

A2 Critical point: diethyl ether or n-pentane

Tasks:

1. Determine the critical pressure and temperature of diethyl ether (apparatus A 2a) or of n-pentane (apparatus A2b), as appropriate.
2. The vapor pressure curve of diethyl ether or n-pentane should be determined

Basics:

The following knowledge is required to understand the experiment:

1. Definition of the critical point
2. Isotherms of a real gas near the critical point in a p-V diagram.
3. Vapor pressure curve in a p-T diagram.
4. Description of the real gas behavior by a state equation (e.g. Van der Waals equation).

The simplest way to determine the critical data is to begin first with the critical pressure, p_k and then continue with the determination of the critical temperature, T_k . It is however not possible to use this apparatus and determine the critical volume, V_k . For this purpose the substance placed in the vertically oriented capillary should be driven in the region of the temperature gradient, $T_{oben} > T_{unten}$. When currently $T_{oben} < T_k$ and one reduces the pressure p of the substance from $p < p_k$ down to a value which corresponds to T_{oben} , then one observes a spontaneous formation of a meniscus in the upper end of the capillary, i.e. this behavior signalizes that the phase separation drives the system towards a thermodynamic equilibrium between gas and liquid phases.¹ The impressive meniscus in the upper end of the capillary disappears immediately when increasing the pressure. When in a small region of the capillary, somewhere around the center, the temperature of the substance approaches the critical value T_k then the following relation is obvious, $T_{unten} < T_k < T_{oben}$. By slowly reducing the pressure, $p < p_k$, when $p = p_k$ one gets in this region turbidity (critical opalescence). When continuing this pressure reduction one observes the meniscus again. When driving the system in opposite direction and increasing gradually the pressure one observes first that the meniscus disappears and subsequently also the critical opalescence is entirely quenched. The pressure p measured at the conditions leading to the visible critical opalescence corresponds to the real critical pressure p_k value. The related T_k value can be determined only when the capillary reached a homogeneous temperature distribution along the whole length. One starts with a slow reduction of the pressure when $p > p_k$ and precisely record the vapor pressure curve, $p(T)$, by stepwise increasing the temperature and read out the pressure at the moment when the meniscus appears again. When no meniscus can be formed by further temperature increase then the critical temperature T_k has been reached. The best way to determine T_k : one should first plot the vapor pressure curve, $p(T)$ (sometimes this curve has to be extrapolated first) and subsequently determine the intercept point between the $p(T)$ curve and the straight line $p = p_k = \text{const}$, which defines the critical temperature T_k .

¹ By a careful and slow pressure reduction one relaxes the liquid phase in a metastable way. The pressure drops then below the equilibrium vapor pressure without to activate the phase segregation. Somewhere along this line the stability limit will be reached, the gas phase forms itself and the pressure increases abruptly up to the equilibrium value.

Functional description of the apparatus

The substance whose critical data are to be determined is located in the back light equipped glass capillary. This is connected to a high pressure apparatus screwed on so that the filled ether or hydrocarbon can also be used at approx. 60 bar the overpressure cannot escape to the outside. The apparatus screwed together from high-pressure components is U-shaped and filled with liquid mercury as a separating liquid. For a spindle press with a large hand wheel is used to generate pressure. The part of the apparatus, on which the screw press, the high-pressure manometer and the filling device are screwed on is filled with hydraulic oil. Turning the hand wheel clockwise allows the pressure in the apparatus. It is transferred from the oil to the mercury and from the mercury to the substance under investigation. The apparatus has been filled once and can be operated many measuring cycles without maintenance and repair work. The double valve (valves 1 and 2) must not be operated. If the apparatus is not operated, a buffer volume must be connected. The reason for this is the relatively large isochoric expansion coefficient $\alpha = (\partial p / \partial T)_V$ of the involved Liquids (oil, Hg and ether or pentane) at room temperature. Slight temperature fluctuations lead to relatively strong pressure changes in the not operated apparatus.

The pressure should not exceed 60 bar in stand-by mode and should never fall below 10 bar. At the beginning of the experiment, the buffer volume must be reduced by closing the valve 3 (on the left side of the apparatus). To do this, first apply the spindle press to a pressure of approx. 15 bar. After completion of the experiment, the buffer volume must be switched on again - again at a pressure of about 15 bar. The measuring capillary is located in a two-part furnace with top and bottom heating. The supply voltage for the two heaters is set with toroidal core transformers to max. 44 V to 48 V alternating voltage. One thyristor controller each can be connected to the heaters voltages between 0 V and the maximum value can be applied.

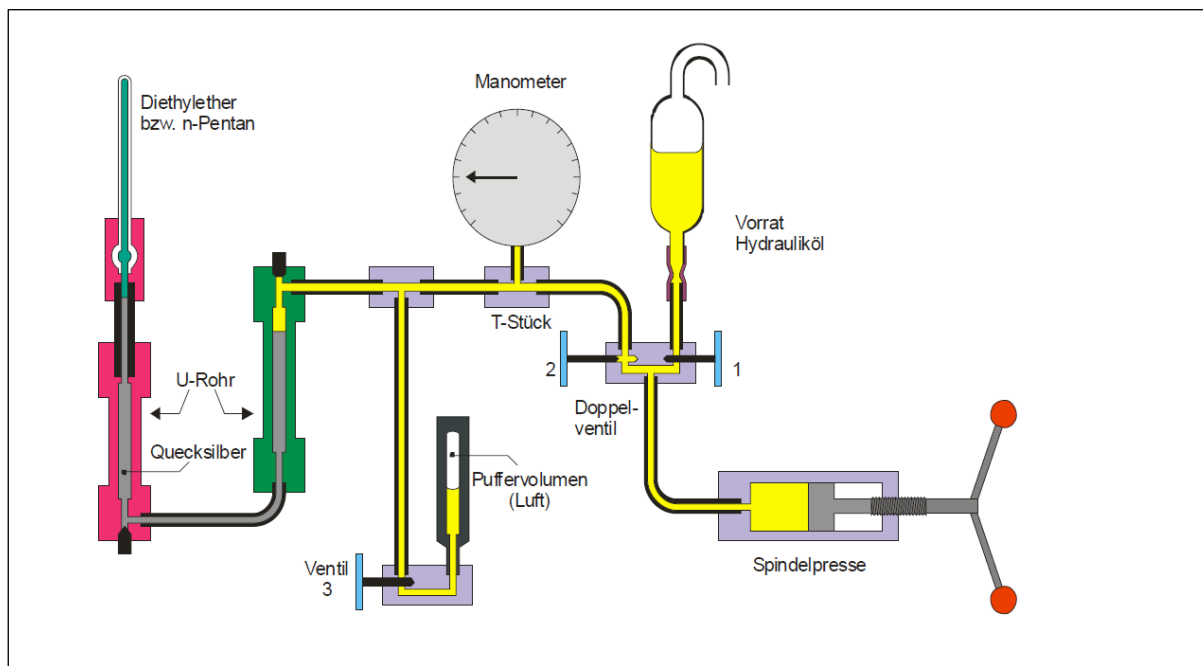


Figure 1: High-pressure apparatus for measuring the critical data of diethyl ether and n-pentane. Pressure generation: screw press, pressure measurement: manometer, separation fluid: mercury. The double valve must not be operated.

Performing the experiment

The apparatus is already completely wired and filled for measurement. Insert into the bore of the

A thermometer (0 °C to 250 °C) protrudes from the furnace surrounding the capillary. The one on the right. The control box on the side contains the main switch, a control for the brightness of the backlight, the two thyristor controllers and the ammeters for the upper and lower lower heating. Before starting the test, a pressure of approx. 15 bar must be set with the aid of the spindle press and close valve no. 3 located on the left side of the apparatus.

1. Determination of the critical pressure

First, both heaters of the furnace are put into operation and are evenly heated with max. 2 A heated up slowly for approx. 11 minutes to 180 °C. Then you turn the current flow in the lower heating back to zero, the lower heating is thus switched off. The upper end of the Now heat the capillary with 2.8 A for approx. 3 minutes until the thermometer reaches 200 °C to 210 °C. (App. A2a) or 205 °C to 215 °C (App. A2b). To maintain the temperature, reduce the current strength to 1.7 to 1.8 A (App. A2a) or to 1.6 to 1.7 A (App. A2b). It is to make sure that the pressure does not rise above 50 to 60 bar during heating. Now switches the lamp is turned on for backlighting, the light output of which is also regulated. The illuminance of the lamp must be adjusted in such a way that the light to be observing phenomenon becomes optimally visible. This can be different for the two tried parts and is also individually different. One reduces now the pressure, begun at about 50 bar, slowly by means of the large hand wheel of the spindle press, until the position of the capillary, which has just the critical temperature, shows a turbidity: the critical Opalescence. This disappears immediately with a small increase in pressure. By repeating this procedure, the mean value of the critical pressure p_k can be determined. The heating is then switched off (both ammeters must indicate zero) and the furnace is allowed to cool down to about 100 °C. The temperature of the furnace is then reduced to about 100 °C. The temperature of the furnace is then reduced to a minimum.

2. Determination of the critical temperature

After the furnace has cooled down to approx. 100 °C, the capillary is heated up again with both heaters and a current of approx. 2 A. The capillary is then heated up again with the two heaters. From 140 °C on, the current should be reduced to 1.4 A. Starting at about 160 °C, the vapour pressure is determined at intervals of about 5 K depending on the temperature. For this purpose one reduces, in each case begun at about 50 bar the pressure and reads at the first appearance of a meniscus at the upper end of the capillary at the same time pressure and temperature. After reading, the pressure is to about 50 bar again.

3. Termination of the experiment

After completion of the experiments, a pressure of approx. 15 bar must be set in the apparatus again. The buffer volume is then reattached to the apparatus by opening valve 3. connected.

Safety instructions

1. Protective goggles must of course be worn.
2. The Plexiglas pane must always remain closed during the test. All Operating elements within the test apparatus must not be operated. They are used for filling the apparatus with diethyl ether or n-pentane, mercury as separating liquid and hydraulic oil as pressure transmitting medium.
3. The pressure in the apparatus must not exceed 60 bar during the test, the temperature 220 °C not to exceed.
4. The pressure in the apparatus must not drop below 10 bar.
5. Make sure that the meniscus is not deeper than 3 cm below the upper end of the meniscus of the capillary, otherwise increase the pressure.
6. The maximum current of the upper heater is 3 A, that of the lower heater is 2.2 A (the limitation is realized by the design of the wiring)
7. After the end of the experiment, wait until the oven has reached room temperature cooled down. The pressure in the apparatus must now not fall below 10 bar sink.

8. If the capillary should break during the experiment, the current at the emergency stop switch is to shut down the lab row. Ask the other trainees to switch off and to leave the lab. Inform the assistants and the internship management immediately.

Data evaluation

Evaluation

1. The vapor pressure curve of the diethyl ether or n-pentane between 160 °C and the critical temperature. Determine the critical temperature by extrapolation the temperature T_k .
2. Plot the vapor pressure curve in the form $\log_{10}(p/p_0)$ against $1/T$ ($p_0=1$ bar). Determine the parameters A and B according to the equation $\log_{10}(p/p_0) = B - A/T$. Enter the critical pressure and temperature in this drawing and estimate their error limits.

Calculate the van der Waals constants a and b for diethyl ether and n-Pentane, respectively, and derive the necessary relationships. Calculate the critical Mol volume $V_{m,k}$. Discuss the results. Compare your results with literature data (e.g. CRC Handbook). Discuss any deviations that may occur.

Additional questions:

1. Order the following compounds according to increasing critical temperature and explain they follow the order: He, H₂O, NaCl, CHCl₃, Xe and C₂H₆.
2. How to liquefy air? What are the particular difficulties with the Liquefaction from H₂ to?
3. Calculate and compare the gravitational force with the Coulomb force between a Na⁺ ion and a Cl⁻ ion at a distance of 1 Å, 1 nm and 1 µm.

What you should know:

- equations of state of real gases, especially the van der Waals equation and the Virial equation;
- vapor-liquid phase transition;
- stable, metastable and unstable condition areas; behavior of the densities of the liquid and gaseous phase approaching the critical point;
- rule of Cailletet-Mathias;
- basis of origin of critical opalescence; Lennard-Jones potential.