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THERMODYNAMIC PROPERTIES OF A van der WAALS FLUID, PARTICULARLY NEAR THE CRITICAL POINT

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As a result of the Conference on Phenomena in the Neighborhood of Critical Points, National Bureau of Standards, Washington, D. C., 5-8 April 1965, we became interested in the numerical values of various thermodynamic functions, at the critical point, as predicted by the van der Waals equation of state.

The van der Waals equation of state, in reduced variables, is

$$\beta = 8\alpha\gamma/(3-\alpha)-3\alpha^2, \tag{1}$$

where $\beta = P/P_c$ is the reduced pressure, $\alpha = \rho/\rho_c$ is the reduced density, and $\gamma = T/T_c$ is the reduced temperature.

Using Maxwell's[1] relationship to ensure that the chemical potential is the same for coexisting phases, we have derived the following formula:

$$\frac{3(\alpha_3-\alpha_1)(6-\alpha_1-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1+\alpha_3)} = \ln\frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)}, \tag{2}$$

where α_1 is the reduced density of saturated vapor, and α_3 is the reduced density of saturated liquid. Other thermodynamic properties are given by

$$\gamma = \frac{(3-\alpha_1)(3-\alpha_3)(\alpha_1+\alpha_3)}{8}; \tag{3}$$

$$\beta = \alpha_1\alpha_3(3-\alpha_1-\alpha_3); \tag{4}$$

$$\frac{d\alpha_1}{d\gamma} = \alpha_1' = \frac{\alpha_1(3-\alpha_1)}{\gamma(3-2\alpha_1-\alpha_3)}; \tag{5}$$

$$\frac{d\alpha_3}{d\gamma} = \alpha_3' = \frac{\alpha_3(3-\alpha_3)}{\gamma(3-\alpha_1-2\alpha_3)}; \tag{6}$$

$$\frac{d\beta}{d\gamma} = \beta' = \frac{\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{\gamma}; \tag{7}$$

$$\frac{d^2\beta}{d\gamma^2} = \beta'' = \frac{3}{\gamma}(\alpha_3\alpha_1' + \alpha_1\alpha_3'); \tag{8}$$

$$\frac{\Delta H_v}{RT_c} = \frac{3(\alpha_3-\alpha_1)(6-\alpha_1-\alpha_3)}{8}, \tag{9}$$

where ΔH_v is the heat of vaporization;

$$\frac{C(\text{sat. vap.})-C_v{}^0}{R} = -\frac{3\gamma\alpha_1'}{\alpha_1(3-\alpha_1)}, \tag{10}$$

where $C_v{}^0$ is the heat capacity at constant volume in the ideal gas state at zero density;

$$\frac{C(\text{sat. liq.})-C_v{}^0}{R} = -\frac{3\gamma\alpha_3'}{\alpha_3(3-\alpha_3)}; \tag{11}$$

$$\frac{-Td^2\mu/dT^2-C_v{}^0}{R} = -\frac{9}{8}(\alpha_1' + \alpha_3'), \tag{12}$$

where μ is the chemical potential or Gibbs free energy;

$$\frac{C_v(2\text{ phases, }\rho=\rho_c)-C_v{}^0}{R} = \frac{9}{8}[(\alpha_3-1)\alpha_1' + (\alpha_1-1)\alpha_3']. \tag{13}$$

Equations (2)-(13) are exact for a van der Waals fluid and apply to the two-phase region.

Near the critical point, the solution to Eq. (2) is given by

$$-(1-\alpha_3)=(1-\alpha_1)[1+\tfrac{1}{5}(1-\alpha_1)+\tfrac{1}{25}(1-\alpha_1)^2+\cdots]. \tag{14}$$

By substituting Eq. (14) into the formulas given above, we have determined the following limits as the critical point is approached from the two-phase region:

$$\lim\alpha_1'=+\infty, \tag{15}$$

$$\lim\alpha_3'=-\infty, \tag{16}$$

$$\lim(\alpha_1'+\alpha_3')=-0.80, \tag{17}$$

$$\lim\beta'=4, \tag{18}$$

$$\lim\beta''=9.6, \tag{19}$$

$$\lim\frac{\Delta H_v}{RT_c}=0, \tag{20}$$

$$\lim\frac{C(\text{sat. vap.})-C_v^{\,0}}{R}=-\infty, \tag{21}$$

$$\lim\frac{C(\text{sat. vap.})-C_v^{\,0}}{R}=+\infty, \tag{22}$$

$$\lim\frac{-T(d^2\mu/dT^2)-C_v^{\,0}}{R}=0.90, \tag{23}$$

$$\lim\frac{C_v(2\text{ phases},\ \rho=\rho_c)-C_v^{\,0}}{R}=4.5. \tag{24}$$

From Eq. (1), we can derive

$$(\partial\beta/\partial\gamma)_{\alpha\,\text{c.p.}}=4, \tag{25}$$

and thus the first derivative of the vapor-pressure curve is continuous with the first derivative of the critical isometric.

However,

$$(\partial^2\beta/\partial\gamma^2)_\alpha=0, \tag{26}$$

and the second derivative of the vapor-pressure curve is discontinuous with the second derivative of the critical isometric.

As there is no change of C_v with density for a van der Waals gas,

$$T(\partial^2\mu/\partial T^2)_\rho=C_v^{\,0}, \tag{27}$$

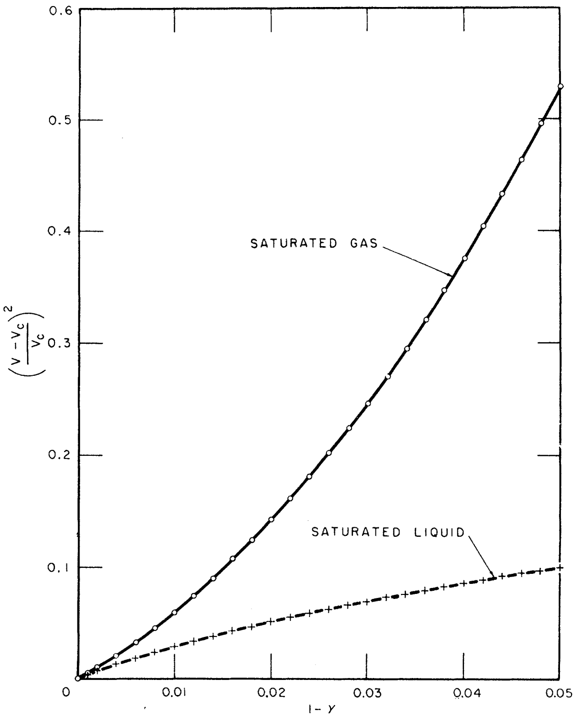

FIG. 1. van der Waals fluid, V-T coexistence curves; $\gamma=T/T_c$.

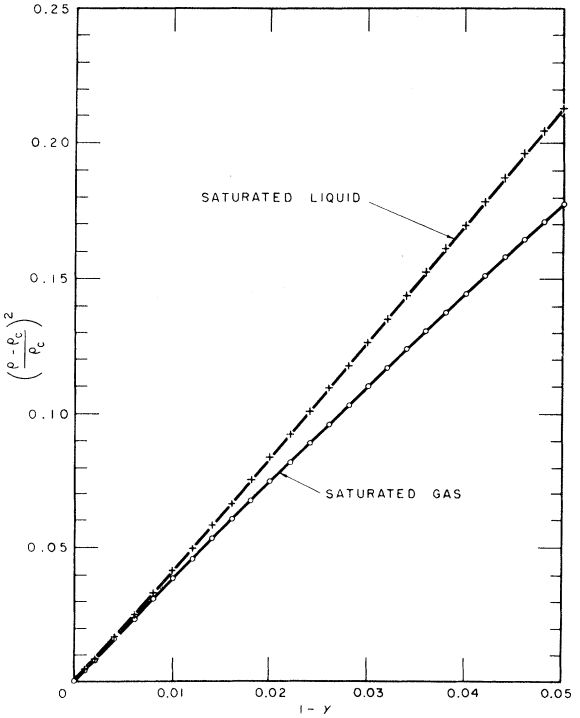

FIG. 2. van der Waals fluid, ρ-T coexistence curves; $\gamma=T/T_c$.

and we see that there is a discontinuity in the second derivative of the chemical potential.

Also as $C_v = C_v{}^0$ we see that there is a finite discontinuity in the heat capacity at constant volume when a calorimeter filled to the critical density is heated through the critical point.

Equation (17) shows that the rectilinear diameter of a van der Waals fluid is not a horizontal line near the critical point.

When Edwards and Woodbury[2] first presented and treated their data on the coexistent curves of helium near its critical temperature, they used the variables of volume and temperature. Recently, Tisza and Chase[3] have re-examined these data using the variables of density and temperature. Tisza and Chase show that the use of the density and temperature leads to functions that are more linear and more coincident than when the volume and temperature variables are used. We would like to point out that the same statement is true for a van der Waals gas. In Fig. 1 we show the plot of the same function as plotted by Edwards and Woodbury, in reduced variables, for a van der Waals gas. In Fig. 2, we show the plot of the same function as plotted by Tisza and Chase. On comparing Figs. 1 and 2, it is clear that the curves are more coincident and have less curvature using the variables of density and temperature. In other words, Tisza and Chase's discovery is predicted by van der Waals' equation.

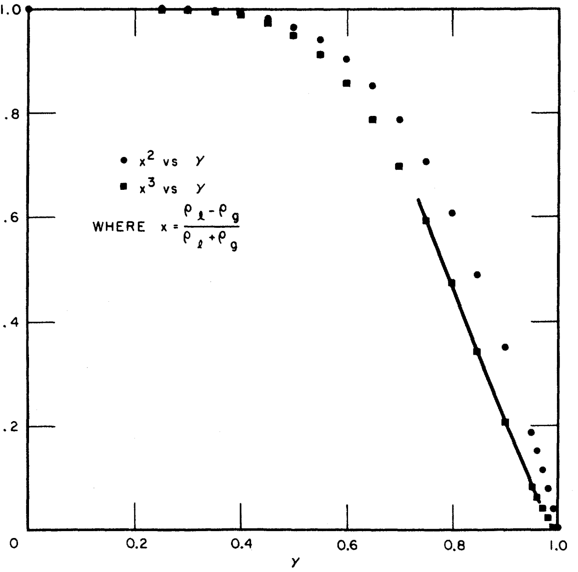

FIG. 3. Temperature dependence of X^2 and X^3 for a van der Waals fluid. X^3 is nearly linear above $0.8T_c$; $\gamma = T/T_c$.

However, it is well known that van der Waals' equation is not quantitatively in agreement with experimental data. The range of linearity, of coincidence, and the initial slope of the lines in Fig. 2 are not quantitatively in agreement with the curves on helium as presented by Tisza and Chase.

More recently, Edwards[4] has used a function suggested by Buckingham[5] to re-examine his original data on helium. Edwards uses the variable X, defined by

$$X = (\rho_1 - \rho_g)/(\rho_1 + \rho_g). \tag{28}$$

He presents graphs of X^2 and X^3 versus temperature for helium. We present similar graphs for a van der Waals gas in Fig. 3.

Edwards says, "Fig. 1 shows how plots of X^2 (or $\beta = \frac{1}{2}$), and X^3 (or $\beta = \frac{1}{3}$), appear for helium-four over the whole range of measurements from 0.3 to $0.99T_c$. Clearly, X^3 is nearly linear (or $\beta = \frac{1}{3}$) above about $0.8T_c$ (but not too near T_c; see later), in agreement with many other measurements for many fluids. Note that the classical X^2 is not linear over any extended

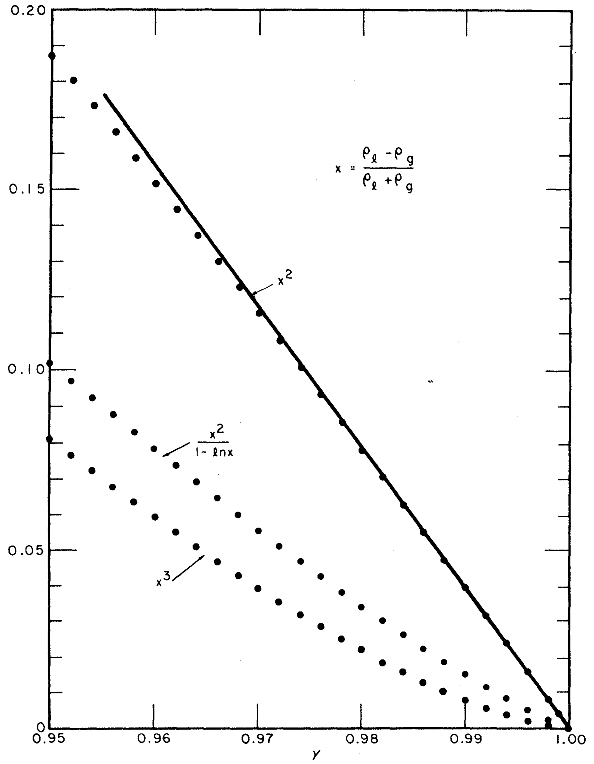

FIG. 4. Tests of the asymptotic form of the coexistence curve for a van der Waals fluid above $0.95T_c$; $\gamma = T/T_c$.

range of temperature." Our Fig. 3 shows that when the classical van der Waals gas equations are solved exactly, X^3 is nearly linear between $0.8T_c$ and $0.95T_c$.

Edwards also presents plots for helium of X^2, X^3, and $X^2/(1-\ln X)$ within 250 mdeg of T_c. In our Fig. 4, we present similar plots for a van der Waals gas above $0.95T_c$. Figure 4 shows that X^2 is accurately linear above $0.98T_c$.

Edwards concludes that the functional form $X^2/(1-\ln X)$ is the best asymptotic form for the coexistence curve of helium, with the critical point lowered 6 to 8 mdeg below the T_{58} value. Moldover and Little[6] have obtained experimental evidence from their specific-heat work that the critical point on the T_{58} scale is 10 mdeg below the presently accepted value.

The details of derivations and numerical values of the various thermodynamic functions calculated for a van der Waals gas will be published as a Bureau of Mines publication.

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EFFECTS OF A LONG-RANGE OSCILLATORY POTENTIAL ON THE RADIAL DISTRIBUTION FUNCTION AND THE CONSTANT OF SELF-DIFFUSION IN LIQUID Na†

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Johnson, Hutchinson, and March[1] (JHM) have recently reported the striking observation that an analysis of the experimental radial distribution functions of liquid metals yields a long-range oscillatory (LRO) interatomic pair potential for a number of metals but gives the usual van der Waals potential for liquid argon. While LRO potentials have been derived theoretically[2] and observed experimentally[3] for solids, it is not obvious that these results can be extrapolated to the liquid state. Further, the JHM analysis of the data is based on the Born-Green[4] and Percus-Yevick[5] equations which in themselves may not be capable of yielding accurate enough information[6] to give the pair potentials quantitatively.

In addition to the time-independent study of JHM, there is some information about the time-dependent behavior of the motions of the atoms in liquid Na. Randolph[7] has analyzed the slow-neutron inelastic spectrum of liquid Na and obtained the time-dependent mean square displacement of the atoms, $\langle r^2\rangle$. He concludes that at times less than 10^{-13} sec the displacements show a gaslike behavior, while at longer times the displacements increase slowly and show a high degree of solidlike behavior. It has been conjectured that such a solidlike behavior of $\langle r^2\rangle$ might result from the existence of a LRO potential in a liquid metal.

It has been demonstrated by Rahman[8] that the radial distribution function and $\langle r^2\rangle$ can be calculated on a computer using the method of molecular dynamics. In particular, he solved the classical equations of motion with periodic boundary conditions for a system of 864 particles interacting with a Lennard-Jones potential. Applying this method to argon, he was able to reproduce the experimental radial distribution function and D, the constant of self-diffusion, which is simply related to the asymptotic form of $\langle r^2\rangle$. Using the same computation-