Experimental study of the density of the helium-nitrogen gas system at low temperatures.

V.A. Milyutin

The Department Of Theoretical Bases Of Heat Engineering (TOT), National Research University "MPEI", Russian Federation

Email: mva.z@ya.ru

Abstract. At the Department of TOT, an experimental setup was created to measure the density of a binary gas system from 100 to 300 K and pressures up to 16 MPa and with any mixture compositions. Experimental density for the helium-nitrogen system were determined by the piezometer of constant volume method. The amount of substance in the piezometer was measured by volumetric method. In this setup, the mixture of He – N₂ was prepared in a special mixer for a series of p-v-T experiments, the concentration was determined by calculation using the equations of state of pure components. In the experiment, mixtures were prepared with molar concentrations, lying close to the range: 0.2, 0.4, 0.6 and 0.8.

1. Introduction.
An experimental study of the p-v-T properties of mixtures of technically important gases is of great interest for the development of applied packages for calculating the thermophysical properties of mixtures. This is due to the fact that by the properties of pure components it is impossible to predict the behavior of the mixture with high accuracy. Helium in industrial quantities is obtained from natural gas by the method of separation under deep cooling. One of the low-boiling components released from such a system is nitrogen and neon.

In the literature, the results of research He - N₂ gas system generally at room and elevated temperatures [6, 7, 9, 10 – 13]. At negative temperatures (Celsius), one work [5] was found in open access.

At the Department of TOT, an experimental setup was created to measure the density of a binary gas system from 100 K to 300 K and pressures up to 16 MPa and with any mixture compositions [1]. This experimental setup has been upgraded. In the installation, the constant-displacement piezometer method is implemented. Determination of the amount of substance in the piezometer is carried out by a volumetric method. In this setup, the mixture is prepared in a special mixer for a series of p-v-T experiments, the concentration is determined by calculation the equations of state of pure components.

2. Apparatus and experimental technique.
The main installation systems are:
- cryostating system with piezometric cell;
- system for preparing the mixture;
- system for measuring the amount of matter in a piezometer;
- Temperature measurement and control system;
- pressure measuring system.

These unit nodes are shown in Figure No1.

![The scheme of the experimental installation for the investigation of the density of the He - N\(_2\) system](image.png)

### 2.1. Cryostatics system with piezometric cell.

Unloaded from the pressure cylinder piezometer 1 (figure No1) placed in a cryostat 2. Piezometer is made of Chrome-Nickel steel and has a volume of approximately 62 cm\(^3\). To equalize the temperature field over the surface of the piezometer, it is inserted into a thick-walled cylindrical copper block. In the drilling of the copper block are platinum and copper thermometers of the system for measuring and controlling the temperature, respectively. In this installation gas cryostatting is realized.

The coolant is low-temperature nitrogen, obtained from liquid nitrogen in a metal vessel Dewar 3 (Figure No1), type SK-25. The adjustment of the flow of gaseous refrigerant is carried out by means of a heater placed in the liquid phase of nitrogen in the Dewar vessel. The refrigerant is removed from the Dewar vessel through a copper tube into a gas cryostat. The refrigerant flow is arranged so that it shields the outer surface of the copper block. For this, the piezometer cooling system consists of the following elements: a two-way coil and two shielding covers. The entire system is placed in a thick layer of thermal insulation made of low-density foam. The coil is made of two copper tubes, tightly wound on the cylindrical surface of the copper block. The refrigerant in the coil runs in opposite directions. Each shielding cover is made of Plexiglas (polymethylmethacrylate) and has two rows of cylindrical channels along which the coolant moves. Gaseous nitrogen enters the lower shielding cover into the inner (upper) row of channels, passes them. Then it enters the first run of the copper coil, along which it moves from bottom to top. Then the gas enters the inner (lower) row of channels of the upper shielding cover, and then into the outer (upper) row. Now the gas enters the second run of the copper coil. Passing it from the top down, through the external (lower) system of the holes of the lower shielding cap, nitrogen leaves the cooling system of the piezometer. Thus, the refrigerant
subsequently flushes the entire outer surface of the copper block, passing first in one direction and then in the opposite direction. This provides the more accurate temperature equalization over the outer surface of the copper block. A complete elimination of the temperature gradient along the height of the copper block is carried out with the aid of a heater located at the lower end of the copper block.

With the help of a capillary, the piezometer is connected to four valves (V13 to V16) and a pressure transducer of the IPD type. The valves and IPD are located in the room temperature region. Thus, the piezometer has a ballast volume. The ballast volume is approximately 3% of the volume of the piezometer. It consists of capillary volumes, an IPD bellows and internal volumes of V13 - V16 valves. The capillary going from the piezometer to the valve bank is in the temperature range from experimental to room temperature. The amount of substance in the ballast volume of the piezometer is determined by calculation. To more accurately calculate this value, the temperature of the different parts of the ballast volume is measured.

2.2. System for preparing the mixture.
A mixture of the given concentration is prepared in a special assembly - mixer 4 (Fig. 1). The concentration of the resulting mixture is determined by calculation. The mixture is prepared from pure gas components. The purity of nitrogen is 99.999% by volume, helium is not less than 99.993% by volume.

The mixer consists of two vessels 5 and 6, eight valves B1-B8 and two pressure transmitters of the type IPD No1 and No2. In general, only one IPD No1 was used to prepare the mixture. Vessels and valves were placed in a liquid thermostat. The temperature in the mixer is maintained at the room temperature (usually +20°). The volumes of vessels 5 and 6 are identical and are equal to about 500cm³. The mixture is prepared as follows. Suppose that it is necessary to prepare a mixture of nitrogen poor. Then the vessel 6 (Figure No1) will be filled with He, and the container 5 - N₂ (for preparing a mixture rich in nitrogen filling of the mixer vessel is reversed). If the pressure in the cylinders 9 (He) and 12 (N₂) is not enough to increase the pressure then thermocompressors 11 are used. Lowering the temperature, which is carried out using liquid nitrogen. Suppose that for measurement of gas pressure in the preparation of a mixture, only IPD No1 is used, then valve V5 is closed. V8 is also closed, all the rest - V1, V2, V3, V4, V6, V7 - are open. The mixer is evacuated, valves V1, V2 are closed. First, the vessel 6 is filled (in this example - He), the valve V7 is closed. The system is thermostated to an equilibrium state, the temperature of the mixer and pressure in the vessel is measured. 6. The valve V6 closes. Comb with valves and bellows IPD No1 evacuated, and the vessel 5 filled to its gas (in this example - N₂, therefore the valve V2 - open). The valve V2 closes. The equilibrium gas pressure in vessel 5 is measured. Then, the thermostatic liquid from the mixer thermostat is removed and the vessel 6 is cooled by liquid nitrogen. Then the gas from the vessel 5 is transferred to the vessel 6 by means of the valve V6. The valve V6 is closed. The temperature control system of the mixer is restored, brought to an equilibrium state, the pressure of the remaining gas in the vessel 5 is measured. The concentration of the obtained mixture in the vessel 6 is calculated by decreasing the amount of substance in the vessel 5. The equilibrium concentration of the mixture in the vessel 6 is achieved through diffuse mixing. This takes three days (the mixing time is estimated using the differential diffusion equation). The use of cooling the vessel 5 before allowing the second component to pass thereto makes it possible to prepare the mixture at a pressure higher than the pressure of the upper part of the IPD measurement. This method allows prepare the mixture in quantities sufficient for several experiments.

The mixer has a ballast volume, defined by the capillary to the IPD and the IPD bellows. But since the volume of the bellows is a small fraction of the volume of each vessel of the mixer 5 or 6, and the bellows temperature is slightly different from the temperature of the mixer thermostat (20°C), the temperature difference between the bellows and the mixer can be neglected.

2.3. System for measuring the amount of substance in a piezometer.
The prepared mixture was transferred from the mixer to the piezometer, and the experiment is carried out along the isotherm with a decrease in pressure during the transition from point to point. The gas is released from the piezometer into a special vessel – the gasometer 6 (Fig. 1). Gasometer volume is approximately 2200 cm$^3$. The gasometer is placed in its liquid thermostat 7. The gasometer temperature is set at room temperature (usually at +20°C). The gasometer is controlled by three valves - V17 - V19. Gas pressure measurement in the gasometer is carried out using a mercury U-shaped manometer 8 and a laboratory mercury barometer. The difference in mercury heights in the U-shaped manometer is determined by a vertical type catheter V-630. The right knee of the U-shaped manometer is filled with mercury above the mercury. Since the volume of the right knee of the U-shaped manometer varies depending on the position of the mercury in it, a circuit was constructed to measure this volume. As a result of the experiment, a functional dependence of the volume of the right knee on the level of the meniscus of mercury in it was obtained. Since the gas pressure in the gasometer is not more than 1.85 bar, the gas state in it is not much different from the ideal gas, which allows to determine the amount of matter in the gasometer with high accuracy.

2.4. Temperature measurement and control systems.

The temperature is regulated and measured in three systems:

1. the piezometric cell;
2. the mixer;
3. the gasometer.

In the cryostat, the automatic temperature control system is implemented. It includes the following elements.

A) Temperature regulator VRT-3 (blocks I-102; R-111, BUT-01, BT-01). A sensitive element in the control system is a copper resistance thermometer. The thermometer is made in the laboratory of the department of TOT and has a resistance of 100 Ohms at +20°C. The thermometer is included in the bridge circuit, created on the basis of UPIP-60M. The mismatch signal of the bridge is fed to the I-102 input. The control signal VRT-3 with BT-01 is fed to the primary winding of the transformer, and then to the control heater. The regulating heater is made of manganese wire in silk braid and glued to a copper tube supplying coolant from the Dewar SC-25 vessel to the cryostat. Before the regulating heater, the main heater is located, power is supplied to it from a high-precision stabilized power source. The voltage can be varied from 0 to 100% of the nominal value. In the regulatory system, the PID-regulation law is implemented.

B) The system for maintaining the specified refrigerant flow rate - gaseous nitrogen on the basis of a heater in liquid nitrogen, a laboratory autotransformer of the LATR type and an ammeter of class 0.1.

C) A system for removing the temperature gradient from the height of a piezometer consisting of a heater at the bottom of a copper block, LATR. The temperature skew is controlled by an eight-spaced differential copper-constantan thermocouple complete with a digital voltmeter SCH-1516. The thermocouple junctions are glued to the ends of the copper block of the piezometer.

Experience has shown that this cryostating system makes it possible to reliably provide any temperature of the piezometer in the temperature range 100-300 K with an accuracy of ±0.01 K.

To measure the temperature, a platinum thermometer of the TSPN-1 type, manufactured in VNIIFTRI, is used. This thermometer allows reproducing the international practical temperature scale IPTS-68 with an accuracy of ± 0.01 K in the temperature range from 13.81 to 273.15 K. The temperature measurement circuit is based on a semi-automatic self-testing potentiometer type P-348 class 0.002. This system also includes: a model resistance coil of resistance P331 class 0.01; Normal element of NE65 class 0.01; Store resistance MCP-63 and switch the direction of current P308.

The temperature of the thermostat of the mixer and the gas meter is measured with a ten-ohm platinum resistance thermometer type PTS-10 VNIIFTRI, the device reproduces the scale IPTS-68 with an accuracy of ±0.02 K in the temperature range 0-630°C. The measurement system is assembled on the basis of a semi-automatic two-row potentiometer P363-2 with a device for autonomous
calibration of class 0.002, including the voltage stabilizer P36-1. The circuit also contains a ten-ohm coil P321 class 0.01; Normal element NE65; Store resistance MCP-63.

However, now the international temperature scale ITS-90 operates. There is no need to rework the work, since the discrepancy between ITS-90 and IPTS-68 is not more than ±0.014 K in the temperature range 100-300 K. And it is enough to make a correction for this deviation.

The temperature of different parts of the ballast volume of the piezometer was measured by six copper-constantan thermocouples complete with a digital voltmeter of the type SCH-1516. Five thermocouples were placed on the lead capillary in the transition zone from the test temperature to room temperature, the sixth thermocouple was glued to the IPD bellows.

The temperature of the U-shaped manometer (both mercury and ballast volume of the gas meter) was measured by a mercury laboratory thermometer with a scale division value of ±0.1°C.

2.5. The pressure measuring system.
The pressure in the vessels of the installation is measured by means of a pressure transducer of the IPD type, the indication of which is displayed on a digital voltmeter of the type SCH-1516 (cumulatively - IPTC). The IPDC class is 0.06. The pressure in the gas meter is determined by means of a mercury U-shaped manometer. Since there is an overpressure when measuring all pressures, a mercury laboratory barometer is used.

To verify and calibrate the SDI, a system was created on the basis of piston manometers MP-600 13 (Figure No1) and MP-60 14. This system also included: a window 12, a reciprocating press 15. The window provides the ability to measure the oil / gas separation level and make a correction for the hydrostatic oil column.

3. Results.
Based on the described setup, a series of experimental points was obtained. Mixtures were prepared with molar concentrations close to the row: 0.2; 0.4; 0.6 and 0.8. Measurements were made on isotherms: 100, 110, 120, 130, 140, 160, 200, 240 K, at pressures up to 16 MPa. 400 experimental points were obtained. The results of this work demonstrate good consistency with the data of other authors. The error in the experimental density of this work is estimated as 0.2%.

Based on these data and the results obtained by other authors thermal state equation describing the surface thermodynamic system He - N\textsubscript{2} at temperatures of 77 - 373 K at pressures up to 20 MPa.

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