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Coexistence Behavior of the Vapor–Liquid–Solid Equilibrium States for Argon

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Experimental measurements available in the literature for the saturated states of argon have been critically evaluated to establish the boundaries of all three coexistence regions. This treatment has permitted the description of the vapor–liquid coexistence region over the complete domain ranging from the critical point (T_c = 150.65 K, P_c = 4.886 MPa (48.02 atm), ρ_c = 529.1 kg/m^3) to the triple point (T_t = 83.79 K, P_t = 68.82 kPa (516.17 mmHg)). The vapor–solid coexistence region has been investigated from absolute zero to the triple point. For the liquid–solid coexistence region, sufficient experimental information was available to enable the development of the saturated-liquid and -solid equilibrium curves from the triple point up to 323 K (T_R = 2.15). At the triple point, this treatment yielded values for the saturated densities of 1623, 1416, and 4.117 kg/m^3 for the solid, liquid, and vapor states, respectively. All saturated equilibrium relationships have been expressed analytically and represent the boundaries for these three coexistence regions.

In order to establish the boundaries of the two-phase coexistance regions for a typical substance, argon has been selected as a test case for the following reasons. The properties of this fluid have been well studied experimentally. Because of its simple nature, this spherical monatomic molecule in its fluid state possesses only a translational degree of freedom and is devoid of rotational and vibrational contributions. Although any one of the noble gases possesses these characteristics, helium and neon of necessity are unique to themselves due to the presence of quantum effects and therefore these substances cannot be representative of general fluid behavior. Since the amount of experimental information available for krypton and xenon is limited, these two substances cannot be studied as comprehensively as argon, for which ample experimental information is presented in the literature.

The behavior of a two-phase coexistence region must satisfy the Clapeyron equation since this relationship is a rigorous thermodynamic expression relating saturation pressure to temperature as follows:

$$\mathrm{d}P/\mathrm{d}T = \lambda/(T\Delta v) \qquad (1)$$

where λ is the latent heat of transformation and Δv the corresponding molar volume change. If the temperature dependence of λ and Δv is known, integration of eq 1 yields the saturation pressure behavior. Generally, this information is not readily available and therefore integration of the Clapeyron equation is not usually possible without recourse to simplifying assumptions.

Table I. Critical Point Measurements Reported in the Literature for Argon

year	ref	T_c, K	P_c, MPa (atm)	ρ_c, kg/m^3
1910	Crommelin (*3*)	150.68	4.863 (47.994)	
1968	Grigor and Steele (*4*)	150.6	4.864 (48.0)	529.5
1912	Mathias et al. (*5*)			530.78
1967	McCain and Ziegler (*6*)	150.65	4.855 (47.92)	
1958	Michels et al. (*7*)[a]	150.87	4.898 (48.34)	535.91
1895	Olszewski (*8*)[a]	152.0	5.127 (50.6)	
1901	Ramsay and Travers (*9*)[a]	155.7	5.360 (52.9)	
1969	Streett and Staveley (*10*)[a]	150.9		
1968	Teague and Pings (*11*)	150.705	4.882 (48.18)	
1969	Terry et al. (*12*)	150.6		527
av		150.65	4.866 (48.02)	529.1

[a] Data excluded when averaging.

Along any path on the *PVT* surface of a single-component system, it can be shown through mathematical arguments (*1*) that the relationship between the partial derivatives is

$$(\partial P/\partial T)_s(\partial T/\partial v)_s(\partial v/\partial P)_s = 1 \qquad (2)$$

where the subscript s denotes the designated path. This path can be taken as any one of the saturation curves where the partial derivative $(\partial P/\partial T)_s$ is the slope of the saturated pressure function which is the most easily obtainable partial derivative of eq 2. Thus, if a density–temperature relationship is accessible, the slope $(\partial v/\partial P)_s$ can be determined.

Model and Data Selection

The discrimination between data represents a perennial problem that must be handled in a manner consistent with the nature of the data. Ideally, this discrimination should be independent of any analytical model in order to avoid an unintentional bias that can easily creep into the analysis. However, more often than not, this is not possible, thus necessitating the use of a model from which deviations can be calculated in order to determine the relative behavior between data sets.

The selection of data, without the involvement of a model, was possible for the screening of vapor pressure measurements for the vapor–liquid and vapor–solid coexistence regions. In this context, Wilsak and Thodos (*2*) take advantage of the essentially linear nature of the vapor pressure function when expressed as ln *P* vs. 1/*T*, to obtain a graphical representation of high resolution suitable for screening purposes. The selec-

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Table II. Literature Sources and Comparison between Calculated and Experimental Values for the Vapor–Liquid Coexistence Region

		all data			selected data		
year	ref	points	av dev, %	max dev, %	points	av dev, %	max dev, %
		Vapor Pressure—Eq 6					
1973	Ancsin (*13*)	9	0.025	0.028	9	0.025	0.028
1922	Born (*14*)	13	1.590	2.057			
1969	Bowman et al. (*15*)	36	0.107	0.330	22	0.047	0.206
1971	Chen et al. (*16*)	16	0.010	0.017	16	0.010	0.017
1975	Chen et al. (*17*)	44	0.032	0.077	44	0.032	0.077
1951	Clark et al. (*18*)	40	0.081	0.375	32	0.061	0.363
1963	Clusius et al. (*19*)	27	0.035	0.088	27	0.035	0.088
1910	Crommelin (*3*)	7	0.167	0.482	4	0.030	0.055
1913	Crommelin (*20*)	9	0.298	0.405			
1961	Flubacher et al. (*21*)	7	0.060	0.080	7	0.060	0.080
1956	Freeman and Halsey (*22*)	12	0.040	0.096	12	0.040	0.096
1916	Holst and Hamburger (*23*)	6	0.176	0.441			
1970	Lee et al. (*24*)	89	0.165	1.216			
1967	McCain and Ziegler (*6*)	21	0.277	0.811			
1958	Michels et al. (*7*)	23	0.047	0.091	23	0.047	0.091
1895	Olszewski (*8*)	12	1.890	10.875			
1901	Ramsay and Travers (*9*)	17	3.046	9.770			
1961	Rogovaya and Kaganer (*25*)	1	0.117	0.117	1	0.117	0.117
1970	Sorokin and Blagoi (*26*)	5	2.266	4.183			
1969	Streett and Staveley (*10*)	10	0.440	1.179			
1964	Van Itterbeek et al. (*27*)	34	0.519	1.775			
1963	Van Itterbeek et al. (*28*)	9	0.219	0.370			
1969	Verbeke et al. (*29*)	9	0.061	0.102	9	0.061	0.102
1973	Wagner (*30*)	57	0.045	0.115	57	0.045	0.115
av		513	0.333		263	0.042	
		Liquid Density—Eq 11					
1980	Alburquerque et al. (*32*)	15	0.35	0.59			
1902	Baly and Donnan (*33*)	12	0.28	0.34	12	0.28	0.34
1971	Chui and Canfield (*34*)	1	0.29	0.29			
1910	Crommelin (*35*)	4	3.07	4.36			
1967	Davies et al. (*36*)	1	0.42	0.42			
1971	Gladun (*37*)	13	0.29	0.50			
1969	Goldman and Scrase (*38*)	36	0.12	0.30	36	0.12	0.30
1978	Haynes (*39*)	6	0.30	0.39			
1927	Herz (*40*)	7	0.22	0.61	7	0.22	0.61
1912	Mathias et al. (*5*)	8	0.23	0.73	8	0.23	0.73
1958	Michels et al. (*7*)	11	0.19	0.70	11	0.19	0.70
1975	Pan et al. (*41*)	4	0.19	0.32			
1964	Saji and Kobayashi (*42*)	5	0.46	0.49			
1970	Sorokin and Blagoi (*26*)	5	0.13	0.29	5	0.13	0.29
1969	Streett and Staveley (*10*)	10	0.12	0.62	10	0.12	0.62
1969	Terry et al. (*12*)	16	0.12	0.26	16	0.12	0.26
1960	Van Itterbeek and Verbeke (*43*)	2	0.02	0.03	2	0.02	0.03
av		156	0.28		107	0.16	
		Vapor Density—Eq 12					
1910	Crommelin (*35*)	4	5.29	9.08			
1912	Mathias et al. (*5*)	5	2.55	4.42	4	2.09	3.66
1958	Michels et al. (*7*)	10	0.39	1.48	9	0.27	0.57
av		19	1.99		13	0.83	

trion of a model then depends on the nature of the fit of the screened data as determined by the linear and nonlinear regression subroutines of the Vogelback Computing Center of Northwestern University.

Critical Constants for Argon

Experimental measurements for the critical state of argon have been reported in the literature by a number of investigators (*3*–*12*). The earliest work in this direction dates back to 1895 performed by Olszewski (*8*) and extends to the work of Streett and Staveley (*10*) and Terry et al. (*12*) reported in 1969. All work reported for the critical state of argon is presented in Table I. Since the work of Olszewski (*8*) and Ramsay and Travers (*9*) is in complete disagreement with all the others, their values were not considered further. Although the critical values reported by Michels et al. (*7*) and Streett and Staveley (*10*) are in substantial agreement with the remaining sources, their values are somewhat systematically higher and therefore were not included in the averaging process which yielded T_c = 150.65 K, P_c = 4.866 MPa (48.02 atm), and ρ_c = 529.1 kg/m^3.

Vapor–Liquid Coexistence Region

Vapor Pressure. A comprehensive literature search for vapor pressure measurements yielded a total of 513 experimental values from 24 sources. These sources (*3*, *6*–*10*, *13*–*30*) are presented in Table II. All temperatures in this investigation have been expressed in terms of the International Practical Temperature Scale of 1968. The necessary temperature conversions can be found elsewhere (*31*). A rigorous screening procedure was developed for the selection of internally consistent values. The development of this procedure exploits the linear trend of the vapor pressure data when expressed on a ln P_R vs. $1/T_R$ plot. Although the selection of any two points can be used to establish this linearity, a convenient choice is the critical point and the triple point. If one selects the critical point to represent the origin for a translated coordinate system, the ordinate remains unchanged while the abscissa becomes $1/T_R - 1$. A rotation of this coordinate system

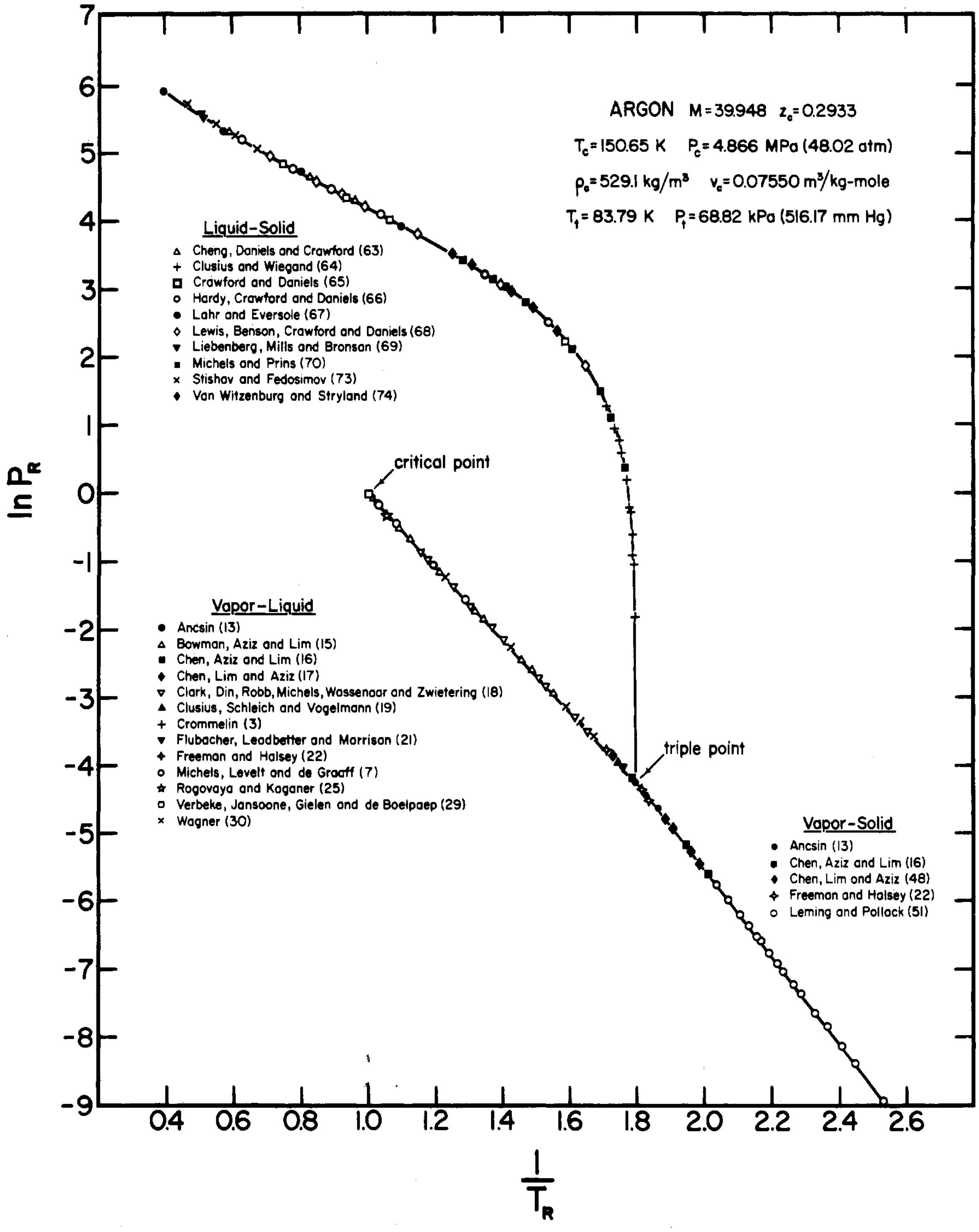

Figure 1. Dependence of saturated pressure on temperature for argon.

about its origin until its abscissa coincides with the line joining the origin and the triple point is subjected to an angular displacement φ defined as

$$\tan \varphi = \frac{\ln P_{Rt}}{1/T_{Rt} - 1} \tag{3}$$

These transformations define a new coordinate system whose abscissa and ordinate are

$$x = (\sin \varphi) \ln P_R + (\cos \varphi)(1/T_R - 1) \tag{4}$$

$$y = (\cos \varphi) \ln P_R - (\sin \varphi)(1/T_R - 1) \tag{5}$$

where P_R and T_R represent normalized experimental measurements. This xy-coordinate system produces a plot of high resolution which accentuates differences between experimental points. Details relating to the application of this approach for the screening of vapor pressure data for argon are presented by Wilsak and Thodos (*2*). Their treatment resulted in the acceptance of 263 selected points capable of defining the vapor pressure function from the triple point to the critical point. Selected values for the vapor-liquid saturation pressure are shown in Figure 1. It should be noted that this screening procedure is independent of any vapor pressure model.

The screened vapor pressure data now can be fitted by an appropriate analytical function. A number of such vapor pressure functions are available as representative candidates. The application of the screened data to four five-parameter models indicated that each was equally capable of representing the vapor pressure behavior (*2*). For the purpose of this investigation the following model with its associated parameters for argon was adopted:

$$\ln P_R = 4.6334 - 4.5397/T_R - 0.22715/T_R^2 + 0.13114 T_R^{5.741} \quad (6)$$

where $P_R = P/P_c$ and $T_R = T/T_c$ in which P_c = 4.866 MPa (48.02 atm) and T_c = 150.65 K. Equation 6 reproduces the vapor pressure measurements with an overall average pressure deviation of 0.042% (263 screened points). These deviations are well scattered about zero over the entire region between the triple point and the critical point. Of these, only 13 of the 263 screened points are associated with absolute deviations exceeding 0.10%. The average pressure deviation associated with each source is presented in Table II. It should be noted that these deviations and others that will follow are defined as the arithmetic average of the absolute value of the differences between the experimental and calculated values divided by the corresponding experimental value multiplied by 100.

When eq 6 is evaluated at T_R = 1.000, the associated ln P_R value is found to be -0.00231 rather than 0. This value corresponds to a calculated critical pressure of 4.854 MPa (47.91 atm). This calculated value lies within the uncertainty associated with the average critical pressure value from Table I and furthermore is very similar to the measurement reported by McCain and Ziegler (*6*).

Liquid Density. For establishing the saturated-liquid-density behavior of argon, 17 sources (*5*, *7*, *10*, *12*, *26*, *32*–*43*) of experimental data were available which yielded 156 unscreened measurements. Of these, the four values reported by Crommelin (*35*) were in obvious disagreement with all others and were not considered further. These references are presented in Table II. The screening of these data is not as straightforward as was the case for vapor pressures. This stems from the fact that there is no convenient method for transforming the density-temperature function into a linear form so that experimental measurements can be screened without the involvement of a prescribed model. In this context, four saturated-liquid-density models have been fitted to the unscreened data (152 points) in order to differentiate between these data. The four models and their parameters resulting from the regressions on these unscreened data were found to be as follows:

$$\ln \rho_R = 1.24731(1 - T_R)^{0.290965} \quad (7)$$

$$\rho_R = 1 + 1.8842(1 - T_R)^{0.35} + 0.17764(1 - T_R) + 1.1382(1 - T_R)^{4/3} - 0.81221(1 - T_R)^{5/3} \quad (8)$$

$$\rho_R = 1 + 1.3188(1 - T_R)^{0.6274} + 1.1012(1 - T_R)^{0.2766} \quad (9)$$

$$\rho_R = 1.1338 + 2.2575(1 - T_R)^{0.7436} - 0.1338 e^{-37.75(1-T_R)^{1/2}} \quad (10)$$

where $\rho_R = \rho/\rho_c$ and ρ_c = 529.1 kg/m^3. Equation 7 is the simplest model of the four and is of the same form as the equation proposed by Rackett (*44*) while eq 8 was first suggested by Haynes (*39*) and extended by Alburquerque et al. (*32*). The form of eq 9 was applied in a generalized manner by Campbell (*45*) while that of eq 10 was used by Wilsak (*31*).

Density deviations were calculated for each of the 152 unscreened measurements, using in each case eq 7–10. Plots of these deviations vs. T_R were constructed and all four exhibited the same relative orientation between sets of data. The deviations associated with the experimental data, calculated by using eq 7, are presented in Figure 2. The five measurements reported by Saji and Kobayashi (*42*) are obviously far removed from all the others and therefore were not considered further. The values reported by Gladun (*37*) lack internal consistency as exhibited by their broad scattering and consequently these data were also rejected. The remaining 14 sources of data segregate themselves into two distinct groups. The upper group which includes the work of Alburquerque et al. (*32*), Chui and Canfield (*34*), Davies et al. (*36*), Haynes (*39*), and Pan et al. (*41*) and the lower group involving the remaining nine sources differ systematically by about 0.3%. To seek an explanation for this discrepancy between these two groups, this matter was examined further. Alburquerque et al. (*32*) point out that "the volume of the cell was calibrated with nitrogen at 93.93 K by extrapolating a $p-V$ isotherm to the vapor pressure given by Wagner (*30*) and forcing agreement with the data of Haynes et al. (*46*, *47*)". Alburquerque et al. (*32*) go on to state that Pan et al. (*41*) calibrated their equipment by using also the data of Haynes et al. (*46*, *47*). These data of Alburquerque et al. (*32*), Haynes (*39*), and Pan et al. (*41*) account for 25 of the 27 points of the upper group.

At this stage, it must be decided which group in Figure 2 is to be given preference. The preponderance of the data in the upper group is directly or indirectly linked with the work of Haynes, while the data in the lower group span a period of 68 years and were performed at different independent research centers. Consequently, the data of the lower group, shown in Figure 2, have been favored in this study since they represent a broader coverage of investigators whose work is not necessarily related to that of each other.

Although the screened data can be fitted to obtain new values for the parameters of each of eq 7–10, this reevaluation was limited to the model represented by eq 7 because of the simplicity of this relationship and the fact that the more complex models did not offer a significant advantage in this analysis. Therefore, a reevaluation of the parameters of eq 7 using the screened data of the lower group in Figure 2 yielded the following expression:

$$\ln \rho_R = 1.24738(1 - T_R)^{0.291439} \quad (11)$$

Equation 11 has been applied over the entire saturated-liquid region and reproduces the experimental measurements with an average deviation of 0.16% (107 screened points). Equation 11 represents the selected data to within ±0.2% from the triple point up to T_R = 0.95. The deviations decrease to a minimum of -0.8% at T_R = 0.98 and increase to a maximum of +0.65% at T_R = 0.997. At the critical point, eq 11 yields the averaged critical density presented in Table I. The deviations associated with each source are presented in Table II. The hypothetical liquid density at absolute zero becomes ρ_R^0 = 3.481 (1842 kg/m^3) as calculated from eq 11.

Vapor Density. The establishment of the saturated-vapor-density function of argon is not straightforward due to the lack of experimental data. A total of 19 experimental measurements from the work of Crommelin (*35*), Mathias et al. (*5*), and Michels et al. (*7*) were available. Of these, the four values of Crommelin (*35*) were in complete disagreement with the others and therefore these values of Crommelin were rejected. Of the other two remaining references, the values reported by Michels et al. (*7*) show excellent internal consistency and therefore were considered as more reliable over those given by Mathias et al. (*5*). The final selection of 13 measurements considered dependable is included in Table II and these values are shown in Figure 3. These measurements ranged from T = 122 K (T_R = 0.81) to the critical point and represent 45% of the temperature range included between the triple point and the critical point. To extend the information contained in these 13 points, the compressibility factor concept was applied to take advantage of the hypothetical limiting ideal gas behavior at low temperatures. From the vapor pressure relationship of eq 6 and the selected 13 points, the compressibility factor, $z = z_c P_R/\rho_R T_R$, for the saturated vapor has been established to be

$$z = 1 + (0.99769 z_c - 1) T_R^4 \exp[-0.6161(1 - T_R)^{0.2809}] \quad (12)$$

where z_c = 0.2933. At T_R = 1.00, eq 6 yields a value of P_R = 0.99769 rather than unity and therefore in order to maintain

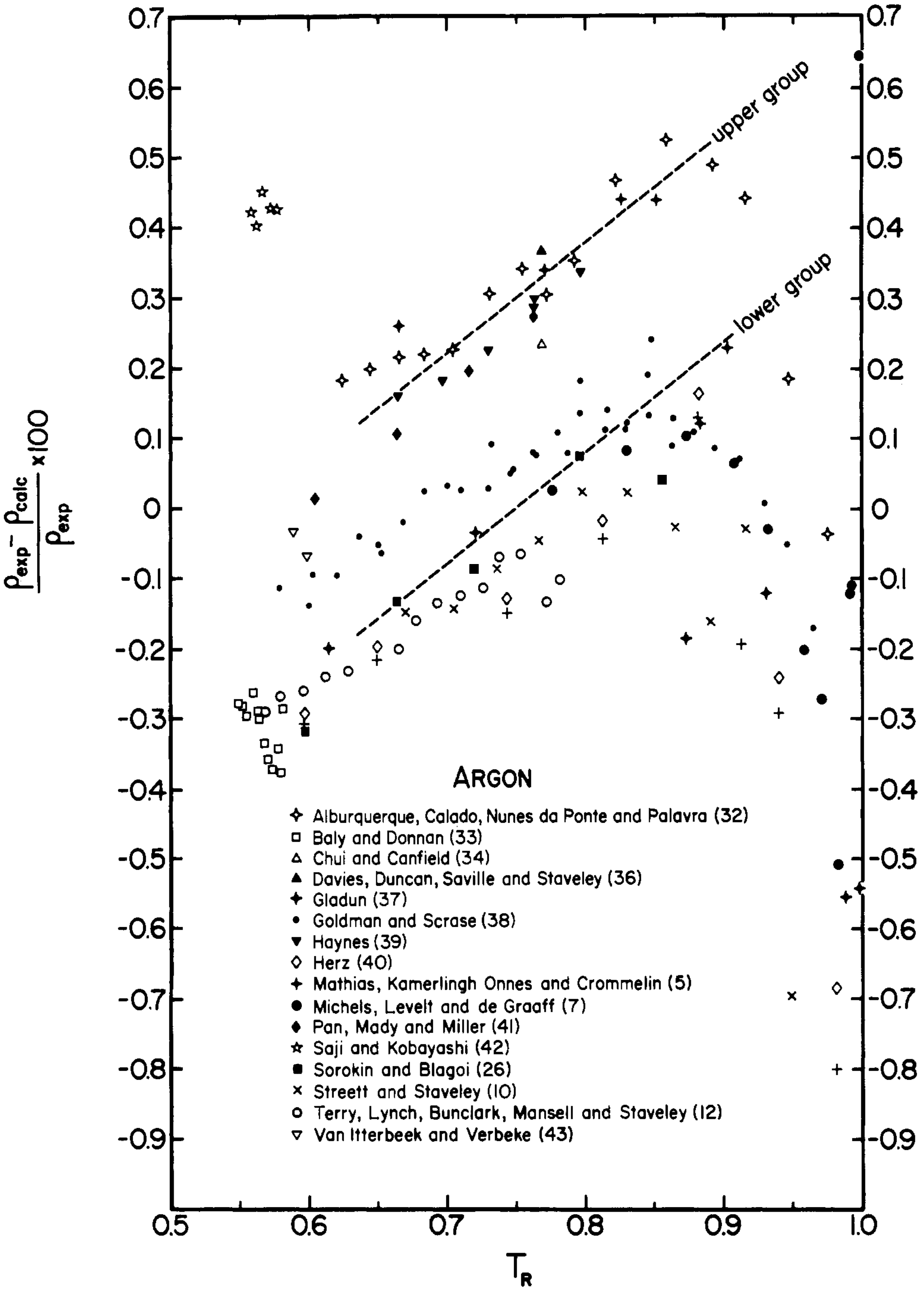

Figure 2. Deviations for liquid densities in the vapor-liquid coexistence region calculated with eq 7.

internal consistency between eq 6, 11 and 12, this value of 0.997 69 was incorporated into eq 12 instead of unity for the coefficient of z_c. Equation 12, coupled with eq 6, is capable of producing saturated-vapor densities, $\rho_R = z_c P_R / z T_R$, with an overall average deviation of 0.83% (13 points). The average deviation from the work of Michels et al. (*7*) was found to be 0.27% (nine points) while that resulting from the work of Mathias et al. (*5*) was 2.09% (four points). These deviations lend credence to the vapor density measurements of Michels et al. (*7*) over those reported by Mathias et al. (*5*) in 1912. Therefore, eq 12 represents the vapor density behavior between $T_R = 0.81$ and the critical point to within ±0.3%. This information is documented in Table II.

Vapor-Solid Coexistence Region

Below the triple point temperature, the only coexistence region for argon consists of saturated vapor and saturated solid. For this region, 14 sources of data (*9*, *13*, *14*, *16*, *18*, *20–24*, *48–51*) reported 506 measurements for the sublimation pressure of argon. After these measurements were subjected to a similar screening procedure as outlined for the pressures of the vapor-liquid coexistence region, these 506 sublimation pressures were reduced to 150 reliable values, ranging from 59 K to the triple point. Selected values for the vapor-solid saturation pressure are shown in Figure 1. This information is summarized in Table III and these screened values were utilized to develop the sublimation pressure relationship

$$\ln P_R = 5.427708 - 5.095585/T_R - 0.2486302/T_R^2 + 1.084844 T_R^{2.3142} \quad (13)$$

Equation 13 reproduces sublimation pressure measurements with an average deviation of 0.023% (150 points). From 59

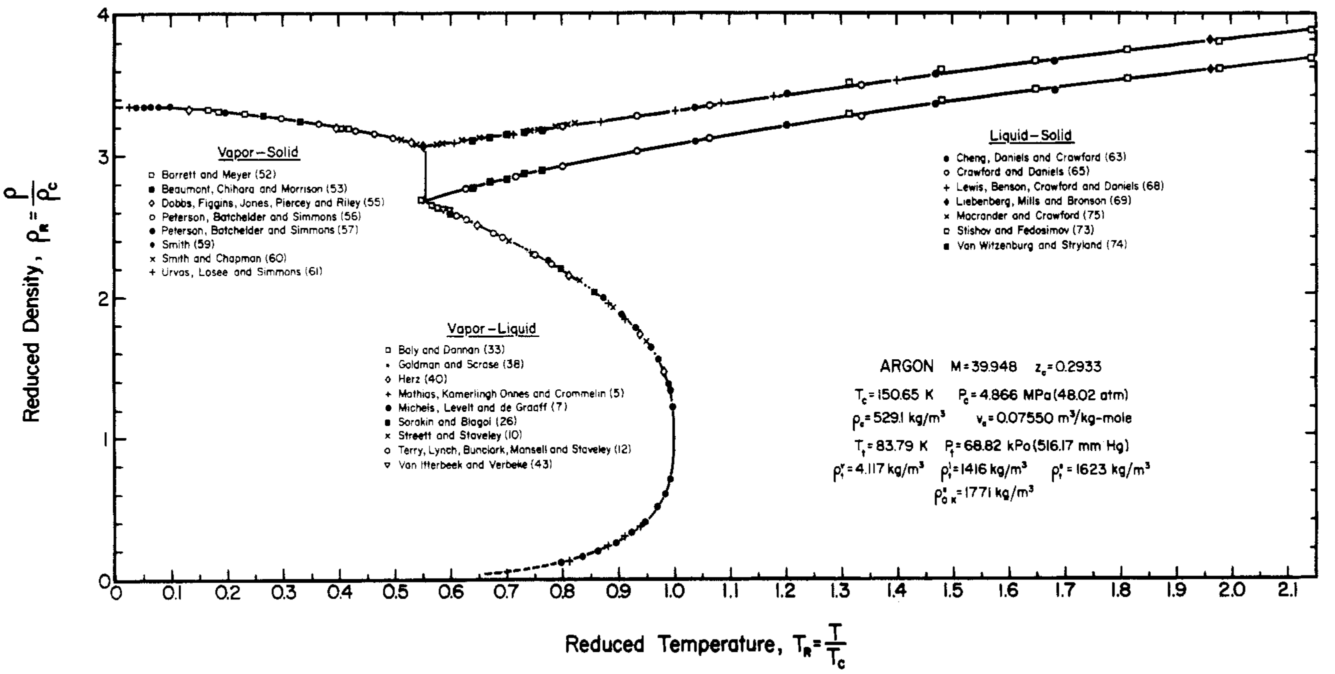

Figure 3. Dependence of saturated density on temperature for argon.

Table III. Literature Sources and Comparison between Calculated and Experimental Values for the Vapor–Solid Coexistence Region

		all data			selected data		
year	ref	points	av dev, %	max dev, %	points	av dev, %	max dev, %
		Vapor Pressure—Eq 13					
1973	Ancsin (*13*)	7	0.004	0.006	7	0.004	0.006
1922	Born (*14*)	26	1.254	4.698			
1971	Chen et al. (*16*)	71	0.008	0.022	71	0.008	0.022
1978	Chen et al. (*48*)	39	0.027	0.274	38	0.021	0.066
1951	Clark et al. (*18*)	8	2.813	5.676			
1913	Crommelin (*20*)	5	14.337	55.495			
1914	Crommelin (*49*)	8	3.930	9.107			
1965	Fender and Halsey (*50*)	4	0.100	0.160			
1961	Flubacher et al. (*21*)	26	0.304	1.508			
1956	Freeman and Halsey (*22*)	5	0.051	0.108	5	0.051	0.108
1916	Holst and Hamburger (*23*)	4	0.190	0.301			
1970	Lee et al. (*24*)	216	0.340	5.316			
1970	Leming and Pollack (*51*)	81	13.519	99.995	29	0.062	0.465
1901	Ramsay and Travers (*9*)	6	4.606	7.202			
av		506	2.698		150	0.023	
		Solid Density—Eq 14					
1964	Barrett and Meyer (*52*)	14	0.040	0.115	13	0.035	0.115
1961	Beaumont et al. (*53*)	9	0.189	0.296	2	0.029	0.036
1925	De Smedt and Keesom (*54*)	1	5.027	5.027			
1956	Dobbs et al. (*55*)	5	0.061	0.091	4	0.065	0.091
1965	Peterson et al. (*56*)	10	0.021	0.032	10	0.021	0.032
1966	Peterson et al. (*57*)	20	0.018	0.038	20	0.018	0.038
1924	Simon and von Simson (*58*)	1	4.131	4.131			
1961	Smith (*59*)	7	0.162	0.217	1	0.067	0.067
1967	Smith and Chapman (*60*)	6	0.069	0.092	6	0.069	0.092
1967	Urvas et al. (*61*)	1	0.020	0.020	1	0.020	0.020
av		74	0.187		57	0.033	

K to the triple point, only 12 measurements of the selected 150 values showed deviations in excess of 0.05%.

No saturated-vapor densities below the triple point are reported for argon. In order to obtain an order of magnitude estimate, eq 12 can be extrapolated since this relationship satisfies the limiting condition $z \rightarrow 1.00$ as $T \rightarrow 0$ K. Equation 12 enables the calculation of saturated-vapor densities by using the sublimation pressure relationship of eq 13 and the definition of the compressibility factor.

For the solid state, 10 sources of information (*52–61*) were consulted which yielded 74 saturated-solid densities which were reduced to 57 reliable values after screening. Typical screened values are shown in Figure 3. All this information is presented in Table III. These values range from absolute zero to the triple point and were used to obtain the following expression for the saturated-solid densities of argon:

$$\rho_R = 3.3467 - 0.83209T_R^{1.8376} \exp[-0.0024838/T_R^{2.8636}] \tag{14}$$

Equation 14 reproduces the experimental solid density measurements with an overall average deviation of 0.033% (57 points) where the point deviations are well distributed about zero and where all but two are within ±0.08%. Equation 14 predicts

Table IV. Literature Sources and Comparison between Calculated and Experimental Values for the Liquid-Solid Coexistence Region

		all data			selected data		
year	ref	points	av dev, %	max dev, %	points	av dev, %	max dev, %
		Saturated Pressure—Eq 15					
1935	Bridgman (*62*)	7	99.300	691.1			
1973	Cheng et al. (*63*)	4	0.117	0.241	4	0.117	0.241
1940	Clusius and Weigand (*64*)	28	2.330	31.61	27	1.246	6.372
1968	Crawford and Daniels (*65*)	11	0.359	0.926	11	0.359	0.926
1971	Hardy et al. (*66*)	84	0.160	0.463	84	0.160	0.463
1962	Lahr and Eversole (*67*)	15	1.545	4.202	15	1.545	4.202
1974	Lewis et al. (*68*)	8	0.252	0.927	8	0.252	0.927
1974	Liebenberg et al. (*69*)	2	1.284	1.369	2	1.284	1.369
1962	Michels and Prins (*70*)	13	7.928	57.63	11	0.398	0.599
1954	Robinson (*71*)	11	4.595	12.47			
1930	Simon et al. (*72*)	24	6.026	14.52			
1971	Stishov and Fedosimov (*73*)	12	0.292	0.741	12	0.292	0.741
1968	Van Witzenburg and Stryland (*74*)	6	0.613	0.650	6	0.613	0.650
av		225	4.939		180	0.504	
		Liquid Density—Eq 16					
1935	Bridgman (*62*)	4	4.138	8.078			
1973	Cheng et al. (*63*)	4	0.179	0.409	4	0.179	0.409
1968	Crawford and Daniels (*65*)	11	0.207	0.521	11	0.207	0.521
1962	Lahr and Eversole (*67*)	15	8.398	9.693			
1974	Liebenberg et al. (*69*)	1	0.286	0.286	1	0.286	0.286
1971	Stishov and Fedosimov (*73*)	9	0.185	0.494	9	0.185	0.494
1968	Van Witzenburg and Stryland (*74*)	6	0.141	0.194	6	0.141	0.194
av		50	2.966		31	0.187	
		Solid Density—Eq 17					
1935	Bridgman (*62*)	4	6.205	11.261			
1973	Cheng et al. (*63*)	4	0.270	0.560	4	0.270	0.560
1968	Crawford and Daniels (*65*)	8	0.230	0.460	8	0.230	0.460
1962	Lahr and Eversole (*67*)	14	8.763	10.485			
1974	Lewis et al. (*68*)	8	0.212	0.468	8	0.212	0.468
1974	Liebenberg et al. (*69*)	1	0.058	0.058	1	0.058	0.058
1977	Macrander and Crawford (*75*)	15	0.134	0.264	15	0.134	0.264
1971	Stishov and Fedosimov (*73*)	9	0.394	0.985	9	0.394	0.985
1968	Van Witzenburg and Stryland (*74*)	6	0.242	0.514	6	0.242	0.514
av		69	2.307		51	0.229	

at absolute zero a solid density of $\rho_R^0 = 3.347$ (1771 kg/m^3).

Liquid-Solid Coexistence Region

The liquid-solid two-phase region begins at the triple point and extends continuously to higher temperatures. In this region, the saturated-liquid and -solid density curves approach each other with increasing temperature, but do not converge to define a liquid-solid critical point, based on the experimental measurements. For the establishment of the equilibrium pressure, 13 references (*62-74*) provided 225 experimental values. After screening, 180 determinations from 10 references were considered reliable. Selected values for the liquid-solid saturation pressure are shown in Figure 1. Table IV summarizes the initial and final source selections. The screened data were used to develop the saturated pressure function

$$P_R = P_{Rt}(1 + 4872.8X)(1 + 0.28360X) - 775.93X^{1/2} \exp(-7.0152/T_R) \quad (15)$$

where $P_{Rt} = P_t/P_c$ and $X = (T/T_t) - 1$. The application of eq 15 is valid from the triple point temperature up to $T_R = 2.4$ (362 K). This temperature corresponds to $P_R = 376$ (1830 MPa (18 060 atm)). Equation 15 reproduces the selected values with an overall average deviation of 0.50% (180 screened points). The point deviations are well scattered about zero except in the immediate vicinity of the triple point. Because of the steepness of the saturated pressure function in this region as demonstrated in Figure 1, substantial deviations between a model and actual measurements are to be expected. Of the 180 selected points, only 19 exhibited associated deviations in excess of 1%. A summary of the average deviations is presented in Table IV.

For saturated-liquid densities, seven sources (*62*, *63*, *65*, *67*, *69*, *73*, *74*) were available and reported 50 measurements. Of these, the information presented by Bridgman (*62*) and Lahr and Eversole (*67*) was rejected because their values were completely incompatible with those reported by the others. This elimination left a total of 31 screened points (Table IV). Typical saturated-liquid densities are shown in Figure 3. The screened values, which extended up to $T_R = 2.15$ (323 K), were utilized to establish the saturated-liquid relationship

$$\rho_R = 3.0471T_R^{1/4} + 17.884T_R^4 \exp(-6.5492T_R) \quad (16)$$

Equation 16 reproduces the selected measurements with an overall average deviation of 0.19% (31 screened points) for liquid densities. The point deviations are well distributed about zero with all but five within ±0.30%. The average deviations for each source are presented in Table IV.

For the saturated-solid densities, nine references (*62*, *63*, *65*, *67-69*, *73-75*) were consulted which involved 69 experimental points. As before, it was found necessary to reject the work of Bridgman (*62*) and that of Lahr and Eversole (*67*). The remaining seven references contained 51 experimental values (Table IV). Typical saturated-solid densities are included in Figure 3. These values were used to develop the relationship for the saturated-solid density

$$\rho_R = 3.2233T_R^{1/4} + 4.7932T_R \exp(-4.0308T_R) \quad (17)$$

Equation 17 reproduces the selected values with an overall average density deviation of 0.23% (51 points) and is valid up to $T_R = 2.15$ (323 K). The point deviations are well scattered about zero and only those for six of the 51 selected points exceed 0.40%. The deviations are summarized in Table IV.

It should be noted that eq 16 and 17 are valid for the same range of temperature.

Triple Point

The triple point represents the unique state where vapor, liquid, and solid can coexist. Therefore, eq 6 and 11–17 are valid at this univariant point so that the intersection of any two appropriate relationships can be used to specify the corresponding two quantities of the triple point. For example, eq 6 and 13 can be solved simultaneously for pressure and temperature. Likewise, eq 11 and 16 produce the liquid density and temperature, while eq 14 and 17 yield the solid density and temperature. In all cases the triple point temperature was found to be 83.79 K. This triple point temperature gives rise to the following unique pressure value P_t = 86.82 kPa (516.17 mmHg) and densities ρ_t = 4.117, 1416, and 1623 kg/m^3, for the vapor, liquid, and solid states, respectively. The vapor density represents an extrapolated value.

Glossary

P	pressure
R	gas constant
T	temperature
v	molar volume
X	temperature variable, $(T/T_t) - 1$
z	compressibility factor, Pv/RT

Greek Letters

λ	latent heat of phase transformation
ρ	density
φ	angle of rotation

Subscripts

c	critical point
R	reduced
s	saturated curve
t	triple point

Superscripts

0	absolute zero, 0 K
l	liquid state
s	solid state
v	vapor state

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