

Speaker's
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Introduction

A laboratory workshop is one of the important components in preparing students for a technical discipline.

The purpose of this laboratory work is to study the algorithm of how tables of thermodynamic properties of technically important substances are obtained from experimental data. To process the empirical array using mathematical packages, such as MathCad or Mathematica. The lab program is written in VBA in Excel.

To reproduce the error of devices, a pseudo-random number generator (Rnd VBA function) is used. The teacher can change the upper limit of the gauge, class. You can specify the system of units in which measurements are made, as well as the type of pressure gauge - it measures the absolute or gauge pressure.

The main advantage of computer emulation over physical laboratory work is the ability to study almost any technically important substance in a wide range of pressures and temperatures. And at the same time, much more experimental data can be obtained in 2 academic hours than on a real installation. This form of laboratory work is easily implemented online.

The use of computer modeling to emulate laboratory work on the study of thermodynamic properties of substances

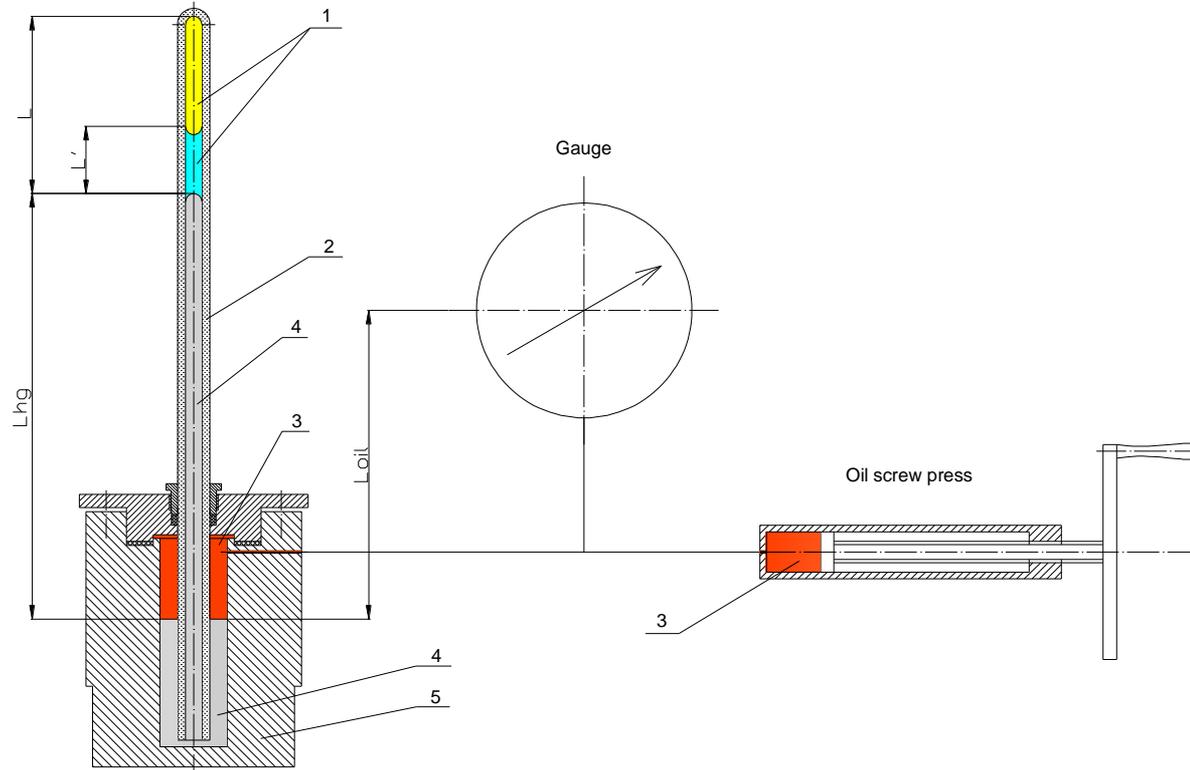


Fig. 1. Installation scheme. The column of the test substance and hydrostatic columns of mercury, oil.

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The laboratory bench layout is shown in Fig. 1. At the moment, the test substance is in a two-phase state. Designation of installation nodes.

1. Test substance.
2. Glass capillary.
3. Transformer oil, transfers pressure from the screw press “Oil screw press” to mercury.
4. Mercury is a separator between transformer oil and the test substance.
5. Steel casing installation.

Linear dimensions:

1. L_{Hg} – is the hydrostatic column of mercury;
2. L – is the height occupied by the test substance in the capillary;
3. L' – is the height of the liquid phase for a two-phase state;
4. L_{oil} – is a hydrostatic transformer oil column.

“Gauge” is a pressure gauge for measuring the pressure of the test substance.

The capillary is covered with a sealed transparent case (not shown in Fig. 1). Inside it, a uniform temperature is maintained by circulating water through an external thermostat. There is also a temperature measurement. For each installation, the internal diameter of the capillary d_{cap} and the mass of the test substance in the capillary are m .

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Conducting the experiment.

Measurements are carried out on isotherms. Three isotherms (t_i) are measured, two are subcritical, one is supercritical. The independent variables are: barometric pressure B ; thermostat temperature t_i ; the height of the test substance in the capillary L or the pressure of the pressure gauge p_{man} . The program displays either the pressure of the pressure gauge p_{man} or the height of the test substance in the capillary L . If the test substance is in a two-phase state, then the height of the liquid phase of the substance L' is also given.

Processing the experiment.

The absolute pressure of the test substance is calculated:

$$p_{\text{sub}} = p_{\text{man}} + B - g_M \cdot (\rho_{\text{hg}} \cdot L_{\text{hg}} - \rho_{\text{oil}} \cdot L_{\text{oil}}). \quad (1)$$

Specific volume of the test substance is determined :

$$v = 1/\rho = V_{\text{sub}}/m = 0,25 \cdot \pi \cdot d_{\text{cap}}^2 \cdot L/m. \quad (2)$$

Compressibility factor is calculated :

$$z = p \cdot v / (R \cdot T). \quad (3)$$

For the isotherm, a plot of $p(v)$ is plotted; the saturation pressure $p_s = p_s(t)$ of the isotherm is determined from the horizontal portion of the plot. Using the two isotherms and the critical point of the substance, we find the equation of the boiling curve in the form of Antoine :

$$\ln(p_s/p_K) = a + b/(T_s/T_K + c), \quad (4)$$

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For two points on one isotherm in a two-phase region, we can construct a system of equations:

$$\rho = L'_1/L_1 \cdot \rho' + (L_1 - L'_1)/L_1 \cdot \rho'' \quad (5)$$

$$\rho' = (\rho - \rho'') \cdot L_2/L'_2 + \rho'' \quad (6)$$

to find v' and v'' (ρ' and ρ'').

The heat of vaporization for two isotherms is found according to the Clapeyron - Clausius equation:

$$r = T_s \cdot (v'' - v') \cdot dp_s/dT_s \quad (7)$$

The derivative in (7) is calculated from the analytical expression (4). In fig. Figure 2 presents a comparison of experimental data with the Altunin equation of state and the Antoine equation (4).

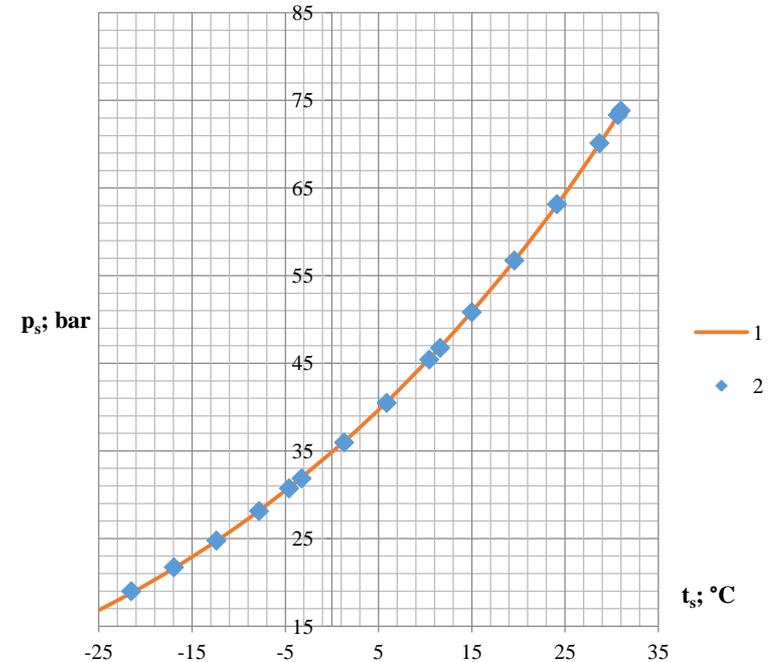


Fig.2. The boiling curve of CO₂. 1 - V.V. Altunin's equation [2]; 2 - Antoine equation (7)

An example of the experimental dependence $z = z(p)$ for subcritical and supercritical isotherms.

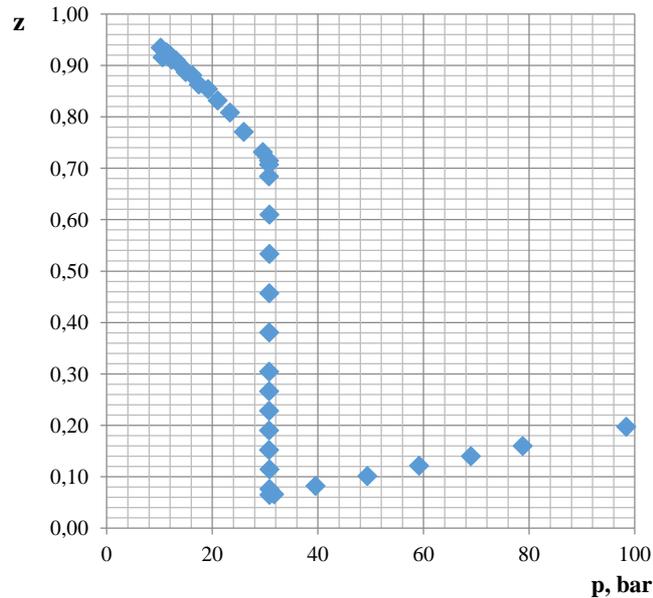


Fig. 3. CO₂. z, p-diagram for superheated vapor and subcritical isotherm $t_1 = -4.6^\circ\text{C}$

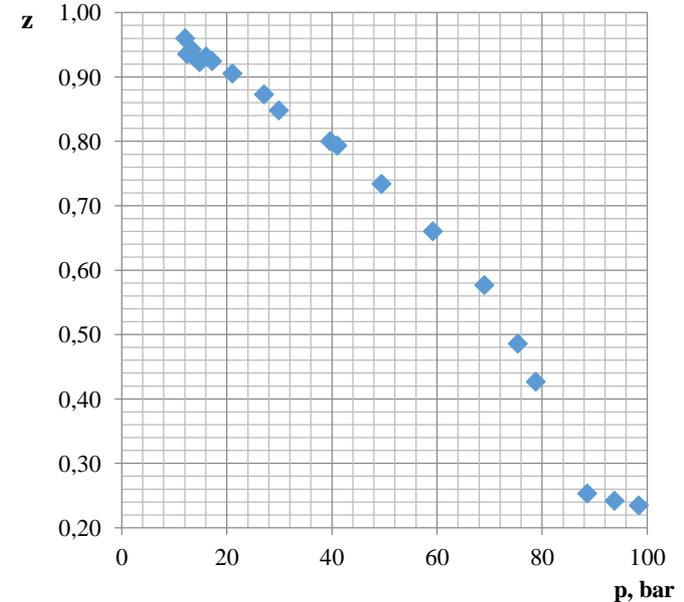


Fig. 4. CO₂. z, p-diagram for supercritical temperature $t_3 = 36.1^\circ\text{C}$

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The second virial coefficient. Density expansion.

For not very dense gases, one can construct the equation of state in virial form (expansion in a series in density ρ):

$$z = 1 + B(T) \cdot \rho + C(T) \cdot \rho^2 + D(T) \cdot \rho^3 + \dots, \quad (8)$$

The second virial coefficient $B(T)$ is equal to $B = \partial z / \partial \rho$ at $\rho = 0$. Therefore, it can be obtained from experimental data; for this, experimental z should be extrapolated to $\rho = 0$ (graphs or functional dependence $z = z(\rho)$). To do this, approximate the function according to experimental data :

$$y = 1 - z = b_1 \cdot \rho + b_2 \cdot \rho^2, \quad (9)$$

b_1 in which is an estimate of the second virial coefficient for a given isotherm. The constants of equation (9) are determined by the least squares method.

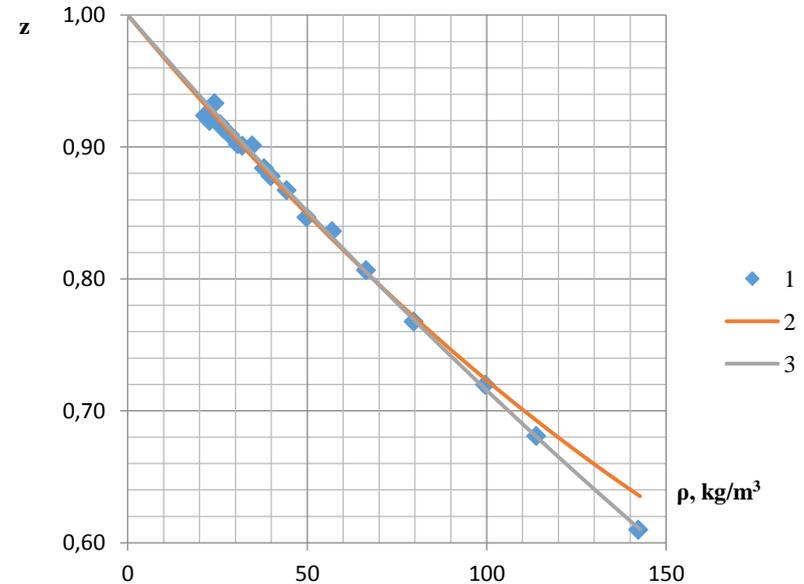


Fig. 5. CO₂, dependence of compressibility factor on density for isotherm 12.6°C. Approximation of experimental data according to (9). 1 - experimental points; 2 - approximation by equation (9); 3 - the equation of Altunin V.V. [2]

Creating a thermal equation of state for a gas region in virial form.

The equation of state of the test substance in the region of superheated steam can be obtained in virial form (12) or (14). Consider a series in density.

Since a limited number of isotherms were obtained in the experiments and the accuracy of the experimental data is small, the equation of state $z = z(T, \rho)$ it makes sense to write in the following simplified form :

$$z(T, \rho) = 1 + B(T) \cdot \rho + C(T) \cdot \rho^2, \quad (10)$$

$$B(T) = c_1/T + c_2/T^2, \quad (11)$$

$$C(T) = c_3/T + c_4/T^2, \quad (12)$$

The experimental data are approximated by the least squares method using the equation

$$y(T, \rho) = z(T, \rho) - 1 = B(T) \cdot \rho + C(T) \cdot \rho^2, \quad (13)$$

Using the ideal gas function of the test substance $h_{IG}(T)$ and differential equations of thermodynamics

$$(\partial h / \partial v)_T = T \cdot (\partial p / \partial T)_v + v \cdot (\partial p / \partial v)_T. \quad (14)$$

the enthalpy of the test substance can be calculated:

$$h(\rho; T) = h_{IG}(T) + R \cdot \rho \cdot [2 \cdot c_1 + 3 \cdot c_2 / T + (3/2 \cdot c_3 + 2 \cdot c_4 / T) \cdot \rho]. \quad (15)$$

Comparison of the calculation results according to equations (10) and (15) with modern reference data.

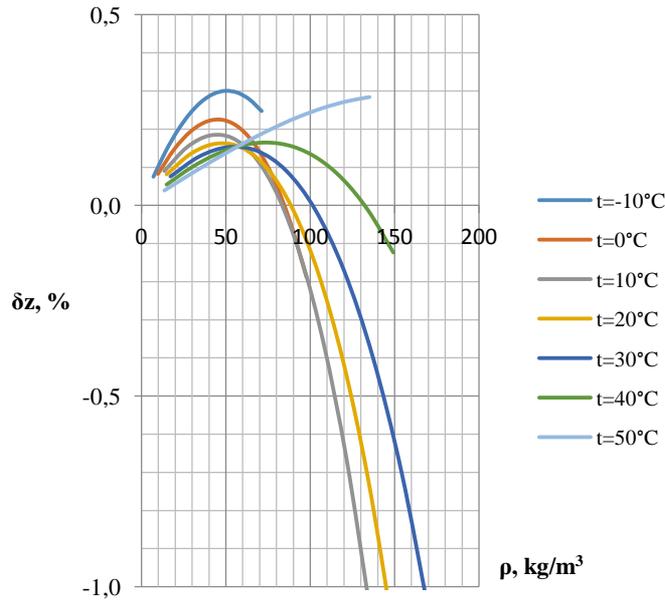


Fig. 6. CO₂. Deviation of the compressibility coefficient calculated by (10) from the reference data V.V. Altunin [2]

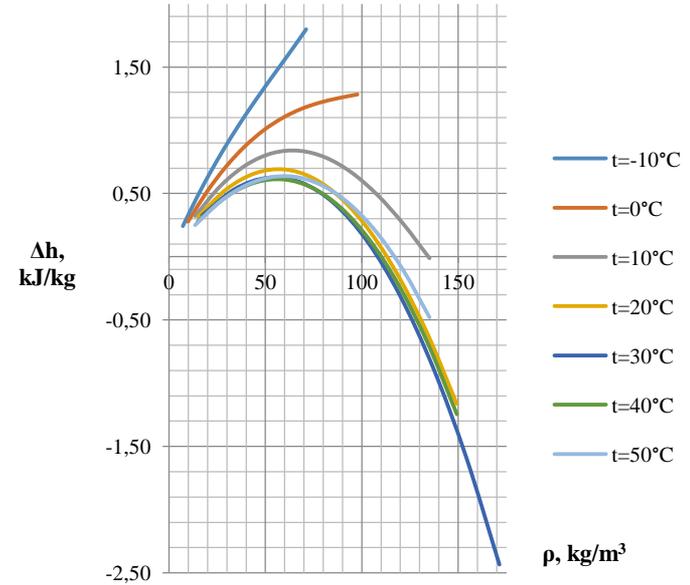
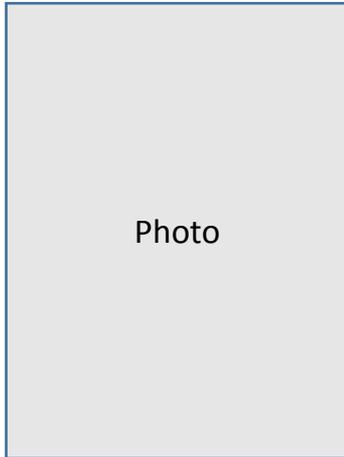


Fig. 7. CO₂. Deviation of enthalpy calculated according to (15) from the reference data V.V. Altunin [2]

Thank you for attention!

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