A METHOD OF FORECASTING BINARY-SOLUTION SUPERHEATING

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A method is considered for estimating the boiling point of a solution from the component critical parameters.

Extensive data have accumulated on boiling kinetics and the related attainable superheating [1]. Mostly, pure or specially purified materials were used. However, one often has to deal with multicomponent systems, and information on superheating for them is scanty. Forecasting spontaneous boiling has therefore to be based on restricted data. In particular, we consider the scope for extending approximation for the homogeneous nucleation frequency J(T, p) to two-component systems, as J corresponds to a certain attainable superheating temperature T*, where the formula is derived from the one-parameter similarity theory [1]:

$$\lg J(\tau,\ \pi) = a\{1 - \exp[-(\tau - \tau_0) G_{\tau_0}(\pi)/a]\}. \tag{1}$$

The pressure dependence of τ_0, $G\tau_0$, and a is provided by six fitting parameters, two of which are correlated with the thermodynamic similarity criterion A [2].

When one transfers from a one-component system to a two-component one, the T*(p; x = const) relationship remains simple and almost linear (Fig. 1) not only for the ideal pentane-heptane system [3] but also for gas-liquid solutions: CO_2 in water [4], pentane, decane, and nitrobenzene [5, 6], Ar and NH_3 in water [7], and N_2 in water and heptane. This will be required subsequently.

The reduced attainable superheating $\tau_a = T^*_a/T_c$ at atmospheric pressure usually falls in the narrow range from 0.89 to 0.91; some segregation occurs within this interval, which is incorporated via parameter A. Substantially lower $\tau_a(x)$ are obtained for these solutions by extrapolating the attainable-superheating line to atmospheric pressure T^*_a and to the critical curve T_c: $\tau_a(x) = 0.71$-0.91. There is the following relation between $\tau_a(x)$ and the critical curve. The greater the relative deviation (along the p axis) for the critical curve for the solution for a straight line joining the critical points for the components, the greater the difference in $\tau_a(x)$ from τ_a for the initial substances (Table 1 and Fig. 2). Then (1) has to be modified for binary systems.

The T*(p; x = const) curves give auxiliary points having coordinates T_a, p_a satisfying a condition analogous to that for the one-component case:

$$T_a(x) = T^*_a(x)/\bar{\tau}_a(x). \tag{2}$$

Here $\bar{\tau}_a(x)$ is a value linearly interpolated between the τ_a for the components. These points lie near the straight line joining the critical points K_1 and K_2 for the initial substances in the T − p diagram (Fig. 1). The $T_a(p_a)$ relations for all solutions examined at elevated pressures are similar, which shows that there is thermodynamic similarity in the attainable-superheating lines in $\tau' = T^*/T_a$, $\pi' = p/p_a$ coordinates. One therefore has a simple method of evaluating the course of T*(p) for a solution from the known critical component parameters. The straight line K_1K_2 (Fig. 3) is an approximation for $T_a(p_a,\ x = 0$-$1)$, and on it one locates a point K corresponding to the required concentration. We assume that T_a is linearly dependent on the molar fraction:

$$T_a = T_{c_1}(1 - x) + T_{c_2}x. \tag{3}$$

K is joined by a straight line to N, which has coordinates $0.9T_a$, 0.1 MPa. The T*(p) for the solution with a given concentration lies on that line. NK is extrapolated to meet the crit-

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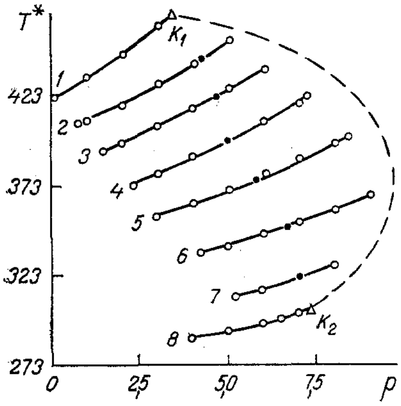

Fig. 1

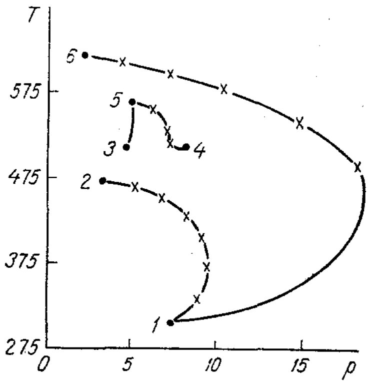

Fig. 2

Fig. 1. Attainable superheating temperature K for a pentane—CO_2 solution as a function of pressure (MPa) for various concentrations for a heating time to boiling of 450 μsec (open points): 1) x = 0; 2) 0.17; 3) 0.32; 4) 0.47; 5) 0.6; 6) 0.77; 7) 0.9; 8) 1. K_1 and K_2 are the critical points for pentane and CO_2 correspondingly, while the dashed line shows the critical curve, where the filled points are auxiliary ($T_a(x)$, p_a) calculated from (2).

Fig. 2. Critical curves for solutions in Table 1: 1-6) critical points corresponding for CO_2, pentane, acetone, methanol, benzene, and decane (T in K and p in MPa). The crosses show the values of $T_c(x)$ and $p_c(x)$ obtained by extrapolating the observed $T^*(p;\ x = \text{const})$ lines and used in calculating $\tau_a(x)$ in Table 1.

TABLE 1. Reduced Attainable Superheating Temperatures $\tau_a(x) = T_a^*/T_c$ for Certain Binary Systems

Pentane—CO_2 [8]*		Decane—CO_2 [9]		Methanol—benzene [10]		Acetone—benzene [11]†	
x	$\tau_a(x)$	x	$\tau_a(x)$	x	$\tau_a(x)$	x	$\tau_a(x)$
0	0,90	0	0,91	0	0,91	0	0,89
0,17	0,87	0,13	0,86	0,36	0,91	0,12	0,89
0,32	0,85	0,26	0,81	0,49	0,90	0,22	0,89
0,47	0,83	0,42	0,76	0,82	0,89	0,49	0,89
0,60	0,83	0,63	0,72	1,0	0,90	0,74	0,89
0,77	0,84	0,77	0,71			0,90	0,89
0,90	0,87	1,0	0,90			1,0	0,89
1,0	0,90						

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*The number quotes the source from which the critical curve is derived.

†The data for $T_a^*(x)$ for acetone-benzene have been taken from [1, 11].

ical curve. With known critical parameters for the solution ($T_c(x)$, $p_c(x)$), it is possible to modify the position of NK by successively displacing K along K_1K_2 in the required direction.

Table 2 compares measurements with our results. The method was tested directly by selecting K at the point of intersection between the K_1K_2 straight line and the $T^*(p;\ x = \text{const})$ line constructed from experiment (ΔT_1). To test (3) for actual systems, the position of K on K_1K_2 was chosen in accordance with (3) (ΔT_2). The ΔT_3 in Table 2 have been obtained by comparing the observed T* with those calculated from (1) with τ and π replaced by τ' and π' ($\pi' < 0.95$) and linear interpolation for A. When the second component is added, the binodal family ceases to be a single-parameter one such as is characteristic of a wide class of unassociated substances, so one cannot calculate A exactly for solutions.

It is reasonable to use (1) only for $p < p_a(x)$. The method of evaluating T*(p) for a solution from the component critical parameters operates throughout the region in the T—p diagram bounded by the critical curve and the component attainable-superheating lines. The error increases as one extends the ranges in the variables, particularly for $p > 2p_a$ (Table 2, with the double vertical bar separating two regions: $p < p_a$ and $p > p_a$). Nevertheless, the rela-

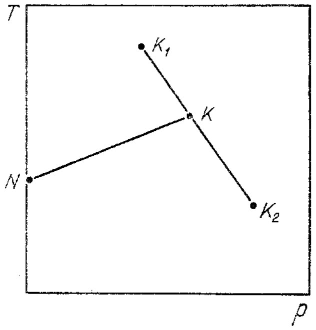

Fig. 3. Construction of the attainable-superheating line NK for a two-component system from the critical points K_1 and K_2 for the pure substances.

TABLE 2. Comparison of Measured Attainable Superheating Temperatures for Solutions with Results Obtained by Various Approximate Methods, $\Delta T = T^*_{exp} - T^*_{est}$; $\Delta T_c = |T_{c_1} - T_{c_2}|$

Pentane — CO_2, $x = 0{,}6$, $\Delta T_c = 165$ K

p, MPa	3	4	5	6	7	8
ΔT_1, K	—2	—2	—1	1	2	4
ΔT_2, K	4	5	6	8	10	12
ΔT_3, K	—0,5	0	1			

Decane — CO_2, $x = 0{,}63$, $\Delta T_c = 313$ K

p, MPa	3,2	4,8	6,4	8,0	9,6	11,2	12,8	14,4
ΔT_1, K	—1	—1	0	3	8	14	22	31
ΔT_2, K	—23	—24	—23	—22	—18	—13	—6	2
ΔT_3, K	1	1						

Acetone—benzene [1], $\Delta T_c = 54{,}5$ K

x	0,12	0,22	0,49	0,75	0,90
ΔT_2, K (p=0,1 MPa)	+1	—1	—4	—4	—3
ΔT_2, K (p=0,98 MPa)	0	—2	—6	—5	—3

tive error $\Delta T/\Delta T_c$ does not exceed 10% for the systems examined in [4-7]. The ΔT_2 of Table 2 indicate that a linear approximation for $T_a(x)$ is usable as a first approximation.

The method is effective when there is a substantial difference between the component critical temperatures. For solutions with small ΔT_c, there may be a minimum on the critical curve or on $T^*_a(x)$ (hexane-hexafluorobenzene [12]). The scope for using this method there has not been examined.

We thus have a method of estimating the attainable superheating temperature $T^*(p)$ from the component critical points. The auxiliary parameters T_a and p_a extend the scope for using a standard approximation for the nucleation frequency to two-component systems.

NOTATION

J, homogeneous nucleation frequency; T, temperature; T*, attainable superheating temperature; p, pressure; τ and π, temperature and pressure referred to the critical values; A, similarity parameter; G, Gibbs number, $G\tau_0 = (\partial \lg J/\partial\tau)\pi$ $(\tau = \tau_0)$, where $\lg J(\tau_0, \pi) = 0$; x, molar fraction of second component; τ' and π', temperature and pressure referred to the auxiliary values. Subscripts: c, relates to the critical value and a to an auxiliary value or atmospheric pressure.

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NONSTATIONARY HEAT TRANSFER IN A CHANNEL CONTAINING SATURATED He II: STEPPED HEAT LOADING

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Measurements have been made on the nonstationary temperature distribution in a channel containing saturated superfluid helium with local stepped heat input. A numerical method has been developed, which incorporates the variable thermophysical parameters for the helium.

Recently, superfluid helium has been used in superconducting devices [1, 2], and there has been extensive research on nonstationary heat transfer in it, mainly for superconductor stabilization. The most detailed studies have been made on nonstationary heat transfer in such helium at atmospheric pressure (unheated He II) in adiabatic channels having pulsed local heating under countercurrent conditions ($\rho v = 0$), which simulate the heat production in superconducting magnets [3-6]. Underheated He II has very good heat-transfer characteristics: it can accept heat pulses several times larger than the stationary critical flux without crisis or superfluidity loss [3, 4].

Much less use has been made of nonstationary heat transfer in saturated superfluid helium, since from the start preference has been given to using underheated He II.

We have examined nonstationary heat transfer in a channel containing saturated He II under countercurrent conditions ($\rho v = 0$) with local heat input to the middle of the channel as a stepped function.

It is considered that the transfer in such a case can be described by a one-dimensional nonstationary energy equation [3, 5]:

$$\rho c_p \frac{\partial T}{\partial \tau} = \frac{\partial q_T}{\partial x}. \qquad (1)$$

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