

INVESTIGATING A LIQUID-VAPOR MIXTURE OF SULFUR HEXAFLUORIDE AT THE CRITICAL STATE

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Rezumat: În această lucrare se prezintă dependența dintre temperatura și presiunea de vaporizare, stabilită pe cale experimentală, observarea disoluției liniei de separație între faza lichidă și gazoasă când substanța este încălzită deasupra temperaturii critice, observarea formării liniei de separație când substanța este răcită înaintea temperaturii critice și de asemenea observarea fenomenului de opalescență critică. Pentru observarea comportării substanței la starea critică este analizată hexafluorură de sulf, SF₆, care se introduce în camera de presiune, ceea ce permite atât demonstrarea cât și vizualizarea acestor fenomene. Pentru achiziția și prelucrarea datelor este utilizat un dispozitiv portabil cu afișaj digital LCD, Mobile Cassy, dotat cu sensor de temperatura NiCr – Ni și calculator de proces cu soft licențiat CASSY Lab. Pe baza perechilor de valori p și t obținute experimental, se calculează presiunea de saturație cu ajutorul relației *Hoffmann – Huminic*. Pentru substanța aleasă, între valorile experimentale și cele calculate cu această relație s-au obținut abateri sub 5%.

Cuvinte cheie: starea critică, temperatură, opalescență critică.

Abstract. The work aims to establish experimentally the dependence between the temperature and vaporisation pressure, to observe the phase boundary dissolution between liquid and gas when the substance is heated above the critical temperature, to observe the phase boundary formation when the cooling is performed below the critical temperature and to observe the critical opalescence phenomenon. For to observe of the substance behaviour at critical state is analysed the sulphur hexafluoride, SF₆, which it introduce into pressure chamber, which these phenomena can be demonstrated and visualised. For the data acquisition is used a portable hand-held device with a digital LCD display, Mobile Cassy, with temperature sensor NiCr – Ni, which can be also connected to the USB port of a PC running the CASSY-Lab software. On the basis of the obtained values pairs p and t , using *Hoffmann – Huminic equation*, the saturation pressure is calculated. For this substance, deviations between experimental and calculated data are under 5%.

Keywords: critical state, temperature, critical opalescence.

1. INTRODUCTION

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 spacing 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.

The relationships between the pressure p , the temperature T and the molar volume V of an ideal gas are described by the state equations. There are several state equations, some simple and other very complex. The simplest and best – know state equation for substances in the vapor phase is the ideal gas state equation:

$$P = R \left(\frac{T}{v} \right) \quad (1)$$

or

$$Pv = RT \quad (2)$$

where the constant of proportionality $R = 8.314 \text{ kJ}/(\text{kmol} \cdot \text{K})$ is the gas constant, P is absolute pressure, T is absolute temperature and v is the specific volume.

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 for 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:

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT \quad (3)$$

where the term a/v^2 is a correction for the mutual attraction of the molecules and b is a correction for the actual volume of the molecules themselves.

For determination of the two constants appearing in this equation is based on the observation that the critical isotherm on a $P - V$ diagram (see Fig. 1).

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.

Below the critical temperature, the situation is much more complicated. If the volume is large enough (in Fig. 1

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 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.

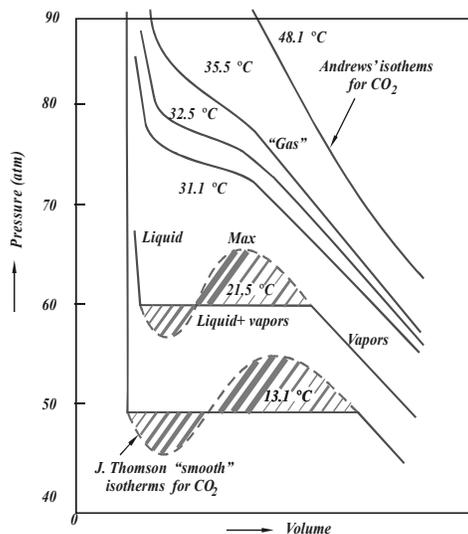


Fig. 1. P - V diagram with the isotherms of a real substance.

2. EXPERIMENTAL SETUP

An experimental system (see Fig. 2) was set up to measure the critical temperature, 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 and observing the critical opalescence.

The experimental system was composed of pressure chamber for demonstrating the critical temperature, small optical bench, and circulation thermostat, 30 ... 100 °C.

The data acquisition system is composed from LCD portable device, Mobile Cassy, with temperature sensor and the software CASSY Lab.

The pressure chamber (see Fig. 3) contains a filling of sulphur hexafluoride SF_6 . Thermo - physical properties of the sulphur hexafluoride are: molecular weight: $M = 146.06$ kg/mol; critical temperature: $T_C = 318.733$ K; critical pressure: $P_C = 37.5455$ bar; critical molar volume: $v_C = 200$ cm³/mol.

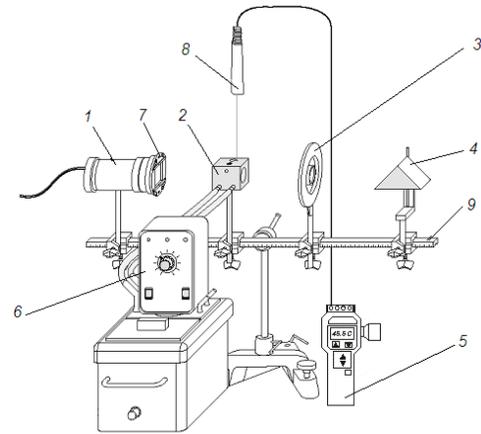


Fig. 2. Schematic of the experimental setup:
1 – lamp 6 V/30 W; 2 – pressure chamber; 3 – lens in holder, $f = 100$ mm; 4 – right angled prism; 5 – LCD portable device; 6 – circulation thermostat, 30 ... 100 °C; 7 – aspherical condenser; 8 – temperature sensor NiCr-Ni; 9 – small optical bench.

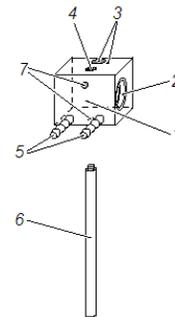


Fig. 3. Pressure chamber for demonstrating the critical temperature:

1 – steel pressure chamber filled with liquefied gas, with heating channel integrated in steel casing; 2 – pressure-resistant view windows on both sides; 3 – holes for thermometer and temperature sensor; 4 – screw plug for liquefied-gas filling opening; 5 – heating channel inlet and outlet as hose fittings (8 mm); 6 – stand rod (130 mm long, $\phi 10$ mm), for screwing into one of the holes.

3. RESULTS AND DISCUSSION

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 phenomena can be observed directly in the chamber or projected on the wall.

As the temperature increases, condensate begins to form and run down the glass panes; a further temperature increase causes the water to boil, i.e. vapor emerges from the volume. The liquid, which is no longer homogeneous due to the gas bubbles, diffuses the incident light. As a result, the projected image becomes darker.

When the critical temperature is reached, the liquid boils vigorously. The phase boundary between the liquid

and the gas becomes unstable, and the image becomes almost completely dark. Finally, the phase boundary disappears completely. The image becomes lighter again, as the chamber once again contains a homogeneous phase.

When the temperature is further, we can only observe increased formation of a condensation film on the flat glass panes.

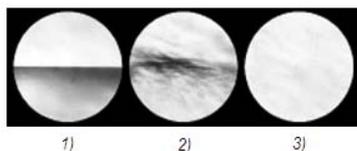


Fig. 4. The contents of the pressure chamber: 1 – below the critical temperature; 2 – at the critical temperature (dissolution of the phase boundary); 3 – above the critical temperature.

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 formation of a mist.

The entire pressure-chamber unit appears increasingly red-brown (critical opalescence) and the streaking increases further (see Fig. 5).



Fig. 5. Critical opalescence phenomena.

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.

Data acquisition, proceeding and visualization system (see Fig. 6) was composed from portable hand-held device

with a digital LCD display (non-graphic), which can also connect to the USB port of a PC running the CASSY-Lab software for further analysis and graphical display.



Fig. 6. Data acquisition system.

CASSY-Lab is the data-analysis and graph-plotting software that supports all the sensors, sensor boxes, and up to eight devices. It can display graphs (with cartesian or polar coordinates), tables and meter readings (digital and analogue).

In Figure 7 shows the saturation temperature versus pressure compared with experimental dates and Hoffmann – Huminc Equation.

4. CONCLUSIONS

The aim of the present work was investigating a liquid-vapor mixture of sulfur hexafluoride at the critical state, namely: 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 and measured temperatures.

Experimental date has been verified with Hoffmann – Huminc Equation and has shown good agreement.

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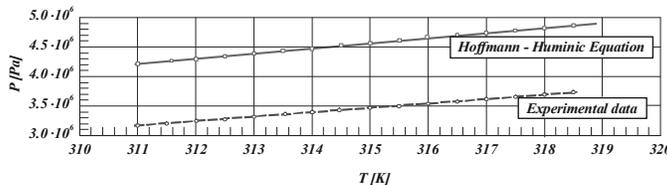


Fig. 7. Saturation temperature – pressure variation.

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