

# A Calorimetric Study of Phase Behavior of the Methane-Propane-Nonane System

V. M. Buleiko (✉ [buleikof@rambler.ru](mailto:buleikof@rambler.ru))

National University of Oil and Gas «Gubkin University»

D. V. Buleiko

National University of Oil and Gas «Gubkin University»

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## Research Article

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# Abstract

The recent results of the accurate calorimetric measurements of phase equilibria in ternary mixtures of methane, propane, and nonane have been presented. The heat capacity, internal energy, pressure, and temperature derivative of pressure at constant volume were measured in the range 160 – 340 K, up to 30 MPa. The phase transitions were localized by the finite discontinuities in temperature derivatives of the thermodynamic potentials. The phase diagrams for ternary mixtures of methane, propane, and nonane have been plotted based on the experimental data. These data are supplemented with the earlier measurements of two ternary hydrocarbon systems for the low concentration of octane and decane. Our investigations show that hydrocarbon mixture for the low concentration of nonane as well as the hydrocarbon mixtures for the low concentration of octane and decane split into two phases, the nonane-lean macrophase and the microphase formed by nonane. Besides, nonane provokes a split of the liquid part of a ternary mixture into two liquid phases, the nonane-rich phase and the nonane-lean phase.

## 1 Introduction

Petroleum reservoir fluids are multicomponent mixtures consisting primarily of hydrocarbons [1]. An experimental study of the phase behavior of hydrocarbon mixtures for the low concentration of heavy components attracts special attention due to possibility to get the credible information about the nature of intermolecular forces in mixtures. An effective modeling of these mixtures has been realized by means of their representation as a combination of simple mixtures which consist of components forming the macrophase (a mixture of  $C_{1-3}$  components) and microphase (one of  $C_{4+}$  components). In the earlier papers we presented the simple hydrocarbon mixtures for the low concentration of octane and decane [2, 3], and quaternary mixtures of methane, propane, octane, and decane for the low concentration of octane and decane, which are a combination of the simple hydrocarbon mixtures for the low concentration of octane and decane [4]. We reported a split of these mixtures into two and three phases, namely, the octane-lean and decane-lean macrophase and microphases formed by octane and decane. Some important experimental data of the accurate calorimetric measurements of phase equilibria in ternary and quaternary mixtures of methane, propane, heptane, octane, and decane including heptane, octane and decane as heavy components have been presented in papers [5–7]. Only few experimental data of vapor-liquid equilibria in ternary mixtures of methane, propane, and octane and methane, propane, and decane one can find in the data archive of the NIST Thermodynamics Research Center [8–16].

The data of phase equilibria in ternary mixtures of methane, propane, and nonane are necessary for the proper description of hydrocarbon mixtures for the low concentration of heavy components in the region of the microphase formation by octane, nonane, and decane. Unfortunately, there are not many data of phase equilibria in these mixtures, in particular, no experimental data of the vapor-liquid, liquid-liquid or solid-liquid equilibria & solubility in the data archive of the NIST Thermodynamics Research Center. The objective of this paper is to make up a deficiency in these data and describe the results of recent calorimetric research of phase equilibria in ternary mixtures of methane, propane, and nonane for the low concentration of nonane. The phase behavior of these mixtures is qualitatively similar (isomorphic) to the

phase behavior of earlier studied ternary hydrocarbon mixtures. A phase diagram for each ternary mixture, equally with the typical phase envelopes for binary and ternary mixtures, includes the line of the microphase formation by nonane. Nonane provokes a split of the liquid part of a ternary mixture into two liquid phases, the nonane-rich phase and the nonane-lean phase.

## 2 Experiment And Results

A method of the precision adiabatic calorimetry is applied for the adiabatic calorimeter setup (the isochoric calorimeter). A detailed description of the adiabatic calorimeter setup and experimental procedure can be found elsewhere [17, 18].

Ternary mixtures of methane, propane, and nonane of constant composition presented as quasi-binary mixtures have been studied. A purity of hydrocarbon components was between 0.9995 – 0.9999 mole fractions. A summary of gas parameters and composition of ternary mixtures has been depicted in Table 1 and Table 2. The first quasi-component is a binary mixture with the constant methane/propane ratio. The second quasi-component is nonane. Measurements have been performed for the different values of  $x_{C9}$ , 0.00100, 0.00250, 0.00500, 0.01012, 0.02007, and 0.04003 mol fractions. The mixtures No 1-7 as well as the ternary mixtures presented in Ref. [2, 3] are the examples of simple hydrocarbon mixtures for the low concentration of heavy hydrocarbons. The phase diagrams for mixtures of methane, propane and nonane, presented in Figs. 1, 2, 3, and 5 and Table 3, have been plotted using the procedure described in Ref. [2]. The phase transitions those occur for these mixtures have been depicted in Table 4.

Figure 1 shows the phase diagram for a ternary mixture of methane, propane and nonane. The phase diagram, equally with the typical phase envelopes for binary (I) and ternary (II) mixtures, includes the line of the microphase formation (branches III and III') and the immiscibility area (IV), presented by the line AKB. The line AKB is the  $P, T$  – projection of the immiscibility area (see the inset of Fig. 1). The line of the microphase formation consisting of two branches, III and III', starts at the point  $Q_2$ . The branch III stretches upward into the high pressure area. The branch III' goes downward, intersecting the phase envelope surrounding the two-phase region of the nonane-lean macrophase (the point  $Q_1$ ) and further it stretches into the region of the low temperature and pressure (the branch  $Q_1Q'_1$ ).

The branches III and III' divide the phase diagram into two parts. A ternary mixture of methane, propane, and nonane is on the right of these branches. A binary system which consists of the nonane-lean macrophase and microphase formed by nonane is on the left of these branches.

The phase envelope for the ternary mixture (II), conjugated to the line of the microphase formation, also starts at the point  $Q_2$ . The solubility of nonane in the macrophase on the branch III equals to the concentration of nonane in the ternary mixture, presented by the phase envelope II. On this phase envelope, the ternary mixture is in the single-phase state and in equilibrium with an incipient amount of the second phase. On the branch III, the liquid phase of the ternary mixture is in equilibrium with an incipient amount of the microphase formed by nonane.

Figures 2 and 3 show the  $P, T$ - projection of phase diagrams for the simple hydrocarbon mixtures No 1-7. The red lines in these Figures are the lines of the nonane microphase formation. The red numerals in Fig 3 are the concentration of nonane in solution for the definite value of pressure and temperature. These lines show the limits of nonane volume which can solve in the macrophase. In fact these lines are the lines of solubility of nonane in the macrophase, so as the lines of the octane and decane microphase formation presented in papers [2, 3] are the lines of solubility of octane and decane in the macrophase. The composition of the macrophase is strongly determined by the pressure and temperature. If the nonane content of solution for the definite value of pressure and temperature is more then its solubility at this pressure and temperature, the surplus of nonane forming the microphase is rejected from the solution. In fact the diktat of the microphase on the phase behavior of the macrophase takes place (in detail see further). The phase diagram for the simple hydrocarbon mixture contains the phase envelope for a ternary mixture conjugated to the line of the microphase formation. For the same mixture the solubility of nonane in the macrophase (branch III) equals to the concentration of nonane in the ternary mixture (the phase envelope II, on the right of the point of conjugation). As result, the macrophase is the single-phase fluid (in the presence of the microphase formed by nonane) in the area which bounded by branches III, III', and I, as well as the ternary mixture is the single-phase fluid in the area which bounded by branches III and II.

Let's see the microphase formation for the mixture No 6 presented in Fig. 3. Cooling takes place along the isochores I ( $r = 407.503 \text{ kg}\times\text{m}^3$ ), II ( $r = 395.178 \text{ kg}\times\text{m}^3$ ), III ( $r = 377.250 \text{ kg}\times\text{m}^3$ ), and IV ( $r = 356.428 \text{ kg}\times\text{m}^3$ ). The microphase can be formed in the single-phase mixture (the isochore I) or two-phase mixture (the isochores II, III, and IV).

The microphase formation in the single-phase mixture starts on the branch III (at the point A). As noted above, on the branch III the liquid phase of the three-component mixture of methane, propane, and nonane is in equilibrium with an incipient amount of the microphase formed by nonane. If the temperature is reduced (cooling AB along the isochore I) the microphase formation in the macrophase takes place due to decrease in the nonane solubility. As result, the nonane content of solution decreases from 0.04003 mol fractions (at the point A) to 0.00050 mol fractions (at the point B). We believe that microphase formation is qualitatively similar to the traditional crystallization of a pure component in solution. As opposed to the traditional concept, the solid phase (microphase) formed by the low concentrated component (nonane).

The microphase formation in the two-phase mixture starts on the branch III' (at the point A'). As opposed to the first case, the microphase formation of nonane goes through the branch III' at the constant temperature until the nonane content of solution decreases from 0.04003 mol fractions, which takes place on the right of the branch III', to 0.01809 mol fractions, which takes place on the left of the branch III'. The forced crystallization takes place at the point A'. The composition of the macrophase is strongly determined by the solubility of nonane in the macrophase at this pressure and temperature. Further, if the temperature is reduced (cooling A'B' along the isochore III) the microphase formation in the macrophase takes place due to decrease in the nonane solubility similar to the first case.

The heat capacity at constant volume for the mixture No 6 has been presented in Fig. 4 and Table 5. The microphase formation in the single-phase mixture takes place on the isochore I. The isochore I depicted in Fig. 3 shows the singularity  $C_I$  of the heat capacity presented in Fig. 4. The microphase formation in the two-phase mixture takes place on the isochores II, III, and IV depicted in Fig. 3. The heat capacity at constant volume on the isochores II and IV have been presented in Fig. 4. Each isochore shows two singularities of the heat capacity. The singularities  $C_{II}$  and  $C_{IV}$  correspond to the microphase formation in the nonane-lean phase, the singularities  $C'_{II}$  and  $C'_{IV}$  correspond to the microphase formation in the nonane-rich phase. The singularity and finite discontinuity of heat capacity of fluid systems have been described in Refs. [19-21].

The comparison of experimental phase diagrams and phase diagrams calculated with the ThermoFast software from the University of Western Australia for the ternary mixtures No 1-3 is shown in Fig. 5 (the calculated data points are listed in Table 6). As shown in Fig. 5, a good approximation by the ThermoFast software takes place for the phase envelopes of the binary mixtures No 1-3 (branch I). A satisfactory approximation takes place for the phase envelope of the ternary mixtures No 1-3 (branch II), as well as a satisfactory approximation takes place for the line of solidification (branch III) for mixtures including the low concentrated nonane (less than the nonane concentration of the mixture No 1). If the nonane content of solution increases the error is increased too. The more the concentration of nonane the more is the shift. Unfortunately, the three-phase  $L_2L_1V$  area is not predicted.

In conclusion, it should be note that temperature of nonane microphase formation is sufficiently less than the temperature of crystallization of pure nonane (219.65 K) (compare with Fig. 2) as well as the temperature of microphase formation of octane and decane is sufficiently less than the temperature of crystallization of pure octane (216.37 K) and decane (246.50) respectively (see refs. [2-4]).

### 3 Conclusion

Studies of phase equilibria in hydrocarbon mixtures elucidate the nature of intermolecular forces and fundamental properties of matter. Our future studies by the adiabatic calorimetry will focus on the accurate measurements of phase equilibria in hydrocarbon mixtures for the low concentration of heavy components represented as a combination of simple mixtures. Each of the simple mixtures consists of the macrophase and microphase. The accurate measurements of phase equilibria will be done both for ternary, quaternary, quinary mixtures and mixtures consisted of more than five hydrocarbon components.

### Abbreviations

$P$  – Pressure [MPa]

$T$  – Temperature [K]

$U$  – Internal energy [J]

$x$  – Concentration [mole fraction]

$\rho$  – Density [ $\text{kg} \cdot \text{m}^{-3}$ ]

V – Vapor phase

L(S) – Single-phase, nonane-lean macrophase

LV(S) – Two-phase, nonane-lean macrophase

$L_1$  – Liquid, nonane-lean phase of the methane-propane-nonane ternary mixture

$L_2$  – Liquid, nonane-rich phase liquid phase of the methane-propane-nonane ternary mixture

S – Microphase

$C_V = (\partial U / \partial T)_V$  – Heat capacity at constant volume [ $\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ]

$(\partial P / \partial T)_V$  – Temperature derivative of pressure at constant volume (the thermal pressure coefficient)  
[MPa · K<sup>-1</sup>]

## Declarations

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### Ethical Approval

“not applicable”

### Competing interests

I declare that the authors have no competing interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

### Authors' contributions

V.M. Buleiko wrote the main manuscript text and prepared figures 1-5.

D.V. Buleiko wrote the main manuscript text and tables 1-6.

All authors reviewed the manuscript

Dual publication

The results/data/figures in this manuscript have not been published elsewhere, nor are they under consideration (from you or one of your Contributing Authors) by another publisher.

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## Availability of data and materials

“not applicable”

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## Tables

Tables 1-6 are available in the Supplementary Files section.

## Figures



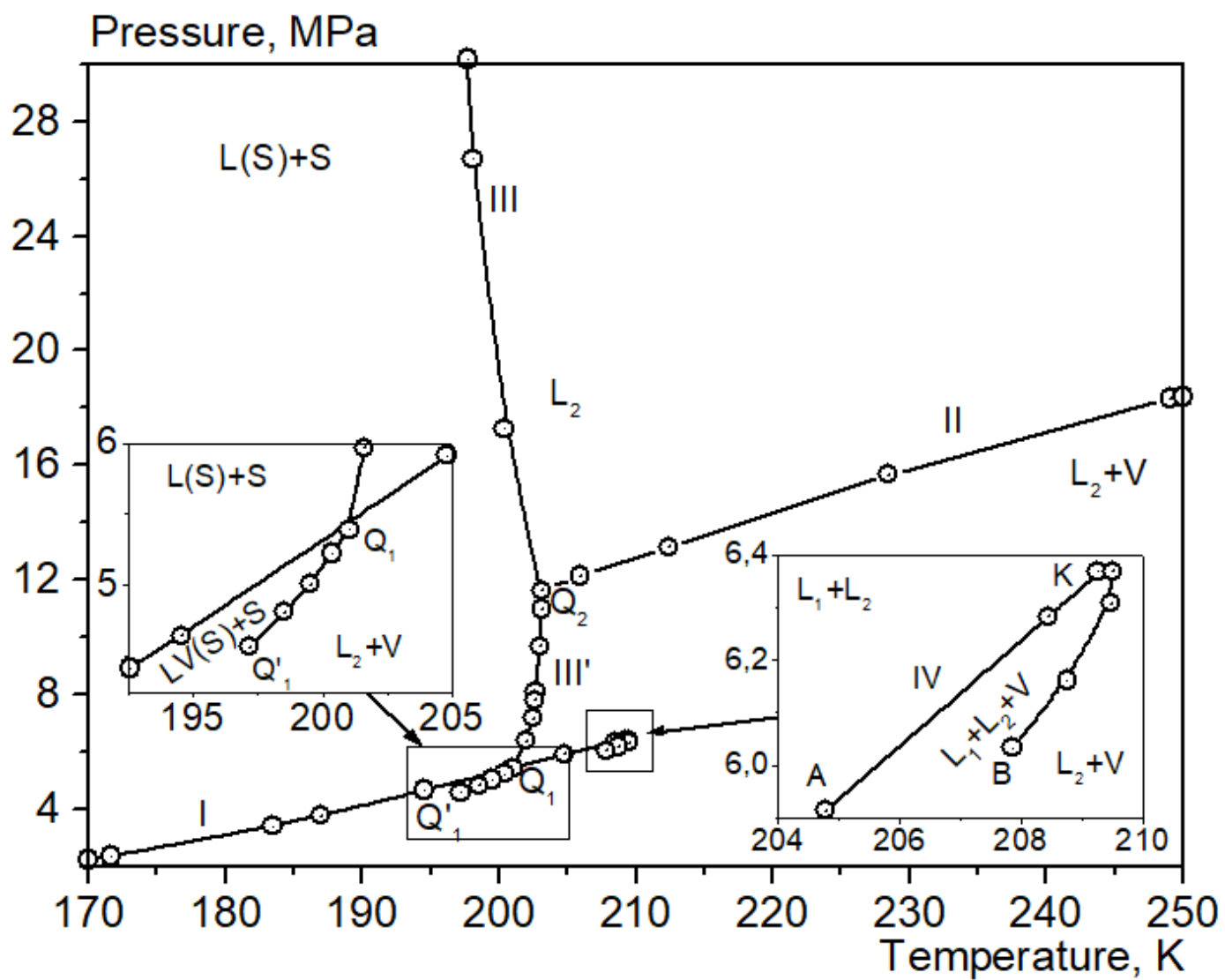


Figure 1

Experimental phase diagram for the mixture No 5 presented in Table 2

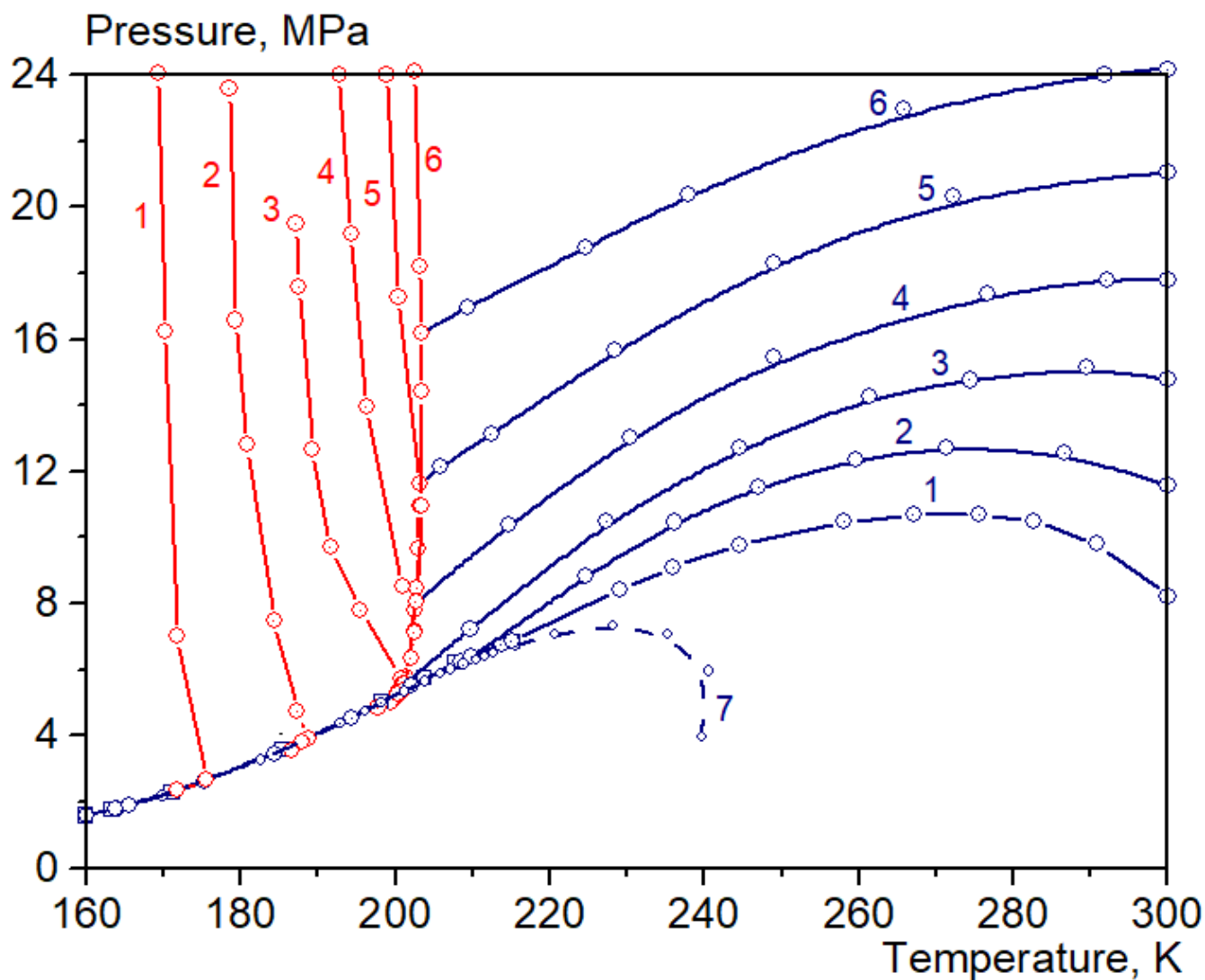
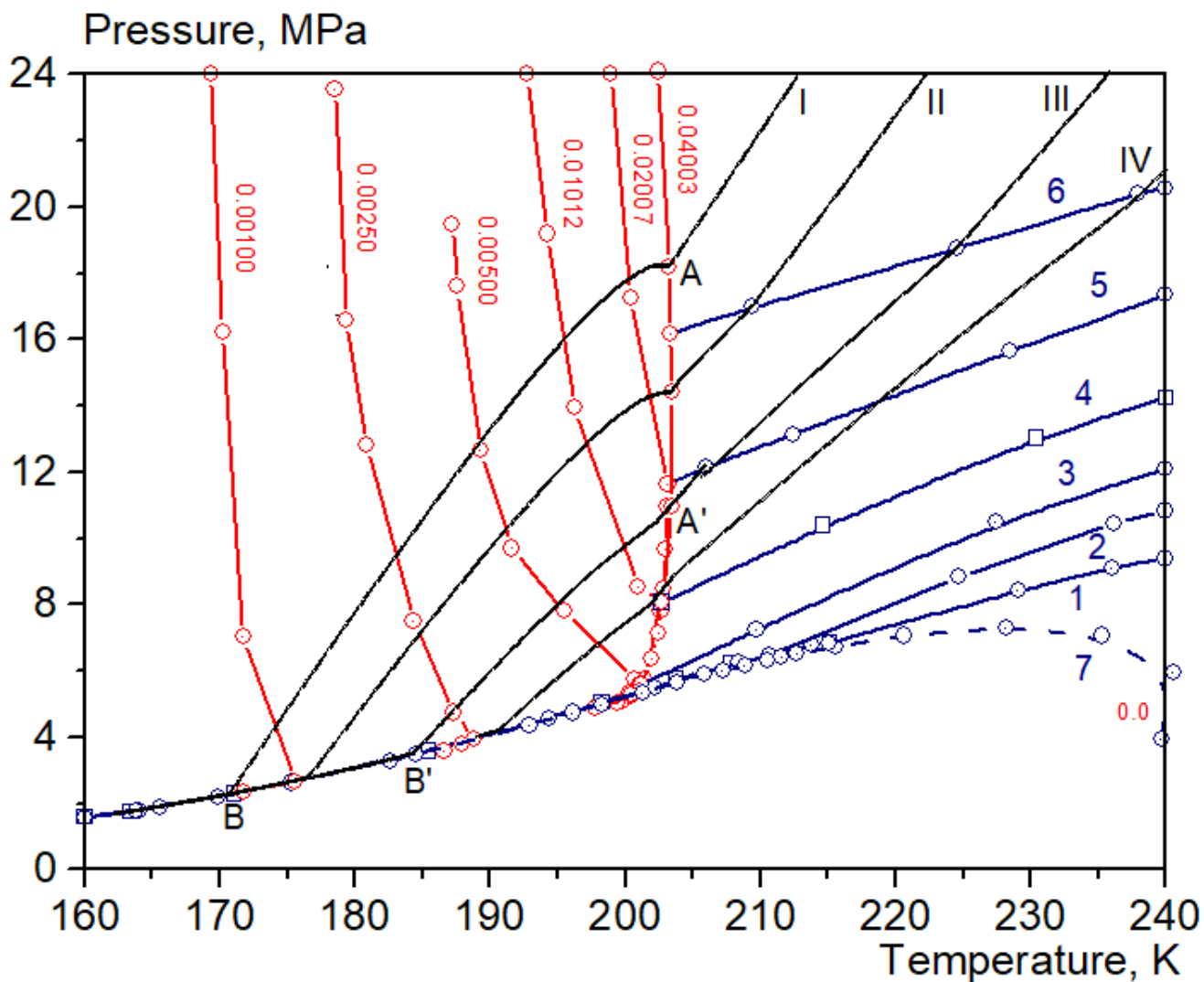


Figure 2

Experimental phase diagrams for the mixtures No 1-7. Red and blue numerals are the numbers of mixtures presented in Table 2



**Figure 3**

Experimental phase diagrams for the mixtures No 1-7, which show the nonane microphase formation in the single-phase (the isochore I) and two-phase (the isochores II-IV) mixture No 6. Densities of the isochores are: I -  $r = 407.503 \text{ kg} \times \text{m}^{-3}$ , II -  $r = 395.178 \text{ kg} \times \text{m}^{-3}$ , III -  $r = 377.250 \text{ kg} \times \text{m}^{-3}$ , IV -  $r = 356.428 \text{ kg} \times \text{m}^{-3}$

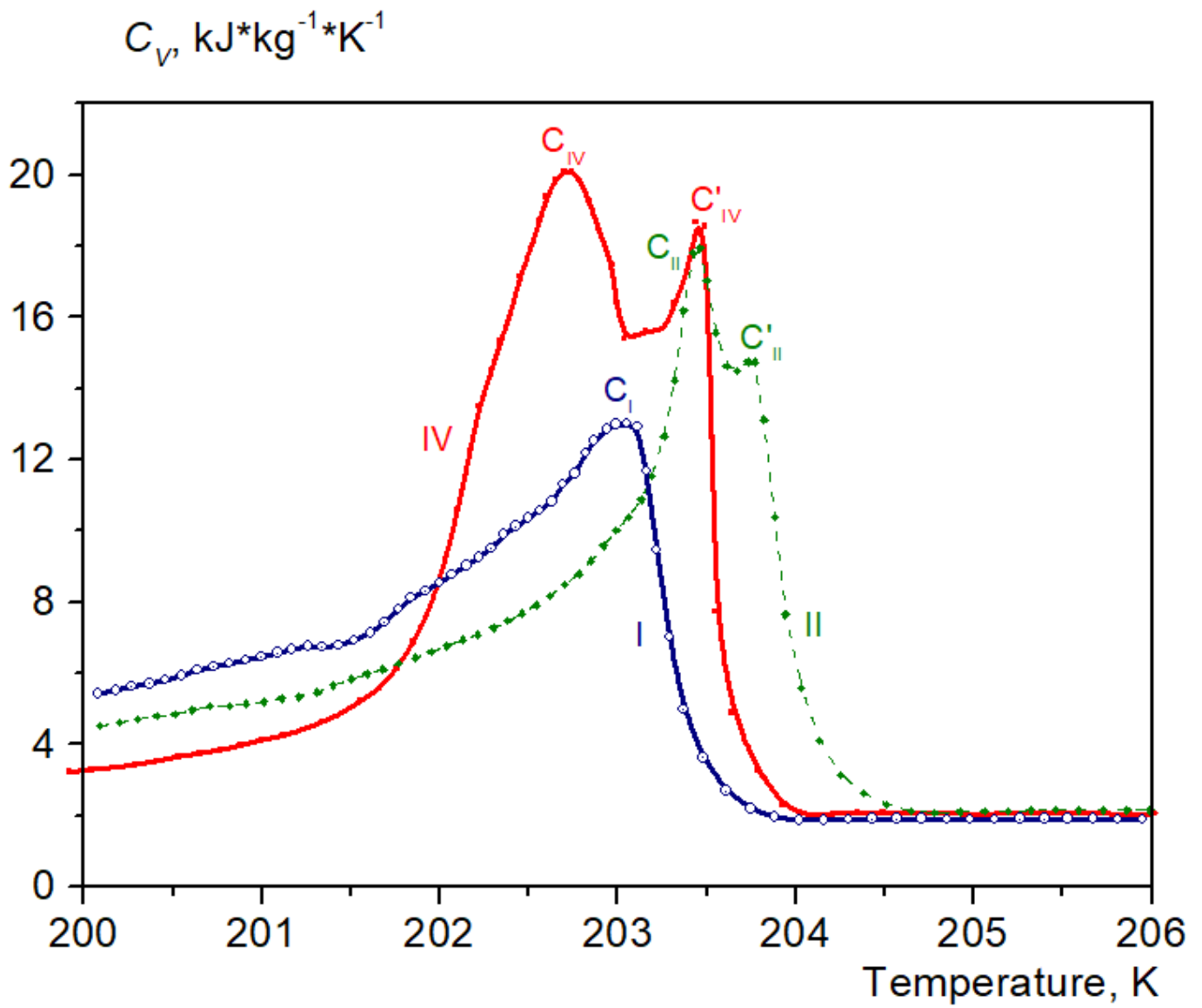


Figure 4

Heat capacity at constant volume for the mixture No 6. Numbers of the isochores are the same as in Fig. 3.

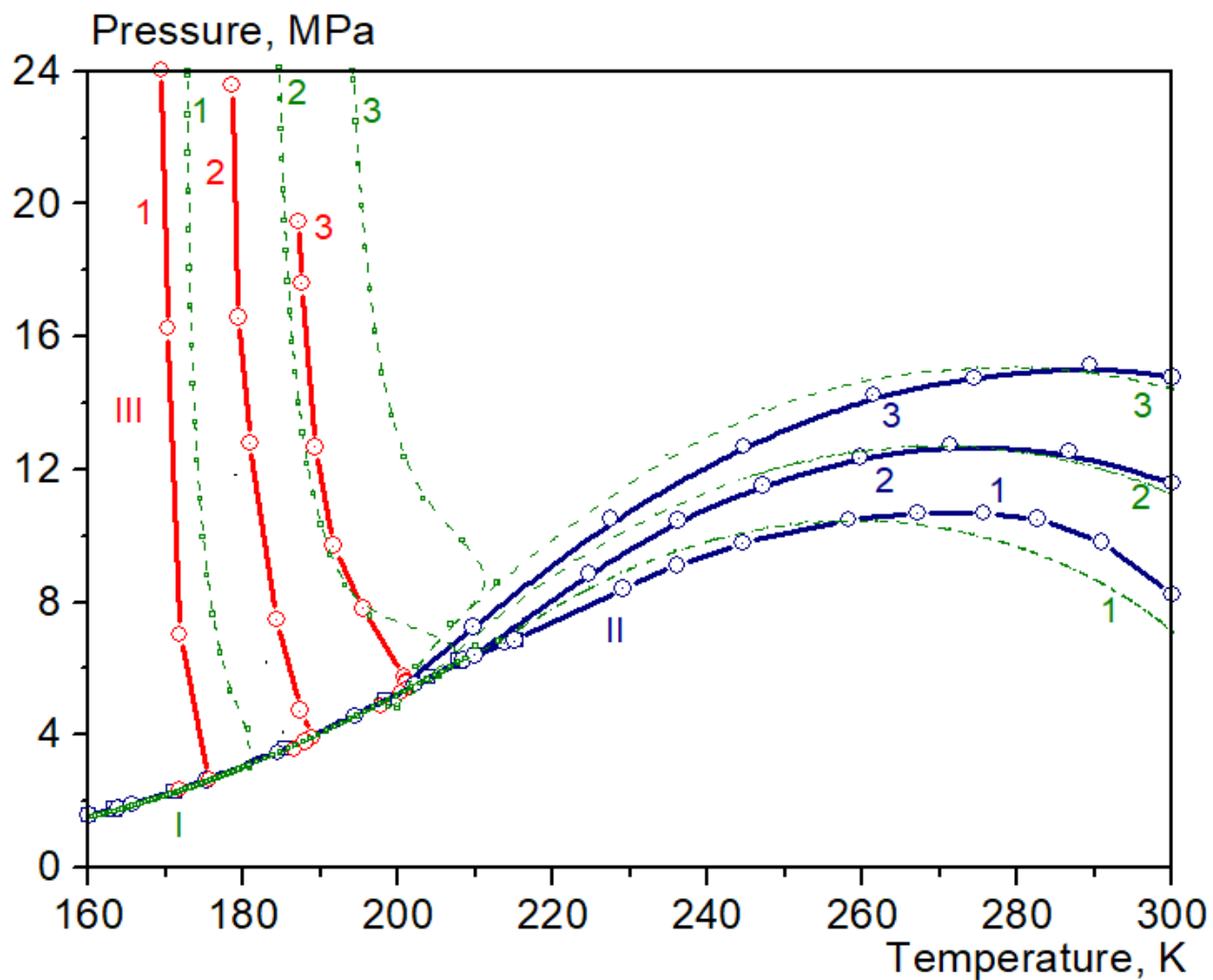


Figure 5

Comparison of experimental (solid) phase diagrams and phase diagrams calculated (dash) with the ThermoFast software from the University of Western Australia for the ternary mixtures No 1-3

## Supplementary Files

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