An experimental study of the density of the helium – neon – nitrogen gas system at low temperatures

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Abstract. An experimental installation has been created at the Department of TOT to measure the density of ternary gas mixtures from 100 to 300 K and pressures up to 16 MPa. The experimental density for the He–Ne–N\textsubscript{2} system is determined by the constant volume piezometer method. The amount of substance in the piezometer is measured by the volumetric method. He–Ne–N\textsubscript{2} mixtures are prepared in a special mixer at 20\textdegree C for the \(p\)-\(v\)-\(T\) series of experiments, the concentrations are calculated using the equations of state of pure components. In the experiment, 3 mixtures were prepared, which had mole concentrations: \((x_{\text{He}} = 0.24; x_{\text{N}_2} = 0.17), (x_{\text{He}} = 0.33; x_{\text{N}_2} = 0.34), (x_{\text{He}} = 0.16; x_{\text{N}_2} = 0.60)\). 70 experimental points on 7 isotherms were obtained.

1. Introduction
Experimental study of thermal properties (for example, \(p\)-\(v\)-\(T\) data) of mixtures of technically important gases is necessary to create applied packages for calculation of thermophysical properties of mixtures. Only the availability of experimental data can guarantee the high accuracy of these applications.

This article describes an experimental measurement of the density of the He-Ne-N\textsubscript{2} gas system at low temperatures. No experimental studies of this gas system have been found in the available literature.

An experimental setup for measuring the density of the He-N\textsubscript{2} binary gas system at temperatures of 100–300 K and pressures up to 16 MPa and at any composition of the mixture was created at the Department of TOT [1, 2]. This unit has been upgraded for the study of ternary gas systems. The mixture preparation procedure was changed partially. The installation implemented a method of a piezometer of constant volume. The amount of substance in the piezometer was measured by the volumetric method. The mixture of a given composition is prepared in a special unit in a mixer. The concentration of components is determined by calculation using the equations of state of pure components at 20\textdegree C.

2. Equipment and experimental techniques
The main installation systems are:
- cryostat system with piezometric cell;
- system of preparation of the mixture;
- system for measuring the amount of substance in the piezometer;
2.1. Cryostat system with piezometric cell

The cylindrical piezometer 4 unloaded from pressure (figure 1) is placed in the cryostat 5. The piezometer has a volume of 62 cm\(^3\). In this installation gas cryostatting is realized. The refrigerant is low-temperature nitrogen obtained from liquid nitrogen 11 in a metal vessel Dewar 9 (figure 1) type SK-25 using a heater 10.

The piezometer is connected by a capillary with four valves (V9–V12) and an IPD pressure transducer. Valves, IPD transducer and their connecting lines are at laboratory temperature. Consequently, the piezometer has a ballast volume, parts of which are at different temperatures.

2.2. The system of preparation of a mixture

The mixture of a given concentration is prepared in a special unit, which is mixer 1, figure 1. To work with ternary mixtures, the mixer was upgraded. A third line has been added for the third component with a neon 17 cylinder, pressure gauges, auxiliary valves, trap and thermocompressor. Mixtures were prepared from pure gases-components. Nitrogen with a purity of 99.999 vol.%, helium with a purity of not less than 99.993 vol.%., and neon with a purity of not less than 99.974 vol.% were used. The concentration of the resulting mixture is determined by calculation using the equations of state of the pure components He, Ne, N\(_2\).

The mixer consists of two vessels 2 and 3 (each with a volume of about 500 cm\(^3\)), eight
valves V1 – V8 and two IPD pressure transducers Nos. 1 and 2. In most cases, only pressure transducer No. 1 was used for preparation of a mixture, whereas transducer No. 2 was attached to the piezometer instead of transducer No. 3. Vessels and valves are placed in a water thermostat, where the temperature is usually maintained at +20°C. A ternary mixture was prepared according to the preparation procedure of a binary mixture. This procedure is described in [2]. First, a binary mixture was prepared according to the described procedure. Then the dosing vessel 2 was vacuumed, filled with a third clean component and the procedure for its bypass into the mixing vessel 3 and the measurement procedure were carried out by analogy with the second component.

The mixer has a ballast volume determined by the capillary volumes to the IPD pressure transducer and the its bellows.

2.3. System for measuring the amount of substance in the piezometer

The prepared mixture was passed from the mixer to the piezometer, and the experiment is performed by isothermal decrease of pressure in the piezometer during the transition from one experimental point to another. The release of gas from the piezometer is made in the gasometer 7, figure 1. The volume of the gasometer is approximately 2200 cm³. The gasometer is placed in its water thermostat 6. The temperature control of the gasometer is usually carried out at a temperature of +20°C. The gas pressure in the gasometer is measured by a mercury U-shaped manometer 8. The right knee of the U-shaped pressure gauge is connected to the gasometer. Left knee is open to atmosphere. The gasometer has a ballast volume, and this volume varies depending on the position of mercury in the right knee, that is, the pressure of the mixture in the gasometer.

2.4. Temperature measurement and control systems

The system of regulation and measuring the temperature of the piezometer, the mixer and the gasometer is described in [2]. The quality of piezometer temperature control is the following: the temperature fluctuation in the piezometer within one experimental isotherm was not more than ±0.005 K.

2.5. Pressure measurement system

The pressure in the vessels of the installation is measured by means of an IPD pressure transducer, the indication of which is displayed on a SHCH-1516 digital voltmeter (total – IPDC). IPDC class is 0.06. The pressure in the gasometer is determined by a mercury U-shaped manometer. The height difference of the meniscus of mercury in the knees of the U-shaped manometer is measured by a vertical type catheter B-630. Because the excess pressures were determined when measuring all pressures, the laboratory mercury barometer was used. The scheme of pressure measurement in the units is described in [2].

The reliability and accuracy of the IPD pressure transducer was tested using a system based on MP-60 and MP-600 piston pressure gauges. In figure 1, this scheme is presented: 19 – gas and oil separator; 20 – MP-600 piston pressure gauge; 21 – MP-60 piston pressure gauge; 22 – threaded press; 23 – storage of transformer oil. The experimental setup is supplied with gas – it creates pressure in the IPD pressure transducer. MP-60 and MP-600 piston pressure gauges work on oil (transformer and castor, respectively), the gas pressure is transferred to the oil of piston pressure gauges in the separator 19. Since the piston pressure gauges and the gas-oil interface are located at different levels, the pressures measured by the piston pressure gauges and the IPD will vary. The 19 oil separator has a transparent window through which the oil level position can be observed. This allows you to accurately adjust for the hydrostatic oil column.

For various upper limits of pressure, the data obtained using IPD pressure transducers Nos. 1, 2, and 3 were compared with those obtained with the MP-60 and MP-600 pressure gauges. For
example, in figure 2, the results obtained with IPD transducer No. 1 at the upper pressure limit of 16 MPa are compared for two experiments. Here, the DM is an increase in pressure during calibration from 0 to 16 MPa, the RM is pressure decrease from 16 MPa to 0. In figure 2 $\Delta p = p_{IPD} - p_{MP}$, where $p_{IPD}$ is the pressure reading of the IPD pressure transducer, $p_{MP}$ is the pressure reading of the piston manometer. Here, IPD pressure transducer No. 1 has an upper limit of 16 MPa, the class of the device is 0.06; the maximum error of the IPD pressure transducer is equal to $\pm0.0096$ MPa. The device has a small nonlinearity in the readings. But since the accuracy of the readings is much higher than the class of IPD pressure transducer, we can take into account this nonlinearity as an amendment. This curve was approximated by a quadratic parabola.

3. Determination of ballast volumes of the installation
3.1. The ballast volume of the piezometer
The ballast volume of the piezometer includes the following units: communications of four valves V9–V12; connecting capillaries; bellows of IPD pressure transducer No. 3. The ballast volume is approximately 3% of the piezometer volume. The capillary connecting the piezometer with the valve V10 is located in the region of large temperature gradients from the temperature of the piezometer to the temperature in the laboratory. For a more accurate account of the amount of substance in the ballast volume, its temperature field is measured. The entire ballast volume was divided into 7 parts. To measure the average temperature of each part, 6 copper–constantan thermocouples and a mercury thermometer are used. Temperature field of capillary between the piezometer and valve V10 is measured by five thermocouples (Nos. 1–5). Valves V9–V12 and part of the communications (part of the capillaries) are at a laboratory temperature, which is determined by a mercury thermometer. The temperature of the bellows IPD is measured by thermocouple 6.

The internal volume of the connecting capillary from the piezometer to the valve V10 was measured by weighing. Before the capillary was attached to the installation, the empty capillary and the capillary filled with distilled water were weighed. As a result of these measurements, the average internal diameter of this capillary was obtained. Depending on the position of thermocouple junctions Nos. 1–5 on the capillary, the capillary volume was divided into five parts.

The volumes of the two remaining parts of the ballast volume of the piezometer were found by the volumetric method for the release of the substance into the gasometer.
3.2. Ballast volume of the gasometer

The ballast volume of the gasometer consists of the following units: a part of the right knee of the U-shaped manometer above the mercury meniscus (glass tube); a part of the valve V15; and communications (steel capillary) connecting the U-shaped manometer with V15. The ballast volume is kept at the laboratory air temperature, which is measured by a mercury thermometer. The valve V15 and part of the communications are at the temperature of the thermostatic fluid of the gasometer (usually equal to +20°C, which is almost equal to the temperature of the laboratory).

The volume of the right knee of the U-shaped manometer occupied by the substance under study depends on the level of the mercury meniscus, which is determined by the gas pressure in the gasometer. To determine the dependence of the ballast volume of the gasometer on the position of the mercury meniscus, an experimental setup was created. The idea of the experiment was as follows. In the right knee of the U-shaped manometer, a certain amount of nitrogen was locked with the V15 valve. Changing the gas pressure in the left knee will change the position of the mercury level in the right knee. In this case, the ratio between the locked nitrogen volumes for the two different mercury level positions in the right knee will be equal to

\[ \frac{V_{BG2}}{V_{BG1}} = \frac{\rho_{BG2}}{\rho_{BG1}}, \]

where, \( V_{BGi} \) and \( \rho_{BGi} \) \((i = 1, 2)\) are the volume and density of nitrogen in the right knee of the U - shape pressure gauge when the V15 valve is closed at the mercury meniscus level of \( h_{r1} \). The pressure of nitrogen in the right knee was determined by barometric pressure, the data of the MO-2.5 manometer and mercury column. The experimental results for different levels of \( h_{Ri} \) were processed by the least squares method in the form of a quadratic dependence:

\[ \frac{V_{BG}}{V_{BG0}} = 1 + a \cdot (h_r - h_0) + b \cdot (h_r - h_0)^2, \]

where \( V_{BG} \) is the value of the ballast volume of the gasometer for the level of mercury in its right knee \( h_r \); \( V_{BG0} \) is the value of the ballast volume for the mercury level \( h_0 \); \( h_0 \) is the level of the marker. The marker was applied to the right knee. The mercury and marker levels are determined by the catheter. The value of \( V_{BG0} \) was measured by the volumetric method for the release of nitrogen into the gasometer.

3.3. Ballast volume of the mixer

The ballast volume of the mixer is determined by the volume of the capillary up to the IPD pressure transducer and its bellows. But since the volume of the bellows is a small part of the volume of each vessel of the mixer 2 or 3, the temperature of the bellows is slightly different from the thermostat temperature of the mixer (+20°C). So, is possible to neglect the difference of the temperatures of the bellows and the mixer.

4. Experimental data

Three mixtures were prepared in the mixer, 15 experiments were carried out on 7 isotherms (100 K, 115 K, 125 K, 140 K, 190 K, 250 K, 294.2 K) to 16 MPa, 70 experimental points were obtained. figure 3–5 show graphs of the compressibility factor \( z \) of the mixture pressure on the isotherms for experimental data.

The experimental density error of this work is estimated at 0.3%. The analysis of the received results will be provided in the subsequent papers.

Acknowledgments

We dedicate this work to the good memory of our teacher Zubarev Vladimir Nikolaevich.
Figure 3. Experimental isotherms for $x_{\text{He}} = 0.24; x_{\text{Ne}} = 0.59; x_{\text{N}_2} = 0.17$.

Figure 4. Experimental isotherms for $x_{\text{He}} = 0.33; x_{\text{Ne}} = 0.33; x_{\text{N}_2} = 0.34$.

Figure 5. Experimental isotherms for $x_{\text{He}} = 0.16; x_{\text{Ne}} = 0.24; x_{\text{N}_2} = 0.604$.

References
[1] Zubarev V N, Prusakov P G, Barkovskii V V and A M V 1984 Proceedings of Moscow power engineering Institute 622 94–101
[2] Milyutin V A 2017 Journal of Physics: Conference Series 1–6