percent density deviation is plotted as a function of temperature.

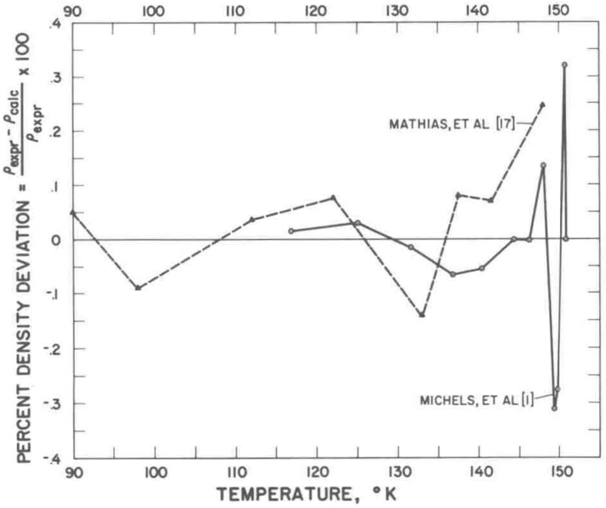

FIGURE 1. *Deviations between calculated (eq (9)) saturation liquid densities and experimental saturated liquid densities.*

In figure 1, it is seen that both sets of data exhibit almost the same characteristics with the Mathias data showing a wider envelope of density deviations. The maximum deviation of the saturated liquid density data from that calculated by eq (9) is 0.32 percent which occurs within 1/2 deg of the critical point. The mean of the absolute values of density deviations for Michels' data is 0.099 percent, and for the data of Mathias, 0.098 percent.

However, the three Michels' data points which exhibit the largest density deviations are all within about a degree and a half of the critical point where the experimental determination of saturated liquid densities becomes most difficult. If these three points are not included, then the mean density deviation is 0.039 percent. On the other hand, the single data point of the Mathias data which exhibits the maximum deviation is within about two and a half degrees of the critical point. If this point is omitted, the mean density deviation for the Mathias data is 0.076 percent.

With these comparisons, it can be concluded that eq (9) adequately represents the data, with precision approaching the precision of the data. In addition, the data of Michels et al. [1] display a precision about twice that of Mathias et al. [17].

The coefficients of eq (9) which resulted from the fit with $n=6$ are shown in table 4.

TABLE 4. *Coefficients for saturated liquid densities for eq (9)*

Temperature in K, coefficients are dimensionless	
$d_0=0.99995448$ $d_1=0.47354891$ $d_2=11.238328$ $d_3=-43.741090$	$d_4=91.361470$ $d_5=-93.773992$ $d_6=37.769045$

Use of the coefficients in table 4 produces a root-mean-square deviation in ρ^l/ρ_c of 0.002 for the data considered.

6. Vapor Pressure

The purpose of developing a vapor pressure equation was twofold. When used in conjunction with an independently obtained equation of state, the vapor pressure equation could be used to define the coexistence boundary. Also, the vapor pressure equation could be used in conjunction with the equation of state to calculate some of the derived thermodynamic properties.

The coexistence boundary may also be defined without the use of a vapor pressure equation, as discussed in section 11. However, this method requires a sufficient number of highly precise experimental *P-V-T* data points along the boundary. Since saturation densities are difficult to measure with a high degree of precision, and since there was only one source of satisfactory coexistence data, it was difficult to perform a critical evaluation of this data for the purpose of establishing the coexistence boundary.

Instead, there was in the literature a relatively large number of experimental *P-T* data points along the coexistence boundary. With these data a vapor pressure equation could be developed. An examination of the literature indicated the existence of many vapor pressure equations which have been used. Some of these have been studied, compared, and listed by Stewart [19].

For this evaluation of argon, a vapor pressure equation was developed which would represent the argon data with sufficient precision and at the same time permit consistency with the equation of state at the critical point.

The argon vapor pressure equation was developed from the application of the Clapeyron equation to a first order phase transition. The Clapeyron equation is

$$\left(\frac{dP}{dT}\right)_{\text{sat}}=\frac{H^g-H^l}{T(V^g-V^l)}. \tag{10}$$

If appropriate expressions for the changes in enthalpy and volume as functions of temperature and pressure are substituted in eq (10), the equation can then be integrated to give the desired vapor pressure equation. Some of the simpler and more commonly used vapor pressure equations were obtained with the assumptions of

$$V^g \gg V^l;\ V^g=\frac{RT}{P};\ H^g-H^l=\text{constant}. \tag{11}$$

The first assumption of eq (11) is valid only for coexistence states which are considerably below the critical point. In addition, figures 2 and 3 illustrate that the second and third assumptions of eq (11) are in substantial error.

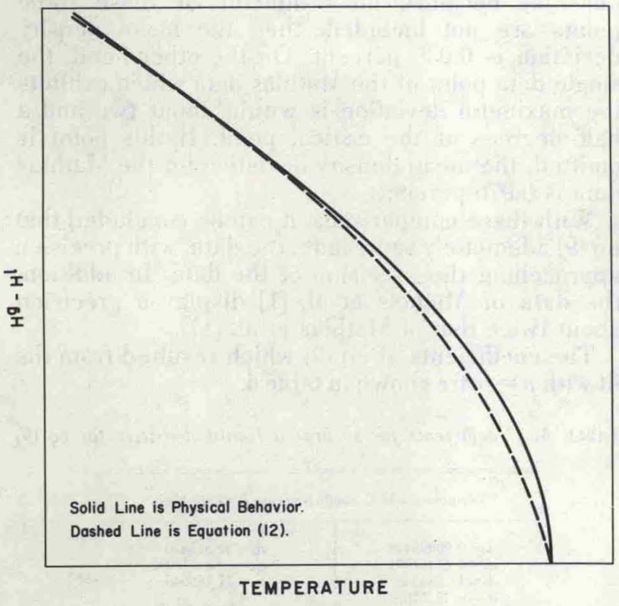

FIGURE 2. *Latent heat of vaporization as a function of temperature.*

Therefore, for this work on argon, the following two approximations were proposed:

$$H^g - H^l = K_1 + K_2 T + K_3 T^2 \tag{12}$$

and

$$V^g - V^l = \left(1 - \frac{P}{P_c}\right)\frac{RT}{P}. \tag{13}$$

The approximations suggested by eqs (12) and (13) are compared with the assumptions of eq (11) and are shown in figures 2 and 3.

Figure 2 illustrates a typical plot of the latent heat of vaporization as a function of temperature. It is observed that the third assumption of eq (11), which approximates the latent heat as a constant, is unsatisfactory both in magnitude and in characteristic nature. It is thus proposed that eq (12) represent the latent heat of vaporization. Equation (12) is shown in figure 2 as the dashed line and is seen to represent more closely the characteristic nature of the physical behavior. The constants in eq (12) may be adjusted to change slightly the nature of the curve. Therefore, it was concluded that the quadratic nature of eq (12) satisfactorily represented the physical behavior in figure 2, and no higher degree temperature terms were considered necessary.

Figure 3 illustrates a typical plot of the volume of vaporization as a function of temperature. It is clear that the perfect gas assumption of eq (11) becomes quite unsatisfactory as temperature increases. In addition, it is noted that the characteristic curvature of the perfect gas representation is incorrect. In figure 3, it is seen that the approximation proposed by eq (13) represents the physical behavior more closely and maintains the proper curvature for the entire temperature range. In addition, eq (13) permits the volume of vaporization to reduce to zero as the pressure approaches critical pressure. It should be noted that the deviations between the different models shown in figures 2 and 3 are used only for purposes of illustrating qualitative trends and are not indicative of the actual deviations of the calculated vapor pressure properties.

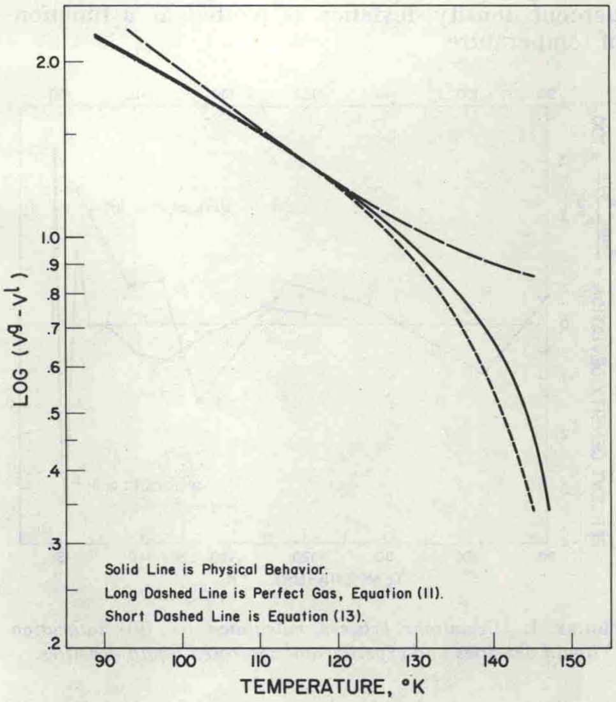

FIGURE 3. *Volume of vaporization as a function of temperature.*

Substitution of eqs (12) and (13) into eq (10) and integrating give

$$\ln P = A/T + B \ln T + CT + D + EP. \tag{14}$$

Equation (14) was then the equation which was proposed for representing the vapor pressure data, with five constants to be determined by a least-square fit to the data.

In order to fit the vapor pressure eq (14) to the data, considerations were given to the expermental errors in the observed data points so that each of the data points could be appropriately weighted. The weighting scheme, as described by Hust and McCarty [20], is outlined below.

Let a function with "Q" variables

$$y_n = f(x_{1n}, x_{2n}, \ldots, x_{qn}, \ldots, x_{Qn}) \quad \text{for } n = 1, 2, \ldots, N \tag{15}$$