

Observing the phase transition between the liquid and the gas phase at the critical point

Objects of the experiment

- Observing the dissolution of the phase boundary between liquid and gas when heating above the critical temperature.
- Observing the formation of the phase boundary when cooling below the critical temperature.
- Observing the critical opalescence.

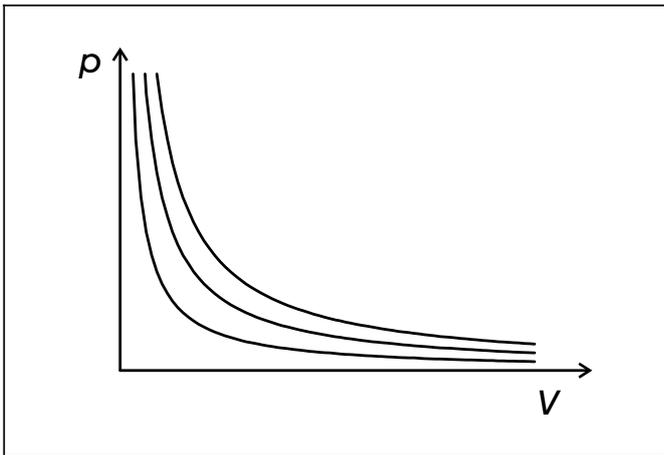
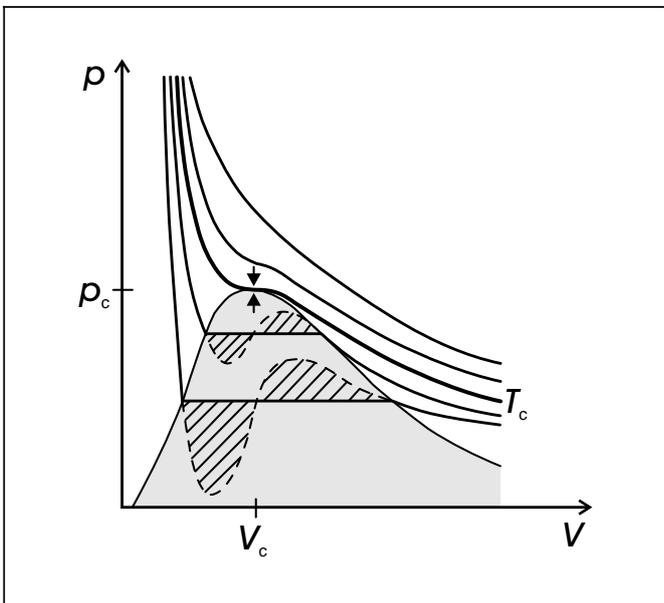


Fig. 1: pV diagram with the isotherms of an ideal gas

Fig. 2: pV diagram with the isotherms of a real substance. A liquid-vapor mixture exists in the shaded range. The arrows mark the critical point.



Principles

One important characteristic of an ideal gas is that it does not condense, not even when the temperature approaches absolute zero. Such a gas does not exist in nature, as it would have to consist of particles which are small in relation to their mean spacings even at low temperatures, and, except for elastic collisions, do not interact with each other. When an ideal gas is compressed at a constant temperature, the pressure increases inversely proportional to the volume (see Fig. 1). The relationship between the pressure p , the temperature T and the molar volume V of an ideal gas is described by the state equation for ideal gases:

$$pV = RT \quad (I)$$

$$(R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} : \text{gas constant})$$

Most real gases approach the properties of an ideal gas when they are far enough away from their condensation or liquefaction point, e.g. at room temperature and atmospheric pressure. As the gas approaches the condensation point, i.e. at high pressure p or low temperature T , its properties deviate significantly from those of an ideal gas. The density of the gas increases and the particles are on average extremely close together. The behavior of real gases is approximately described by the *van der Waals* equation of state

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

In this equation, the substance-dependent *van der Waals* constants a , b signify the mutual attraction of the gas particles and their effective volumes.

Fig. 2 shows the isotherms of a real gas in a pV diagram. The isotherm to which a horizontal tangent can be applied at the turning point is of particular importance. The turning point is referred to as the critical point; the quantities associated with this point are called the critical pressure p_c , the critical molar volume V_c and the critical temperature T_c . Above the critical temperature, the substance is gaseous at all pressures, and the isotherms conform to the *van der Waals* equation, which approaches the equation of state for ideal gases here. The substance is termed a gas.

Apparatus

1 Pressure chamber for demonstrating the critical temperature	371 401
1 Lamp, 6 V/30 W	450 51
1 Lamp housing	450 60
1 Aspherical condenser	460 20
1 Transformer, 6 V AC, 12 V AC, 30 VA	562 73
1 Small optical bench	460 43
1 Lens in holder, $f = 100$ mm	460 03
1 Right angled prism	461 11
4 Leybold multiclamps	301 01
1 Large stand base, V-shape	300 01
<i>for heating:</i>	
1 Circulation thermostat, 30 ... 100 °C	666 768
2 Silicone tubing, i.d. 7×1.5 mm, 1 m	667 194
or	
1 Steam generator, 550 W/230 V	303 28
1 Silicone tubing, i.d. 7×1.5 mm, 1 m	667 194
1 Beaker, 400 ml	664 104
<i>temperature measurement:</i>	
1 Digital thermometer with one input	666 190
1 Temperature sensor, NiCr-Ni	666 193
or	
1 Thermometer, -10 to 150 °C e.g.	382 33

Below the critical temperature, the situation is much more complicated. If the volume is large enough (in Fig. 2 to the right of the shaded range), the substance is gaseous, and is referred to as a vapor. In very small volumes (to the left of the shaded range), the substance is liquid and virtually incompressible. The shaded range corresponds to a liquid-vapor mixture, in which

Safety notes

The pressure chamber for demonstrating the critical temperature is under high pressure (minimum 20 bar).

- Read and observe the safety notes contained in the Instruction Sheet.
- Never unscrew the assembly screws.

The gaskets used to seal the glass panes also act as a safety valve in the event of extreme overheating. They can be used up to a maximum temperature of 100 °C.

- To ensure a long service life of the gaskets, do not allow the pressure chamber to become hotter than 90 °C.

Particularly when heating with the steam generator, there is a danger of burns and scalding due to contact with the pressure chamber, the steam generator, the tubing and the receptacle.

- If you are using the steam generator (303 28), observe the safety notes contained in the Instruction Sheet.
- Do not touch the hot experiment apparatus.

the vapor proportion increases from left to right. This is where the *van der Waals* equation deviates from reality: at a constant temperature, a change in the volume changes the vapor proportion of the mixture, but not its pressure. The curve sections drawn with dashes, which correspond to the van der Waals equation, must be replaced by horizontal curve sections. These show the vapor pressure at which the vapor and liquid are at equilibrium with respect to each other. As the liquid and the gas have different densities, they are normally separated by gravity. The density of the vapor increases with the temperature, while that of the liquid decreases. At the critical temperature, these densities are identical. Liquid and vapor can no longer be distinguished; they are completely mixed.

As the mixture approaches the critical point, the light scattering within the pressure chamber reaches an extremely high level. This phenomenon is called the critical opalescence, and is caused by variations in density, which increase significantly close to the critical point because the compressibility is great and the resistance to density changes is low. Short-wavelength light is scattered, while long-wavelength light continues in its path.

The pressure chamber for observing the critical temperature allows us to demonstrate these phenomena. The cladding of the chamber is heated by a flow of hot water or steam. The two high-pressure resistant flat glass panes allow us to observe the behavior of the filling inside the chamber when it exceeds the critical temperature T_c due to heating, and again during cooling. The phenomena can be observed directly in the chamber or projected on the wall.

The pressure chamber contains a filling of sulfur hexafluoride SF_6 . At room temperature, its critical density – the inverse of the critical volume – is a close approximation of the average of the liquid and gas densities. At room temperature, the pressure chamber is filled about half-way with liquefied gas, so that the system passes through the critical point when heated.

SF_6 has the following thermodynamic variables in the critical point:

Critical temperature: $T_c = 318.7$ K

Critical pressure: $p_c = 37.6$ bar

Critical molar volume: $V_c = 200 \frac{\text{cm}^3}{\text{mol}}$.

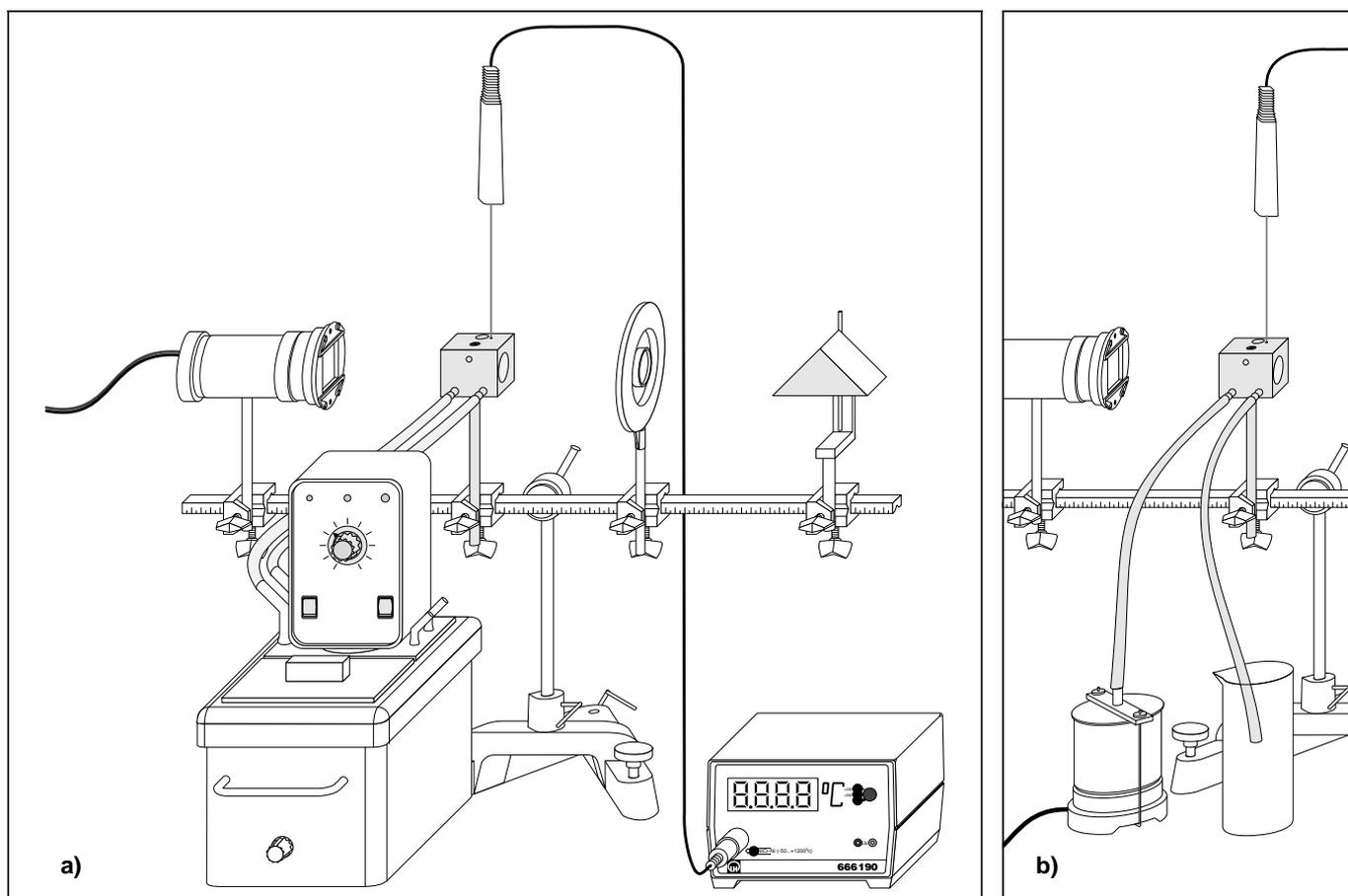
Setup

Fig. 3 shows the experiment setup.

Note on using the steam generator:

Cut the silicone tubing into two sections 0.5 m long to prevent condensation in the tubing.

- Before connecting the silicone tubing, check the heating channel of the pressure chamber for obstructions by blowing through it.
- Before inserting the temperature sensor, add e.g. a little water in the corresponding hole for better heat transfer.
- Mount the aspherical condenser on the lamp housing.
- Set up the assembly as shown in Fig. 3 so that the lamp, the glass panes of the pressure chamber, the lens and the right angled prism are all along one axis.



- Check the seating of the silicone tubing every time before putting the apparatus into operation, to ensure that no steam or hot water can escape in an uncontrolled manner and cause damage or injury.
- Connect the lamp to the transformer and project the contents of the pressure chamber on a light-colored surface (e.g. a sheet of white paper tacked to the wall). Readjust the setup as necessary.
- Focus the image of the liquid meniscus by moving the lens on the small optical bench.

Fig. 3: Experiment setup for observing the critical point

a) Complete setup with circulation thermostat for heating the pressure chamber. The exact position of the individual components on the optical bench depends on the distance of the projection surface and can be found most easily by moving the lens

b) Section of the setup with the steam generator for heating the pressure chamber

Carrying out the experiment

Note on using the steam generator:

When heating with steam, the temperature in the pressure chamber for observing the critical temperature increases very quickly and is very difficult to control. The water in the reservoir must not boil so intensely that steam and water are both forced into the heating channel together.

Do not fill the reservoir of the steam generator above the 2 cm level.

Switch off the steam generator immediately when the water begins to boil.

Make sure that the condensed water in the beaker cannot reach the level of the tubing, so that the water is not sucked back in when the system cools; this could cause damage to the pressure chamber due to thermal shock.

The following description is based on the use of the circulation thermostat:

- Darken the room to observe the projected image.
- Switch on the circulation thermostat and initially set it to a temperature of 40 °C.
- Starting from about 40 °C, increase the set temperature on the circulation thermostat slowly to ensure more even heating of the substance and enable clear observation of the disappearance of the phase boundary.
- After the system exceeds the critical temperature, set the circulation thermostat to a level below the critical temperature.
- To reduce the effects of troublesome temperature gradients over the volume of the chamber, it may be advisable after the system falls below the critical temperature to again slowly increase the temperature and repeat the experiment.

Measuring example and evaluation

The occurrence of the phenomena described in the following depends on the speed with which the critical temperature is exceeded. The effects noted under "Heating" occur when the circulation thermostat is used; when the steam generator is used, the reaction is more violent and over more quickly.

Heating:

Shortly after you start heating, characteristic streaking (sometimes called "schlieren") appears in the liquid phase. Next, the liquid begins to boil, and condensate drips from the top sections of the chamber walls. Finally, we can also see streaking in the gas phase, particularly at the boundary.

ous and liquid phase in the projected image. After this occurs, the image becomes brighter again, as the chamber now contains one homogeneous phase. The contents of the pressure chamber demonstrate intensive turbulence with streaking, which dissipates somewhat as the temperature increases further. These are due to a temperature gradient in the pressure chamber.

Cooling:

When the heating is switched off, the streaking initially disappears almost completely, before becoming stronger again as the system approaches the critical temperature. At the bottom of the chamber, we can observe a slight darkening caused by the

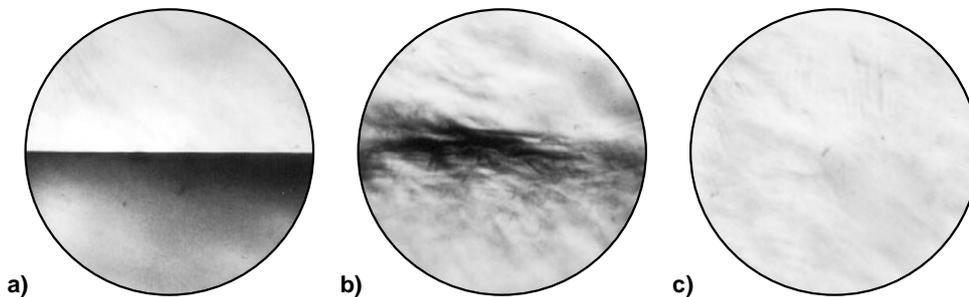


Fig. 4: The contents of the pressure chamber:
 a) below the critical temperature
 b) at the critical temperature (dissolution of the phase boundary)
 c) above the critical temperature

Shortly before the critical temperature is reached, the boiling is so violent that the liquid, which is inhomogeneous due to the gas bubbles, scatters the light diffusely. This makes the projected image of the liquid phase darker. The streaking becomes more intense, initially in the gas phase directly above the boundary, then in the entire gas phase and finally in the remaining liquid phase as well.

When the system exceeds the critical temperature slowly, the phase boundary between liquid and gas becomes agitated, broadens and finally disappears. Just before the boundary disappears, the liquid phase appears slightly brownish. We can observe the disappearance of the boundary between the gas-

formation of a mist. The entire pressure-chamber unit appears increasingly red-brown (critical opalescence) and the streaking increases further. Suddenly, the inside of the pressure chamber darkens, the gas condenses and a rise in the liquid level can be observed. The gas phase contains a mist, which gradually condenses. Finally, the gas phase becomes clearer, while the liquid phase continues boiling.

Reheating:

The liquid boils more intensely again, then the gas phase appears yellowish and the liquid phase is reddish-brown (critical opalescence). The phase boundary becomes broader, then disappears completely. Just above the critical temperature, the entire contents of the pressure chamber becomes a uniform yellow-brown, together with intensive streaking and violent turbulence. Finally, the temperature range in which critical opalescence occurs is exceeded and we can see only the turbulence-related streaking in the pressure chamber.