to the extended time spent in the cryogenic bath prior to starting the experiment. Because of this extended time, experimental runs 1 and 2 were much closer to each other throughout the experiment. However, the internal vessel temperature never reached the cryogenic bath temperature of 113 K.

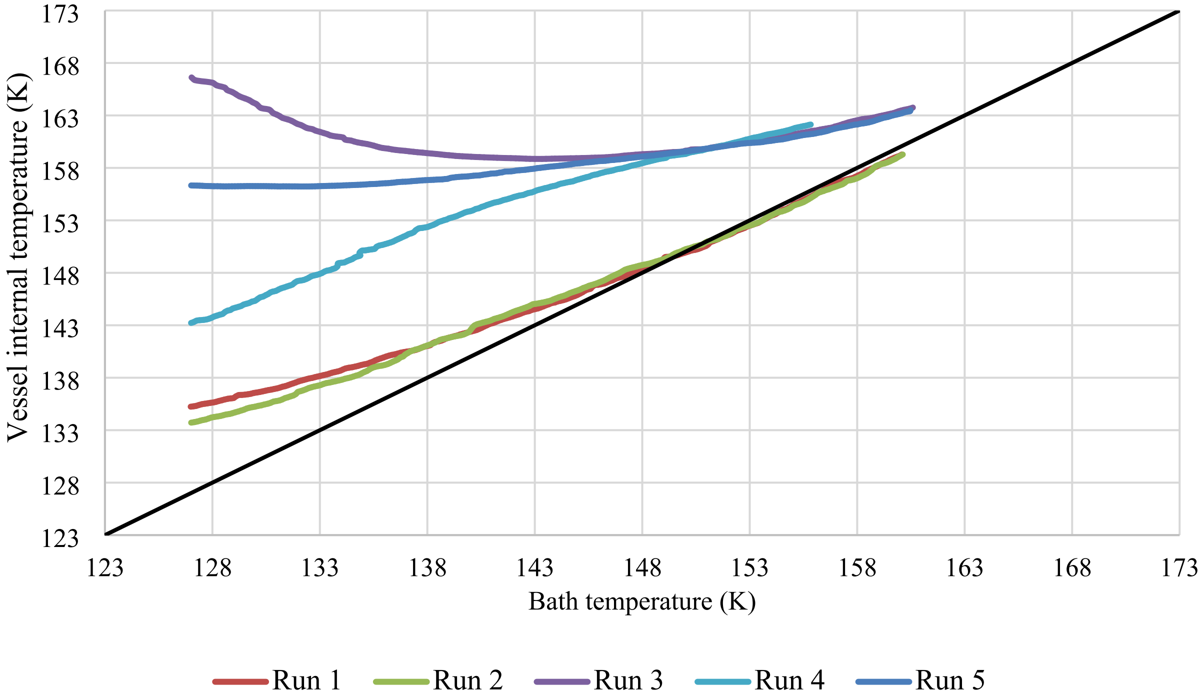

Figure 4. Relationship between cryogenic bath temperature and vessel internal temperature. The black line represents a one-to-one relationship.

A full review of all temperature data indicates that the higher internal vessel temperature contributed to the reduced experiment duration for experimental run 3 (discussed in Section 3.3), but there is no indication that a difference in the two temperatures caused the data to be unreliable.

Although the inside of the test vessel could not be observed during this experiment for true verification of this phenomenon, it is understood that as desublimation occurs, the gaseous material forms solid crystals on a cold surface. Based on the discrepancy between the bath and vessel internal temperatures, it is assumed that some solid formed on the probe, which skewed the internal temperature measurement. The measured pressures in the same temperature range as existing historical data agree with the historical points when associated with the bath temperatures rather than the vessel temperatures. It is therefore assumed that the bath temperature, not the vessel internal temperature, is more representative of the actual SiF_4 vapor temperature. This assumption is justified by both the consistency and level of agreement (e.g., minimal error) between historical and collected data using the bath temperature. Although the bath temperature is not the exact vapor temperature, error associated with these values is minimal, as discussed in following paragraphs and shown in Figure 5, and is therefore acceptable for this engineering-level experiment.

The 10 and 100 torr aggregated data sets were evaluated separately for pressure range validity. Typically, data below 1% of PT full scale are unreliable for data analysis because of the PT signal-to-noise ratio at the low end of the pressure range. Based on an analysis of the data, the 1% limit held true for the 100 torr PT, resulting in reliable data above approximately 127 K (±0.1). The 1% limit did not hold true for the 10 torr PT, though, and data variability occurred below 2% of full scale. However, the 10 torr PT still provided meaningful results down to approximately 122 K (±0.2).

The 0.1 torr gauge was used for the LAr and LN_2 experimental runs. For the 0.1 torr gauge, data collected during the LAr run were just below 0.5% of full scale. Because this is below the 1% full scale threshold, there is variability in the data which manifested during the experimental runs as a sinusoidal pattern within the pressure measurement. Both this trend and data set will be discussed further later in this section and in Section 5. Data for the LN_2 experimental runs were well below the 1% threshold of the 0.1 torr gauge and could not be reliably collected.

The data collected in this work are shown in Figure 5 and are displayed as continuous lines for the 10 and 100 torr data to represent the experimental methodology of continuous collection. New data that were below the historical experimental values were collected using the 10 torr PT.

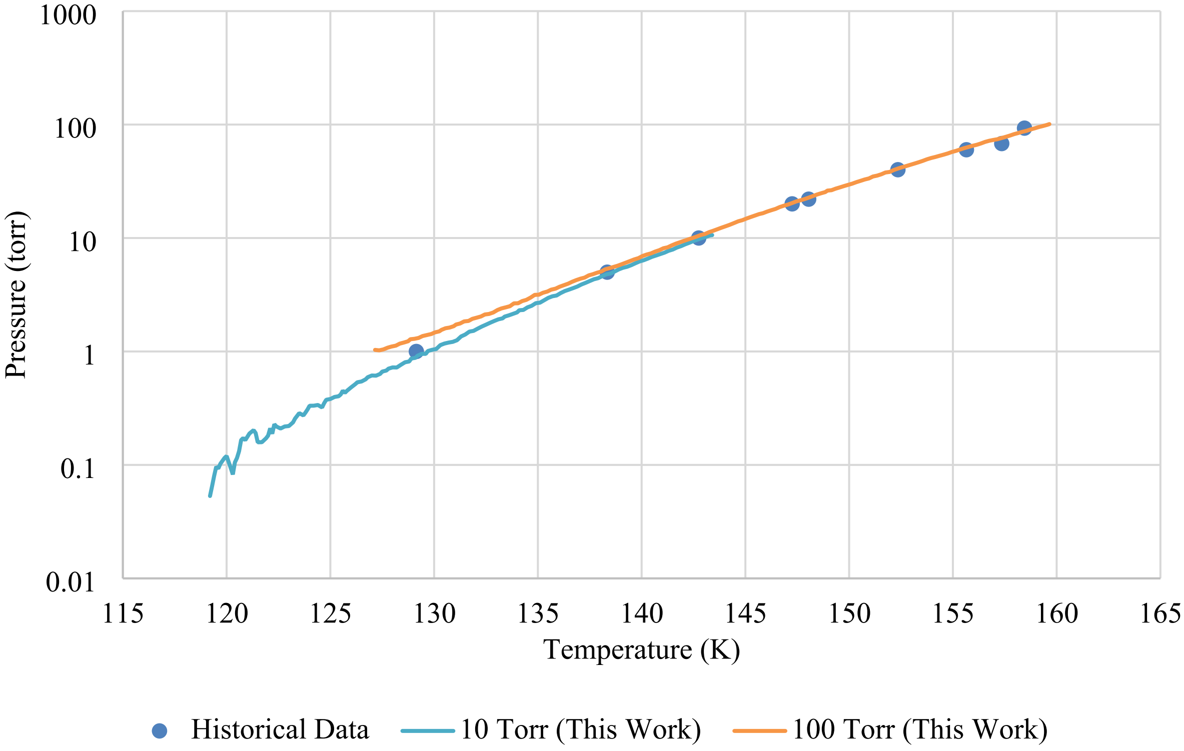

Figure 5. Historical and experimental VP data for SiF_4. Error is so low at most points that error bars are masked by the data and therefore are not shown. Error was 0.12% of reading for pressure, 0.1 K for temperature.

The error between the measured values with the 100 torr PT and the historical data are less than 10% in the applicable measurement range (>1% full scale) with the exception of two data points that are both from a different data set than the majority of the historical data. Based on this, the error can be attributed to noncondensable gases within the vessel or a slight offset of temperature between the SiF_4 vapor and the bath temperature. Without reliable information regarding the temperature of the SiF_4 vapor due to the issues with the internal RTDs, an exact determination of the cause of this difference cannot be made. Despite the undetermined source difference, the methodology used to measure VP using the 100 torr gauge is a reliable method for determining VP for this engineering-level experiment because of its repeatability between multiple experimental runs and its agreement with historical data with an average error of 5% or less.

Data collected between 122 and 143.2 K using the 10 torr PT are also shown in Figure 5. The data collected above 129 K are consistent with historical data, while data below 129K have no comparison. Only three data sets were used in the analysis of this temperature range. The data from experimental run 1 indicated the presence of noncondensable gases within the vessel, leading to erroneous pressure measurements. The noncondensable gases were determined by analyzing the initial vessel pressure and the temperature of the cryogenic bath when the limit of the PT was reached. Both were inconsistent with historical data and with the other three data runs.

There are only three data points that can be compared to historical data in the 10 torr gauge temperature range. Like the measurements with the 100 torr PT, the error of the measured pressures for all runs was less than 11% when compared to the historical pressure of 1 torr at 129 K and less than 5% for the two warmer points. Since the historical value was directly between the measured values of both the 100 torr and 10 torr gauges at 129 K (with the 100 torr gauge value being 10% higher and the 10 torr gauge value being 11% lower), this suggests that the actual SiF_4 VP at 129 K is somewhere in between the two measured values and is very close to the historical value. However, in general given the lower error between the measured values and the historical data with the 10 torr PT, and the greater resolution of the PT at these pressures, the 10 torr data are considered more representative of the actual VP at these temperatures compared to the 100 torr data.

Comparing the 10 and 100 torr PTs reveals that the agreement between the two PTs when the temperature is between 139 and 143.4 K, where the corresponding vapor pressure is in a measurable range for both PTs, is better than 90%. As the temperature decreases below this range, the vapor pressure also decreases below the reliable range of the 100 torr PT. Thus, the agreement between the two PTs decreases as well. In the ranges that are applicable to each, the trends between the two PTs are consistent with each other and historical data.

For the tests with LAr and LN_2, the temperature of the bath was constant ($\pm < 1.0$ °C) at 88 K and 77 K, respectively. While attempting to measure the VP at the LAr temperature, a sinusoidal pattern was observed in the data, which is typical when measuring a value at the end of the gauge range, as also seen with the 10 and 100 torr gauges. Examples of the sinusoidal pattern are shown in Figure 6 and Figure 7.

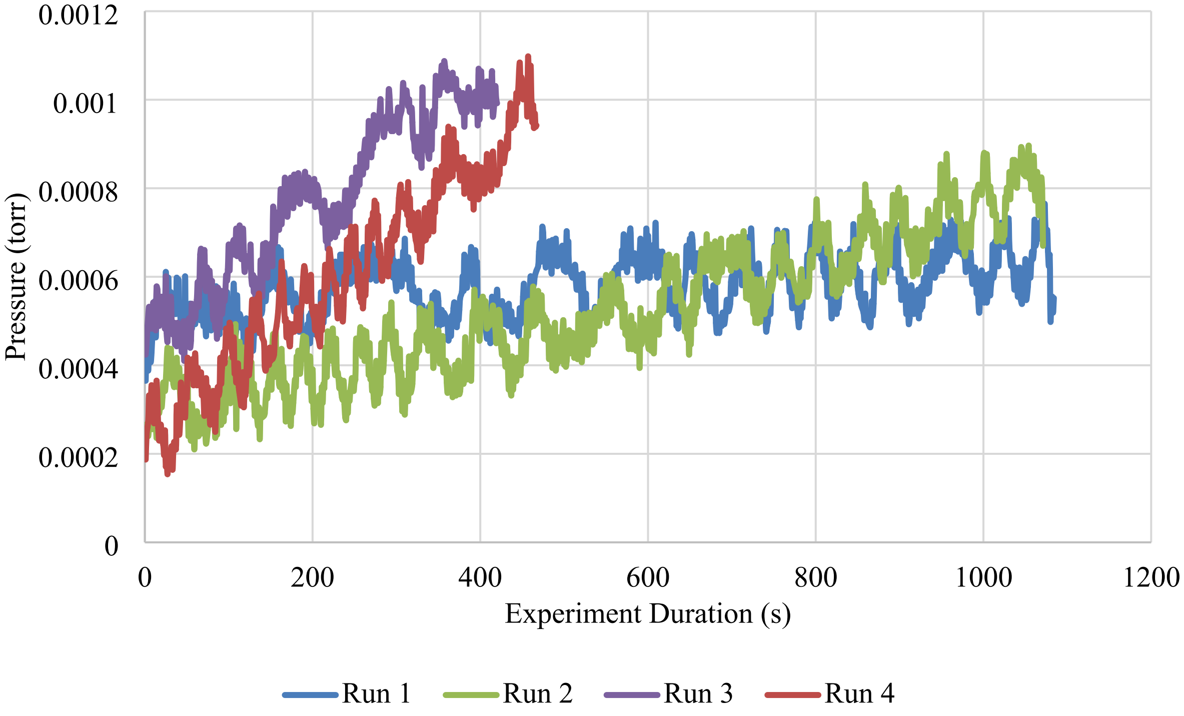

Figure 6. Raw pressure data from LAr experimental runs.

In addition to the sinusoidal function observed in the 0.1 torr data set, a linear increase as a function of time was also observed. This was attributed to in-leakage of noncondensable gases. The test vessel rig was bumped and readjusted while making a LAr addition to the dewar between run 2 and 3. The rate of in-leakage between these two runs increased, as shown in Figure 6, and the suspected cause is this physical interference. The presence of noncondensables was fairly consistent throughout the experiment, so the system was proven to have leak points. Bumping and readjusting the test vessel is thought to have impacted a leak point, which then allowed for a higher inflow of nonprocess gas. This suspicion is supported by the comparability in results both before and after the movement. To calculate the impact of in-leakage, a linear curve was fit to each of the four experimental runs for LAr. Once the rate of in-leakage was determined, the rate was subtracted from each of the data points from the run to create in-leakage corrected data and form the basis of the LAr data. The corrected data are shown in Figure 7.

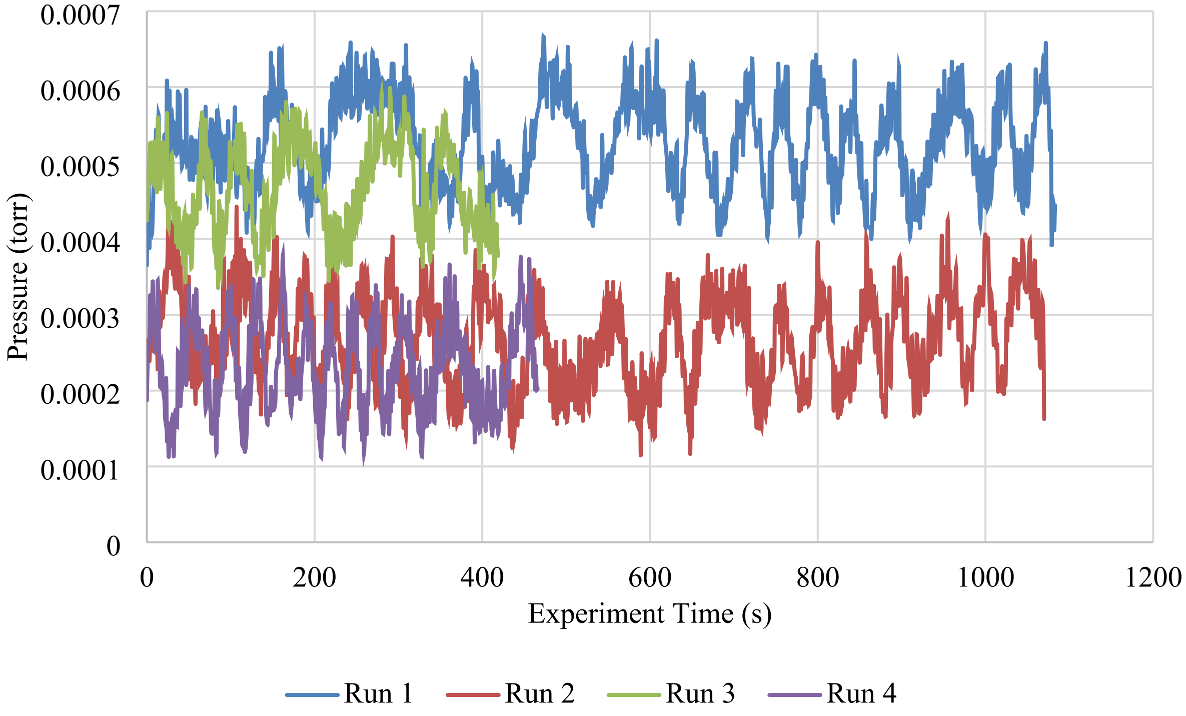

Figure 7. In-leakage corrected pressure data for LAr experimental runs.

Even with the in-leakage corrected for, the noise in the data persists at 88 K with the 0.1 torr gauge. Because of this noise, the only conclusive statement about the VP at this temperature is that is it less than 0.001 torr. Further investigations with higher resolution PTs, improved vacuum tightness, and more consistent temperature control are required to make more conclusive statements about the VP of SiF_4 at temperatures below 122 K. However, as this is an engineering-level experiment, the data collected are sufficient to project an order of magnitude value of the VP at this temperature. This order of magnitude value is not meant as a definitive value, but rather serves to answer the initial question of whether LAr or LN_2 is a sufficient cold-trapping method for SiF_4. This is discussed further in Section 5.

Removal of noncondensable and non-SiF_4 gases was a primary concern during testing. As observed in one experimental run with the 10 torr PT, and during the LAr and LN_2 testing, insufficient purging and in-leakage of gases hampered reliable data collection. The in-leakage of noncondensable gases, like that observed in the LAr experimental runs, was a concern throughout all experimental runs. However, the data from the LAr experimental runs indicates the maximum noncondensable in-leakage rate calculated was 0.0057 torr per hour, which is a concern for the LAr and LN_2 experimental runs, but too small to influence the 10 and 100 torr experimental runs.

5. ANALYSIS

The Clausius-Clapeyron (CC) equation is a relationship that can be used to analyze vapor pressure data [4]. The equation, as

$$lnP = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + C,$$

where *P* is the vapor pressure, Δ*H* is the latent heat of the applicable phase change, *R* is the universal gas constant, *T* is the temperature, and *C* is some constant, is applicable when three assumptions are valid. These assumptions are: (1) the volume occupied by one mole of the condensed phase is negligible compared to the volume occupied by one mole of the vapor, (2) the vapor behaves as an ideal gas, and (3) Δ*H* does not change with temperature. By accepting these three assumptions, the Δ*H*/*R* term becomes a constant slope, and the equation yields a linear relationship in some temperature range. Data from this experiment can be fit to this trend to validate vapor pressure data collected down to some temperature, as well as potentially determine a new value for the latent heat of sublimation in a lower temperature range than what is currently available in literature.

Historical data from References 1, 2, and 3 were fit to the CC relationship as shown in Figure 8. From the fit for each, and accounting for the universal gas constant, the latent heat of sublimation was determined in the respective temperature ranges shown in Table 2.

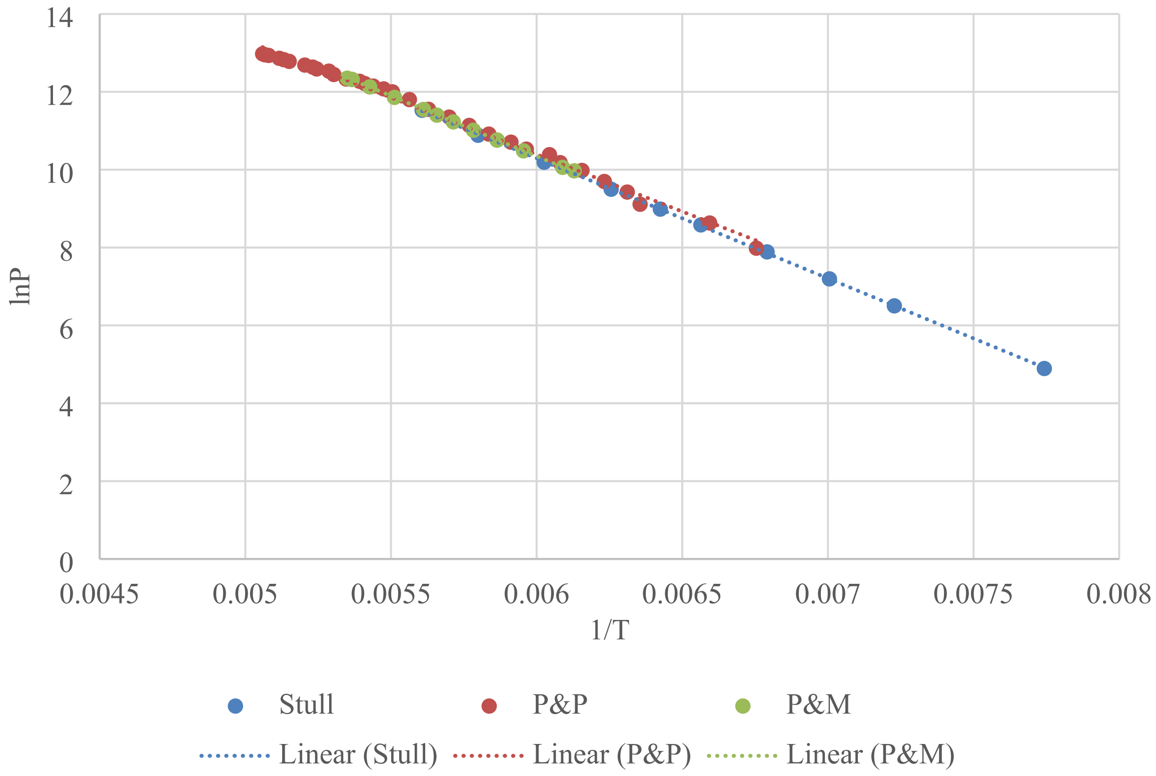

Figure 8. CC fit for historical data. The trendline equations and R^2 values are included for verification of values and fit. P&P stands for Patnode & Papish data set, and P&M stands for Pace & Mosser data set.

Table 2. Δ*H* from historical data

Data set	Δ*H* (kJ/mol)	*C*	Temperature range (K)
Pace & Mosser	25.8	28.94	163–187
Patnode & Papish	24.4	27.97	148–198
Stull	25.7	28.81	129–178

When comparing the data collected in this experiment from 129 to 160 K, which is the same range as the Stull data set, the latent heat of sublimation is determined to be 25.8 kJ/mol, which agrees with the values from the historical data above and validates the data collected in this engineering-level experiment. From this, the applicable temperature range for the latent heat value can be explored.

Data from this experiment was collected using the 10 and 100 torr gauges between 116 and 160 K. However, as previously discussed, the 10 torr PT was only reliable down to 0.2% of the full scale range, or approximately 0.2 torr, before variability started to occur. The associated temperature with this pressure limit is approximately 122 K. Also, as previously discussed, the 100 torr PT was reliable down to 0.1% of the full scale before variability occurred; however, because this coincides with the range of the 10 torr PT, data from both transducers overlap. Therefore, there is consistent and reliable data in the temperature range between 122 and 160 K. The experimental data in this temperature range fit to the CC relationship are shown in Figure 9.

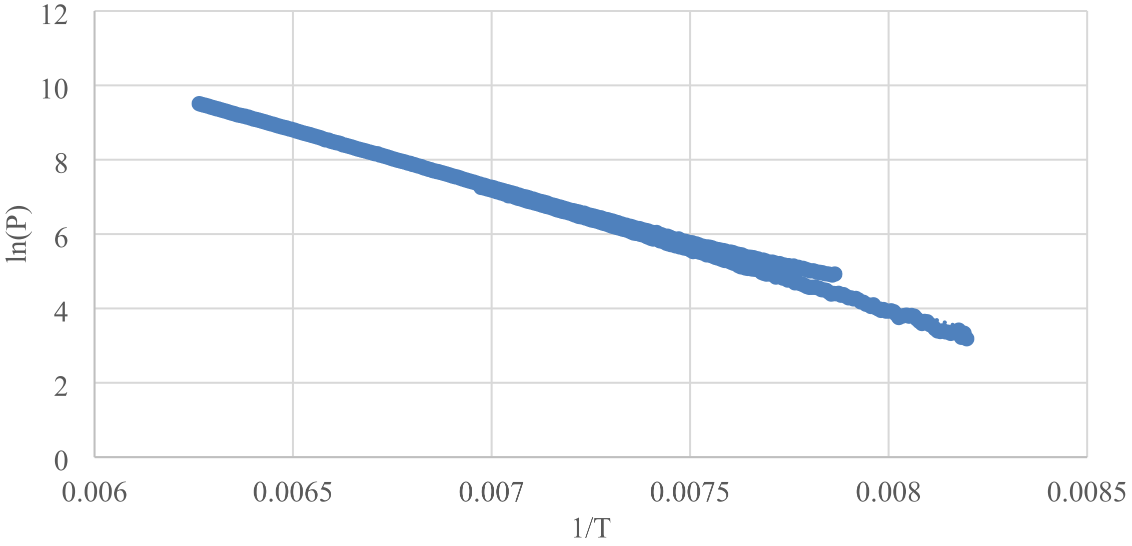

Figure 9. CC fit for experimental data.

This yields a latent heat of sublimation obtained from experimental data of 26.3 kJ/mol between 122 K and 160 K. This 26.3 kJ/mol value is less than 3% higher than those values obtained from both the Pace & Mosser and the Stull data sets, which is less variation than the value obtained from the Patnode & Papish data set when compared to the other two data sets (5% lower). This 3% discrepancy can be attributed to experimental error associated with the 10 torr gauge in the extended temperature range, but is small enough to validate the data collected in this engineering level experiment. The Patnode & Papish data set is excluded from this analysis herein, since the focus of this analysis is at lower temperatures and the ΔH obtained from this data is not applicable in the lower range, which is proven by the larger variance from the other two historic data sets in this range.

It should be noted that the discrepancy in experimental data between 0.0077 K^{-1} and 0.0079 K^{-1} in Figure 9 is where the 100 torr gauge approaches the end of its reliability. In the overlapping temperature range where valid data were collected from both the 10 torr and 100 torr gauges, there was a consistent offset in data with the 100 torr values being slightly higher. To offset any instrument bias in this CC analysis, and based on the error discussion in Section 4, the lower end of the 100 torr data set was still included to provide an average value. It should also be reiterated here that the experimental data used in this analysis for both the 10 torr and 100 torr data sets are averaged from all experimental runs per gauge used, as explained in Section 4. While using each individual data point would provide a larger population for statistical reviews and analysis and could affect the results, it is more likely the noise associated with the multiple runs would increase the overall error. Thus, the averaged values for the experimental data were used throughout this analysis.

The CC analysis can also be used to predict the vapor pressure value of SiF_4 at temperatures where data are not available. Using the Δ*H* value of 26.3 kJ/mol stated previously and the *C* term of 29.37 shown in Figure 9, VP values were estimated at one-degree intervals between 88 K (LAr) and 160 K (maximum measured temperature during this experiment). These results were then plotted over the experimental data between 122 K and 159.6 K. This comparison is shown in Figure 10.

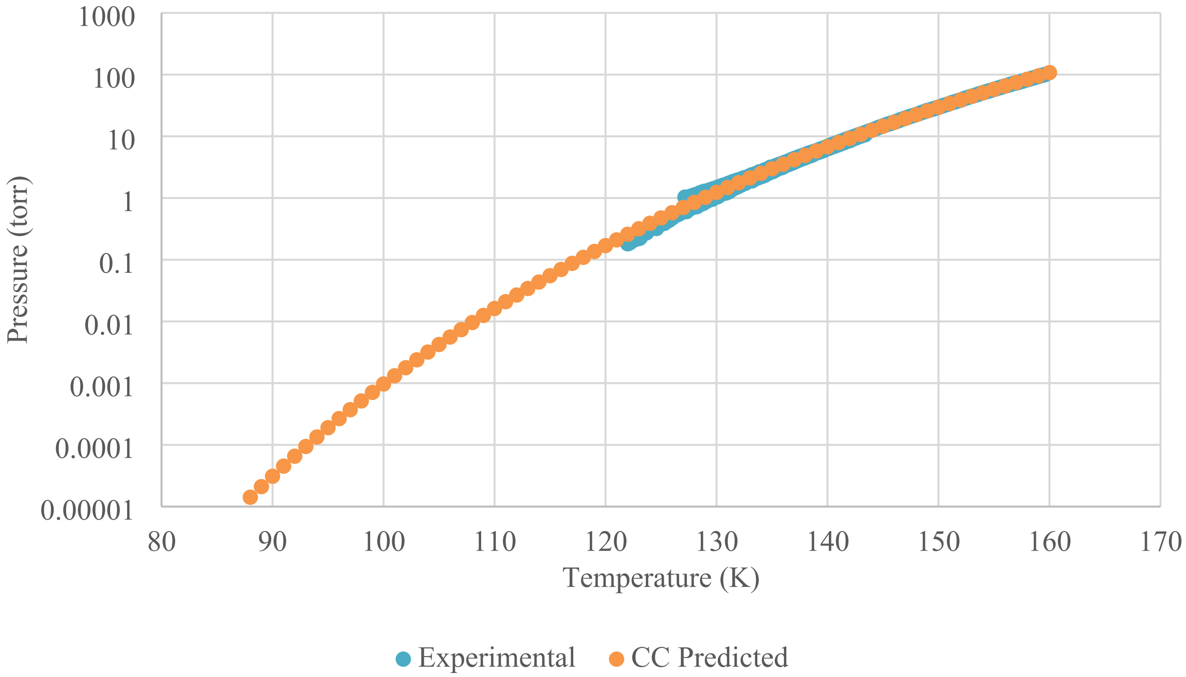

Figure 10. VP between 88 K and 160 K. VP values are estimated at 1 K intervals rather than actual measured temperatures to show a trend rather than direct point comparison.

As discussed previously, the average between the 10 torr and 100 torr data sets was used to obtain the latent heat of sublimation value, so the calculated VP falls between the collected sets and fits well. The discrepancy between the experimental values at the lower temperatures was due to instrument error, also as discussed previously. Since the calculated values are derived from the experimental data, the good fit is expected. Thus, the calculated VP range was extended to 190 K, and the historical values were added to the plot for comparison, as shown in Figure 11.

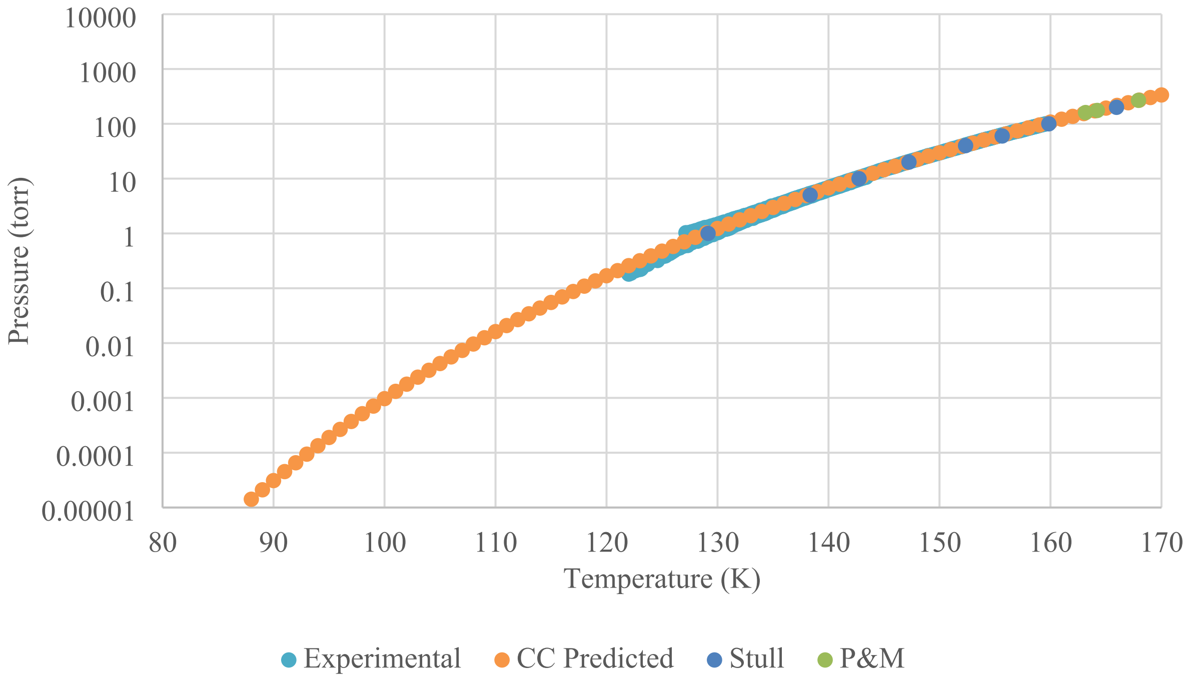

Figure 11. VP between 88 K and 190 K.

The VP was then estimated via the CC equation using the respective Δ*H* and *C* terms in Table 2 for the Pace & Mosser and Stull data sets to validate the estimated VP based on experimental data. The Pace & Mosser and Stull VPs were calculated at 88 K and 10 K intervals from 90 K to 190 K. A comparison of these data sets against the experimental based VPs is shown in Table 3.

Table 3. Estimated VP between 88 K and 190 K

Temperature (K)	**VP (torr)**			**Mean with std dev**
	Pace & Mosser	**Stull**	**Experiment**	
88	1.42×10^{-5}	1.44×10^{-5}	1.05×10^{-5}	$1.30 \times 10^{-5} \pm 1.76 \times 10^{-6}$
90	3.10×10^{-5}	3.14×10^{-5}	2.34×10^{-5}	$2.86 \times 10^{-5} \pm 3.65 \times 10^{-6}$
100	9.69×10^{-4}	9.67×10^{-4}	7.87×10^{-4}	$9.07 \times 10^{-4} \pm 8.54 \times 10^{-5}$
110	1.62×10^{-2}	1.60×10^{-2}	1.39×10^{-2}	$1.54 \times 10^{-2} \pm 1.02 \times 10^{-3}$
120	1.69×10^{-1}	1.66×10^{-1}	1.35×10^{-1}	$1.63 \times 10^{-1} \pm 6.96 \times 10^{-3}$
130	1.23	1.20	1.16	$1.20 \pm 2.93 \times 10^{-2}$
140	6.77	6.52	6.60	$6.63 \pm 1.03 \times 10^{-1}$
150	2.96×10^{1}	2.83×10^{1}	2.98×10^{1}	$2.92 \times 10^{1} \pm 6.37 \times 10^{-1}$
160	1.08×10^{2}	1.03×10^{2}	1.11×10^{2}	$1.07 \times 10^{2} \pm 3.56$
170	3.36×10^{2}	3.19×10^{2}	3.56×10^{2}	$3.37 \times 10^{2} \pm 1.50 \times 10^{1}$
180	9.25×10^{2}	8.74×10^{2}	1.00×10^{3}	$9.33 \times 10^{2} \pm 5.16 \times 10^{1}$
190	2.29×10^{3}	2.15×10^{3}	2.52×10^{3}	$2.32 \times 10^{3} \pm 1.51 \times 10^{2}$

The applicable temperature range of the CC equation for SiF_4 can be determined by this analysis. The average (mean) VP with the standard deviation for the three sets of data indicates the level of agreement between the historic- and experimental-based data sets. Although the historic values have been accepted, the historic-based estimates at lower temperatures (below 129 K) are still just estimates, as are the estimates based on data from this experiment. Therefore, agreement among all three sets is necessary to validate the applicability of the governing CC assumptions over a temperature range. Owing to the relationships used in the CC equation (i.e., logarithmic), increased deviation will occur between data sets at the lower end of the temperature range because the initially small discrepancy in input values (ΔH and C) have a larger impact on the smaller resulting pressure. Therefore, good agreement between data sets for this engineering-level experiment is indicated by a mean VP value that is a factor of ten or more higher than the standard deviation. Based on this criterion, the CC equation is valid for providing a relatively accurate estimate of the VP of SiF_4 between 100 and 190 K.

Although 88 K is below the applicability of the CC equation (as was just determined), this equation can still be used to estimate an order of magnitude value for the VP. As this is an engineering-level effort, with several sources of error identified, the intention is not to use the CC analysis to definitively state the VP of SiF_4 at 88 K, but rather to provide a sound estimate for future application. From the results in Table 3, the VP of SiF_4 at 88 K is on the order of approximately 1×10^{-5} torr.

There initially appears to be a discrepancy between this calculated VP at 88 K and the measured VP shown in Figure 7. During the experiment, the measured values were questioned due to the measurement range of the gauge. Although it appears as though some VPs were measured, the sinusoidal-like trend of the data actually indicates the measurements were below the capabilities of the instrument, where the instrument was on, but there was not enough applied force to cause a deflection/strain/etc. to produce an output (measurement), so the indication is really signal noise from the instrument. As mentioned above, the transducer used for the LAr measurements was a 0.1 torr gauge. Knowing this, the only definitive conclusion that can be drawn from the data shown in Figure 7 is that the VP of SiF_4 is below 0.1 torr. Although this does not support the exact value calculated with the CC equation, this does support the conclusion that the VP of SiF_4 is at least a much lower value than what could have been measured in this experiment.

The VP of LN_2 was not explored in this analysis. As explained previously and demonstrated with the LAr values, the variation between VP values depending on source inputs increases with decreasing temperature. Since the LAr temperature is below the applicability of the CC equation and already shows deviation in estimated values, it can be assumed that VP values estimated at LN_2 temperatures would deviate too significantly to provide an accurate enough order of magnitude value. For the VP of SiF_4 at LN_2 temperature to be estimated with confidence, more data at lower temperatures would need to be collected to extend the applicability range of the CC equation.

6. CONCLUSIONS

This study evaluated the VP of SiF_4 at temperatures between 88 K and 159.6 K, increasing the known VP range down to 122 K, with VP trends understood down to 100 K. Issues with the experimental setup prevented further data capture. However, the investigators have identified methods (mentioned throughout this paper and captured in a separate document) to improve the physical setup to further extend the known VP range of SiF_4 in a future experiment.

The method of allowing the bath temperature to warm to collect a continuous pressure trend, as opposed to the historical method of capturing pressure values at single bath temperatures, was proven to be a reliable method for obtaining VP values over a wide temperature range. The experimental continuous data was in acceptable agreement with the historical single point values throughout the temperature range explored. Therefore, a new functional relationship between VP and temperature for SiF_4 was developed based on the data collected in this experiment:

$$lnP = -3162.4\left(\frac{1}{T}\right) + 29.4$$

This new relationship follows the form of the CC equation discussed in Section 5, but simplifies the *ΔH/R* term. Results of this equation yield a VP in Pascals. This relationship is applicable for the temperature range of 100 to 190 K.

Although a valid VP vs temperature relationship could not be determined from this experiment at temperatures as low as 88 K or 77 K, the experiment was still successful in resolving the initial engineering question about if LAr or LN_2 are sufficient mediums for cold-trapping SiF_4. Based on the relationship shown previously for temperatures as low as 100 K, the conclusion is that the VP of SiF_4 at these cryo temperatures is sufficiently low enough for either LAr or LN_2 to be used as cold-trapping coolants for this gas in a practical application where a roughing pump (vacuum on the order of $\leq 1 \times 10^{-3}$ torr) is used.

7. REFERENCES

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APPENDIX A. DATA TABLES

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Table A-1. Tabular data for the 100 torr PT

100 Torr			
Bath temperature (K)	**Temperature error (K)**	**VP (torr)**	**VP Error (torr)**
127.0	0.1	1.01	0.01
127.6	0.1	1.04	0.01
128.0	0.1	1.13	0.01
128.5	0.1	1.20	0.01
129.1	0.1	1.29	0.01
129.5	0.1	1.36	0.01
130.0	0.1	1.47	0.01
130.5	0.1	1.60	0.01
131.1	0.1	1.73	0.01
131.6	0.1	1.87	0.01
132.1	0.1	2.00	0.02
132.6	0.1	2.14	0.02
133.0	0.1	2.27	0.02
133.5	0.1	2.49	0.02
134.0	0.1	2.66	0.02
134.6	0.1	2.98	0.02
135.0	0.1	3.16	0.02
135.5	0.1	3.44	0.03
136.0	0.1	3.72	0.03
136.5	0.1	4.01	0.03
137.1	0.1	4.46	0.03
137.5	0.1	4.69	0.04
138.0	0.1	5.01	0.04
138.5	0.1	5.50	0.04
139.0	0.1	5.88	0.04
139.5	0.1	6.28	0.05
140.0	0.1	6.95	0.05
140.6	0.1	7.48	0.06
141.0	0.1	8.00	0.06
141.5	0.1	8.62	0.06
142.0	0.1	9.45	0.07
142.5	0.1	10.01	0.08
143.0	0.1	10.85	0.08
143.5	0.1	11.74	0.09
144.0	0.1	12.52	0.09
144.5	0.1	13.79	0.10
145.1	0.1	14.85	0.11
145.5	0.1	15.76	0.12
146.0	0.1	16.71	0.13
146.5	0.1	18.06	0.14
147.0	0.1	19.72	0.15

100 Torr

Bath temperature (K)	**Temperature error (K)**	**VP (torr)**	**VP error (torr)**
147.5	0.1	21.27	0.16
148.0	0.1	22.41	0.17
148.6	0.1	24.47	0.18
149.0	0.1	26.22	0.20
149.5	0.1	27.92	0.21
150.0	0.1	29.70	0.22
150.6	0.1	31.93	0.24
151.1	0.1	34.39	0.26
151.6	0.1	36.47	0.27
152.0	0.1	38.99	0.29
152.5	0.1	42.03	0.32
153.0	0.1	44.21	0.33
153.6	0.1	47.91	0.36
154.0	0.1	50.73	0.38
154.6	0.1	54.29	0.41
155.0	0.1	58.06	0.44
155.5	0.1	62.00	0.46
156.0	0.1	65.04	0.49
156.5	0.1	68.96	0.52
157.1	0.1	73.71	0.55
157.5	0.1	77.97	0.58
158.1	0.1	83.33	0.62
158.5	0.1	87.70	0.66
159.0	0.1	94.20	0.71
159.6	0.1	100.95	0.76

Table A-2. Tabular data for the 10 torr PT

10 torr

Bath temperature (K)	Temperature error (K)	VP (torr)	VP error (torr)
122.0	0.2	0.18	0.0
122.5	0.2	0.21	0.0
123.0	0.2	0.22	0.0
123.5	0.1	0.29	0.0
124.0	0.1	0.33	0.0
124.5	0.1	0.33	0.0
125.0	0.1	0.38	0.0
125.5	0.1	0.42	0.0
126.0	0.1	0.48	0.0
126.5	0.1	0.54	0.0
127.0	0.1	0.61	0.0
127.5	0.1	0.67	0.0
128.0	0.1	0.72	0.0
128.5	0.1	0.79	0.0
129.0	0.1	0.88	0.0
129.5	0.1	0.96	0.0
130.0	0.1	1.03	0.0
130.5	0.1	1.17	0.0
131.0	0.1	1.24	0.0
131.5	0.1	1.41	0.0
132.0	0.1	1.56	0.0
132.5	0.1	1.72	0.0
133.0	0.1	1.89	0.0
133.5	0.1	2.06	0.0
134.0	0.1	2.21	0.0
134.5	0.1	2.45	0.0
135.0	0.1	2.65	0.0
135.5	0.1	2.97	0.0
136.0	0.1	3.19	0.0
136.5	0.1	3.51	0.0
137.0	0.1	3.81	0.0
137.5	0.1	4.18	0.0
138.0	0.1	4.51	0.0
138.5	0.1	4.86	0.0
139.0	0.1	5.37	0.0
139.5	0.1	5.76	0.0
140.0	0.1	6.31	0.0
140.5	0.1	6.83	0.1
141.0	0.1	7.30	0.1
141.5	0.1	7.92	0.1
142.0	0.1	8.49	0.1
142.5	0.1	9.41	0.1
143.0	0.1	10.10	0.1

Table A-3. Tabular data for the four LAr experiments corrected for gas in-leakage

0.1 torr

Bath temperature (K)	Temperature error (K)	VP (torr)	VP error (torr)
88	0.2	5.26×10^{-4}	7.89×10^{-7}
88	0.2	2.67×10^{-4}	4.01×10^{-7}
88	0.2	4.64×10^{-4}	6.97×10^{-7}
88	0.2	2.30×10^{-4}	3.45×10^{-7}