

Investigative Design Exercise: Critical Point of Ethane

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1 INTRODUCTION

Isotherms of ethane have been previously measured and the critical temperature, pressure and molar volume have been determined, as well as values for the Van der Waals constants. In this report, the agreement between empirical predictions made using theoretical gas models and experimental data for isotherms of ethane is discussed, and modifications to the experimental setup to measure the critical points of carbon dioxide, xenon and methane are given.

2 A COMPARISON OF EXPERIMENTAL DATA TO THEORETICAL GAS MODELS

Figure (1) shows plots of the $24.5 \pm 0.5^\circ\text{C}$ and $38.0 \pm 0.5^\circ\text{C}$ isotherms of ethane measured during the experiment, as well as plots of the ideal gas equation and the Van der Waals equation, given by

$$pV = nRT \quad (1)$$

and

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \quad (2)$$

respectively, where p is pressure, V is volume, n is the number of moles, R is the gas constant, T is temperature in Kelvin, and a and b are the Van der Waals constants. The theoretical curves have been plotted using values determined from the experiment including $n = 2.62 \pm 1.05 \times 10^{-3}$ moles, $a = 0.545 \pm 0.051 \text{ m}^6\text{Pamol}^{-2}$, and $b = 6.37 \pm 0.27 \times 10^{-5} \text{ m}^3\text{mol}^{-1}$, and the literature value of $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ [1]; the errors have been propagated using the general formula for error propagation in each case [2].

Neither the ideal gas nor the Van der Waals equation correctly predict how pressure increases as $V \rightarrow 0$ compared to experimental data. The 24.5°C isotherm shows no difference between Eqs. (1) and (2), whereas Van der Waals equation provides a slight improvement to the 38.0°C isotherm. There is agreement at higher volumes and lower pressures which suggests that these equations breakdown at and around the critical point or, more precisely, at the phase transition from vapour/gas to liquid/supercritical fluid.

There is an assumption in the derivation of the n^2a/V^2 term of the Van der Waals equation that the number of nearest neighbour

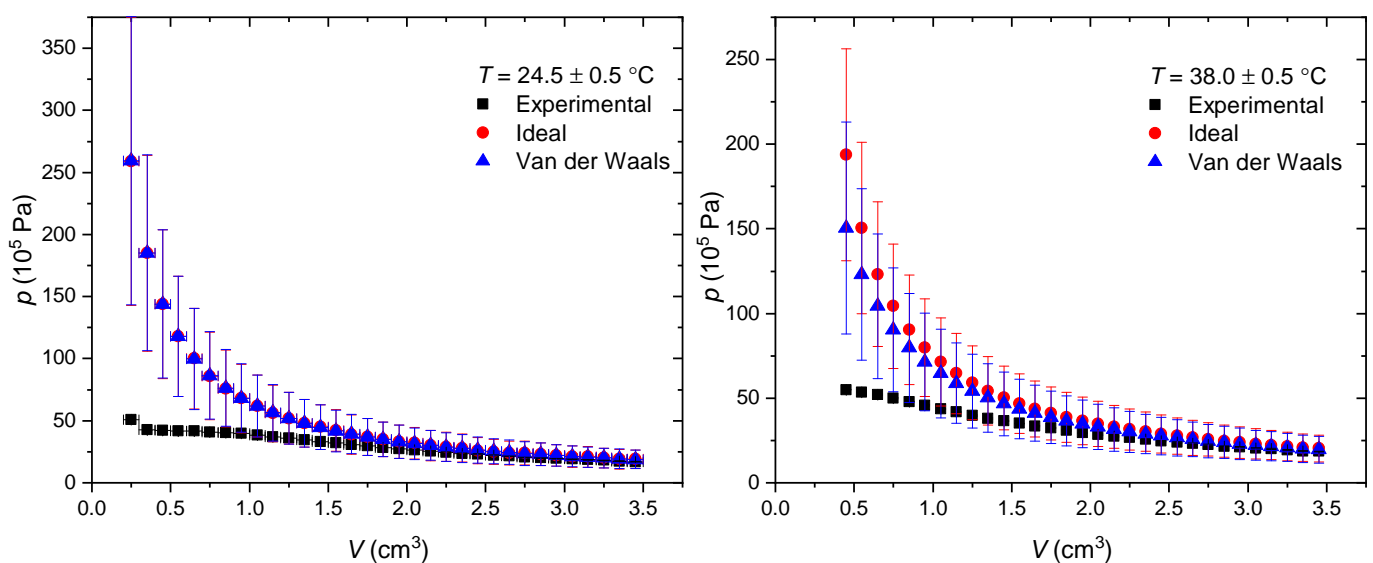


Figure 1. Pressure as a function of volume for the $24.5 \pm 0.5^\circ\text{C}$ and $38.0 \pm 0.5^\circ\text{C}$ isotherms of ethane, with the ideal gas and Van der Waals equations' predictions using experimentally determined parameters.

Gas	T_C (K)	p_C (MPa)	$V_{m,C}$ (cm ³ mol ⁻¹)
Carbon dioxide	304.13	7.375	94
Xenon	289.77	5.841	118
Methane	190.56	4.599	98.60

Table 1. Values of the critical temperature, pressure and volume for carbon dioxide, xenon and methane, obtained from the CRC Handbook of Chemistry and Physics [1].

molecules is proportional to n/V [3]. However, during a phase transition, as liquid or supercritical fluid begins to form, the number of nearest neighbours may not continue to be homogenous, as was assumed in the gaseous state. As a result the value of a may not be expected to remain constant during this process, which could explain the discrepancy between the theoretical curves and the experimental data.

3 MODIFICATIONS TO THE EXPERIMENTAL SETUP

The lack of agreement between experiment and theory indicates that more data needs be collected and analysed to better understand the behaviour of gases at and around the critical point. Three gases which have been previously investigated are carbon dioxide, xenon and methane, the critical data of which is given in table (1).

In its current configuration, the experimental setup used to test ethane is not capable of measuring critical point data of these gases for several reasons: (i) the maximum tensile strength of glass is typically around 7 MPa [4] and the maximum pressure measurable by the pressure gauge is 6 MPa, both of which are exceeded by the critical pressure of carbon dioxide; (ii) the water bath used to control the gas temperature has a stated range of -20 to 100 °C which is insufficient to reach the critical temperature of methane; (iii) mercury, used vary the volume by compressing the gas, has a melting point of -38.8290 °C [1], and, consequently, would solidify before reaching the critical temperature of methane.

To overcome these limitations, it is proposed that a Poly (Methyl Methacrylate) (also known as acrylic) tube should replace the glass capillary tube whilst testing carbon dioxide and xenon because the polymer is both strong (with a tensile strength of ≈ 72 MPa [5]), and transparent, meaning that the phase transition into a supercritical fluid can still be directly observed. Low temperature baths can be made using dry ice (for temperatures ≥ -78 °C) or liquid nitrogen (for temperatures < -78 °C) to cool compounds such as acetone, which has a melting point of -94.8 °C [1]. In a similar experiment, Jones *et al.* measured warming rates of 0.06 °min⁻¹ at 200 K with a highly-insulated experimental setup [6]. Based on previous measurements of ethane, tests can take up to 10 minutes per isotherm, which could lead to temperature fluctuations > 1 °C. Therefore, it is suggested that pressure as a function of temperature is measured for isochores of methane, avoiding a potentially large source of error in temperature. Additionally, exchanging mercury for ethanol (which has a melting point of -114.1 °C [1]) as the compression fluid will enable the volume of methane to be varied at low temperatures. A thermometer and pressure gauge of greater range will also be required to take measurements of temperatures around -100 °C and pressures ≥ 8 MPa, of which there are many available online. Although the acrylic capillary tube should also be used for xenon (due to the proximity of the critical pressure to the tensile strength of glass), it should not be used for methane because compounds such as acetone strongly attack acrylic [5], which can affect the strength of the material.

4 CONCLUSION

This report has used p – V isotherms of ethane to compare predictions of theoretical gas models with experimental data around the critical point, and determined modifications required for the experimental setup to be capable of obtaining critical point data for carbon dioxide, xenon and methane. The ideal gas and Van der Waals equations were shown to have poor agreement with the experimental results at small volumes. The cause of this is thought to stem from the assumption that a is constant during a phase transition.

To test carbon dioxide and xenon, it has been suggested that the glass capillary tube should be replaced with an acrylic one because it would have approximately $10\times$ the tensile strength, and retains the transparency required to observe the supercritical phase transition. A low temperature bath made using an organic compound such as acetone, cooled by liquid nitrogen, is recommended to measure isochores of methane, rather than isotherms, due to the unavoidable warming of the gas back to room temperature.

References

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