properties of the liquid in the first case is more weakly expressed than in the second case. In contrast to capillary-transport conditions, in which there are two boiling zones with a boundary defined by Eq. (2) of [8], in free-motion conditions there is a single boiling zone extending right up to the critical heat flux density corresponding to the maximum heat-transfer coefficient.

NOTATION

α, heat-transfer coefficient; q, heat flux density; δ, coating thickness; Π, porosity of coating; λ, thermal conductivity; d, diameter; ℓ, length; c, specific heat; ρ, density; r, heat of vaporization; ν, kinematic viscosity; σ, surface tension; T, temperature. Indices: F, fiber; bo, boundary; L, liquid; sat, saturation; v, vapor; hs, heating surface; li, limiting; ef, effective.

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TWO-PHASE FLOW SINGULARITIES IN THE CRITICAL STATE DOMAIN

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An analytical proof is presented of the possibility of rarefaction shockwave formation for a two-phase flow in states near the critical point. Results of a theoretical analysis are compared with experimental data available in the literature.

A two-phase flow, that in the simplest case is a moving pair with fluid drops of the same substance contained therein, should possess quite interesting features when the stream temperature and pressure are near the critical parameters T_c, p_c of the moving substance. It will be shown below that the formation of rarefaction shockwaves becomes possible in the stream in this case.

As is known, the entropy increment in a shock wave is according to Jouget

$$S_2 - S_1 = \frac{T}{12}\left(\frac{\partial^2 V}{\partial p^2}\right)_S (p_2 - p_1)^3. \tag{1}$$

From this it is seen that the difference $p_2 - p_1$ should be positive for $(\partial^2V/\partial p^2)_S > 0$ because of the condition $S_2 > S_1$, i.e., a compression shock is formed, while for $(\partial^2V/\partial p^2)_S < 0$ the difference is $p_2 - p_1 < 0$, and therefore, formation of a rarefaction shock is possible. In both cases the conditions

$$w_1 > c_1; \ w_2 < c_2, \tag{2}$$

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are satisfied for the motion velocities where c is the speed of sound [1].

Therefore, the nature of the shock is determined uniquely by the sign of the derivative $(\partial^2V/\partial p^2)_S$. In the overwhelming majority of cases in real substances, the derivative $(\partial^2V/\partial p^2)_S$ is positive, and therefore the shocks will be compression waves as a rule. However, this does not mean that substance states do not exist in which this derivative will be negative. One of the authors showed [2] that the derivative $(\partial^2V/\partial p^2)_S$ is negative in a two-phase domain near the liquid-vapor critical point, and therefore rarefaction shocks can occur here in particular in a moist vapor flow. The deduction about satisfaction of the condition $(\partial^2V/\partial p^2)_S < 0$ in a two-phase domain near the critical point was made by starting from analysis of experimental data on the properties of steam, however, it was noted that this deduction is valid even for other substances. A strict analytic proof of the negativity of the derivative $(\partial^2V/\partial p^2)_S$ in the domain of the critical point is presented in this paper for $p < p_c$. Before going over to this proof it is impossible not to remark that in 1946 Zel'dovich [3] arrived at the conclusion that the condition $(\partial^2V/\partial p^2)_S < 0$ will be satisfied in the gaseous state outside the domain of condensation for values $1.2 < V/V_c < 1.8$ of the volume and the pressure $0.8 < p/p_c < 0.97$, on the basis of numerical computations in which it is assumed that the Van der Waals equation is satisfied strictly for a gas while its specific heat c_V is constant and exceeds 20 cal/(mole·deg). According to Zel'dovich, rarefaction shocks could exist here. The single-phase domain mentioned by Zel'dovich where rarefaction shocks are possible is shifted to the right of the critical point into the domain of volumes considerably exceeding the critical volume and does not include the neighborhood of the critical point. The circumstance that the domain of rarefaction shock existence does not agree with the domain of the critical point is due, it must be assumed, to the fact that the exact Van der Waals equation was not used by any means* in the Zel'dovich computations (as was clear to Zel'dovich himself, who especially noted in his paper that the numerical computations were made under quite rough assumptions). Nevertheless the Zel'dovich research was quite important since it indicated with obvious definiteness that the real possibility of rarefaction shock formation existed in certain substance states (in a gas according to Zel'dovich), and attracted attention to this interesting problem.

Let us now elucidate the proof of the inequality $(\partial^2V/\partial p^2)_S < 0$ in the domain of the critical point. According to the modern theory of the critical state and its experimental foundations the isochoric specific heat c_V becomes infinite at the critical point. Since the values of c_V and the derivative $(\partial p/\partial V)_S$ are connected by the thermodynamic relationship

$$\left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial p}{\partial V}\right)_T - \frac{T}{c_V}\left(\frac{\partial p}{\partial T}\right)_V^2,$$

then at the critical point where $(\partial p/\partial V)_T = 0$ while $(\partial p/\partial T)_V$ is finite and not equal to zero, the derivative $(\partial p/\partial V)_S$ vanishes. That the derivative $(\partial p/\partial V)_S$ vanishes implies that the second derivative $(\partial^2p/\partial V^2)_S$ also vanishes. Indeed, the derivative cannot be positive by the stability condition. But then the change in $(\partial p/\partial V)_S$ along the critical isentrope is displayed by a bell-shaped curve with apex (maximum) at the critical point from which it indeed follows that the derivative $(\partial^2p/\partial V^2)_S$ at the critical point equals zero. Another, more formalized proof of the equality of $(\partial^2p/\partial V^2)_S$ to zero at the critical point is presented in [4].

Now let us examine the isentrope passing through the critical point. To find its equation near the critical point in the p, V variables we expand p in a power series in $(V - V_c)$. Let us note that the expansion of thermodynamic quantities in a power series in the difference of the governing parameters in this state and at the critical point in the domain of the critical point, although it requires care, is nevertheless completely allowable and is used to some degree in all theories of the critical state. Selection of the variables V, S as governing parameters is apparently most justified since the series coefficients do not here become infinite.

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*Let us note that the requirement of a large value of the isochoric specific heat c_V is satisfied automatically in the domain of the critical point since c_V becomes infinite at the critical point itself. This important result was established experimentally much later than 1946.

At the critical point $(\partial p/\partial V)_S = (\partial^2 p/\partial V^2)_S = 0$, consequently, the equation of the critical isentrope $S(V) = S_c$ resulting from the series expansion of p will have the form

$$p = p_c + \frac{1}{6}\left(\frac{\partial^3 p}{\partial V_c^3}\right)_S (V - V_c)^3,$$

where $(\partial^3 p/\partial V^3)_S < 0$ [since otherwise the derivative $(\partial p/\partial V)_S$ could turn out to be positive].

Solving this equation for $V - V_c$ we obtain

$$V - V_c = A\sqrt[3]{p - p_c} \tag{3}$$

and after differentiating twice with respect to p

$$\left(\frac{\partial^2 V}{\partial p^2}\right)_S = -\frac{2A}{5}(p - p_c)^{-5/3}, \tag{4}$$

where $A = \sqrt[3]{6/(\partial^3 p/\partial V^3)_S}$. Hence, it is seen that the derivative $(\partial^2 V/\partial p^2)_S$ is negative at points of the isentrope corresponding to the pressure $p < p_c$. Because of the continuity of this quantity it will be negative even near the isentrope. On the other hand, by rewriting (3) in the form

$$p - p_c = A^{-3}(V - V_c)^3,$$

we conclude that $(\partial^2 p/\partial V^2)_S < 0$ below the critical point for $V > V_c$. Since $(\partial^2 V/\partial p^2)_S = -(\partial V/\partial p)_S{}^3 \cdot (\partial^2 p/\partial V^2)_S$, then it is valid to conclude that the derivative $(\partial^2 V/\partial p^2)_S$ will be negative in every case in the part of the domain defined by the conditions $p \le p_c$, $V \ge V_c$ adjoining the critical isentrope $S = S_c$ on the right (in the p–V plane) and lying in the two-phase domain.

A theoretical analysis therefore shows that since the critical isentrope is in a two-phase domain for $p \le p_c$, then the derivative $(\partial^2 V/\partial p^2)_S$ has the negative sign in the neighborhoods of the critical point enclosing the two phase domain (including the point itself). Therefore, the formation of rarefaction shocks is possible in this domain. It is pertinent to note that the theoretical analysis presented here for the behavior of the derivative $(\partial^2 V/\partial p^2)_S$ can also be extended to the domain of the critical point of a crystal (tricritical, in particular) since the original relationships are most common and hold for all aggregate states of a substance.

The derivative $(\partial^2 V/\partial p^2)_S$ is possibly, although hardly probably, negative also near the critical point in a narrow domain lying above the right branch of the liquid-vapor phase equilibrium curve. As is known, the equation of the phase equilibrium line near the critical point has the form [5]

$$p - p_c = a(T - T_c);\ T - T_c = b(V - V_c)^3,$$

where $a = dp/dT_c$, b = const. On the other hand, it can be shown (see [6]) that on the critical isentrope

$$T - T_c = b'(V - V_c)^3,$$

where in conformity with a result obtained earlier

$$p - p_c = a'(V - V_c)^3.$$

It hence follows that the equation of the critical isentrope can be written also as

$$\frac{p - p_c}{T - T_c} = \frac{a'}{b'}.$$

But $dp/dT = (\partial p/\partial T)_S$ at the critical point, consequently $a'/b' = dp/dT_c$, and therefore, in direct proximity to the critical point the equation of the critical isentrope does not differ from the equation of the phase equilibrium line, i.e., both these lines are in agreement on a certain small section starting at the critical point. And since the derivative $(\partial^2 V/\partial p^2)_S < 0$ on the critical isentrope for $p < p_c$, then it will have the same sign on the mentioned section also and apparently somewhat above, i.e., above it (let us note that values of the derivatives on the right, i.e., on the approach to the phase equilibrium line from the single-phase states, actually figure in the relationships presented, which removes, at least partially, the question of their jump on the phase equilibrium line). Therefore, it can be considered proved that near the critical point in a two-phase domain, and possibly even on a small section of the gaseous state above the phase equilibrium line, the derivative $(\partial^2V/\partial p^2)_S$ is negative, and consequently rarefaction shocks can be formed here.

Experiments were recently performed to observe rarefaction shocks. The authors of [7] determined rarefaction shocks in Freon-13. These waves were formed in the critical point domain for initial values of the temperature and pressure equal to the critical values and in complete conformity with those as was assumed in [2].

NOTATION

p, pressure; V, volume; T, temperature; S, entropy; p_C, V_C, T_C, S_C are the p, V, T, S values at the critical point; w, flow velocity; c, speed of sound; c_V, isochoric specific heat; A, a, b, a', b', constants.

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MODELING AND PREDICTION OF THE THERMODYNAMIC PROPERTIES OF LIQUID PETROLEUM PRODUCTS

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A method for predicting the thermal properties and heat capacity of liquid petroleum fractions and gas condensates is described. The method employs only the data on the density ρ_{20}, the molecular mass, and the average boiling point of the petroleum product as the starting information.

The thermodynamic properties of pure substances are now successfully predicted using methods based on the law of corresponding states with three parameters. According to this law the equation of state of a single-phase substance has the form

$$z = z(\omega, \tau, \beta). \tag{1}$$

The acentricity factor combined with the well-known linear correlation of Pitzer [1] is often employed as the correlation parameter β:

$$z = z^{(0)}(\omega, \tau) + \beta z^{(1)}(\omega, \tau). \tag{2}$$

The expansion (2) is valid, however, for small β, $\beta < 0.4$ [2]. However, a significant number of substances, in particular heavy hydrocarbons, that are widely employed in practice, are characterized by larger values of β. For such substances we proposed [3] a method for predicting the thermal properties from the generalized equation of state (ES) of the liquid.

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