Shape of the coexistence curve of pure matter near the critical point

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A precision P-V-T installation with visual observation was used to investigate the shape of the coexistence curve of pure sulfur hexafluoride near the critical point. Asymmetry of the coexistence curve as well as deviations from the linear diameter variation law were observed in the range $10^{-6} \leq \tau < 10^{-5}$.

The question of the coexistence curve has been the subject of many publications, [1,3,5,7] but there is still need for further research.

We report here preliminary results of the study of the coexistence curve of pure SF_6 near the critical point, using an experimental P-V-T installation in which a glass piezometer of constantly-variable volume[2] is employed (the height of the piezometer is 8 mm). The accuracies with which the state parameters were measured were as follows: pressure— $\pm 4\times10^{-9}$ N/m² (1×10^{-3}%), temperature— $\pm 2\times10^{-4}$ °C, volume— $\pm$ 0.02%. The sulfur hexafluoride was purified by multiple successive distillation in two high-pressure rectification columns. The degree of purity obtained in this manner (~99.9995%) conformed fully with the accuracy of the P-V-T measurements.

The experimental values of the points of the coexistence curve were obtained by visual observation of the appearance and vanishing of a two-phase state of the matter in the piezometer, up to value $\tau \equiv |(T - T_c)/T_c| \geq 10^{-6}$. So close an approach to the critical point and the increase of the overall accuracy of the measurements have made it possible to establish certain new regularities in the shape of the coexistence curve, in comparison with the available results, [1,5,7] and particularly in comparison with earlier work[3] by one of the authors.

Figure 1 shows the coexistence curve of pure SF_6 in terms of the coordinates T and ρ, and the line shape corresponding to the linear diameter $\rho_d = (\rho_{liq} + \rho_g)/2$.

Attention is called to the fact that the coexistence curve is asymmetrical near the critical point. We see also that the value of the critical density (ρ_c) obtained with the aid of the visual observations[4] and by extrapolating the linear diameter curve (ρ_c') differ by ~0.4%. In addition, whereas the "linear" diameter justifies its name far from the critical point ($\tau \geq 3\times10^{-5}$), a noticeable deviation from linearity towards lower densities is observed near $\tau < 3\times10^{-5}$.

The fact that the indicated singularities have not been noted by other authors, particularly in[7], where data are given on the coexistence curves of CO_2, N_2O and $CClF_3$, may apparently be attributed both to the lower accuracy of the experiments discussed in[7] ($\Delta T \geq \pm 1\times10^{-3}$ °C), and to the smaller penetration into the critical region ($\tau \geq 10^{-5}$). At the same time, far from the critical region, the agreement between our results and the conclusions of[7] can be regarded as good.

In our opinion, a possible explanation of this behavior of the coexistence curve of pure matter in the immediate vicinity of the critical point may be connected to a considerable degree with allowance for the influence of gravitation. A distinction should be made between two cases: distortion of the shape of the curve by the action of gravitation in vessels of "large" and "small" height. In the former case, the gravitational effect leads to a strong flattening of the top of the coexistence curve.[5]

In the latter case, its influence is apparently somewhat different. Assuming, in first-order approximation, that the asymmetry of the coexistence curve is determined entirely by the action of the gravitation, let us examine its influence on the temperatures of the appearance and vanishing of one of the phases of the matter in the piezometer on both sides of the critical density. (The method of establishing the transition of the substance from the two-phase state into the single-phase state and vice versa does not seem to play a special role.) It is reasonable to assume that the force of gravity, by making the substance denser under conditions of strongly increasing compressibility ($K_T \to \infty$ as $T - T_c$), "facilitates" the formation of the liquid phase from the gas phase and "hinders" the inverse transition. Continuing this reasoning, we can conclude that in this case experiment should reveal the point A' in place of the point A (Fig. 2) and B' in place of B, so that the coexistence curve becomes asymmetrical (dashed line of Fig. 2.).

In the case of "large" piezometer heights, the predominant effect is that of the flattening of the top of the

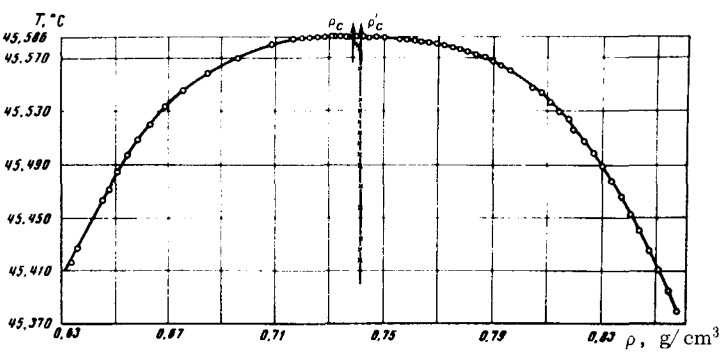

FIG. 1. Coexistence curve of sulfur hexafluoride.

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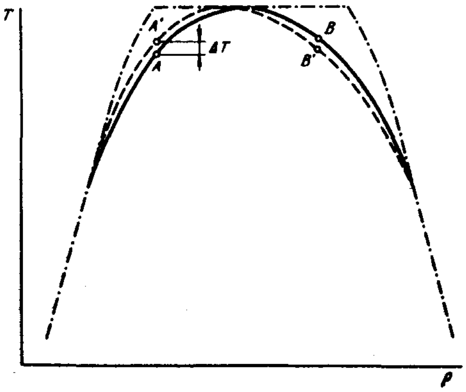

FIG. 2. Influence of the gravitational effect on the shape of the coexistence curve.

curve (dash-dot line in Fig. 2). In all probability, both effects are present in the real case, and the height of the piezometer only determines the ratio of their influence on the shape of the coexistence curve near the critical point. In particular, in our case we note likewise a certain flattening of the top of the curve (Fig. 1) amounting only to ~± 1% in terms of density, in view of the small height of the piezometer, whereas the asymmetry becomes manifest in a density variation range ~± 4%, and in a range of temperature variation $\Delta T \geq 6\times 10^{-3}$ °C.

The arguments advanced here with respect to the influence of the gravitational effect on the shape of the coexistence curve are of course only qualitative in character and their confirmation calls for both a theoretical investigation of this question and special experiments.

Figure 3 shows, in a log-log scale, the results reduced in the spirit of the scaling hypothesis, [6] in accordance with Eqs. (1)—(3)

$$(\rho_{liq} - \rho_g)/\rho_c = B\tau^{\beta}; \tag{1}$$

$$(\rho_{liq} - \rho_c)/\rho_c = B_{liq}\tau^{\beta_{liq}}; \tag{2}$$

$$(\rho_c - \rho_g)/\rho_c = B_g\tau^{\beta_g}. \tag{3}$$

Equation (1) is more traditional, while the two others make it possible to describe separately the branches of the coexistence curve on the right and on the left of the critical point. With such a data reduction, the asymmetry of the coexistence curve becomes even more strongly pronounced (Fig. 3). In the region $10^{-6} \leq \tau < 10^{-5}$, the value of β_{liq} greatly exceeds β_g. Far from the critical point ($\tau \geq 10^{-5}$), the difference between the exponents is negligible, in good agreement with the results of the cited papers. [1,7]

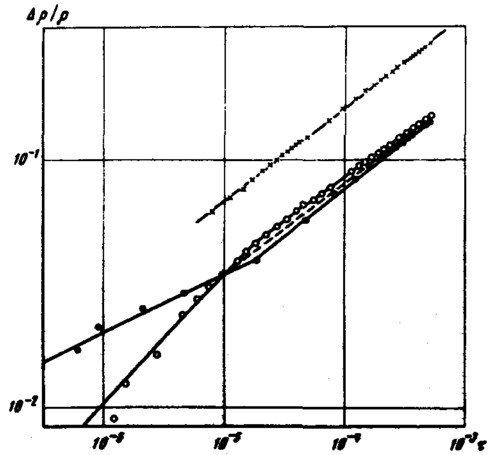

FIG. 3. Plot of $\log(\Delta\rho/\rho)$ against $\log\tau$ for SF_6 near the critical point: ●—$\rho < \rho_c$ (Eq. 3), ○—$\rho > \rho_c$ (Eq. 2), ×—Eq. (1).

It follows from the calculation that in the region $10^{-6} \leq \tau < 10^{-5}$ we have

$\beta_{liq} = 0.50 \pm 0.04$, $\beta_g = 0.25 \pm 0.03$

for $\tau \geq 10^{-5}$ $\beta_{liq} = 0.342 \pm 0.008$, $\beta_g = 0.358 \pm 0.006$, $\beta = 0.363 \pm 0.007$.

It should be noted that Widom and Stillinger[8] obtained recently the asymmetry of the coexistence curve and the deviation from the straight-line diameter rule, within the framework of the "interpenetrating spheres" model, an essential premise of which was the nonexistence of particle-hole symmetry.

In conclusion, the authors thank I. R. Krichevskiĭ for constant interest in the work, and also V. K. Fedyanin and B. N. Provotorov for a discussion of the question touched upon here.

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