Temperatures of the Attainable Superheat of Some Thermally Unstable Liquids

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The paper gives the results of measuring the temperatures of the attainable superheat of some liquids that are thermally unstable at these temperatures. The technique of heating a thin wire probe placed into a liquid under study with electric-current pulses has been used. The length of pulses is from $10^{-5}$ to $10^{-3}$ s, which corresponds to a heating rate of $10^5$ to $10^8$ K·s$^{-1}$. The influence of a chemical reaction in the liquid phase on the temperature of the attainable superheat has been considered. In particular, it has been shown that boiling initiated by an elementary act of an exothermic chemical reaction is of a low probability. A method of calculating the temperature of the attainable superheat of thermally unstable liquids under conditions of quick heating has been developed. A method for the determination of the kinetic parameters of thermal decomposition from the measurements of the temperature of the attainable superheat is discussed.

KEY WORDS: attainable superheat; boiling; homogeneous nucleation; kinetic parameters; pulse heating; thermal decomposition; wire probe.

1. INTRODUCTION

A chemical reaction in the liquid phase affects the bubble formation in a superheated liquid. The method of describing nucleation in multicomponent systems with chemical reactions suggested by Cherepanova and Ushkans [1] is too general and does not allow numerical calculations. The aim of the present paper is to develop a simple method for estimating the temperature of the attainable superheat of thermally unstable substances.
using the results of experiments. We restrict ourselves to the reactions of thermal decomposition, although some of the conclusions of this paper are true for reactions of an arbitrary type. We also assume that a chemical reaction is a primary process and nucleation is a secondary one in the sense that bubble formation does not influence the course of a chemical reaction.

If a chemical reaction has nonzero heat as a result of the reaction in the liquid phase, domains appear for which the temperature and the composition differ from those of the bulk. The initial size of these domains is very small; it is of the order of molecule dimensions. Then these domains spread out over the whole liquid volume as a result of molecule interactions. So this inhomogeneity should be taken into account in developing a rigorous nucleation theory in chemically reacting systems.

However, we consider only two limiting cases: (i) the critical bubble arises as the result of a single, elementary act of an exothermic chemical reaction, and (ii) the products and the heat of a chemical reaction have spread over the whole volume so that such a system can be considered as a mixture, the temperature and the composition of which are uniform but time dependent.

Only several new molecules may be born due to an elementary act, which does not change considerably the composition of the critical nucleus because, even at the temperature of the attainable superheat, it consists of no fewer than 100 molecules [2–4]. However, if a chemical reaction is endothermic, the originated molecules may have energy that is sufficient for the formation of the critical bubble. Several approaches have been developed for calculating the conditions under which a local heat release leads to the birth of the critical bubble. One of these approaches is known as the thermal theory of the initiation of boiling-up of superheated liquids with high-energy particles [5, 6]. According to the thermal theory, zones or so-called thermal spikes are formed in the liquid along the track of the particle. The temperature in the spikes is higher than that in the bulk. To form the critical bubble, it is necessary to evaporate the volume of liquid that is equal to

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V_1 = \frac{4}{3} \pi r_c^3 \rho'' \rho'\]

Here \( \rho' \) and \( \rho'' \) are the densities of the liquid and the vapor, respectively, and \( r_c \) is the radius of the critical bubble at the temperature of the bulk. In the framework of the thermal theory it is suggested that if the volume \( V_1 \) has the energy \( W_a + W' \), the formation of the critical bubble occurs with a probability that is equal to 1. Here \( W_a \) is the adiabatic work of the critical bubble formation, and \( W' \) is the irreversible energy losses connected with