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Study of non-equilibrium behavior of gas-condensate system in free volume

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Abstract. The results of experiments on the investigation of the non-equilibrium behavior of a multicomponent hydrocarbon gas condensate mixture $\text{CH}_4$–$\text{C}_3\text{H}_8$–$\text{C}_5\text{H}_{12}$–$\text{C}_7\text{H}_{16}$ in a free volume are presented in the article. The calculation of the thermodynamic properties of this mixture with a volume change (adiabatic compression–expansion) and sharp pressure drops in the container cell with a floating piston (recombiner) is presented. The phase equilibrium establishment time of 4-component mixture is determined. The mathematical model of the process in the context of the linearized problem of continuum mechanics using the phase diagram of the investigated mixture is developed. The reliability of the results obtained by calculation is confirmed by experimental studies in the cell of the recombiner.

1. Introduction

The need for in-depth theoretical and experimental research of the features of non-equilibrium processes in hydrocarbon mixtures is growing to improve existing and introduce new methods of hydrocarbon production, as well as for more efficient management of the field development process. Hydrodynamic processes and features of the phase diagrams of such mixtures under natural conditions and in physical experiments are considered in [1–4]. At the same time, the process of establishing a phase equilibrium in mixtures of alkanes, which is specific for gas-condensate fields, has not been studied enough. There is no mathematical description of this process. Experimental research and development of mathematical model of similar processes were the aims of this work.

A series of experiments on adiabatic compression–expansion and sharp pressure drops in a cell of a container with a floating piston (recombiner) was carried out to study the processes of phase transition in gas-condensate systems under adiabatic pressure changes in a free volume. The dependence of the phase equilibrium establishment time on the rate of volume change of the experimental cell and on the initial and final pressures in the cell of the recombiner was observed during the experiment. A mathematical model of the process was developed to describe the experimental results in the context of the linearized problem of continuum mechanics using the phase diagram of the investigated mixture. The results of the numerical solution made
it possible to describe the results of the experiment adequately and to determine the phase equilibrium establishment time under experimental conditions.

2. The experimental part

To study the processes of phase transition under adiabatic pressure change in gas-condensate systems, an experimental setup was assembled, the principal scheme of which is shown in figure 1.

The experimental setup consists of following components:

- container with a floating piston (recombiner);
- one pair of measuring pumps with control unit-controller;
- electronic system for collecting, processing and storing operating parameters for pressure, temperature and flow, the values of which are fixed by sensors during the experiment at predetermined intervals.

In the experiment, the study of the relaxation time of phase transitions in an open volume was performed by a static method. In this case, the phase transition occurs in a stationary gas in a closed volume. During the studies, the pressure in the $PVT$-cell ($P$ is pressure, $V$ is volume, $T$ is temperature) was drastically reduced or increased by different values relative to the initial pressure corresponding to the equilibrium gas state.

The recombiner is a high-pressure cylinder with a floating piston in it and two side retaining nuts, through which the inlet and outlet pistons are fixed. The floating piston divides the recombiner into two chambers isolated from each other—a chamber with diethylene glycol (DEG), into which working fluid is supplied from measuring pumps. The second chamber is the gas-condensate mixture (GCM) chamber in which the GCM under study is located. The recombiner is thermostatically controlled by a special case with heating elements. Two thermocouples are installed to monitor and maintain the set temperature—one on the outside of the recombiner housing, the other in a special pocket of the output piston on the side of the GCM chamber.

The use of measuring pumps in the scheme of piping with the recombinator has allowed to set the required flow rate of the working fluid quite accurately and in a wide range. Three pump modes are programmed in the pump controller:

- continuous maintenance of a constant volume feed;
- continuous maintenance of constant pressure;
- independent mode while maintaining a constant volumetric flow (or constant pressure).

During the research, all indications were measured at a specified interval, automatically recorded in a working spreadsheet. The main parameters controlled during the study are the current pressure in the recombiner and the temperature. Changing the pressure in the chambers above and below the piston was automatically recorded throughout the study by pressure sensors.

To conduct experiments on the study of the non-equilibrium behavior of the GCM in a free volume, a model mixture was prepared consisting of four components of the following composition (table 1).

The measurements showed (table 2) the nonmonotonic behavior of the pressure—a decrease with increasing volume and a slight increase in stabilization. With a decrease in volume, the opposite picture was observed: the growth of pressure during the first phase and a slight decrease in the stabilization phase. The reason for this behavior could be a non-equilibrium phase transition or non-isothermal process due to the inertia of the thermostating system.

The first series of experiments covered the gaseous state of the mixture and the zone of maximum condensation. The operating pressure in the recombiner varied from 14.4 to 20.5 MPa. Pressure stabilization in the GCM chamber occurred in 50 min. The second series of experiments
Figure 1. Scheme of the piping of the recombinator in the study of GCM by the static method: 1—pressure sensor at the outlet of the recombiner (pressure in the GCM, above the piston); 2—pressure sensor at the inlet of the recombiner (pressure in the chamber with ethylene glycol, under the piston); 3—the valve is installed on the connection line of the press and recombiner, opens when the press is pressed; 4—thermocouple installed in the pocket of the output piston; 5—thermocouple installed on the body of the recombinator; 6—a group of pumps for pressure regulation in the hydraulic system (measured values: volumetric flow, pressure at the entrance to the core holder).

Table 1. Loading of a mixture of CH$_4$–C$_{3}$H$_8$–C$_{5}$H$_{12}$–C$_{7}$H$_{16}$ into a recombinator by a measuring press.

| Component  | Temperature, K | Volume fraction |
|------------|----------------|-----------------|
| Methane CH$_4$ | 348 | 0.75 |
| Propane C$_4$H$_{10}$ | 348 | 0.15 |
| Pentane C$_5$H$_{12}$ | 348 | 0.05 |
| Heptane C$_7$H$_{16}$ | 348 | 0.05 |

covered the zone of single-phase state of the mixture and transition into a zone below the maximum condensation pressure. The pressure was lowered from 20.5 to 12.8 MPa (the volume of DEG coming from the recombiner was 166 cm$^3$).
Table 2. The experimental value of the pressure in the upper section of the recombiner cell.

| t, min | P, Pa          |
|-------|---------------|
| 10.00 | 2.05 × 10⁷    |
| 17.13 | 1.28 × 10⁷    |
| 24.26 | 1.28 × 10⁷    |
| 31.39 | 1.28 × 10⁷    |
| 38.52 | 1.28 × 10⁷    |
| 45.64 | 2.16 × 10⁷    |
| 52.77 | 2.16 × 10⁷    |
| 59.90 | 2.16 × 10⁷    |
| 67.03 | 2.16 × 10⁷    |
| 74.16 | 2.16 × 10⁷    |
| 81.28 | 1.53 × 10⁷    |

The pressure stabilization in the GCM chamber occurred in 30 min. The third study returned to a single-phase region. The pressure in the recombiner was increased from 12.8 to 21.6 MPa by pumping 155 cm³ of DEG. The stabilization of the pressure occurred in 55 min. Further, the pressure in the recombiner was reduced from 21.6 to 15.3 MPa, creating the conditions of maximum condensation in the GCM chamber. The volume of the released DEG is 158 cm³. Pressure stabilization occurred in 30 min. In the last study, the pressure was reduced from 21.6 to 15.3 MPa, which corresponded to the region below the pressure of maximum condensation. The volume of the released DEG is 555 cm³. Pressure stabilization occurred in 75 min.

3. Problem statement
One can obtain the resolving equation with respect to the phase velocities from the system of equations of fluid motion for the recombiner problem under the linearized formulation of the problem:

\[
\frac{\partial^2 v_\alpha}{\partial t^2} + \frac{q_\alpha}{\rho_\alpha} \frac{\partial v_\alpha}{\partial t} - \frac{1}{\rho_\alpha \beta_\alpha} \frac{\partial^2 v_\alpha}{\partial x^2} + g_\alpha \frac{\partial v_\alpha}{\partial x} = \frac{q_\alpha g_\alpha}{\rho_\alpha},
\]

where \(v_\alpha\) is the velocity of the \(\alpha\)-phase, \(q_\alpha = \sum_{i=1}^{n_e} q_{i\alpha} = \sum_{i=1}^{n_e} \rho_{i\alpha} / \tau_{i\alpha} = \rho_\alpha / \tau_\alpha\), \(l(t)\) is the mobile boundary of the lower section of the cell of the recombiner, \(\rho_\alpha\) is the value of the phase density, are known (calculated) from the thermodynamic part of the problem, \(\tau_\alpha\) is the phase equilibrium establishment time, \(\beta_\alpha\) is the coefficient of phase compressibility (for the first approximation \(\beta_1 = (2.7–5) \times 10^{-10}\), \(\beta_2 = 1/P_0\)), \(g_\alpha\) is acceleration, \(t\) is time, \(x\) is coordinate along the axis of the recombiner; for liquid \(\alpha = 1\), for gas \(\alpha = 2\).

One can calculate the variation of the coordinate of the lower section of the recombiner cell \(l(t)\) knowing the experimental law of the change in the volume of the recombiner cell in time:

\[
l(t) = \frac{4V_{\text{exp}}(t)}{\pi D_{\text{piston}}^2},
\]
Figure 2. Change in the mobile coordinate of the piston in the cell of the recombiner during the whole experiment.

Figure 3. Comparison of the mixture pressure, calculated from the mathematical model with the experimental values.

\( D_{\text{piston}} = 64 \, \text{mm} \) numerically differentiating of that, one can find the velocity of the lower section of the recombiner cell throughout the entire experiment.

The character of this motion is stepwise in accordance with the experimental actions for a discrete decreasing and increasing of the volume of the recombiner cell during the experiment. The corresponding experimental graphs of the change in the volume of the recombiner cell are shown in figure 2.

The unknown density of the \( \rho_\alpha \) phases and the phase equilibrium establishment time \( \tau_\alpha \) of the phases in equations (1) can be found from the thermodynamic part of the problem. The initial molar volumes of phases can be found by solving the cubic equation with respect to the compressibility \( z \) from the thermodynamic part of the problem for a given initial working pressure \( P_0 \) and temperature \( T \). There are two volume values corresponding to the liquid and gas
phases in the case of stratifying of the mixture into phases and there is one value for the molar volume of the gas phase in the case of the absence of the separation under given initial operating pressure $P_0$ and temperature $T$. Further, according to the known procedure, the phase density $\rho_\alpha$ can be found as well as the saturation and composition. These values of volumes, density of phases, saturation and compositions are the first iteration approximation of the problem.

The first approximation of the phase equilibrium relaxation time can be estimated knowing the experimental law of the change of the volume of the mixture $V_{\text{exp}}(t)$ in the cell of the recombiner and the density of the phases $\rho_\alpha$ (if the mixture is stratified, then there are two different densities for the liquid and gas phases) from the equation of conservation of mass:

$$\frac{1}{\rho_\alpha} \frac{d\rho_\alpha}{dt} = \frac{1}{\tau_\alpha} - \frac{1}{V_{\text{exp}}(t)} \frac{dV_{\text{exp}}(t)}{dt}.$$

Thus, the phase velocities $v_\alpha$ can be found solving equations (1) with known values of phase density and phase equilibrium establishment time in the first approximation, then the expression
Figure 6. Molar volume of the gas phase.

Table 3. The phase equilibrium establishment time of gas–liquid phase transitions in a mixture of CH$_4$–C$_3$H$_8$–C$_5$H$_{12}$–C$_7$H$_{16}$.

| $t$, min | $x$, m | 0.00 | 0.02 | 0.03 | 0.05 | 0.06 | 0.08 | 0.10 | 0.11 | 0.13 | 0.14 | 0.16 |
|--------|-------|------|------|------|------|------|------|------|------|------|------|------|
| 10.00  | 8.0   | 8.0  | 8.0  | 8.0  | 8.0  | 8.0  | 8.0  | 8.0  | 8.0  | 8.0  | 8.0  | 37.2 |
| 17.13  | 152.4 | 152.4| 152.4| 152.4| 152.4| 152.4| 152.4| 152.4| 14.1 | 14.1 | 14.1 | 38.3 |
| 24.26  | 0.0   | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| 31.39  | 0.0   | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| 38.52  | 141.0 | 141.0| 141.0| 141.0| 141.0| 141.0| 141.0| 141.0| 13.9 | 13.9 | 13.9 | 37.0 |
| 45.64  | 102.0 | 102.0| 102.0| 102.0| 102.0| 102.0| 102.0| 102.0| 9.3  | 9.3  | 9.3  | 9.3  |
| 52.77  | 0.0   | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 15.8 | 15.8 | 15.8 | 15.8 |
| 59.90  | 0.0   | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 15.8 | 15.8 | 15.8 | 15.8 |
| 67.03  | 0.0   | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 15.8 | 15.8 | 15.8 | 15.8 |
| 74.16  | 284.7 | 284.7| 284.7| 284.7| 284.7| 284.7| 284.7| 284.7| 25.9 | 25.9 | 25.9 | 25.9 |
| 81.28  | 18.3  | 18.3 | 18.3 | 18.3 | 18.3 | 18.3 | 18.3 | 18.3 | 18.3 | 18.3 | 18.3 | 18.3 |
| 62.28  | 0.0   | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 31.6 | 31.6 | 31.6 | 31.6 |
| 67.03  | 0.0   | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 31.6 | 31.6 | 31.6 | 31.6 |
| 71.78  | 189.8 | 187.6| 185.4| 183.3| 181.2| 179.2| 179.2| 14.5 | 14.5 | 14.5 | 14.5 | 14.5 |
| 76.53  | 231.9 | 233.9| 236.0| 238.1| 240.2| 242.4| 246.1| 8.7  | 16.8 | 16.8 | 16.8 | 16.8 |
| 81.28  | 36.6  | 36.6 | 36.5 | 36.5 | 36.4 | 36.4 | 36.3 | 36.2 | 36.1 | 36.1 | 36.1 | 36.1 |

for the pressure can be obtained from the equations of phase motion:

$$P(x, t) = P_0 + \frac{1}{\beta} \int_0^t \left( \frac{q_\alpha}{\rho_\alpha} - \frac{\partial v_\alpha}{\partial x} \right) dt,$$

where $P_0$ is the integration constant, which is the specified working pressure at the initial instant of time by definition. In this case, $P_0$ can also be a function of the coordinate of the recombiner cell, if this distribution at the initial instant of time is known. The boundary conditions on the pressure are not specified in the solution of the problem. The boundary values of the pressure are calculated from the known changes of the phase velocity, density, and relaxation time. The pressure distribution $P(x, t)$ at each point $x$ of the recombiner cell and at any time $t$ during the
entire experiment can be obtained knowing only the experimental change of the volume of the recombiner cell. This theoretical value of the pressure \( P(x, t) \) at \( x = 0 \) and the experimental pressure values measured by the pressure sensors in the upper section of the recombiner cell practically coincide throughout the time of the experiment (figure 3).

The next approximation of the problem can be obtained knowing the pressure distribution \( P(x, t) \) by solving the thermodynamic part of the problem (cubic equation) at the pressure \( P(x, t) \) and thereby obtaining the molar volumes of the phases formed and, consequently, adjust the phase densities \( \rho_\alpha \) (if the mixture is phase-separated), and also saturation and composition. Then the procedure of solving the problem of determining the phase velocities and the pressure field in the recombiner cell repeats until the specified accuracy is reached.

The algorithm for solving the problem is implemented in the FlexPDE environment [5, 6]. In this case, the numerical algorithm of calculations in the FlexPDE environment for solving differential equations is based on the finite element method and its modifications.

4. Calculation results
The results of calculation of the pressure and the law of volume change are shown in figures 3–6 and table 3.

Comparison of the obtained pressure distribution in the presented mathematical model at the boundary sections of the recombiner cell with experimental data on pressure measurements at the corresponding points of the recombiner cell yields an error of less than 5%, which is a satisfactory result of the approbation of the hydrodynamic part of the mathematical model.

5. Conclusion
The choice of a four-component mixture \( \text{CH}_4 - \text{C}_3\text{H}_8 - \text{C}_5\text{H}_{12} - \text{C}_7\text{H}_{16} \) for modeling was determined by the need for a more adequate description of real gas-condensate deposits using improved van der Waals state equations.

The amount of the liquid phase formed in the system increases to a maximum value with the pressure decrease under the experimental conditions, and then, with a further pressure decrease, the volume of the liquid phase decreases. The liquid phase disappears with the pressure increase and the multicomponent system again goes into a single-phase state. A similar change in the gas–liquid ratio is characteristic for gas-condensate [1]. The mathematical model proposed by the authors made it possible to adequately describe the results of the experiment, to determine the mole fractions of the gas and liquid phases, and the phase equilibrium establishment time in the free volume.

Further research suggests the development of mathematical models and the experimental investigations of the processes of heat and mass transfer during the filtration of multicomponent hydrocarbon mixtures in porous media.

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References
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1. Vyakhirev R.I., Gricenko A.I. and Ter-Sarkisov R.M. 2002 Razrabotka i Eksplotatsiya Gazovykh Mestorozhdennii (Moskva: Nedra)
2. Grigor’ev B.A., Kachalov V.V., Pazuyuk Yu.V. and Sokotushchenko V.N. 2017 Vesti Gazovoy Nauki (2) 182–202
3. de Groot C.R. and Mazur P. 1962 Non-Equilibrium Thermodynamics (Amsterdam: North-Holland)
4. Zaichenko V.M., Maikov I.L. and Torchinskii V.M. 2013 High Temp. 51 776–84
5. Backstrom G. 2005 Fields of Physics by Finite Element Analysis: Electricity, Magnetism, and Heat in 1D, 2D, and 3D Using FlexPDE Version 5 (Malmo, Sweden: GB Publishing)
6. URL http://www.pdesolutions.com/cgi-bin/getbook50