higher temperatures, especially in the range of the H_2 and D_2 critical temperatures, is also of interest.

NOTATION

V, molar volume; V^E, excess molar volume; p, pressure; T, temperature; c, concentration of components in solution; ε, dielectric constant; α, polarizability of a molecule; P, polarization (Clausius–Mossotti function); N, Avogadro's number; A, B, C, dielectric viral coefficients.

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SPONTANEOUS NUCLEATION FREQUENCY IN SUPERHEATED LIQUID XENON AND KRYPTON

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An experimental study is made of spontaneous boiling up in superheated liquid xenon and krypton. Results are compared with calculations using the Volmer–Zel'dovich–Frenkel homogeneous nucleation theory.

Boiling processes may be accompanied by significant superheating of the liquid involved. The case where boiling up occurs at centers of a fluctuation nature is of physical interest. In the absence of external fields the kinetics of such a process are described by the well-known Volmer–Zel'dovich–Frenkel theory [1], which produces the following expressions for the stationary nucleation frequency:

$$J = N_1 B \exp(-W_*/kT), \tag{1}$$

where

$$W_* = \frac{16\pi\sigma^3}{3(p_s - p)^2 (1 - v'/v'')^2}. \tag{2}$$

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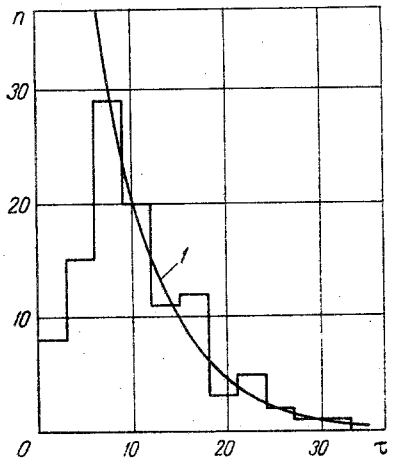

Fig. 1. Histogram of liquid krypton boilup time distribution: p = 1.00 MPa, T = 185.10°K; N = 107; $\bar{\tau}$ = 6.5 sec; τ' = 6 sec; 1) calculation by Eq. (3). τ, sec.

The value of the preexponential factor B was determined in [2-4].

In technological processes boiling up of a superheated liquid can be initiated significantly by preactivated or easily activated boiling centers, and also by γ-quanta, neutrons, and other rapid particles. In the latter case formation of viable bubbles occurs due to local heat liberation caused by transformation of the energy lost by δ-electrons created by the high-energy particles [5,6].

The present study is devoted to an experimental investigation of the kinetics of nucleation in superheated liquid xenon and krypton, and is a continuation of investigations of metastable states of simple liquids performed previously [7,8]. Interest in condensed noble gases is stimulated not only by the simplicity of their molecular structure, but also by the promise of their use in nuclear physics as ionized particle detectors [9,10].

The experiments were performed with equipment operating on the principle of the pure bubble chamber [5]. The liquid was superheated in a glass cell with working volume V = (65-85)·10^{-9} m^3. The material under study was brought into the metastable state by reducing the pressure beyond the phase equilibrium line. The time period τ from pressure removal to commencement of boiling was measured. For fixed T and p not less than N = 50-70 values of τ were recorded, which were then used to produce an average lifetime, $\bar{\tau} = \Sigma\tau_i/N$ for the superheated liquid, whereupon the nucleation frequency $J = (\bar{\tau}V)^{-1}$ was calculated. Uncertainty in temperature measurement did not exceed 0.03°K, with uncertainty in pressure measurement not more than 0.01 MPa. The experimental apparatus and technique are described in detail in [7,11].

For constant T and p, the boilup delay time is a random quantity, distributed by a Poisson exponential law [1]:

$$\omega(\tau) = (\bar{\tau})^{-1} \exp(-\tau/\bar{\tau}). \quad (3)$$

Figure 1 presents a histogram of the τ distribution obtained in the krypton experiments. The significant deviation of the experimental histogram from the Poisson form, Eq. (3), at low τ values may be explained by quasiadiabatic cooling upon removal of pressure from the liquid. The stationary distribution of Eq. (3) is preceded by a transient process produced by temperature relaxation of the system.* The τ distribution calculated by a computer with consideration of spatial and temporal inhomogeneity of the temperature field within the cell agrees qualitatively with that obtained experimentally. To eliminate the transient process an anticipation time τ' was introduced, selected from the form of the experimental histograms. The criterion for correctness in choice of τ', aside from good agreement of the experimental histogram with the theoretical curve (Fig. 1), was the closeness in value of $\bar{\tau}$ and the mean-square error of an individual measurement.

*The time for establishment of pressure upon departure into the metastable region does not exceed ∿0.2 sec.

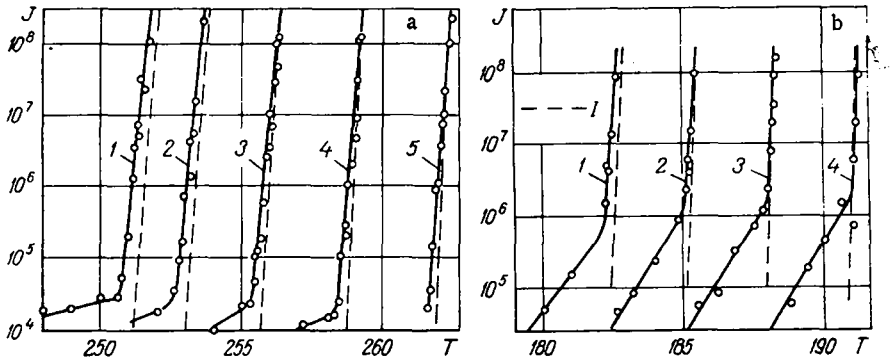

Fig. 2. Nucleation frequency versus temperature in superheated liquid xenon (a) and krypton (b) along isobars: 1) p = 0.24 MPa; 2) 0.55; 3) 0.99; 4) 1.48; 5) 1.98 (a); 1) p = 0.40 MPa; 2) 1.00; 3) 1.60; 4) 2.20 (b); 1) calculation with homogeneous nucleation theory. J, $m^{-3} \cdot sec^{-1}$; T, °K.

High-purity gases were used in the experiments. The label purity of the xenon was 99.98%, of the krypton, 99.87%. The τ measurements were performed along isobars. The mean boiling delay times ranged from 0.1 to 1500 sec. The nucleation frequency values determined in experiment are shown by the open circles of Fig. 2a, b. The dashed lines in the same figure show calculations of J by the homogeneous nucleation theory formulas, Eqs. (1), (2). Thermodynamic parameters of the xenon and krypton were taken from [12-14]. In Eq. (2) the value of surface tension for a planar phase boundary was used. The kinetic coefficient was calculated using Kagan's theory [3]. Use of other methods leads to an insignificant shift of the theoretical lines along the temperature axis with practically no change in their slope. For xenon and krypton this divergence does not exceed 0.5°K.

Table 1 shows values of the temperature attainable by superheating T_{sh}, corresponding to a nucleation frequency of $J = 10^7$ $m^{-3} \cdot sec^{-1}$. One can see the good (within 0.4°K) agreement of the theoretical and experimental T_{sh} values. Using Eqs. (1), (2) and the experimental superheating temperature values, the surface tension σ^* at the phase boundary between the liquid and a vapor bubble of critical size was calculated. The σ^* values agree with the data of [12,13] for a planar phase boundary σ_∞. A vapor bubble containing several hundred molecules can be considered as a macroscopic object in the first approximation.

The deviation of the experimental isobars from the theoretical lines in the range of small nucleation rates (Fig. 2a, b) is due to the initiating effect of background and cosmic radiation [6]. In contrast to all the liquids studied previously [1], xenon has significantly higher stability with respect to the action of ionizing particles. The initiation effect appears at frequencies $J \lesssim 2.2 \cdot 10^4$ $m^{-3} \cdot sec^{-1}$, which corresponds to a mean boilup delay time of $\sim$700 sec. This increased radiation stability of xenon permits measurement of thermodynamic and kinetic properties of the material at superheatings close to the limit of fluctuation nucleation. The horizontal plateau characteristic of many liquids [1,15] is absent from the xenon isobars.

The low radiation sensitivity of superheated liquid xenon was first observed by Glaser et al. [9], who explained the phenomenon by the significant scintillation properties of the element. The latter causes a portion of the ionizing particle energy to be scintillated rather than transformed into thermal energy. The stability of condensed inert gases to ionizing radiation increases with atomic number of the element, as does the scintillation capability of the gas [10,16].

The experimental values of d ln J/dT are close to the theoretical ones. Since in the first approximation

$$\frac{d \ln J}{dT} \approx \frac{d(W_*/kT)}{dT}, \tag{4}$$

the experimental results indicate that Eq. (2) gives the proper temperature dependence of the work required to form a critical bubble. However, the systematic reduction of the derivative d ln J/dT as compared to the theoretical value should be noted. The attainable

TABLE 1. Experimental and Theoretical Values of Temperature Attainable by Superheating, and Characteristic Quantities for Critical Bubble in Liquid Xenon and Krypton ($J = 10^7$ $m^{-3} \cdot sec^{-1}$)

Substance	p, MPa	T_s, °K	T_{sh}, °K		$\sigma \cdot 10^3$, N/m		$r_* \cdot 10^{10}$, m	n_*	$d \ln J/dT$	
			expt.	theor.	σ_∞	σ_*			expt.	theor.
Xe	0,24	181,64	251,41	251,79	4,04	3,97	39	245	8,7	11,1
	0,55	201,47	253,34	253,58	3,78	3,73	40	285	9,0	11,7
	0,99	218,32	256,06	256,17	3,42	3,40	42	360	9,7	13,1
	1,48	231,54	259,03	259,14	3,04	3,02	45	480	10,4	15,2
	1,98	242,11	262,18	262,25	2,64	2,63	49	660	12,0	18,0
Kr	0,40	140,56	182,40	182,67	3,37	3,30	36	275	9,9	16,1
	1,00	159,16	185,24	185,35	2,91	2,88	39	380	12,2	18,9
	1,60	170,72	188,10	188,14	2,47	2,46	43	555	14,3	22,8
	2,20	179,47	191,11	191,04	2,02	2,04	47	845	19,1	28,6

superheating temperatures obtained in this study agree well with T_{sh} measurements for xenon and krypton by the continuous isobaric heating method [8], for a nucleation rate of $J \approx 10^{11}$ $m^{-3} \cdot sec^{-1}$.

NOTATION

J, nucleation rate; N_1, number of molecules per unit volume of metastable liquid; B, kinetic coefficient; W*, critical bubble formation work; k, Boltzmann's constant; T, temperature; σ, surface tension; p_s, saturation pressure; p, pressure in liquid; v', v", specific volumes of liquid and vapor on saturation line; V, system volume; τ, liquid lifetime in metastable state; $\bar{\tau}$, mean lifetime; n, number of liquid boilups in specified time interval; N, total number of tests; τ', count anticipation time; T_{sh}, temperature attainable by superheating; σ_*, surface tension at liquid–critical vapor bubble boundary; σ_∞, surface tension at planar phase boundary; T_s, saturation temperature; r_*, critical bubble radius; n_*, number of molecules per critical bubble.

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