

Thermal equation of State and Critical point of Ethane

There are three parts to this experiment. They are:

1. To measure a number of p-V-isotherms of ethane
2. Determine the critical temperature and pressure of ethane
3. Calculate the constants of the Van der Waals equation and the radius of the molecules

NOTE:

IT IS ESSENTIAL THAT THE PRESSURE IN THE APARATUS NEVER RISES ABOVE 6MPa



Fig. 1: Experimental set-up: Thermal equation of state and critical point.

Set-up and procedure

Figure 1 shows a photograph of the equipment for measuring the thermal equation of state of a gas. The equipment consists of a glass tube which has been filled with ethane gas. This tube is surrounded by a water jacket the temperature of which can be varied using the thermostat in the water bath. This allows you to control the temperature of the gas in the experiment. The pressure of the gas can be controlled using a mercury column which can be forced into the capillary tube containing the gas. Whenever you finish an experiment the piston must be lowered fully (i.e. the wheel turned as far anticlockwise as possible)

The p-V-isotherms of ethane should be measured at 2°C increments from 24° to 38°C. Note that precise control of the temperature is not possible so make small changes on the thermostat and record the actual steady state temperature of your measurements. Record the pressure at volume increments of 0.1 cm³.

It is essential to avoid pressures above 6 MPa!

Theory

Consider a system where p , V and T are the state variables. We know that the equilibrium states of the system in a single phase are uniquely specified by two of these variables and that p , V and T are connected by the equation of state. If we compress a gas isothermally, as we do in this experiment, and the gas is initially in a single vapour phase region as the pressure is increased the volume decreases until at some point we have condensation and drops of liquid begin to appear. In figure 2 at $t=10^{\circ}\text{C}$ for example this occurs as the curve enters the hatched region. What is happening is that the substance is separating into two distinct phases of very different densities, although both are at the same temperature and pressure. As we further compress the substance more liquid forms until at the point where the line leaves the hatched region all the substance is in the liquid phase. After this region a large increase in pressure is required to produce a small change in volume.

There is a critical temperature, T_C , above which an isothermal compression produces no sharp liquid-vapour transition. Upon compression the system becomes more and more dense, moving continuously from a low-density fluid to a high-density fluid. At the critical point (C in figure 2) the vapour and the liquid have become indistinguishable with the same density. It is customary to use the word gas above T_C and the word vapour below T_C . In other words compressing a gas will not produce condensation.

The equation of state of an ideal gas is given by,

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

Where p is the Pressure, V_m the molar volume, T the Temperature in K and R is the Universal Gas constant.

For the description of the real behaviour, molecular interactions (mainly attraction forces) and the volumes of the molecules must be taken into account. One widely used equation of state for real gases is the Van der Waals equation,

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

where a and b are the Van der Waals constants

The term a/V_m^2 refers to the attractive molecular forces (attraction acts like an additional pressure) and is called cohesion pressure. The term b refers to the volume of the molecules and is called covolume. On the basis of the covolume b , the radius of the gas molecule can be calculated according to equation (4):

$$b = 4N_A \frac{4}{3} \pi r^3 \quad (3)$$

Where N_A is Avogadro's constant and r is the Van der Waals radius of the molecule

One way for the experimental determination of the Van der Waals constants and the interaction parameters is the measurement of the critical quantities of the gas. The following relations can be derived:

$$V_{Cr} = \frac{3RT_{Cr}}{8p_{Cr}} \quad (4)$$

$$a = 3p_{Cr}V_{Cr}^2 \quad (5)$$

$$b = \frac{V_{Cr}}{3} \quad (6)$$

Figure 2 shows the measured p-V-isotherms for sulphur hexafluoride SF₆. The isotherms below 46°C are characterized by a plateau caused by the liquefaction of the gas (vapour-liquid equilibrium). The point at which a plateau no longer occurs is the critical point. It has been determined for SF₆ at $T_{cr} = 46^\circ\text{C} = 319\text{ K}$ and $p_{cr} = 3.8\text{ MPa}$.

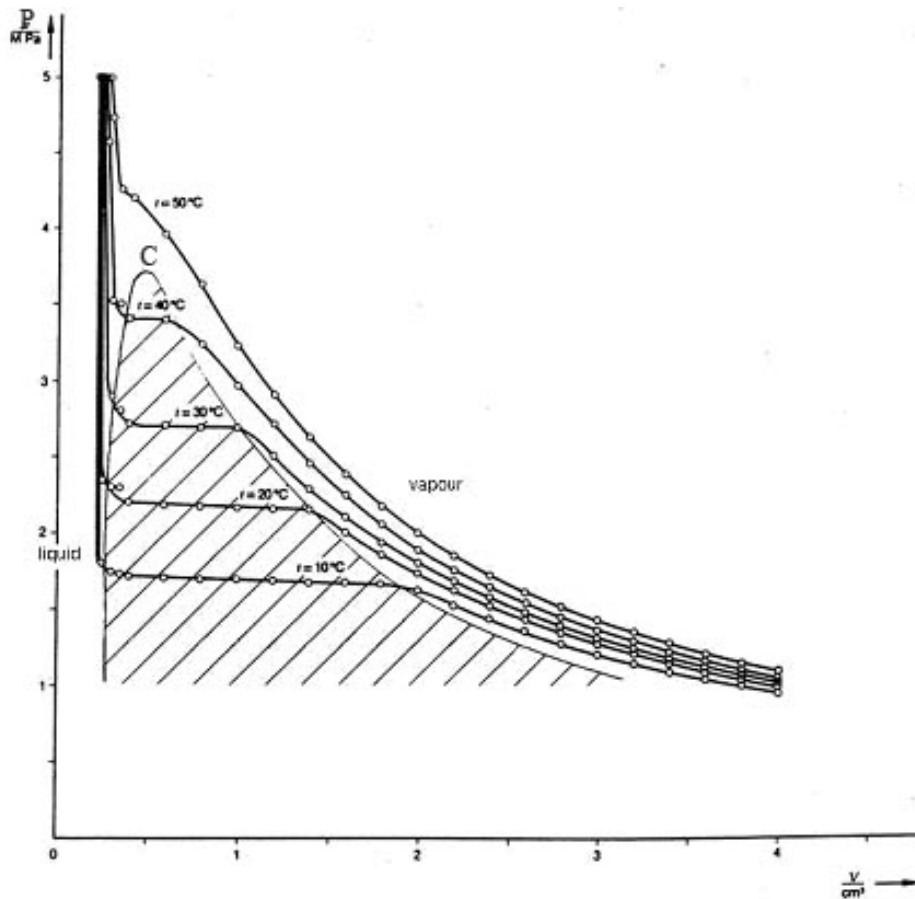


Fig. 2: p-V-isotherms of SF₆.

Having collected your data you should plot the pV-isotherms of ethane and determine the critical temperature and pressure. Use your results to determine the Van der Waals parameters and estimate the molecular radius for ethane.

NOTE.

Observation is essential for this experiment. You must keep a detailed log of exactly what you see at ALL points in this experiment. Without note of everything you observe you will not be able to interpret the data you obtain.