

Determining the critical temperature of Ethane and using it to calculate the Van der Waals constants and approximating molecular radius of Ethane.

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ABSTRACT

Ethane gas under isothermal compression is studied to find out more about its thermophysical properties such as critical temperature and molecular radius. The experimentally obtained values are used to calculate the Van Der Waals coefficients a and b . Standard techniques are applied that involve compressing the volume with a mercury column and reading off the pressure. The results such as $T_{Cr} = 305K$ and $P_{Cr} = 50 \pm 1 * 10^5 Pa$ agreed with the theoretical quantities through 3 sigma test. Similarly, the calculated coefficients a , and b were found and were proven to agree with the literature. The approximated molecular radius had 2.2 correctness from the 3 sigma test and therefore was legitimate. The results satisfied the predictions but some quantities were subjected to a bigger error than expected due to fluctuations.

1 INTRODUCTION

A phase of a substance can be fully described with a region in a (P,V,T) space diagram where P is pressure, V – volume, and T – temperature. Its equilibrium state can be specified by two of those variables e.g. P and V since all 3 of them are connected by the equation of state:

$$PV_m = RT \quad (1)$$

where V_m is the molar volume ($V_m = V/n$) and R is the molar gas constant.

If vapour is compressed isothermally in a cylinder, depending on the temperature, at some point of the compression, a sharp transition into a liquid could be observed. After this point, an ongoing decrease in volume causes further vapour condensation at a constant pressure. The exact boundary point at which the saturated vapour appears moves to lower volumes if a higher temperature is kept constant. In fact, at some higher, critical temperature T_{Cr} , the sharp transition from vapour into liquid is not present anymore. Instead, the gas becomes denser and denser upon compression, and vapor and liquid become indistinguishable [1].

To describe the equilibrium states of a substance more realistically, the equation of state: eq. 1, is often modified with extra terms and has the form of the Van der Waals equation:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT. \quad (2)$$

The constants, a and b , can be experimentally determined by obtaining the critical temperature of a given gas. The following relations can be then used to calculate them:

$$a = 3P_{Cr}V_{m,Cr}^2 \quad (3)$$

$$b = \frac{V_{m,Cr}}{3} \quad (4)$$

where the P_{Cr} and $V_{m,Cr}$ are the pressure and volume at the corresponding critical temperature T_{Cr} .

In this work, the critical temperature of ethane is measured by performing an isothermal compression of the gas at an increasing temperature that is kept constant at each step. The obtained experimental result is used to deduce the parameters a and b from (2) and also to calculate the approximate radius of an ethane molecule.

Precise measurements of such thermophysical data of gases

like ethane are needed in designing liquefaction plants, manufacturing refrigerants [2] or for the strictly theoretical purpose such as approximating the radius of a molecule and finding out more about the limitations of the theory such as Van der Waals equation.

2 METHOD

Figure 1 presents the set up of the apparatus used for the experiment.

To measure the P-V isotherms, the temperature was set at the beginning of the experiment by the thermostat. Then the mercury column was being forced into the tube containing ethane and the pressure was recorded from the barometer at the appropriate step of decreasing volume: $0.1cm^3$. This procedure was repeated at temperatures from $24^\circ C$ to $38^\circ C$ with $2^\circ C$ increment and data was collected at each step.

A crucial part of the experiment was an observation of the changes inside the tube because based on them, the obtained data were interpreted. In relation to this, there were several sources of error from the fact that the measurements were taken by eye. The mercury column has a shape of a meniscus on top, therefore it was not always precisely clear what is the amount of the compressed volume. Further, the barometer was oscillating during the major part of taking the data. Nevertheless, it was decided that the value of uncertainty in the instruments themselves is enough to compensate for those fluctuations and imperfections.

3 RESULTS

Figure 2 shows the plotted isotherms on a P-V diagram. The error bars indicate the instrumental errors, for pressure $\sigma_P = 0.25 * 10^5 Pa$ and for volume $\sigma_V = 0.025cm^3$. Both quantities were calculated as half of the instrumental range.

From the observations, during the experiment, we found out that at $T = 32^\circ C$ for the first time, the sharp transition from vapour into liquid was not clearly noted. Instead, it could be seen as the substance is becoming denser across all available volume. This observation confirms the data on the figure 2. Below $32^\circ C$, the isotherms form a plateau at smaller volumes, where the pressure is approximately constant. This indicates the region where condensation happens. This reasoning points at the temperature of

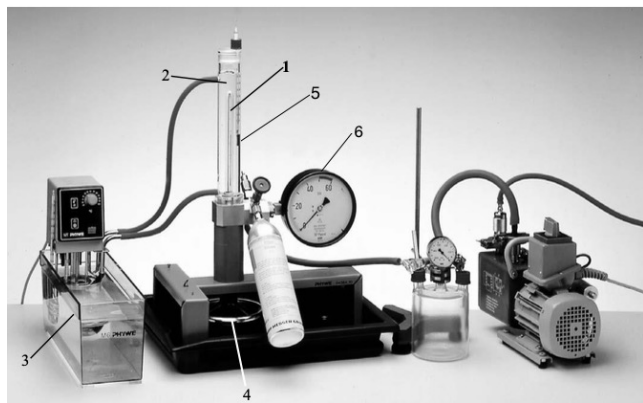


Figure 1. Temperature can be regulated by the thermostat in the water bath (3). The tube with ethane gas and marked volume scale (1). Compression is controlled by forcing the mercury column into the tube by turning the wheel (4). The actual temperature of the water jacket surrounding the tube can be read from the thermometer (5). The pressure in the tube can be gathered from the barometer (6).

$32^{\circ}\text{C} = 305\text{K}$ to be the critical point. Since the initial temperatures were set with the step of 2°C , the error of the critical temperature is $\sigma_{T_{Cr}} = 1^{\circ}\text{C}$. From this, we can also read off the figure 2 that the critical pressure is approximately $P_{Cr} = 50 \pm 1 \times 10^5 \text{Pa}$. The uncertainty on the critical pressure was made bigger than the original error in pressure due to the fact that the actual temperature difference measured by thermometer was quite big ($2.5 \pm 0.25^{\circ}\text{C}$) between the critical temperature and the previous one.

Having the values for P_{Cr} and T_{Cr} , the molar critical volume was calculated from the following equation

$$V_{m,Cr} = \frac{3RT_{Cr}}{8P_{Cr}} = 1.90 \pm 0.07 \text{m}^3 \text{mol}^{-1} \quad (5)$$

In order to compare the obtained value for the critical volume with the results on the figure 2, the number of moles in the tube was calculated from the eq. 1 by using the value for initial volume and its corresponding pressure at $T = 38 \pm 1^{\circ}\text{C}$. Therefore the number of moles in the tube $n = 2.438 \pm 0.073 \times 10^{-3} \text{mol}$. By multiplying this value with $V_{m,Cr}$ we got the quantity that could be compared with plotted results. $V_{Cr} = 0.463 \pm 0.022 \text{cm}^3$. This value coincides with the results on the figure 2.

Using the equations 3 and 4, the van der Waals constants were obtained. The calculated values were respectively: $a = 5.42 \pm 0.42 \text{barL}^2 \text{mol}^{-2}$, $b = 0.0630 \pm 0.0023 \text{Lmol}^{-1}$.

To calculate the approximate radius of a molecule of ethane, a deeper understanding of the van der Waals constant - b had to be introduced. This correction for the volume from the equation of state 1, arises from the fact that ethane molecules are not infinitely small, and their size matters in the calculations. Their molecular shape was approximated to a sphere with a radius of $2r$, since each molecule, cannot come closer to another than the distance of r . With this in mind, the following relation was used for calculations

$$b = 4N_A \frac{4}{3}\pi r^3 \rightarrow r = 1.84 \pm 0.07 \times 10^{-10} \text{m} \quad (6)$$

where N_A is the Avogadro constant.

4 CONCLUSIONS

Both values for the critical temperature and pressure were compared with literature values [3]: $T = 305.33\text{K}$, $P = 48.72 \times 10^5 \text{Pa}$ which were treated as exact values (no error). In both cases,

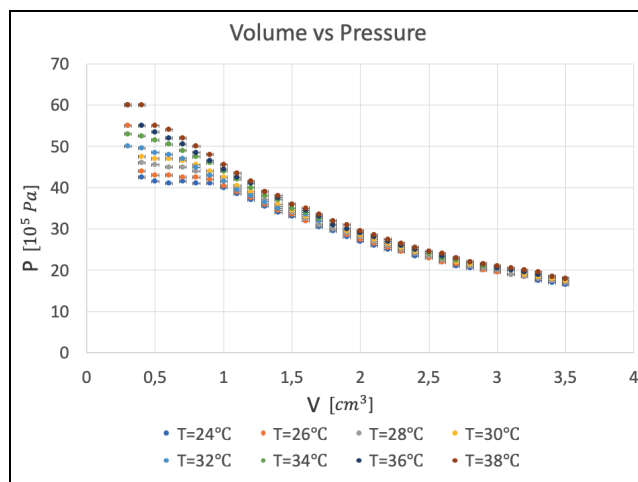


Figure 2. Collected data plotted on the P-V diagram. Each colour corresponds to a separate set of data taken at a different temperature. The error bars were plotted with each data point to indicate uncertainty.

our experimental results passed the 3 sigma test with the following precise outcome

$$\frac{\Delta T_{Cr}}{\sigma_{T_{Cr}}} = 0.33, \quad \frac{\Delta P_{Cr}}{\sigma_{P_{Cr}}} = 1.28. \quad (7)$$

It should be noted here that, whereas the temperature value agrees very precisely with the theoretical quantity, both values for critical pressure are quite different and if the assumed error wasn't increased, the 3 sigma test could result in a worse outcome.

The obtained Van der Waals constants, a and b also passed the 3 sigma tests when comparing them with the following, theoretical values from the lab script [4]: $a = 5.562 \text{L}^2 \text{barmol}^{-2}$, $b = 0.0638 \text{Lmol}^{-1}$. The precise results of the test are:

$$\frac{\Delta a}{\sigma_a} = 0.34, \quad \frac{\Delta b}{\sigma_b} = 0.35. \quad (8)$$

Comparison of the molecular radius with the theoretical value [5]: $r = 1.994 \text{\AA}$ was as well proven to be legitimate:

$$\frac{\Delta r}{\sigma_r} = 2.2. \quad (9)$$

As seen above, all the results agreed with the theoretical predictions. Nevertheless, the 3 sigma test is not only based on the quantity itself, but also the uncertainty. The obtained critical pressure was assumed to have an error of $1 \times 10^5 \text{Pa}$, which was due to the big step of the temperature range. Focusing on making this quantity more precise, could be a good improvement for future experiments.

References

- [1] – A. Rex, Finn, C. B. P. Finn's *Thermal Physics*, CRC Press, Taylor & Francis, Boca Raton FL (2017), 3rd edition, **10**, 239.
- [2] – G. C. Straty, R. Tsumura, *Journal of Research of the National Bureau of Standards* (1976), 80A(1), 35–39,
- [3] – Vesovic Velisa, Ethane, <https://www.thermopedia.com/content/738/11/03/2021>
- [4] – Queen Mary University of London, Physics Laboratory (SPA5201), lab script 2021, Thermal Equation of State and Critical Point of Ethane,
- [5] – Zugang Mao, Susan B. Sinnott, *The Journal of Physical Chemistry*, (2001), 105B(29), 6916–6924