Influence of microadditive of carbon dioxide on the kinetics of boiling-up of superheated $n$-pentane

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Abstract. The effect of a low-boiling impurity (CO$_2$ gas <1.5% mol) on the kinetics of boiling-up of superheated $n$-pentane in a vertical glass tube have been studied by high-speed video (2050 fps). The method of continuous pressure decrease from 2.00 to 0.10 MPa (in the temperature range of 100.2-145.1 °C), as well as the method of measuring the lifetimes of superheated liquids at 0.10 MPa (90.2-134.1 °C) have been used. The inner surface of the tube has two visible defects, one of which defines the boundary of the attainable superheat. After degassing the system, the defects of tube cease to play an appreciable role, the active centers are redistributed. The temperature of the attainable superheat increases from the initial value by 20 °C in tests with gas and by 10 °C in subsequent tests without it. The result obtained may be related to physical gas adsorption on the glass surface during the process of evacuation of the system.

1. Introduction
Boiling-up and subsequent boiling of liquid is a physical phenomenon related to phase transitions of the first kind [1, 2]. The presence of undissolved gas and suspended particulate in the fluid, poorly wetted areas of vessel walls facilitates this process reducing the lifetime of metastable state. From experimental works [3-6] it follows that gas saturation of liquids leads to a decrease in their superheat. On the other hand, it was shown in [7] that the addition of some impurities (up to 1.5 mol.%) including carbon dioxide to distilled water suppress the cavitation centers of the liquid during its impulsive stretching, although in such small amounts they either increase the equilibrium vapor pressure $p_v$ and reduce the surface tension $\sigma$ (CO$_2$, C$_3$H$_6$O), or practically do not change them (HCl, CH$_2$O$_2$). In the opinion of the author of work [7], one of the reasons may be the binding of free hydrogen ions in water by the indicated impurities. In this work, we investigated the effect of small addition of low-boiling impurity (CO$_2$ gas up to 1.5 mol%) on the kinetics of spontaneous boiling-up of superheated $n$-pentane in a glass tube.

2. Materials and methods
An automated installation for studying the kinetics of boiling-up of a superheated liquid with simultaneous high-speed video of this process (2050 fps) is described in detail in [8, 9]. In the current work, the installation has been modified. A system of continuous pressure control with high-precision pressure-vacuum sensors was introduced. As in [9], the moment of boiling-up of superheated liquid was determined by an abrupt change in optical density of the image of the measuring cell.
Figure 1 shows a block diagram of the experimental installation. The investigated liquid (\textit{n}-pentane) is in a glass molybdenum tube with an inner diameter of 5.6 mm. The tube is oriented vertically, its top is sealed. The upper (working) part of the tube with a length of 114.6 mm and a volume of $2.8 \cdot 10^{-6}$ m$^3$ is thermostated in a cell with a coolant from a Huber CC-208B circulation thermostat, but its lower part is kept at room temperature. The temperature difference of between the coolant in the thermostat and the cell is measured with a precision temperature meter MIT-8 using three differential thermocouples. The temperature \( T \) in the thermostated cell is maintained with an accuracy of 0.1 °C. The superheated state of the liquid under investigation is realized by reducing the pressure \( p \) from 2.00 MPa to 0.10 MPa at a fixed temperature \( T \). The pressure in the installation is created by compressed gas and transferred to the liquid through a metal bellows. The pressure maintenance accuracy is 0.01 MPa.

![Block diagram of the experimental installation.](image)

The boiling-up process of a superheated liquid is random, so the experiments are carried out many times. At temperatures below the temperature of the attainable superheating, boiling-up occurs predominantly at a steady-state pressure \( p = 0.10 \) MPa. Then the temperature \( T \) and the lifetime of the metastable liquid \( \tau \) are measured. At higher temperatures, the expected event occurs during the depressurization process. Then the random variable is the pressure at which the liquid boils-up. The first method of studying the kinetics of boiling-up of a superheated liquid is called the method of measuring the lifetimes of the superheated state, the second method is known as the method of continuous pressure decrease [1, 2]. The experiment includes preliminary “running-in” of the surface of the tube with the liquid under investigation. The holding time of the system under the pressure of 2.00 MPa (between tests) is 90 s. The measurement cycle is automated.

Gas saturation of \textit{n}-pentane is as follows. First, the system under study being kept at room temperature and evacuated down to -0.095 MPa (relative to the atmosphere) is filled with carbon dioxide up to -0.087 MPa. Then the vapors of \textit{n}-pentane are added to the system until the mixture pressure is 0.10 MPa. After filling the measuring cell, the resulting vapor-gas mixture is liquefied at
\( p = 2.00 \text{ MPa} \). In a mixture of ideal gases, the mole fraction can be expressed as the ratio of the partial pressure to the total pressure of the mixture [10]. Thus, for the gaseous mixture-filled tube the molar fraction of \( \text{CO}_2 \) in \( n \)-pentane is estimated as \( \sim 8.4 \text{ mol\%} \). This gas concentration is selected empirically. With an increase in the \( \text{CO}_2 \) content in the closed system under study, a poorly soluble vapor-gas bubble is formed at the upper sealed end of the glass tube. The bubble significantly reduces the superheat of the liquid. The experiments were carried out in the temperature range of \( 90.2 - 145.1 \text{ °C} \). From the experimental data on the phase equilibrium of the \( \text{CO}_2 + n \)-pentane system [11] and the equation of state of the mixture [12], it follows that the molar fraction of \( \text{CO}_2 \) in \( n \)-pentane at a pressure of \( \sim 2.00 \text{ MPa} \) does not exceed 1.5 mol\% in this temperature range. Note that the solubility of a gas in a liquid increases with increasing pressure.

3. Results and discussion
The experiments on the study of the boiling-up kinetics of the superheated gas-saturated liquid were carried out by the method of measuring the lifetimes of a superheated liquid, as well as by the method of continuous pressure decrease. Statistical processing of data such as lifetimes is described extensively in [13]. The temperature dependence of the mean lifetime of superheated \( n \)-pentane (with and without \( \text{CO}_2 \) addition) at \( p = 0.10 \text{ MPa} \) is plotted in figure 2a. It is conventional to explain the typical “plateaus” of the dependence by the exposure of background radiation (\( \alpha \)-, \( \beta \)- and \( \gamma \)-particles) [14, 15]. Their positions is practically independent of the pressure and temperature of the liquid. The boundary of the attainable superheat \( 4 \) is calculated according to the theory of homogeneous nucleation for pure \( n \)-pentane. It follows from figure 2a that the temperature of experimentally attainable superheat in series 2 (\( n \)-pentane with gas) increases by 20 °C compared to series 1 (\( n \)-pentane without gas). At a temperature of 120 °C and below, the probability of boiling-up in the \( n \)-pentane + \( \text{CO}_2 \) system does not depend the value of \( T \). In this case, the mean lifetime of the superheated liquid on the “plateau” turns out to be shorter than in experiments with pure \( n \)-pentane and amounts to \( \sim 20 \text{ s} \). After degassing and refilling the measuring cell with pure \( n \)-pentane, the data of series 1 are reproduced (see series 3), but the temperature of the attainable superheat increases by 10 °C.

![Figure 2. The dependence of the mean lifetime of superheated \( n \)-pentane on temperature at \( p = 0.10 \text{ MPa} \) (a) and the phase diagram of \( n \)-pentane (b): points – experimental data: 1, 3 – \( n \)-pentane; 2 – \( n \)-pentane + \( \text{CO}_2 \); 4 – the boundary of the attainable superheat; 5 – spinodal; 6 – binodal.](image-url)
Figure 3. The probability density of boiling-up site distribution on the image plane of the observed region in all range of temperature $T$: (a - c) – boiling-up at 0.10 MPa, (d - e) – at continuous pressure decrease; (a, d) - $n$-pentane, series 1 (see figure 2); (b, f) - $n$-pentane + CO$_2$, series 2; (c, e) - $n$-pentane, series 3. The coordinates are reduced to dimensionless form and are given as a percentage of the size of the observed inner region of the tube.
In figure 2b shows the superheat temperature corresponding to the average pressure at which the investigated liquid boils-up without reaching 0.10 MPa. At some temperatures, part of the events occurs during pressure decrease and part of them occurs at a steady-state value of \( p=0.10 \) MPa. In this range, the \( n \)-pentane + CO\(_2\) system has a special feature. The average pressure at which the gas-saturated liquid boils-up is practically independent of temperature and is \( \sim 0.27 \) MPa. In other cases, active vaporization centers limit the depth of entry into the metastable region \( (p_\text{cr}-p) \) to approximately the same value at different temperatures, therewith its value for series 2 \( (n\)-pentane with gas) is greater than ones for series 1 and 3 \( ("pure" \( n \)-pentane).

The coordinates of the sites of appearance of the first vapor bubbles in the superheated liquid were found from the video frames of the onset of boiling-up. To visualize them, we used the Parzen – Rosenblatt nuclear density estimation method [9, 16]. Figure 3 shows the probability density of boiling-up site distribution over the area of the glass tube image for each series of experiments. Activation centers of boiling-up at steady-state pressure and non-activation centers of boiling-up during the drop of pressure were separately processed. Coordinates \( x \) and \( h \) are reduced to dimensionless form and are given as a percentage of the diameter and height of the observed region of the measuring cell, respectively. Visual analysis of figure 3 shows that initially the total number of active vaporization centers is limited, and they are distributed nonuniformly. The glass tube has two visible defects on the inner surface, one of which defines the boundary of the attainable superheat. The probability distribution of the boiling-up site on the inner surface of the tube outside the defects becomes uniform with the addition of CO\(_2\), i.e. the gas suppresses the other most active centers of vaporization. After re-filling the tube with “pure” \( n \)-pentane, defects cease to play a noticeable role, active centers are redistributed. In this case, the boundary of the attainable superheat, as elsewhere, is determined by one of the most active centers.

4. Conclusion

The kinetics of boiling-up of superheated \( n \)-pentane has been studied by the method of continuous pressure decrease from 2.00 to 0.10 MPa and by the method of measuring the lifetimes at 0.10 MPa by high-speed video. The experiments were carried out in the temperature range of 90.2-145.1 °C with both gas-saturated (CO\(_2\) up to <1.5% mol) and pure \( n \)-pentane (before and after experiments with a volatile impurity). It follows from the video data that initially boiling-up occurs with a high probability on two visible glass defects, one of which determines the boundary of the attainable superheat. The probability distribution of the boiling-up site on the inner surface of the tube outside the defects becomes uniform with the addition of CO\(_2\), i.e. the gas suppresses the other most active centers of vaporization. The temperature of the attainable superheat in tests with gas increases by 20 °C as compared with the initial value for pure \( n \)-pentane. After degassing and refilling the glass tube with pure \( n \)-pentane, the data without gas are reproduced but the temperature of the attainable superheat increases by 10 °C. In this case, two visible defects cease to play a notable role, active centers are redistributed. The result obtained may be related to physical (reversible) gas adsorption on the glass surface during the process of evacuation of the system.

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References

[1] Skripov V P, Sinitstyn E N, Pavlov P A, Ermakov G V, Muratov G N, Bulanov N V, Baidakov V G 1988 Thermophysical Properties of Liquids in the Metastable (Superheated) State (London: Gordon and Breach Science Publishers)
[2] Baidakov V G 2007 *Explosive Boiling of Superheated Cryogenic Liquids* (Weinheim: Wiley-VCH)

[3] Mori Y, Hijikata K, Nagatani T 1976 *Int. J. Heat Mass Transfer*. 19 1153-1159

[4] Forest T W, Ward C A 1977 *J. Chem. Phys.* 66 (6) 2322-2330

[5] Pavlov P A, Skripov P V 1985 *High Temperature* 23 (1) 67–73

[6] Baidakov V G, Kaverin A M 2020 *Int. J. Heat Mass Transfer*. 163 120498

[7] Vinogradov V E 2009 *Tech. Phys. Lett.* 35 (2) 54–56

[8] Lipnyagov E V, Parshakova M A, Perminov S A, and Ermakov G V 2013 *Int. J. Heat Mass Transfer*. 60 612–615.

[9] Lipnyagov E V, Parshakova M A, and Perminov S A 2017 *Int. J. Heat Mass Transfer*. 104 1353-1361

[10] Landsberg G D 1988 *Elementary Textbook on Physics* vol. 1 Mechanics. Heat. Molecular physics (Moscow: Mir Publishers)

[11] Cheng H, Pozo de Fernindez M E, Zollweg J A, and Streett W B 1989 *J. Chem. Eng. Data* 34 319-323

[12] Peng Ding-Yu and Robinson D B 1976 *Ind. Eng. Chem. Fundam.* 15 (1) 319-323

[13] Lipnyagov E V, Parshakova M A, and Perminov S A 2017 *Int. J. Heat Mass Transfer*. 104 1362-1371

[14] Glaser D A 1953 *Phys. Rev.* 91 (3) 762-763

[15] Sinitsyn E N, Uskov V S 1986 *Thermodynamical investigations of metastable liquids* (Sverdlovsk: Urals Scientific Center of the Academy of Sciences of the USSR) 59-62 (In Russian)

[16] Silverman B W 1986 *Density Estimation for Statistics and Data Analysis* (New York: Chapman & Hall / CRC)