

### Related topics

Ideal gas, real gas, equation of state, Van der Waals equation, Boyle temperature, critical point, interaction potential, molecule radius.

### Principle and task

A substance which is gaseous under normal conditions is enclosed in a variable volume and the variation of pressure with the volume is recorded at different temperatures. The critical point is determined graphically from a plot of the isotherms.

### Equipment

Critical point apparatus	04364.10	1
Immersion thermostat A100	46994.93	1
Bath for thermostat, Makrolon	08487.02	1
Accessory set for A100	46994.02	1
Jointing f. GL18, 8 mm hole, 10 pcs	41240.03	1
Vacuum pump, one stage	02750.93	1
Adapter for vacuum pump	02657.00	1
Security bottle 500 ml, 2× GL18/8	34170.01	1
Spring manometer, 0...-1000 mbar	34170.02	1
Stopcock, 3-way, t-shaped, glass	36731.00	1
Tripod base -PASS-	02002.55	1
Support rod, stainl.steel, 500 mm	02032.00	1
Universal clamp	37715.00	1
Right angle clamp	37697.00	1
Rubber tubing, i.d. 8 mm	39283.00	4

Rubber tubing, vacuum, i.d. 8 mm	39288.00	1
Rubber tubing, vacuum, i.d. 6 mm	39286.00	1
Pinchcock, width 15 mm	43631.15	1
Hose clip, diam. 8-12 mm	40996.01	2
Hose clip f. 12-20 diameter tube	40995.00	2
Mercury tray	02085.00	1
Compressed gas, ethane, 14 g	41772.09	1

### Problems

1. Measure a number of  $p$ - $V$ -isotherms of ethane.
2. Determine the critical point and the critical quantities of ethane.
3. Calculate the constants of the Van der Waals equation, the Boyle-temperature, the radius of the molecules and the parameters of the interaction potential.

### Set-up and procedure

The experimental set-up is as shown in Figure 1. The  $p$ - $V$ -isotherms of ethane should be measured at the following temperatures: 20, 25, 28, 30, 32, 35, 40°C.

Detailed descriptions and sketches on evacuating the apparatus and filling it with the appropriate gas are given in the operating instructions.

**Before opening a valve, the screw of the pressure piston must be brought to the lower stop! Furthermore, it is essential to avoid pressures above 6 MPa!**

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



The hoses in the water circulating system between the temperature-controlled bath and the temperature control jacket of the critical point apparatus must be secured with hose clips. The flow of water to the temperature control jacket of the device on the lower hose connection tube (hose olive) is adjusted with a pinchcock in such a manner that just as much water can enter the device as can flow out of the upper hose connection tube. If this adjustment is not made, it is possible that water will flow out of the temperature control jacket's lid. During the measurement of an isotherm perform a reading of the pressure every 0.1 ml of volume difference.

### Theory and evaluation

The equation of state of an ideal gas is given by

$$p \cdot V_m = R \cdot T \quad (1)$$

$$\frac{p \cdot V_m}{R \cdot T} = 1$$

$p$	Pressure
$V_m$	Molar volume
$T$	Temperature in K
$R$	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. This is done formerly by expanding of equation (1) with so-called virial coefficients:

$$p \cdot V_m = R \cdot T + B(T) \cdot p + C(T) \cdot p^2 + \dots \quad (2)$$

$$p \cdot V_m = R \cdot T + B' \cdot V_m^{-1} + C' \cdot V_m^{-2}$$

In practice often only one virial coefficient is used. Another widely used equation of state for real gases is the Van der WAAL's equation:

$$\left(p + \frac{a}{V_m^2}\right) \cdot (V_m - b) = R \cdot T \quad (3)$$

$a, b$  Van der WAALS constants

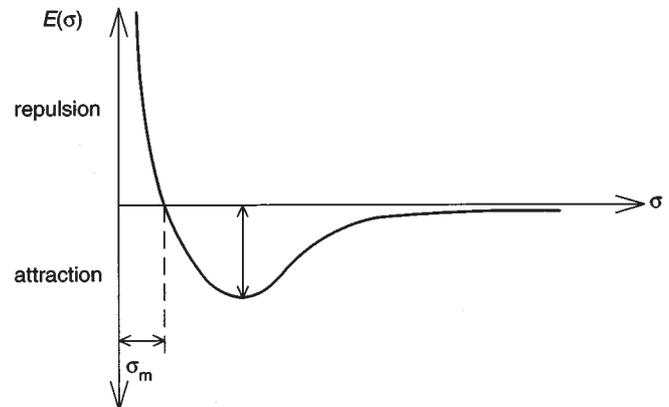
The term  $a/V_m^2$  refers to the attraction forces (attraction acts like an additional pressure) and is called cohesion pressure. The correction term  $b$  refers to the volume of the molecules and is called covolume. On the basis of the covolume  $b$ , the radius of the gas molecule can be calculated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

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

A relation between the second virial coefficient  $B(T)$  of equation (2) and the Van der WAALS constants  $a$  and  $b$  of equation (3) can be derived by simplification of equation (3) and comparison of the coefficients:

$$B(T) = b - \frac{a}{R \cdot T} \quad (5)$$

Fig. 2: Interaction potential in dependence on the molecule distance.



The coefficient  $B(T)$  is a function of the temperature and, according to equation (2), the gas shows a quasi ideal behaviour when  $B$  is equal to zero. This temperature is called BOYLE-temperature and can be calculated by

$$T_B = \frac{a}{b \cdot R} \quad (6)$$

The interactions between the gas molecules can also be described by an interaction potential function

$$E(\sigma) = 4 \cdot \varepsilon \cdot \left[ \left(\frac{\sigma_m}{\sigma}\right)^{12} - \left(\frac{\sigma_m}{\sigma}\right)^6 \right] \quad (7)$$

$\varepsilon, \sigma_m$	Parameters
$\sigma$	Distance of the molecule centres

Such a potential function and the meaning of the parameters  $\varepsilon$  and  $\sigma_m$  are shown in Figure 2.

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:

$$V_{cr} = \frac{3}{8} \cdot \frac{R \cdot T_{cr}}{p_{cr}} \quad (8)$$

$$a = \frac{9}{8} \cdot R \cdot T_{cr} \cdot V_{cr} \quad (9)$$

$$b = \frac{1}{3} \cdot V_{cr} \quad (10)$$

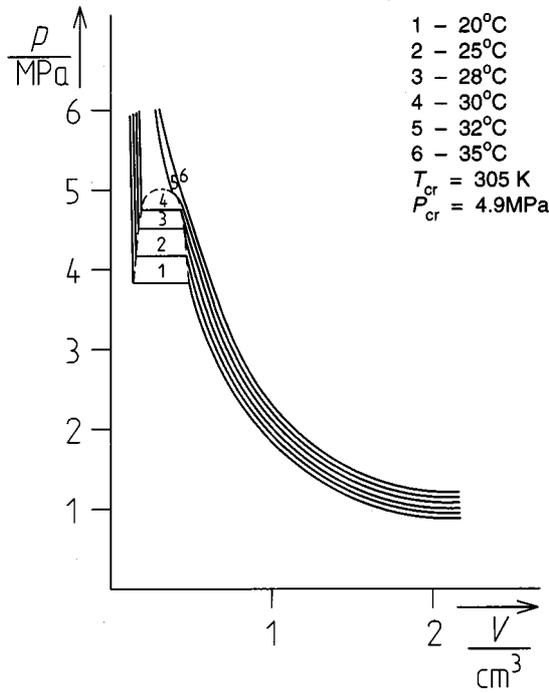
$$\sigma_m = 0.841 \cdot 10^{-8} \cdot V_{cr}^{1/3} \quad (11)$$

$$\varepsilon = 0.77 \cdot k \cdot T_{cr} \quad (12)$$

$k$  BOLTZMANN constant

$$k = 1.381 \cdot 10^{-23} \text{ JK}^{-1}$$

Fig. 3:  $p$ - $V$ -isotherms of ethane.



In order to determine the critical point of ethane, the measured  $p$ - $V$ -isotherms are plotted in a diagram as shown in Figure 3.

The isotherms below 32°C are characterized by a plateau caused by the liquification of the gas (vapour-liquid equilibrium). The point at which a plateau no longer occurs is the critical point. It has been determined for ethane at  $T_{cr} = 32^\circ\text{C} = 305 \text{ K}$  and  $p_{cr} = 4.9 \text{ MPa}$ .