A Reduced Equation of State for Gaseous and Liquid Substances

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Experimental pressure-volume-temperature data available in the literature for argon have been utilized to produce relationships for the prediction of densities for reduced temperatures up to $T_R = 3.38$ and reduced pressures up to $P_R = 50$. A plot of reduced pressure vs. reduced temperature for constant reduced density was made for argon, in which each isochor terminates at the vapor-pressure curve. This information was utilized to develop a third degree polynomial relationship between the normalized pressure and the normalized temperature for each isochor by the method of least squares. This method was also used to establish the dependence of the coefficients of the polynomials on reduced density.

The resulting relationships permitted the calculation of densities for argon from the critical constants, vapor pressure function, and the saturated vapor and liquid densities of the substance with a trial-and-error procedure. For fifty-seven densities for the dense gaseous and liquid phases of argon an average deviation of 1.29% with a maximum value of 3.66% resulted between calculated and reported values. The relationships developed in this study have also been found to be applicable to nitrogen, oxygen, carbon monoxide, and methane, whose critical compressibility factors are similar to that of argon.

Several equations of state of varying complexity are available for the prediction of the PVT behavior of pure substances (*3, 6, 7, 23, 27*). These equations have their limitations, particularly at high pressures and in the critical region, and most of them require the establishment of numerous empirical constants to accurately represent the volumetric behavior of pure substances.

In an attempt to develop a generalized correlation for PVT behavior, Lydersen, Greenkorn, and Hougen (*18*) have introduced the critical compressibility factor as a third correlating parameter for density, to produce the following functional relationship:

$$v_R = f(P_R,\ T_R,\ z_c) \qquad (1)$$

This relationship has been verified by a study of the PVT behavior of the inert gases, argon, krypton, and xenon, whose critical compressibility factors range from 0.290 to 0.292 (*13*). The diatomic gases, nitrogen, oxygen, and carbon monoxide ($0.291 < z_c < 0.294$), have also been shown to exhibit similar PVT behavior in both the gaseous and liquid states (*9*). The results of these three studies are presented in plots of reduced density $\rho_R = 1/v_R$ against reduced temperature for parameters of constant reduced pressure. These plots prove valuable in illustrating the continuity existing between the gaseous and liquid phases and enable the calculation of thermodynamic and transport properties at elevated temperatures and pressures.

The isobars of a reduced density vs. reduced temperature plot cannot be easily expressed analytically. Particular difficulties are encountered for the critical isobar $P_R = 1.00$, which possesses a slope of infinity at $T_R = 1.0$. Also abrupt discontinuities exist for isobars representing reduced pressures of $P_R < 1.00$, where vapor and liquid phases can coexist. For reduced pressures much greater than 1, the dependence between reduced density and reduced temperature can be more easily expressed analytically. Therefore, because of the limitations and complexities of the existing analytical representations of PVT behavior, an attempt has been made in this study to develop a relationship between reduced pressure and reduced temperature for constant reduced density utilizing indirectly the information of the reduced density plots, since this information cannot be easily expressed in analytical form for the low-pressure region.

SOURCES OF EXPERIMENTAL DATA

In this investigation the PVT behavior of argon was arbitrarily selected for study, since this substance is chemically simple in that it is composed of monatomic spherical molecules. A comprehensive literature search produced eight references (*2, 12, 14, 15, 16, 19, 21, 24*), which contained all the basic PVT information available for this substance. Of particular importance was the work of Michels and co-workers (*19, 21*), who report experimental PVT data for argon for temperatures as high as 423°K. and pressures up to 2,889 atm. Michels, Levelt, and de Graaff (*19*) report the critical constants for argon, $T_c = 150.875$°K., $P_c = 48.34$ atm., and $\rho_c = 0.536$ g./cc. These constants are the latest and probably the most precise values reported for this substance and therefore were used in this study. In addition Michels, Levelt, and De Graaff report densities which adequately define the vapor and liquid states of the saturated envelope.

The information of the basic references which were found to be reliable were used to produce the reduced density correlation presented on rectilinear coordinates in Figure 1 and on log-log coordinates in Figure 2. The high-pressure data of Bridgeman (*8*) were excluded in these figures because they were found to be inconsistent with the data reported by the other investigators.

In order to represent the density behavior of argon in the compressed liquid state, for which no experimental values are reported, the data for nitrogen reported by Benedict (*4, 5*) for this region have been used with the

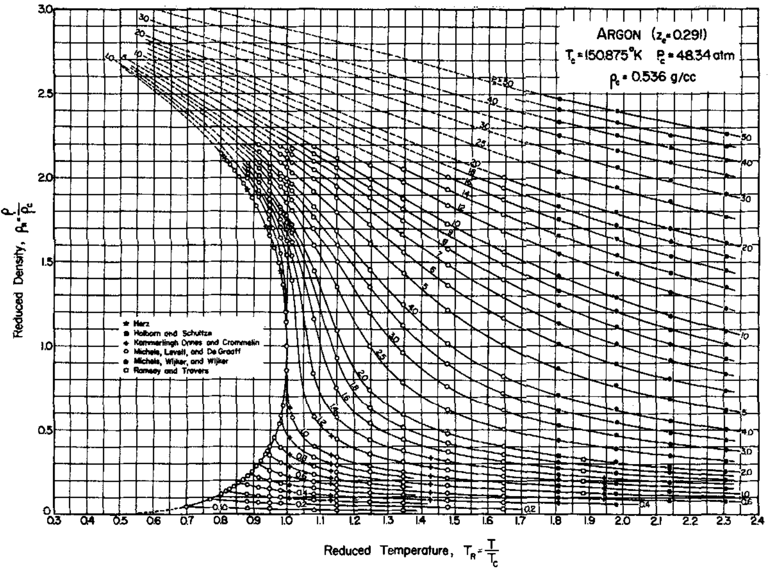

Fig. 1. Reduced density behavior of argon (rectilinear coordinates).

assumption that the ratio $\rho_R/(\rho_{R_l})_s$ at constant temperature was the same for nitrogen and argon below $T_R = 1.00$. For reduced temperatures $T_R > 1.00$ the ratio, $\rho_R/(\rho_R)_{P_R=1.00}$, at constant temperature was assumed to be the same for the two substances. This approach enabled the extension of the density correlation for argon up to reduced pressures of $P_R = 50$. Figure 1 accurately represents the PVT behavior of argon for the liquid and compressed gaseous region, while Figure 2 more adequately accounts for the behavior of the less dense and gaseous states of this substance. In these figures the solid isobars were obtained from experimental data, while the dotted lines represent extrapolations and interpolations based on the PVT data for nitrogen.

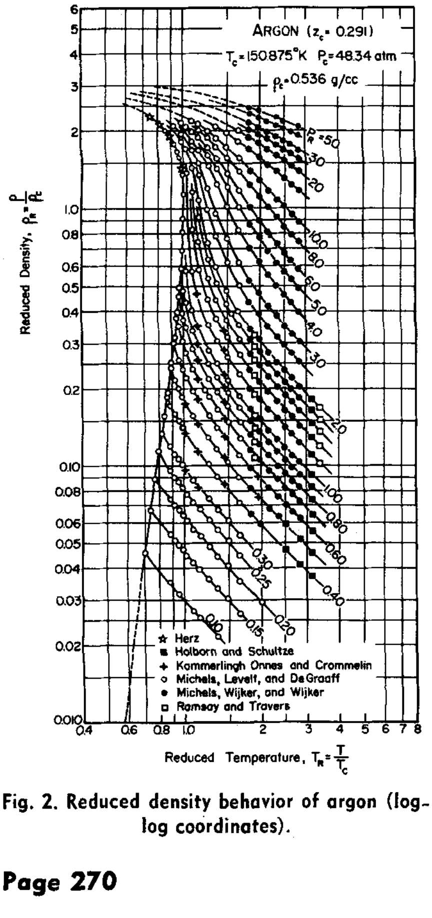

Fig. 2. Reduced density behavior of argon (log-log coordinates).

DENSITIES AT THE SATURATED ENVELOPE

The saturated vapor and liquid densities reported by Michels, Levelt, and De Graaff (*19*) were utilized to establish the rectilinear diameter line proposed by Cailletet and Mathias (*10*). In Figure 3 the sum of the reduced saturated vapor and saturated liquid densities $(\rho_{R_v} + \rho_{R_l})_s$ are plotted against reduced temperature. The saturated density data of Baly and Donnan (*2*), Crommelin (*12*), and Herz (*14*) are included in this figure. The resulting linear relationship can be expressed as

$$(\rho_{R_v} + \rho_{R_l})_s = 3.343 - 1.343\, T_{R_s} \tag{2}$$

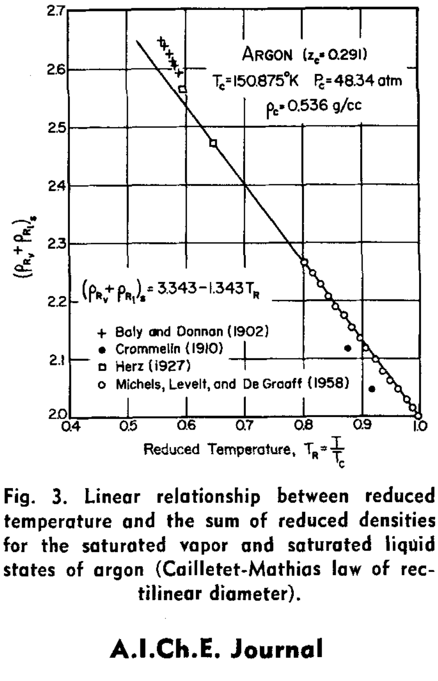

Fig. 3. Linear relationship between reduced temperature and the sum of reduced densities for the saturated vapor and saturated liquid states of argon (Cailletet-Mathias law of rectilinear diameter).

Equation (2) properly defines the sum of reduced densities for the saturated vapor and liquid states for any reduced temperature below $T_R = 1.00$. At low temperatures the reduced saturated vapor density approaches zero, and therefore the reduced saturated liquid density can be obtained directly from Equation (2). At high reduced temperatures the saturated liquid density can be obtained from Equation (2) only if the saturated vapor density is known. Therefore the following relationship was utilized to establish the reduced saturated vapor density of argon:

$$(\rho_{R_v})_s = \frac{P_{R_s}}{z_{R_{vs}} T_{R_s}} \tag{3}$$

The saturated vapor density data of Michels, Levelt, and De Graaff (*19*) were used to calculate values of z_{R_v} for the reported pressure range. In addition z values reported by Lydersen, Greenkorn, and Hougen (*18*) were utilized for reduced pressures of $P_R < 0.3$. The resulting z_R values were related to the corresponding reduced pressure by performing a least-squares analysis on an IBM-650 computer to produce the following expression:

$$z_{R_v} = 3.428 - 3.680\, P_{R_s} + 4.852\, P^2_{R_s} - 3.493\, P^3_{R_s} \tag{4}$$

The reduced saturated vapor density can then be determined from Equation (3) if the corresponding saturation temperature and pressure are known. Therefore it was necessary first to establish the complete vapor-pressure expression for argon relating the saturation pressure to the corresponding temperature.

The vapor-pressure data reported by Michels, Levelt, and De Graaff (*19*) and by Clark et al. (*11*) were used to establish the constants for argon of the reduced vapor-pressure equation proposed by Reynes and Thodos (*26*). The resulting relationship can be expressed as follows:

$$\log P_{R_s} = 2.7690 - \frac{2.9522}{T_{R_s}} - 2.6957 \log T_{R_s} + 0.1832 \frac{P_{R_s}}{T^2_{R_s}} \tag{5}$$

Equation (5) accurately represents the vapor-pressure function of argon over the entire range included between the triple point and the critical point. Thus for a given reduced temperature $T_R < 1.00$ the reduced saturated vapor density was obtained from Equations (3), (4), and (5) and the corresponding reduced saturated liquid density was calculated from Equation (2).

Table 1. Equations for Argon Relating Temperature Coefficients α, β, γ, and δ to Reduced Density

$\alpha = 0.4069 - 1.7687\,\rho_R - 11.3731\,\rho_R^2 + 14.7596\,\rho_R^3 - 6.8088\,\rho_R^4$	$0.08 \leq \rho_R \leq 1.5$
$\log(-\alpha) = -4.8624 + 9.3165\,\rho_R - 5.2029\,\rho_R^2 + 1.0949\,\rho_R^3$	$1.5 < \rho_R \leq 2.5$
$\beta = 0.1751 + 3.2898\,\rho_R + 10.3215\,\rho_R^2 - 15.4964\,\rho_R^3 + 7.2464\,\rho_R^4$	$0.08 \leq \rho_R \leq 1.5$
$\log\beta = -5.3333 + 10.3599\,\rho_R - 5.9272\,\rho_R^2 + 1.2564\,\rho_R^3$	$1.5 < \rho_R \leq 2.5$
$\gamma = 0.3559 - 0.1657\,\rho_R - 2.8497\,\rho_R^2 + 4.3082\,\rho_R^3 - 1.4386\,\rho_R^4$	$0.08 \leq \rho_R \leq 2.1$
$\log(-\gamma) = -100.1792 + 104.8865\,\rho_R - 35.7702\,\rho_R^2 + 4.0978\,\rho_R^3$	$2.1 < \rho_R \leq 2.5$
$\delta = -0.0744 + 0.3311\,\rho_R - 0.6549\,\rho_R^2 + 0.4854\,\rho_R^3 - 0.1573\,\rho_R^4$	$0.08 \leq \rho_R \leq 2.2$
$\log\delta = -50.3217 + 38.7244\,\rho_R - 7.4928\,\rho_R^2 + 0.1346\,\rho_R^3$	$2.2 < \rho_R \leq 2.5$

DEVELOPMENT OF A GENERALIZED EQUATION OF STATE

From Figures 1 and 2 reduced pressures were obtained for constant densities and plotted against the corresponding reduced temperatures to produce the isochoric relationships for argon presented in Figure 4. The isochors of Figure 4 have slight curvatures which diminish with decreasing reduced density. Since these isochors terminate at the vapor-pressure curve, they can be conveniently normalized by dividing the coordinates of their points by the corresponding saturation temperature and pressure. Such a normalization procedure translates the vapor-pressure curve to a single point. Therefore in Figure 5 the normalized temperature is plotted against the normalized pressure for constant reduced densities. Since the normalized pressure becomes very large at high densities, a logarithmic ordinate scale was used for Figure 5, and thus this figure only illustrates the general trend of the normalized pressure–normalized temperature relationships. In Figure 5 the vapor-pressure curve corresponds to the point $\pi = 1.0$, $\tau = 1.0$.

The isochors of Figure 5 can be expressed analytically in the polynomial form

$$\pi = \alpha + \beta\tau + \gamma\tau^2 + \delta\tau^3 \qquad (6)$$

where α, β, γ, and δ are different constants for each reduced density. These constants were established for each isochor of Figure 5 from Equation (6), with the method of least squares. Each constant was then related to reduced density, again with the method of least squares. For low reduced densities fourth-degree polynomial relationships were necessary to define adequately the coefficients of Equation (6) as functions of the reduced density. For high reduced densities third-degree polynomials relating the logarithms of the coefficients to the reduced density were established. The resulting relationships between α, β, γ, δ, and ρ_R are presented in Table 1.

APPLICATION OF EQUATION OF STATE

For a given reduced pressure and temperature the corresponding reduced density can be calculated from Equation (6) only if the saturated reduced temperature and/or the saturated reduced pressure are known at this reduced density. Therefore a trial-and-error procedure utilizing Equations (2), (3), (4), and (5) is required before accurate densities can be obtained from Equation (6). The procedure for the calculation of the density of a substance at a given temperature and pressure is outlined as follows:

1. Calculate the reduced temperature and pressure.
2. Assume a reduced temperature at saturated conditions.
3. With the assumed T_{R_s}, determine the corresponding reduced vapor pressure from a vapor-pressure relationship for the substance.
4. Calculate the reduced saturated vapor density and the reduced saturated liquid density from T_{R_s} and P_{R_s}, with Equations (2), (3), and (4).
5. Calculate two sets of temperature coefficients, α, β, γ, and δ corresponding to ρ_{R_v} and ρ_{R_l}.
6. Calculate $\pi = P_R/P_{R_s}$ and $\tau = T_R/T_{R_s}$.
7. Substitute each set of temperature coefficients into Equation (6), with the assumed τ value calculate corresponding values of π. If either resulting value corresponds to $\pi = P_R/P_{R_s}$, the correct T_{R_s} has been as-

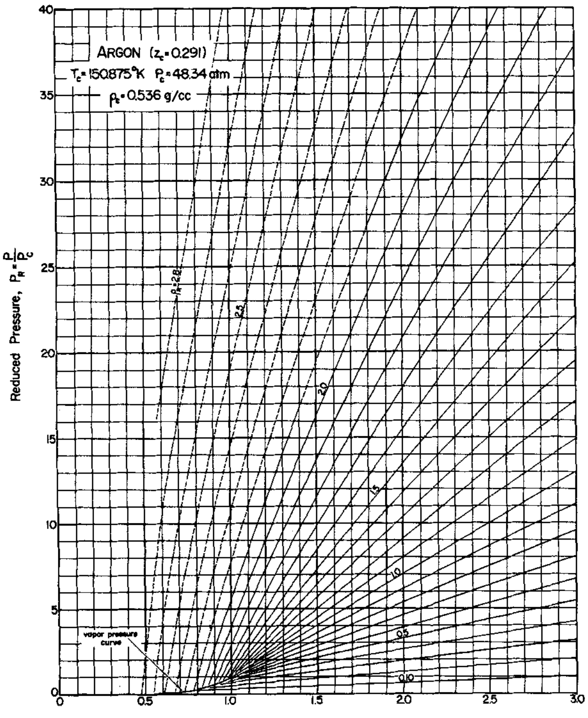

Fig. 4. Isochoric relationships between reduced pressure and reduced temperature for argon.

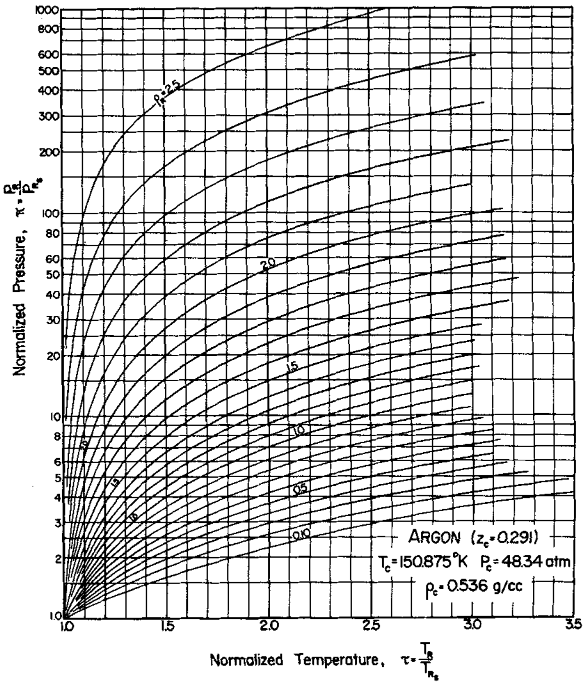

Fig. 5. Isochoric relationships between normalized pressure and normalized temperature for argon (semilogarithmic coordinates).

sumed and the reduced density for the given conditions is the $(\rho_{R_v})_s$ or $(\rho_{R_l})_s$ value which produced the agreement. If neither calculated π value corresponds with the assumed value, a new T_{R_s} must be tried.

In order to expedite these calculations the initial reduced temperature at saturated conditions should be assumed to be 1.00. As this reduced saturated temperature is lowered in increments of $\Delta T_{R_s} = 0.1$, the temperature coefficients for either $(\rho_{R_v})_s$ or $(\rho_{R_l})_s$ will be seen to bracket the correct reduced density. The procedure can then be repeated for $\Delta T_{R_s} = 0.01$, and finally for $\Delta T_{R_s} = 0.001$, with the temperature coefficients for only the proper reduced saturated density.

RESULTS AND CONCLUSIONS

In order to test the validity of this method density values for fifty-seven randomly selected conditions for argon were calculated and compared with the corresponding experimental values by means of an IBM-650 digital computer. For eight values representing conditions on the saturation envelope for both the gaseous and liquid states an average deviation of 1.39% resulted from the data of Herz (*14*) and Michels, Levelt, and De Graaff (*19*). The remaining forty-nine values calculated for the superheated region showed an average deviation of 1.27%. The maximum deviation was 3.66%. The overall average deviation for the fifty-seven points was 1.29%. The maximum reduced pressure was 30.07 (1,454 atm.), and the reduced temperature ranged from 0.803 (121°K.) to 3.384 (511°K.). The highest calculated reduced density was $\rho_R = 2.200$. Since the temperature coefficient relationships were developed for $\rho_R < 2.5$, the method developed in this study is presently limited to this region.

APPLICATION OF METHOD TO OTHER SUBSTANCES

The extension of the method developed in this study to other substances requires the assumption that the relationships for the temperature coefficients α, β, γ, and δ presented in Table 1 are generally applicable. Further studies are necessary to completely test the validity of this assumption. However an attempt has been made to apply the results of this investigation to nonpolar substances having critical compressibility factors similar to that of argon, $z_c = 0.291$.

Density values were calculated for nitrogen, oxygen, carbon monoxide, and methane and were compared with the corresponding experimental PVT data. In these calculations Equations (2) and (4) were assumed to apply to these four substances, and the reduced vapor-pressure relationship

$$\log P_{R_s} = \alpha + \frac{\beta}{T_{R_s}} + \gamma \log T_{R_s} + 0.1832 \frac{P_{R_s}}{T^2_{R_s}} \qquad (7)$$

was employed with the appropriate constants. The average deviation was 3.42% for nitrogen from seven experimental values reported by Benedict (*4, 5*); 2.01% for oxygen for eight values reported by Amagat (*1*); 2.80% for carbon monoxide for ten values of Michels, Lupton, Wassenaar, and De Graaff (*20*); and 2.05% for eighteen experimental values for methane reported by Kvalnes and Gaddy (*17*) and Olds, Reamer, Sage, and Lacey (*22*).

The method of this study should prove particularly useful for the calculation of densities for the critical region, where it does not possess the limitations present in the existing equations of state. These results indicate that the relationships derived for the calculation of densities are applicable for substances having z_c values similar to that of argon. An additional study is necessary to extend this approach to substances having different critical compressibility factors.

NOTATION

P = pressure
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
P_{R_s} = reduced pressure at saturated conditions
R = gas constant
T = absolute temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
T_{R_s} = reduced temperature at saturated conditions
v = molar volume, cc./g.-mole
v_c = critical molar volume, cc./g.-mole
v_R = reduced volume, v/v_c
z = compressibility factor
z_c = critical compressibility factor, $P_c v_c / RT_c$
z_R = reduced compressibility factor, z/z_c
z_{R_v} = reduced compressibility factor at saturated vapor conditions, z_v/z_c
z_{v_s} = compressibility factor at saturated vapor conditions

Greek Letters

α, β, γ = constants for Equation (7)
α, β, γ, δ = temperature coefficients, Equation (6)
π = normalized pressure, P_R/P_{R_s}
ρ = density, g./cc.
ρ_R = reduced density, ρ/ρ_c
ρ_c = critical density, g./cc.
$(\rho_{R_l})_s$ = reduced density of saturated liquid
$(\rho_{R_v})_s$ = reduced density of saturated vapor
τ = normalized temperature, T_R/T_{R_s}

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Manuscript received January 22, 1962; revision received July 9, 1962; paper accepted July 11, 1962.