

# CALORIMETRIC INVESTIGATION OF PHASE BEHAVIOR OF HYDROCARBON MIXTURES WITH LOW CONTENT OF HIGH MOLECULAR COMPONENTS (C4+)

*Buleiko V.M.,\* Grigoriev B.A.*

*Gazprom-VNIIGAZ, Moscow, Russia*

*\*V\_Buleiko@vniigaz.gazprom.ru*

The results of calorimetric investigations of phase behavior of binary mixture (methane-propane), ternary mixtures (methane-propane-heptane and methane-propane-decane) and seven-component mixtures (methane-ethane-propane-butane-pentane-heptane-decane and methane-ethane-propane-butane-isobutane-pentane-octane) are presented. The thermodynamic properties, phase behavior and kinetics of phase transitions of liquid and gaseous hydrocarbons have been studied in the temperature range from 100 to 370 K and in pressure range from 0.1 to 40 MPa. A method of precision adiabatic calorimetry makes possible to construct the phase diagrams of hydrocarbon mixtures, as well to determine with higher accuracy PVT data of condensate dew points. Phase transitions are determined by the discontinuity of directly measured specific heat and temperature derivative of pressure at constant volume. Our particular attention is paid to the hydrocarbon mixtures with low content of high molecular components (condensate-to-gas ratio), due to the fact that standard methods with the use of conventional PVT experiments not guarantee the efficiency and accuracy of phase diagram. Hydrocarbons with four and more carbon atoms are called C4+ components and the entity of all C4+ components is called C4+ fraction. A particular C4+ component will belong to the high molecular component. Our investigations show that if the content of C4+ fraction is less then 2.0 mol %, the phase behavior of hydrocarbon mixtures is qualitatively differed from traditional phase behavior. The region of phase state of hydrocarbon mixtures with low content of high molecular components includes the extensive domain of uncertainty and cannot be studied by conventional PVT experiments and cannot be prognosticate theoretically.

Data of our measurements show that phase diagrams of seven-component hydrocarbon mixture with low content of high molecular components are drastically transformed compared to traditional concepts. For example, hydrocarbon mixture (methane-ethane-propane-butane-pentane-heptane-decane) is separated into a macroscopic phase enriched by methane, ethane, propane and two microscopic phases enriched by isobutane-pentane, and heptane-decane. We define a macroscopic phase as the phase formed and enriched by components of high concentration in the original homogeneous state. A microscopic phase is the phase formed and enriched

by components of low concentration in the original homogeneous state. It is found out that these phases are equilibrium phases. To prove that all phases are equilibrium phases the cooling regime of measurements is used. At cooling regime of measurements the same phase transitions as at heating regime occur. These phase transitions correspond to formation of two microscopic phases enriched by heptane-decane and isobutane-pentane and formation of macroscopic phases (liquid-vapor) enriched by methane-ethane-propane.

To reveal the impact of individual hydrocarbon components on seven-component phase diagram the binary and ternary mixtures, represented as that in a set of quasibinary mixtures, have been studied. The content of decane and heptane in ternary mixtures was less than 2.0 mol %. A ternary mixture methane-propane-decane is separated into a macroscopic phase enriched by methane-propane and a microscopic phase enriched by decane. A liquid phase of ternary mixture methane-propane-heptane is separated into layers (liquid-liquid).

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