W15e Isotherms of Real Gases

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1 Introduction

For real gases, under some sufficient temperature, the critical temperature, the gas behaves differently then the ideal gas relation. The following experiment measure the the pressure and volume of the substance under study, (SF_6) , under some constant temperature (isotherm) and plot the results along a pV graph. The resulting graph is a helpful tool in understanding some of the physical properties of SF_6 , where this paper will explore the following properties;

- Saturated Pressure; Areas of constant pressure within the Pressure-Volume graph. The resulting pressure value set correspond to the range of pressures at which liquid and gas coexist and is a critical region in determining critical parametrs such as the pressure, temperature and molar volume at the critical point
- Average Molar Latent Heat of Vaporisation; Through the approximation that the latent heat of vaporisation is constant, the average (which is also correlative to low temperatures from the critical temperature) latent heat of vaporisation can be determined. Which gives an approximate of how much energy is required to evaporate our substance from its liquid phase.
- The amount of substance: Through the approximation of volume going to infinity for the highest temperature measurement (above the critical temperature), the number of moles of the substance will be determined.
- Molar Latent Heat of Vaporisation; Without the approximation of the laten heat being constant, the values of the latent heat for each temperature will be determined.

All respective results will be compared to literature value, if avaiable, and analysed in depth.

2 Overall Experimental Exploration

As all the following sections utilise the data from the same experiment, the experiment will be explored once at the start.

2.1 Materials

- High Pressure Capillary ± 0.5 :
 - Glass capillary with substance under study SF_6 (1)
 - Plexiglas for temperature control (2)
 - Pipe connection for thermostat fluid (3)
 - Hand wheel for pressure regulation (4)
- Thermostat ± 0.1 (6)
- Manometer ± 0.5 (5)
- Residual items: Connecting Tubes, Laptop, etc...

2.2 Set Up

The High Pressure Capillary is set up in the accordance of the below image. The gas under study, SF_6 is contained within the thick walled glass. The capillary is enclosed by a water bath that allows temperature regulation. The Manometer and the Thermostat are attached to the capillary, for measurement. The pressure is generated by pressing mercury that is located in the chamber below the capillary.



Image 1 Set up for the whole document.

2.3 Methodology

Set the thermostat at room temperature (of $19^{\circ}C$), rotate the hand wheel for pressure correlation to control the volume within the capillary glass. Set it at the volume of $2 cm^3$, record the corresponding pressure value. In the same manner, readjust the hand wheel to the volume $1.9 cm^3$ and record. Repeat it up to the volume measurement of

 $0.2 \ cm^3$ with $0.1 \ cm^3$ increments. If the pressure value approaches the manometer limit of 50 Bars, get the volume as close as safely possible and measure up to that respective volume only.

Repeat the same steps for the following temperatures, $19^{\circ}C$, $25^{\circ}C$, $33^{\circ}C$, $36^{\circ}C$, $39^{\circ}C$, $42^{\circ}C$, $45^{\circ}C$, $47^{\circ}C$, $49^{\circ}C$.

Set-Up and Methodology through the help of the provided lab guide (W15e Isotherms of Real Gases)

3 Pressure-Volume Curve for SF_6 , under different isotherms

3.1 Hypotheses

It is expected that below the critical temperature T_c , there exists a pressure p_s and a volume where both pressure and volume remain constant for a period of time within the coexistence region.

3.2 Theoretical Exploration

The Van der Waals equation describes the behavior of real gases and is given by:

$$(p + \frac{a}{V_m^2})(V_m - b) = RT \tag{1}$$

For temperatures below the critical temperature, Van der Waals isotherms show unphysical oscillations in the pressure vs. volume graph. This corresponds to the region where liquid and vapor phases coexist. The physical behavior is corrected by applying Maxwell's equal-area rule.

Equation 1 can be utilised to find the relation between the critical values (parameters at the critical condition) of T_k , p_k and V_{mk} and the Van der Waals constants a and b, the isotherm would have an inflection point at the critical point. As such, where $\frac{\partial p}{\partial V_m} = 0$ and the second derivative $\frac{\partial^2 p}{\partial V_m^2} = 0$. The exact steps will not be explored, as irreverent to the analysis, but the resulting answer yields;

$$p_k = \frac{a}{27b^2} \quad T_k = \frac{8a}{27Rb} \quad V_{mk} = 3b$$
 (2)

Where the above equations can be used to determine the literary values of p_k, T_k and V_{mk} . The literary values of 'a' and 'b' were provided as $a = 0.79m^4 \text{mol}^{-2}$ and $b = 0.88 \cdot 10^{-4} m^3 \text{mol}^{-1}$. The values of 'a' and 'b', when the above equations rearrange, would be;

$$a = \frac{27R^2T_k^2}{64p_k} \quad b = \frac{RT_K}{8p_k} \tag{3}$$

where the above equation will be utilised to measure the corresponding literary values of the found critical point.

All derivations through the help of the provided lab guide (W15e Isotherms of Real Gases)

3.3 Results

3.3.1 Data and analysis

From the measured data, the following figure presents the relation between Pressure, P (Pa), against Volume, V (cm^3) ;

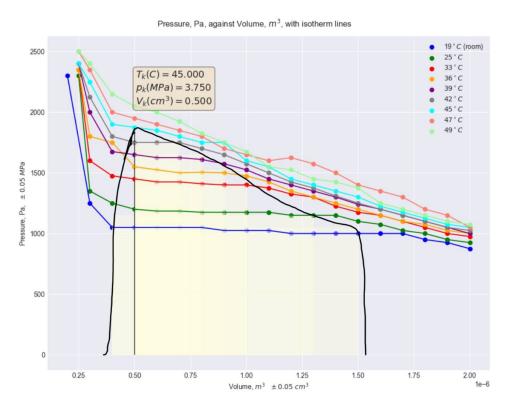


Figure 1: Pressure, Pa, against Volume, m^3 , with isotherm lines

The figure presents the relation between Pressure, P, and Volume, V, under real gas conditions. Areas of constant pressure, or to an extent within a 0.5 difference between each other, after the formation of gas within the tube has been highlighted on the figure. The black line was hand drawn, following the edges of the highlighted boxes. As can be seen from the graph, for temperatures within the range of $19^{\circ}C$ to $42^{\circ}C$, there is a real gas behaviour. With a decrease in volume leading to a point of constant pressure and then leading to a large jump right after the region of constant pressure. For temperatures above $45^{\circ}C$, they exhibit an almost linear like relationship, with a more $\frac{1}{x}$ relationship for $47^{\circ}C$ and $45^{\circ}C$ while $49^{\circ}C$ being almost linear - as expected from the theoretical section, Section 3.1. Uncertainties seen on the graph. More detail in the Discussion.

The isotherm of the critical temperature T_k can be attributed to $45^{\circ}C$, as it as at $45^{\circ}C$ the region of constant pressure disappears, with (from the experiment) no gas being produced. The line which correlated to the point $45^{\circ}C$ can be seen as the black line at volume $0.5 \cdot 10^{-6}$.

In comparing to the literary values, as derived from the theoretical section, and using the provided values of a and b as $a = 0.79Nm^4mol^{-2}$ and $b = 0.88 \cdot 10^{-4}m^3mol - 1$, the following table presents the calculated values at the critical point;

Value	Literary	Calculated	Percentage Difference
T_k° C	$47.08 \approx 47.1$	45	$4.434 \approx 4.4\%$
p_k Pa	$3778313.4 \approx 3.78 \cdot 10^6$	$37.5 \cdot 10^{5}$	$0.755 \approx 0.76 \%$
$V_{mk} cm^3$	$2.64 \cdot 10^{-4}$	$2.438 \approx 2.44 \cdot 10^{-4}$	$7.632 \approx 7.6\%$

Table 1: Parameters at the Critical Point; Comparison between literary and calculated

The values of a and b utilising the measured values, the parameters come out to $a = 0.785613268845 \approx 0.787$ and $b = 8.8 \cdot 10^{-4}$. Which closely align with the provided literary values.

At the beginning of each curve, the slope becomes progressively less steep as the temperature increases. This behaviour suggests that the constant phase corresponds to the Maxwell constant region, which represents the saturation pressure (p_s) . The following values for p_s are observed:

Temperature, $T_s^{\circ}C$	19	25	33	36	39	42
Pressure, p_s Pa	21	23	28	30.5	33	35

Table 2: Value set for the Saturation Pressure, p_s , and the temperatures at saturation, T_s

3.3.2 Discussion

The results obtained align well with the hypothesis that below the critical temperature T_k , a specific pressure p_s and volume exist where both parameters remain constant within the coexistence region. The measured data at various temperatures provide clear evidence of this phenomenon. The set of all temperatures below T_k will be considered as the temperatures at saturation, T_s .

For instance, at temperatures below T_k such as $19^{\circ}C$, $25^{\circ}C$, and $33^{\circ}C$, the observed pressures remained stable at 21 Pa, 23 Pa, and 28 Pa, respectively. This consistency supports the presence of a defined pressure p_s corresponding to each temperature within the coexistence region. Furthermore, as the temperature increased closer to T_k , the pressure continued to rise, reaching 35 Pa at $42^{\circ}C$, consistent with the expected behaviour of a system in equilibrium.

The observed stability in both pressure and volume over time at these temperatures confirms that the system remains in a dynamic equilibrium between phases. This is characteristic of the coexistence region, where both liquid and vapour phases exist simultaneously under the same conditions.

Overall, the results provide strong experimental support for the hypothesis and reinforce the theoretical understanding of phase equilibrium below the critical temperature T_k . More detail in the Discussion.

3.3.3 Error Analysis

The deviation from the literary value can be attributed to errors such as;

(i) Non-ideal Environment

Being in a undergraduate laboratory, with limited control of the whole environment to ensure as accurate of an experiment as possible, creating a controlled environment is not possible. This creates small deviations, and can explain the 2 degree difference of the critical temperature, T_k .

(ii) Not clean Glass capillary

While doing the experiment, it was noticed that there were debris flying around inside the glass while water was flooded in. As the other available set ups had similar problems, the effects of the debris on the result was ignored. However, such small substances could potentially affect the pressure and temperature in some small manner.

(iii) Inaccuracy within the instruments

Possible inaccuracies or slight readjustments of the values (as the reading of the volume and pressure were done with human eye) leads to possible small misalignment with the actual values. Additionally, any instrument leads to some level of inaccuracy in the data showing as they are only calibrated up to some degree only. Which leads to some small variation of the actual value.

Any further resistance, deviation or error can be due to standard imperfection of a non ideal system - i.e external noise, energy lose, imperfect behaviour of the components, and more.

4 Average Molar Latent Heat of Vaporization

4.1 Theoretical Exploration

The relationship between a substance's vapour pressure and temperature is described by the Clausius-Clapeyron equation as;

$$\frac{dp_s}{dT} = \frac{Q_{2,3}}{T\Delta V_m} \tag{4}$$

Where V_m is the molar volume and $Q_{2,3}$ is the latent heat of vaporisation. To understand the relationship between pressure and temperature, equation 4 has to be solved but the result would vary depending on the condition of the temperature. For this section, the approximation that $Q_{2,3}$ is constant will be utilised. This approximation is suitable for low temperatures (in comparison to the critical temperature), but for this section will be applied for all temperatures up to T_k . Solving equation 4 with these approximation, the pressure yields;

$$p_s = p_{s0} \exp\left[-\frac{Q_{2,3}}{RT_p}\right] \tag{5}$$

where equation 5 can be further simplified by taking the natural log of on both sides, leading to;

$$\ln(p_s) = -\frac{\Delta Q_{2,3}}{R} \cdot \frac{1}{T} + p_{s0} \tag{6}$$

Equation 6 would present a linear relationship between $\ln(p_s)$ and temperature, T_s . Where the slope would yield the latent heat of vaporisation, as $Q_{2,3} = \text{slope} \cdot R$. In this context, $Q_{2,3}$ can be thought of as the average latent heat of vaporisation.

Both the graphs of equation 5 and 6 will be explored to better understand the relationship between pressure and temperature.

All derivations through the help of the provided lab guide (W15e Isotherms of Real Gases)

4.2 Results

4.2.1 Data and analysis

From the obtained data, the following figure presents 2 graphs; (A) The pressure, p_s , against temperature, T_s (B) The natural Log of pressure, $\ln(p_s)$, against the reciprocal of temperature, $\frac{1}{T}$;

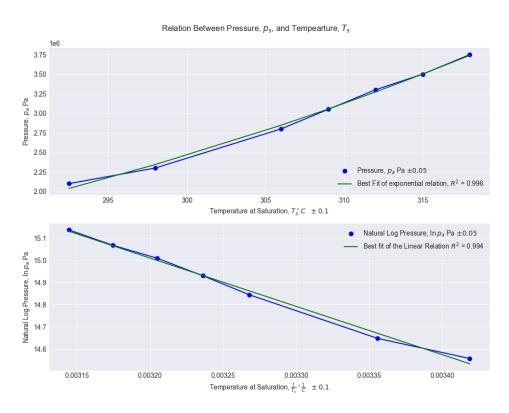


Figure 2: (A) The pressure, p_s , against temperature, T_s (B) The natural Log of pressure, $\ln(p_s)$, against the reciprocal of temperature, $\frac{1}{T}$

Figure 2 presents the two relationship between pressure and temperature. As expected from the equations, the direct computation of pressure against temperature led to an exponential relationship with a R^2 score of 0.996061346617987 \approx 0.996 in regards to equation 5. While the modified natural log of the pressure led the linear relationship, with

an R^2 value of 0.9945402898881939 \approx 0.995 in regards to equation 6. Where a value of 1 means an exact match between the fit and the measured data. Utilising the best fitting of the curves, the linear relationship yielded the value of $Q_{2,3}$ of = 18107.822814029038 \approx 18109 $\frac{J}{\text{moles}}$, and the exponential relation yielded $Q_{2,3}$ of = 18392.80795189327 \approx 18393 $\frac{J}{\text{moles}}$. As both values are close, with a percentage difference of 1.54943790317 \approx 1.5 %, the value from the linear relationship will be taken as the average $Q_{2,3}$ for this section.

Compared to the literary value, 17071 $\frac{J}{\text{moles}}$ (Marcus, Yizhak), 18393 leads to a percentage difference of $|-6.08048737625| \approx 6.1\%$. More details in the Discussion.

4.2.2 Discussion

There was an exponential relationship between pressure and temperature. Which can be resulted to as how at higher temperatures, the average kinetic energy of the system increases, and as such the system becomes more chaotic (due to an increase in individual range of velocities of each particle). This leads to higher pressure, as pressure is the result of force being applied over some region. And with higher range of velocities, the acceleration to lead the particles to those ranges leads to higher force.

Subsequently, a natural log of an exponential relationship leads to linear correlation, as shown in the Theoretical section and further with the data. The existing deviation from the literary value can be attributed to the same system issues as discussed earlier in Section 3.3.3.

4.2.3 Error Analysis

Any experimental error would be the same as the one from Section 3.3.2, as the data is from the same experiment. The error in the found slope (corresponding to $Q_{2,3}$) can be seen in the following table;

	Found Value	Standard Error	Confidence Interval
$Q_{2,3} \frac{J}{\text{mole}}$	18109	72.203	2364.643, 1993.437

Table 3: Uncertainty of found value of $Q_{2,3}$

5 Determining the amount of substance

5.1 Theoretical Exploration

The determination of the amount of substance, n (moles), can be conducted by taking the isotherm which matched the conditions of ideal gases the closest, and taking the limit of $pV \xrightarrow{V \xrightarrow{\infty}} A$, where A, is some constant.

In the regions above the critical point in the pressure volume graph, at higher temperature the substance starts behaving like an ideal gas. Where the parameters a and b lose relevance. As such, taking the results from the highest measured temperature (49° C),

plotting the graph of pV against $\frac{1}{V}$, and finding the value of pV at the limit of $\frac{1}{V} \to 0$, corresponding to $V \to \infty$, leads to the $pV \xrightarrow{V \xrightarrow{\infty}} A$.

Equating A to the conditions of an ideal gas, A = nRT, solving for n, yields;

$$n = \frac{A}{RT_{max}} \tag{7}$$

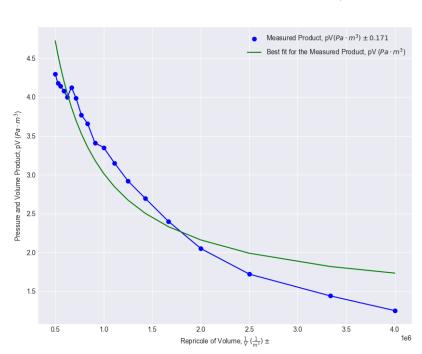
Where equation 7 will be the final equation in determining the amount of substance.

All derivations through the help of the provided lab guide (W15e Isotherms of Real Gases)

5.2 Results

5.2.1 Data and Analysis

From the data of the highest temperature, $T_{max} = 49^{\circ}C$, the following graph with its corresponding fit was seen;



Product of Pressure & Volume, pV, against the Repricole of Volume, $\frac{1}{V}$

Figure 3: Product of Pressure and Volume, pV, against the reciprocal of Volume, $\frac{1}{V}$

Where from the fitting of the curve, the following equation was seen;

$$pV = 1710498 \frac{1}{V} + 1.305 \tag{8}$$

Where utilising equation 8, one gets the following results;

	Result
$pV_{V\to\infty}$	$1.3050030489422302 \approx 1.305 \ (Pa \cdot m^3)$
$n = \frac{A}{BT}$	$0.0004877021058749206 \approx 0.0005 \text{ (moles)}$

Table 4: Data Fitting Results

The value of **0.0005** (moles) presents the amount of substance within the experiment, with an equivalent value in terms of mass, the amount of substance yields to $0.0712337696 \approx 0.0712$ (g). The best fit was fitted with an R^2 value of $0.9153818244676422 \approx 0.915$. Uncertainties in the values of pressure and volume are seen on the graph, and also further analysed the discussion. More details in the Discussion.

5.2.2 Discussion

No Discussion.

5.2.3 Error Analysis

Any experimental error would be the same as the one from Section **3.3.3**, as the data is from the same experiment.

There is no literary value to compare the deviation of the value to, however, error within the found values (such as the uncertainty in the found intercept of equation 8) comes out:

	Found Value	Standard Error	Confidence Interval
$A \operatorname{Pa} m^3$	$1.3050 \approx 1.31$	$0.19731 \approx 0.197$	$0.88870, 1.7212 \approx 0.889, 1.721$

Table 5: Uncertainty of found value of $Q_{2,3}$

6 Latent Heat of Vaporization as a function of reduced Temperature

6.1 Theoretical Exploration

Compared to Section 4, where the measured $Q_{2,3}$ was effective as the average mean latent heat of vaporization, the latent heat of vaporization for each respective temperature can be determined. From the already discussed Clausius-Clapeyron, equation 7, one can find $Q_{2,3}$ as;

$$Q_{2,3} = T_p \cdot \Delta V_M \cdot \frac{dp_s}{dT_p} \tag{9}$$

where equation 9 determines the values of $Q_{2,3}$ for each of the 9 measured temperatures. The values of ΔV_m can be determined by taking;

$$\Delta V_m = \frac{V_g - V_f}{n} \tag{10}$$

where the values of V_g and V_f can be determined as the first and last values respectively of the volume of the isotherm within the region of constant pressure from Figure 1. The amount of substance, n, has been determined from Section 5.

The measurement of $\frac{dp_s}{dt_p}$ can be determined through numerical differentiation (the details of omitted as it is a standard analysis from mathematics) of the fitting curve of the data from Figure 1, the Pressure against Temperature graph of Section 3. As such, yielding the final equation as;

$$Q_{2,3} = T_p \cdot \frac{V_g - V_f}{n} \cdot \frac{dp_s}{dT_p} \tag{11}$$

Note: The equation and code for the numerical differentiation can be found in the appendix if the needed.

All derivations through the help of the provided lab guide (W15e Isotherms of Real Gases)

6.2 Results

6.2.1 Data and Analysis

From the obtained data, the following figure presents the Latent Heat of Vaporization, $Q_{2,3} \frac{J}{moles}$ against the reduced Temperature, $\frac{T_p}{T_K}$ (no units);

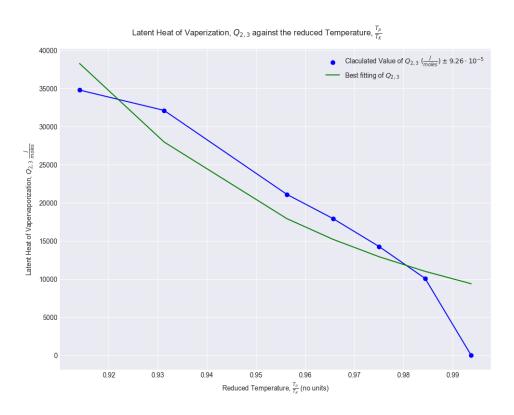


Figure 4: Latent Heat of Vaporization, $Q_{2,3}$ against the reduced Temperature, $\frac{T_p}{T_K}$

The above figure presents the relation between the Calculated $Q_{2,3}$ against the reduced temperature of $\frac{T_p}{T_k}$, where T_k is the temperature at the critical point. There is a clear decreasing relation, where an increase in temperature leads to a decrease in the amount

of energy required to vaporize the substance. Possible reasoning can be found in the Discussion. From the fitting, with an R^2 value of 0.8451494954626187 \approx 0.845, a power law of the order -16.811334863972768 \approx -16.81 was seen. The overall equation came out to as $\approx 8452(\frac{T_p}{T_k})^{-16.81}$. The values of $Q_{2,3}$ came out to;

Temperature (C)	Latent Heat of Vaporization, $Q_{2,3} \frac{J}{moles}$
19 (room)	$34798.360351 \approx 34798$
25	$32134.471112 \approx 32134$
33	$21111.728174 \approx 21112$
36	$17942.163641 \approx 17942$
39	$14277.479782 \approx 14278$
42	$10086.632102 \approx 10087$
45	0

Table 6: Latent Heat of Vaporization, $Q_{2,3} \frac{J}{moles}$ Results

Where the final value of 0 was set in the calculation of ΔV_m , an approximate point would result in nearly value of zero i.e leading the whole equation to zero. The average $Q_{2,3}$ came out to $18621.54788037163 \approx 18621 \frac{J}{moles}$, a percentage difference of $1.2283615194 \approx 1.23 \%$ and $2.7587667236 \approx 2.76\%$ respectively to the two measured values of 18393 and $18109 \frac{J}{moles}$ from Section 3.

In comparison to the literary value, the average $Q_{2,3}$ has a percentage difference of $|-9.08293527252| \approx 9.1\%$. As the source did not provide the temperature at which the latent heat was measured (and were not able to find other reliable sources), the exact comparison to the corresponding temperature value was not done. However, from the value set from Table 6, an approximation to the temperature can be made as towards around $36^{\circ}C$.

In comparison to the relationship presented in the experimental guide (W15e Isotherms of Real Gases), where it was stated that up to a good approximation the relation between $Q_{2,3}$ and $\frac{T_p}{T_k}$ can be related as;

$$Q_{2,3} = Q_{2,3}(0)(1 - \frac{T_p}{T_k})^{\frac{3}{8}}$$
(12)

was not seen. Even a fitting of this equation, with $Q_{2,3}(0)$ and the power left as unknowns to find, lead to no real answer. A fitting with the value of $Q_{2,3}(0)$ inserted as $34798 \frac{J}{moles}$ led to a fitting of an R^2 value of 0.62, a much lower relation rather than the fitting from the original figure. Possible reasoning behind this inconsistency will be further analysed in the Discussion. More details in the Discussion.

6.2.2 Discussion

There is a clear decreasing relationship between reduced temperature (correlative to temperature) and the latent heat of vaporisation. With an increasing T_s , there is a decrease in $Q_{2,3}$. This would be because at a higher temperature, the energy of the system is larger, and as such would require relatively lesser energy to raise the substance from initial temperature to vaporising it. The deviation of the behaviour from the example

behaviour set out in the lab guide can be attributed to standard error deviations as explored in Section 3.3.3. However, such a large misalignment for there to not be any set of constants to map equation 12 with the data cannot be explained. There is no clear large mistakes within the experiment, nor are other values showing any large disparity. As such, it is either a wrong implementation of the values (and our misunderstanding of the explanation in the lab guide) or there is a missing step we did not implement properly. Most likely the former.

6.2.3 Error Analysis

Any experimental error would be the same as the one from Section 3.3.3, as the data is from the same experiment. From the existing uncertainties within the measuring tools, and utilising equation 9, the uncertainty of $Q_{2,3}$ was found by propagating the error through the whole data. Leading to error as follows;

$$\Delta Q_{2,3} = Q_{2,3} \cdot \left(\frac{\partial V_m}{V_m} + T_k \cdot \frac{\partial T_s}{T_s}\right) \tag{13}$$

Where in equation 13, the uncertainty as ∂V_m and ∂T_k where found through the uncertainties in the measurement tool. The final uncertainties being:

Data Set	Mean Error Propagation	Largest Error (Max)
$Q_{2,3} \frac{J}{\text{moles}}$	$\pm 9.26 \cdot 10^{-5}$	± 13.4
$\partial V_m \stackrel{\text{Holos}}{\mathrm{A}}$	$\pm \ 0.01$	± 0.01
∂T_p A	± 0.1	± 0.1

Table 7: Error Propagation; Mean and Maximum Values

The uncertainty in V_m is the result of the additivity of the gas and fluid volume measurements from Figure 1. The uncertainty in T_s is from the lowest measurement value in the Thermostat Machine (because for digital measurements, the smallest measurable value is taken).

7 Conclusion

This study examined the behaviour of SF_6 under varying isothermal conditions, highlighting deviations from ideal gas behaviour. The pressure-volume isotherms revealed coexistence regions below the critical temperature (T_k) , confirming liquid-gas equilibrium. Critical parameters determined experimentally showed agreement with theoretical values. The Clausius-Clapeyron equation provided the molar latent heat of vaporization $(Q_{2,3})$, which decreased with temperature. Deviations from literature values were attributed to experimental limitations, including apparatus precision and environmental control. The relationship between reduced temperature and $Q_{2,3}$ exhibited a power-law trend. Improved experimental methods and data analysis could refine future findings, enhancing consistency with theoretical models.

8 Appendix

Numerical Differentiation; code

9 Bibliography

Author Unknown. W15e Isotherms of Real Gases, 2024

Marcus, Yizhak, Solubility Parameters of Permanent Gases, Journal of Chemistry, 2016, 4701919, 18 pages, 2016. link