1.3 DENSITY AND THERMAL EXPANSION

1.3.1 DENSITY

<u>Summary</u>

Recommended values for the density of liquid sodium and sodium vapor are given in Table 1.3-1 in kg·m⁻³. The recommended equation for the density of liquid sodium in kg/m³ along the saturation curve is

$$\rho_l = \rho_C + f\left(1 - \frac{T}{T_C}\right) + g\left(1 - \frac{T}{T_C}\right)^h$$

$$for 371 \ K \le T \le 2503.7 \ ,$$
(1)

where

$$\begin{array}{l} \rho_C &= 219., \\ f &= 275.32, \\ g &= 511.58, \\ h &= 0.5, \\ T_C &= 2503.7 \ K, \end{array}$$

and $\rho_{\rm C}$ and $T_{\rm C}$ are, respectively, the critical density and critical temperature. The form of Eq. (1), suggested by Hornung,⁽¹⁾ was chosen because it gives proper physical behavior at the critical point. The recommended values are based on the analysis of sodium density data from the melting point to 2201 K by Shpil'rain et al.⁽²⁾ Because Shpil'rain et al.⁽²⁾ fit the data on liquid sodium density to a seven-term polynomial, their results have been refit using the equation with proper temperature dependence at the critical point.

The density of sodium vapor above the saturated liquid was calculated from the enthalpy of vaporization (ΔH_g) , the temperature derivative of the pressure (γ_o) , and the liquid density (ρ_I) using the thermodynamic relation

$$\rho_g = \left(\frac{\Delta H_g}{T\gamma_\sigma} + \frac{1}{\rho_l}\right)^{-1} . \tag{2}$$

Temperature (K)	Liquid Density (kg · m ⁻³)	Vapor Density (kg · m ⁻³)
400	919	1 24 x 10 ⁻⁹
500	897	5.03×10^{-7}
600	874	2.63×10^{-5}
700	852	$4 31 \times 10^{-4}$
800	828	3.43×10^{-3}
900	805	1.70×10^{-2}
	803.	1.70 × 10
1000.	781.	6.03 x 10 ⁻²
1100.	756.	0.168
1200.	732.	0.394
1300.	706.	0.805
1400.	680.	1.48
1500.	653.	2.50
1600.	626.	3.96
1700.	597.	5.95
1800.	568.	8.54
1900.	537.	11.9
2000.	504.	16.0
2100.	469.	21.2
2200.	431.	27.7
2300.	387.	36.3
2400.	335.	49.3
2500.	239.	102.
2503.7	219.	219.

Table 1.3-1 Sodium Density

Recommended values for the densities of liquid sodium and sodium vapor are shown in Fig. 1.3-1. Uncertainty bands have been included as dotted lines in the figures. Uncertainties for the recommended liquid and vapor densities at a number of temperatures are given, respectively, in Tables 1.3-2 and 1.3-3.

Temperature (K)	ρ_1 (kg · m ⁻³)	Uncertainty, $\left(\frac{\delta \rho_l}{\rho_l}\right)$ (%)
$371 \le T \le 700$		0.3
$700 < T \leq 1400$		0.4
$1500 \le T \le 2000^{(a)}$	$210 275 20 \left(1 T\right)$	2.7 - 14 ^(a)
$2000 \le T \le 2200^{(a)}$	$\rho_l = 219 + 275.32 \left(\frac{1}{T_c} - \frac{1}{T_c} \right)$	14 - 19 ^(a)
$2200 \le T \le 2400^{(a)}$	+ 511.58 $\left(1 - \frac{T}{T}\right)^{\frac{1}{2}}$	19 - 24 ^(a)
$2400 \le T \le 2503^{(a)}$	(¹ c)	24 - 26 ^(a)

Table 1.3-2Estimated Uncertainties in the Recommended Values for the
Density of Liquid Sodium

^(a)In the temperature range 1500 K \leq T \leq 2503 K, the uncertainty, $\frac{\delta \rho_l}{\rho_l}$ (%), is approximated by

$$\frac{\delta \rho_l}{\rho_l} (\%) = -32.22 + 0.0233 T$$

Discussion

Liquid Density — Experimental data on the density of sodium are available from the melting point to 2201 K. These data were fit by Shpil'rain et al.⁽²⁾ using a seven-term polynomial. Because an equation up to the critical point is desired and the seven-term polynomial is not appropriate for extrapolation to regions where no data are available, the values given by the polynomial of Shpil'rain et al.⁽²⁾ were refit using a functional form with appropriate behavior at the melting point and at the critical point. Near the melting point, the density has a linear dependence on temperature. As the temperature increases, the curvature of the density increases so that the slope becomes infinite at the critical point. This functional

Temperature (K)	ρ_{g} $(kg \cdot m^{-3})$	Uncertainty, $\left(\frac{\delta\rho_g}{\rho_g}\right)$ (%)
$371 \leq T \leq 400$		25
$400 < T \le 800$		9 - 4
$800 < T \leq 1300$		3
$1300 < T \le 2000$	$\rho_g = \left(\frac{\Delta H_g}{T \chi} + \frac{1}{\Omega}\right)^{-1}$	5 - 15
$2000 < T \le 2200$	$\begin{pmatrix} I Y_{\sigma} & P_{l} \end{pmatrix}$	16 - 20
$2200 < T \le 2400$		20 - 24
$2400 < T \le 2503$		24 - 27

Table 1.3-3Estimated Uncertainties in the Recommended Values for the
Density of Sodium Vapor

form, shown in Eq. (1), was recommended by Hornung.⁽¹⁾ The nonlinear least squares fit to an equation of the form of Eq. (1) used 2503.7 K for the critical temperature, 219 kg·m⁻³ for the critical density, and the constraint that the exponent *h* must be between 0.4 and 0.5. This constraint is based on examination of the behavior of alkali metals in the critical region.⁽³⁾ Classical theory suggests 0.5 for this parameter but the highest temperature sodium data (that of Dillon et al.^(4,5) from 1168 to 2201 K) suggests 0.42. The resulting equation, Eq. (1), with *h* equal to 0.5, reproduces the values given by the seven-term polynomial of Shpil'rain et al.⁽²⁾ to within 1% up to 2200 K. The X² deviation of this fit is 0.00004. Values calculated with Eq. (1), the recommended equation for the density of liquid sodium along the saturation curve, are given in Table 1.3-1.

Comparisons have been made of values calculated with the recommended equation with values from other analyses. The recent assessment of alkali metal thermophysical properties by Bystrov et al.⁽⁶⁾ gives a seven-term polynomial with coefficients differing in the fourth significant figure from those given by Shpil'rain et al.⁽²⁾ Values calculated with the equation recommended by Bystrov et al.⁽⁶⁾ differ from those of Shpil'rain et al.⁽²⁾ in the fourth or fifth significant figure.

In their analysis of sodium density data, Shpil'rain et al.⁽²⁾ gave a three-term polynomial that approximated their recommended seven-term equation. For the temperature range from the melting point to 2000 K, Hornung⁽¹⁾ derived an equation of the form of Eq. (1), which fit the values recommended by Shpil'rain et al.,⁽²⁾ to 2000 K with 2500 K for the critical temperature, 214 kg·m⁻³ for the critical density and the parameter *h* set at 0.45. In their 1979 assessment of sodium density, Fink and Leibowitz⁽⁷⁾ recommended the four-term polynomial due to Stone et al.⁽⁸⁾ from the melting point to 1644 K. For the temperature range between 1644 K and the critical point, they recommended an empirical equation of the form

$$\rho_{l} = \rho_{C} \left[1 + f \left(1 - \frac{T}{T_{C}} \right)^{h} + g \left(T_{C} - T \right)^{2} \right] , \qquad (3)$$

which gives the correct behavior at the critical point. They used 2509.4 K for the critical temperature and $214 \text{ kg} \cdot \text{m}^{-3}$ for the critical density.

Figure 1.3-2 shows the recommended values of the density of liquid sodium along the saturation curve and those from these other assessments. In Fig. 1.3-2 and in subsequent figures, the three-term polynomial approximation given by Shpil'rain et al.⁽²⁾ is designated as "S-approx." At about 1700 K, this approximation begins to deviate from Shpil'rain's recommended seven-term polynomial and from the recommended values calculated with Eq. (1). Because the S-approximation cannot represent the curvature of the density as the critical temperature is approached, deviations of this approximation increase with temperature from 2% at 1700 K to 87% at the critical temperature, 2503.7 K.

Deviations from recommended values, expressed as a percent defined as

Deviations =
$$\left(\frac{\left[\rho(Other) - \rho(Recommended)\right] 100\%}{\rho(Recommended)}\right)$$
 (4)

are shown in Fig. 1.1-3. Lines have been included as a guide between the points at which the percent deviations were calculated. Below 800 K, all recommendations agree within 0.3%. From 800 through 1400 K, agreement is within 0.4%. Up to 2000 K, the recommended values agree within 1% with values from the seven-term polynomials given by Shpil'rain et al.⁽²⁾ and by Bystrov et al.,⁽⁶⁾ and the equation given by Hornung.⁽¹⁾ At 2000 K, values from Fink and Leibowitz⁽⁷⁾ and

from the three-term approximation of Shpil'rain et al.⁽²⁾ differ by 6% from recommended values. The deviation plot in Fig. 1.1-3 shows that deviations become greater as the critical temperature is approached. This is due to the use of different functional forms as well as to the selection of different values for the critical temperature and density. The differences due to the functional forms are clearly shown by the deviations due to the seven-term polynomials of Bystrov et al. and Shpil'rain et al. because the densities given by these polynomials at 2503.7 K are, respectively, 219.0 kg·m⁻³ and 219.5 kg·m⁻³. Maximum deviations from the polynomials recommended by Bystrov et al. and by Shpil'rain et al. are, respectively, 6.8% and 6.6% at 2500 K. The maximum deviation from the recommended equation of Fink and Leibowitz is 32% at 2503.7 K.

Vapor Density — The density of the vapor over saturated liquid sodium has been calculated from the thermodynamic relation given in Eq. (2). The thermodynamic properties used in this equation are defined below. The enthalpy of vaporization, ΔH_g , in kJ·kg⁻¹, is given by

$$\Delta H_g = 393.37 \left(1 - \frac{T}{T_C} \right) + 4398.6 \left(1 - \frac{T}{T_C} \right)^{0.29302}$$

$$for \ 371 \ K \le T \le 2503.7 \ K \quad ,$$
(5)

where T_c is the critical temperature, 2503.7 K, and T is the temperature in kelvins.

Equation (5) is a fit to values of the enthalpy of vaporization from the melting point to 1600 K calculated using the quasi-chemical method of Golden and Tokar.⁽⁹⁾ The recom-mended equation for the enthalpy of vaporization, Eq. (5), has proper behavior at the critical temperature; therefore, it can be used for the entire liquid range.

The temperature derivative of the pressure along the saturation curve, γ_o , defined as

$$\gamma_{\sigma} = \left(\frac{\partial P}{\partial T}\right)_{\sigma} \tag{6}$$

is given by

$$\gamma_{\sigma} = \left(-\frac{b}{T^2} + \frac{c}{T} \right) \exp \left(a + \frac{b}{T} + c \ln T \right) \quad , \tag{7}$$

where the pressure along the saturation curve, P, is given by the equation derived by Browning and Potter:⁽¹⁰⁾

$$\ln P = a + \frac{b}{T} + c \ln T \quad , \tag{8}$$

and the coefficients in Eqs. (7-8) for P in MPa and T in kelvins are

$$a = 11.9463,$$

 $b = -12633.73$
 $c = -0.4672.$

In Fig. 1.3-4, the recommended values of the density of sodium vapor calculated with Eq. (2) are compared with values from assessments by Vargaftik and Voljak,⁽¹¹⁾ by Fink and Leibowitz,⁽⁷⁾ and by Bystrov et al.⁽⁶⁾ Fink and Leibowitz calculated the vapor density from the melting point to the critical point using the thermo-dynamic relation given in Eq. (2). Both Bystrov et al. and Vargaftik and Voljak used equation of state formulations that treated the vapor as mixtures of monatomic and diatomic molecules. Ionization of the gaseous phase was included in their equations. Vargaftik and Voljak calculated vapor densities along the saturation curve from the melting point to 1300 K. Bystrov et al. give results for the temperature range 800 to 2000 K.

Deviations from the recommended values expressed as a percent and defined as in Eq. (4) are shown in Fig. 1.3-5. Except for the large deviations (up to 23%) at low temperatures of values from Fink and Leibowitz,⁽⁷⁾ deviations are within 3%. These large deviations at low temperatures arise from differences in the calculated heat of vaporization at low temperatures. Because the density of the vapor is so low (1 x 10^{-9} kg·m⁻³) at these temperatures, the actual deviations are on the order of 1 x 10^{-10} kg·m⁻³.

<u>Uncertainty</u>

The uncertainties in the recommended values for the density of liquid sodium, shown in Table 1.3-2, were estimated from examination of uncertainties given by other assessments and from deviations between recommendations as a function of temperature. Bystrov et al.⁽⁶⁾ give uncertainties of 0.5% below 1300 K, 1% from 1300 to 1800 K, and 2% above 1800 K. Fink and Leibowitz⁽⁷⁾ give uncertainties of 0.3% below 866 K, 0.4% from 866 to 1644 K, 3% from 1644 to 2300 K, 7% from 2300 to 2400 K, and 15% above 2400 K. The uncertainty is estimated as 0.3% below 800 K, based on the agreement of all recommended equations within 0.3%. From 800 to

1400 K, the uncertainty is estimated as 0.4% based on the 0.4% agree-ment with other recommended values in this temperature region. From 1500 to 2503.7 K, the percent uncertainty as a function of temperature is approximated by the linear equation

$$\delta \rho(\%) = -32.22 + 0.0233 T \quad . \tag{9}$$

This equation gives uncertainties of 2.7% at 1500 K, 14% at 2000 K, and 26% at 2500 K. These estimated uncertainties are above deviations of recommended equations at 1500 and 2000 K but less than the 32% deviation between the recommended value and that of Fink and Leibowitz at 2500 K.

Uncertainties for the vapor densities are given in Table 1.3-3. They were calculated from the uncertainties in the dependent parameters assuming that all uncertainties are independent. If x_i are the dependent parameters, the square of the uncertainty in the calculated vapor densities is given by

$$(\delta \rho_g)^2 = \sum \left(\frac{\partial \rho_g}{\partial x_i} \right)^2 (\delta x_i)^2 , \qquad (10)$$

where δx_i are the uncertainties in the dependent parameters. Thus, the uncertainty in the vapor density ($\delta \rho_g$) is a function of the uncertainty in the enthalpy of vaporization ($\delta \Delta H_g$), the vapor pressure (δP), and the liquid density ($\delta \rho_I$). To simplify the calculation, the partial derivative with respect to the dependent parameters has been assumed to be unity. At each temperature, the uncertainty in the vapor density was calculated from

$$\delta \rho_g = \sqrt{\left(\delta \rho_l\right)^2 + \left(\delta \Delta H_g\right)^2 + \left(\delta P\right)^2} \quad . \tag{11}$$

Uncertainties calculated with Eq. (11), shown in Table 1.3-3, are high at both low and high temperatures. The 25% uncertainty at 371 and 400 K arises from the high uncertainty in the enthalpy of vaporization at these low temperatures. It is consistent with the 25% deviation from values given by Fink and Leibowitz⁽⁷⁾ for these temperatures. Calculated uncertainties decrease to a minimum 3% for the 900 to 1400 K temperature range. The calculated uncertainties increase with temperature to 10% at 1800 K, 14% at 2000 K, 24% at 2400 K, and 26% at 2500 K. These uncertainties are higher than the estimates given by Bystrov et al.⁽⁶⁾ They are consistent with

uncertainties given by Fink and Leibowitz⁽⁷⁾ from 800 to 2400 K, but lower than the uncertainty estimate by Fink and Leibowitz⁽⁷⁾ at 2500 K. Bystrov et al. estimate the uncertainty of their vapor density equation to be 0.4% at 1000 K, 0.8% at 1400 K, and 9% at 1800 K. Fink and Leibowitz estimate the uncertainties of their values for vapor density as 2% from 371 to 1644 K, 12% from 1644 to 2000 K, 20% from 2000 to 2400 K, and 50% above 2400 K.

Polynomial Approximations

Liquid Density — In the SASS code,⁽¹²⁾ a quadratic equation is used to represent the liquid density of sodium. This form of equation is not recommended in this assessment because it does not have proper curvature as the critical temperature is approached. The three-term polynomial approximation given by Shpil'rain et al.⁽²⁾ is an approximation to their seven-term equation and to the recommended equation; it is

$$\rho_l = \rho_C \left[1.01503 - 0.23393 \left(\frac{T}{T_C} \right) - 0.305 \times 10^{-2} \left(\frac{T}{T_C} \right)^2 \right] , \qquad (12)$$

where ρ_c is 218 kg·m⁻³ and T_c is 2505 K. Values from this equation are shown in Fig. 1.3-2 with the legend label "S-approx." Equation (12) is a good approximation at low temperatures but at 1700 K, values from this equation begin to deviate significantly from the recommended values. Deviations of Eq. (12) from the recommended equation are included in Fig. 1.3-3. They increase from 2% at 1700 K to 6% at 2000 K, 30% at 2400 K, and 87% at the critical temperature, 2503.7 K. If agreement within 10% is desired, this equation should not be used above 2100 K. The critical density and critical temperature used in this approximation differ from the values recommended in this assessment ($\rho_c = 219 \text{ kg·m}^{-3}$, $T_c = 2503.7 \text{ K}$). However, because density decreases with temperature, the lower value for the critical density is consistent with the higher critical temperature used in this approximation.

Vapor Density — In the SASS code,⁽¹²⁾ the vapor density is expressed as a polynomial times the vapor pressure. However, the form of the vapor pressure equation used in the SASS code differs from the recommended equation for the vapor pressure because an invertible equation is needed in this computer code. To provide an equation of the desired form, a least squares fit to the recommended values for the density of sodium vapor has been performed using an invertible equation to approximate the vapor pressure. This approximation to the vapor density is given by

$$\rho_g = P\left(\frac{a}{T} + b + cT + dT^2 + eT^3 + fT^4\right) , \qquad (13)$$

where the polynomial coefficients are

$$a = -85.768,$$

$$b = 24951,$$

$$c = 1.2406 \times 10^{-1},$$

$$d = -8.3368 \times 10^{-5},$$

$$e = 2.6214 \times 10^{-8},$$

$$f = -3.0733 \times 10^{-12},$$

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and the pressure, *P*, in MPa is given by the SASS invertible equation for the pressure over saturated liquid sodium:

$$P = \exp\left(A - \frac{B}{T} - \frac{C}{T^2}\right) \quad , \tag{13}$$

where

$$A = 7.8270,$$

 $B = 11275,$
 $C = 4.6192 \times 10^{5}.$

Values for the density calculated with these approximate equations are compared with the recommended values in Fig. 1.3-6. The vapor density approximation (Eq. [13]) reproduces the recommended values of the density of sodium vapor to within 8% in the 400 to 2200 K temperature range. Deviations, shown in Fig. 1.3-7, increase significantly above 2200 K. At 2300 K, the approximation deviates from recommended values by 11%. Deviations are -28% at 2500 K and -66% at the critical temperature, 2503.7 K. The deviations increase as the temperature approaches the critical temperature because the mathematical form for the density used in the SASS code cannot give the proper curvature as the critical point is approached. At the critical point, the slope of the density must be infinite.

1.3.2 THERMAL EXPANSION Summary

Recommended values for the instantaneous volumetric thermal-expansion coefficients of liquid sodium and sodium vapor are given in Table 1.3-4 and shown in Figs. 1.3-8 and 1.3-9. Uncertainties in the recommended values were estimated from the uncertainties in the dependent parameters. These are included as dotted lines in Figs. 1.3-8 and 1.3-9 and given, as a function of temperature, in Tables 1.3-5 and 1.3-6.

For saturated liquid sodium, the instantaneous volumetric thermal-expansion coefficient (α_p) was calculated from the thermodynamic relation

$$\alpha_P = \alpha_{\sigma} + \beta_T \gamma_{\sigma} \quad , \tag{15}$$

where β_T is the isothermal compressibility γ_σ is the temperature derivative of the pressure along the saturation curve, and α_σ is the coefficient of thermal expansion along the saturation curve defined as

$$\alpha_{\sigma} = -\frac{1}{\rho_l} \left(\frac{\partial \rho_l}{\partial T} \right)_{\sigma} \quad . \tag{16}$$

The instantaneous volumetric thermal-expansion coefficient for sodium vapor was calculated from the relation

$$\left(\alpha_{P}\right)_{g} = \frac{\left(\alpha_{\sigma}\right)_{g}}{\left(1 - \frac{\gamma_{\sigma}}{\gamma_{V}}\right)} \quad , \tag{17}$$

where γ_{σ} is the temperature derivative of the pressure along the saturation curve, given in Eq. (7), and γ_{V} is the thermal-pressure coefficient, defined in the discussion below. The coefficient of thermal expansion along the saturation curve for sodium vapor $(\alpha_{\sigma})_{g}$ is defined as

$$\left(\alpha_{\sigma}\right)_{g} = -\frac{1}{\rho_{g}} \left(\frac{\partial \rho_{g}}{\partial T}\right)_{\sigma} \quad . \tag{18}$$

Temperature (K)	$\begin{array}{c} \textbf{Liquid} \\ \alpha_{\rho} \ge 10^{4} \\ (\text{K}^{-1}) \end{array}$	Vapor α _ρ x 10 ³ (K ⁻¹)
400.	2.41	2.55
500.	2.50	2.23
600.	2.60	2.01
700.	2.71	1.85
800.	2.82	1.73
900.	2.95	1.64
1000.	3.10	1.57
1100.	3.26	1.50
1200.	3.45	1.44
1300.	3.66	1.38
1400.	3.90	1.33
1500.	4.20	1.26
1600.	4.55	1.19
1700.	4.98	1.15
1800.	5.52	1.15
1900.	6.23	1.19
2000.	7.18	1.28
2100.	8.56	1.44
2200.	10.7	1.76
2300.	14.7	2.46
2400.	24.9	4.87
2500.	261.	374.

Table 1.3-4Instantaneous Volumetric Thermal-Expansion Coefficients
of Liquid Sodium and Sodium Vapor

Temperature (K)	α _p (K ⁻¹)	Uncertainty, $\left(\frac{\delta \alpha_{\rm p}}{\alpha_{\rm p}}\right)_l$ (%)
$371 \leq T \leq 1000$		10
$1000 < T \leq 1600$		15
$1600 < T \leq 2000$	$\alpha_{\rm P}$ = α_{σ} + β_T γ_{σ}	45
$2000 < T \leq 2200$	$\alpha = -\frac{1}{2}\left(\frac{\partial \rho_l}{\partial \rho_l}\right)$	60
$2200 < T \leq 2400$	$\rho_l \left(\partial T \right)_{\sigma}$	75
$2400 < T \le 2503$		85

Table 1.3-5Estimated Uncertainties in the Recommended Values for the Instantaneous
Volumetric Thermal-Expansion Coefficient for Liquid Sodium

Table 1.3-6	Estimated Uncertainties in the Recommended Values for the Instantaneous
	Volumetric Thermal-Expansion Coefficient for Sodium Vapor

Temperature (K)	α _p (K ⁻¹)	Uncertainty, $\left(\frac{\delta \alpha_{\rm p}}{\alpha_{\rm p}}\right)_g$ (%)
$371 \leq T \leq 500$		50
$500 < T \leq 1600$		15
$1600 < T \leq 2000$	$\alpha = \frac{\alpha_{\sigma}}{1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 +$	30
$2000 < T \leq 2200$	$\left(\begin{array}{c} \alpha_{\rm P} \\ 1 & -\frac{\gamma_{\sigma}}{\gamma_{\sigma}} \end{array}\right)$	40
$2200 < T \leq 2400$	$\begin{pmatrix} \gamma_V \end{pmatrix}$	50
$2400 < T \le 2503$	$\alpha_{\sigma} = -\frac{1}{\rho_g} \left(\frac{\partial \rho_g}{\partial T} \right)_{\sigma}$	55

Discussion

Thermal-Expansion Coefficient for Liquid Sodium — The instantaneous volumetric thermal-expansion coefficient at constant pressure for liquid sodium was calculated from the coefficient of thermal expansion along the saturation curve (α_{σ}), the temperature derivative of the pressure along the saturation curve (γ_{σ}), and the isothermal compressibility (β_T), with the thermodynamic relation given in Eq. (15). The thermal-expansion coefficient along the saturation curve (α_{σ}) is defined in Eq. (16) in terms of the liquid density. The liquid density is given by Eq. (1). The temperature derivative of the pressure along the saturation curve (γ_{σ}) is given in Eqs. (6-8). The isothermal compressibility (β_T) is defined by the thermodynamic relation

$$\beta_{T} = \left[\frac{\beta_{S} C_{\sigma} + \left(\frac{T}{\rho_{l}}\right) \alpha_{\sigma} \left(\alpha_{\sigma} + \beta_{S} \gamma_{\sigma}\right)}{C_{\sigma} - \left(\frac{T}{\rho_{l}}\right) \gamma_{\sigma} \left(\alpha_{\sigma} + \beta_{S} \gamma_{\sigma}\right)} \right] .$$
(19)

In Eq. (19), β_s is the adiabatic compressibility and C_{σ} is the heat capacity along the saturation curve. The adiabatic compressibility is given by

$$\beta_{S} = \beta_{S,m} \frac{\left(1 + \frac{\theta}{b}\right)}{\left(1 - \theta\right)} \quad , \tag{20}$$

with

$$\theta = \frac{(T - T_m)}{(T_c - T_m)}$$

and

$$b = 3.2682 , T_m = 371 K , T_C = 2503.7 K .$$

The adiabatic compressibility at the melting point, $\beta_{S,m}$, is equal to

$$\beta_{S,m} = 1.717 \times 10^{-4} MPa^{-1}$$
.

Equation (20) for the adiabatic compressibility (β_s) was obtained by fitting the adiabatic compressibilities from the melting point to 1773 K, calculated from the density and speed of sound in liquid sodium (v) using the relation

$$\beta_s = \frac{1}{\rho v^2} \quad , \tag{21}$$

where v is the speed of sound in $m \cdot s^{-1}$ is given by the quadratic equation determined by Fink and Leibowitz⁽⁷⁾ from fitting the available data to the quadratic equation

$$v = 2660.7 - 0.37667 T - 9.0356 \times 10^{-5} T^{2}$$
(22)
for 371 K $\leq T \leq 1773$ K.

Equation (21) is not used for the adiabatic compressibility for the entire temperature range because it will not give the proper behavior at the critical point.

The heat capacity at constant pressure along the saturation curve was calculated from the derivative of the enthalpy of liquid sodium along the saturation curve using the thermodynamic relation

$$C_{\sigma} = \left(\frac{\partial H}{\partial T}\right)_{\sigma} - \frac{\gamma_{\sigma}}{\rho_l} \quad .$$
(23)

The enthalpy of liquid sodium in $kJ \cdot kg^{-1}$, is

$$H(l, T) - H(s, 298.15) = -365.77 + 1.6582 T - 4.2395 \times 10^{-4} T^{2} + 1.4847 \times 10^{-7} T^{3} + 2992.6 T^{-1}$$
(24)

for 371
$$K \le T \le 2000 K$$

Above 2000 K, the enthalpy of liquid sodium relative to the solid at 298.15 K is the average enthalpy minus one half the enthalpy of vaporization. In $kJ\cdot kg^{-1}$, the average enthalpy is given by

$$H(AVG, T) - H(s, 298.15) = E + FT$$
for 2000 $K \le T \le 2503.7 K$,
$$(25)$$

where

$$E = 2128.4$$
,
 $F = 0.86496$.

The enthalpy of vaporization, ΔH_{e} , in kJ·kg⁻¹, is given by Eq. (5).

In the data analyses by Shpil'rain et al.⁽²⁾ and by Bystrov et al.,⁽⁶⁾ the coefficient of thermal expansion at constant pressure (α_p) was approximated by the coefficient of thermal expansion along the saturation curve (α_o) . Assessments by Hornung⁽¹⁾ and by Fink and Leibowitz⁽⁷⁾ calculated the instantaneous volumetric thermal-expansion coefficient at constant pressure (α_p) by including the term $(\beta_T \gamma_o)$ in Eq. (15). Results from these four assessments are shown in Fig. 1.3-10. The thermal-expansion coefficient that corresponds to Shpil'rain's cubic approximation to the density has been included in Fig. 1.3-10. It is labeled "S-approx" in the legend. Deviations of these assessments relative to the recommended values, expressed as a percent, are shown in Fig. 1.3-11. The deviations are defined as

Deviations =
$$\left(\frac{\left[\alpha_{p}(Other) - \alpha_{p}(Recommended)\right] 100\%}{\alpha_{p}(Recommended)}\right)$$

Because the equations used by Bystrov et al. and Shpil'rain et al. give values of the thermal-expansion coefficient that are identical to three significant figures, values from these assessments cannot be distinguished on these graphs. The thermal-expansion coefficient given by Hornung agrees within 3% with the recommended values for the entire temperature range given by Hornung (371 to 2000 K). At the melting point, values from the assessments of Bystrov et al. and Shpil'rain et al. are lower than the recommended values by as much as 19%. From 500 through 2400 K, values from these two assessments are within 8.2% of the recommended values. At 2500 K, they differ from recommended values by 82%. Agreement of all assessments are within 9% for the temperature range 500 to 1400 K. Deviations of the values given by Fink and Leibowitz increase with increasing temperature above 1400 K and reach 33% at 2100 K. At 2500 K, the Fink

and Leibowitz values differ by -31%. The similarity in behavior of the deviations of values from Fink and Leibowitz and from the approximation given by Shpil'rain et al. (S-approx) is due to the use of cubic polynomials to represent the density up to 1600 K in both assessments. Above 1600 K, an empirical equation with proper behavior at the critical point was used by Fink and Leibowitz. However, Fink and Leibowitz's use of a higher critical temperature, leads to disagreement at temperatures near the critical temperature because the temperature derivative of the density must approach infinity at a higher temperature in the 1979 assessment by Fink and Leibowitz. The percent deviations of the thermal-expansion coefficient calculated from the cubic polynomial approximation by Shpil'rain et al. (S-approx) become increasingly negative with increasing temperature. At 2500 K, values from the S-approximation differ by -98%. The large deviations of the values from calculations by Bystrov et al. and by Shpil'rain et al. near the critical point arise from the use of a polynomial expression to represent the density. The thermal-expansion coefficient is related to the temperature derivative of the density. Thus, as the slope of the density approaches infinity at the critical temperature, the thermal-expansion coefficient becomes very large. The derivative of the polynomials used to represent the density do not have this behavior near the critical point.

Thermal-Expansion Coefficient for Sodium Vapor — The instantaneous volumetric thermal-expansion coefficient for sodium vapor was calculated from the coefficient of thermal expansion along the saturation curve for sodium vapor $(\alpha_{\sigma})_{g}$, the temperature derivative of the pressure along the saturation curve (γ_{σ}) and the thermal-pressure coefficient (γ_{V}) using Eq. (17). Below 1600 K, the thermal-pressure coefficient was calculated using the quasi-chemical approximation.⁽⁹⁾ Values calculated via the quasi-chemical approximation, shown in Fig. 1.3-12, were fit to an equation so that a functional form is available for calculation of all the vapor properties. This equation for γ_{V} in MPa·K⁻¹ is

$$\gamma_{V} = \left(-\frac{b}{T^{2}} + \frac{c}{T} + d + 2 \ eT \right) \exp\left(a + \frac{b}{T} + c \ln T + dT + eT^{2} \right)$$
(27)
for 371 $K \le T \le 1600 \ K$,

where

$$a = 8.35307,$$

$$b = -12905.6,$$

$$c = -0.45824,$$

$$d = 2.0949 \times 10^{-3},$$

$$e = -5.0786 \times 10^{-7}$$

At the critical point, the thermal-pressure coefficient (γ_V) must equal γ_σ , the slope of the vapor pressure curve. Above 1600 K, the thermal-pressure coefficient was extrapolated to the critical point using the same form of equation used by Fink and Leibowitz:⁽⁷⁾

$$\gamma_{V} = \gamma_{V}^{C} + A \left(1 - \frac{T}{T_{C}} \right)^{\frac{1}{2}} + B \left(1 - \frac{T}{T_{C}} \right)$$
for 1600 K < T < 2500 K ,
$$(28)$$

where

$$\gamma_V^C = \gamma_\sigma^C = 4.6893 \times 10^{-2}$$

$$A = -2.5696 \times 10^{-3} ,$$

$$B = 3.5628 \times 10^{-5} ,$$

$$T_C = 2503.7 K .$$

The superscript or subscript *C* in Eq. (28) denotes the value at the critical temperature (T_c) . The parameters *A* and *B* in Eq. (28) were determined by matching the value and temperature derivative of the thermal-pressure coefficient at 1600 K. The equation fitting the thermal-pressure coefficient below 1600 K and the extrapolation to the critical point are shown in Fig. 1.3-12. The derivative of the vapor pressure, γ_{g} , has been included in the figure.

Instantaneous volumetric thermal-expansion coefficients for sodium vapor are only given in the assessment by Fink and Leibowitz.⁽⁷⁾ Because the differences between the instantaneous volumetric thermal-expansion coefficient at constant pressure (α_p) and the thermal-expansion coefficient along the saturation curve (α_{σ}) are significant for the vapor, α_p cannot be approximated by α_{σ} . Comparisons with values given by Fink and Leibowitz are shown in Fig. 1.3-13. Deviations defined according to Eq. (26) are shown in Fig. 1.3-14. Agreement is within 5% from 400 through 1600 K, and within 10% through 2300 K. The derivative of the vapor density becomes infinite at the critical temperature. Because the recommended critical temperature (2503.7 K) is lower than the one used in the assessment by Fink and Leibowitz (2509.4 K), the deviation becomes large near the critical temperature. At 2500 K, the deviation is -128%.

Uncertainty

The uncertainties for the instantaneous volumetric thermal-expansion coefficients of liquid sodium and sodium vapor have been calculated from the uncertainties in the dependent parameters assuming errors in the dependent parameters are independent. The general equation used is:

$$(\delta \alpha_p)^2 = \sum \left(\frac{\partial \alpha_p}{\partial x_i}\right)^2 (\delta x_i)^2 ,$$
 (29)

where δx_i are the uncertainties in the dependent parameters. To simplify the calculations, the partial derivatives with respect to the dependent parameters have been assumed to be unity. At each temperature, the uncertainty in the instantaneous volumetric thermal-expansion coefficient for liquid sodium was calculated from

$$\left(\delta\alpha_{P}\right)_{l} = \sqrt{4 \left(\delta\rho_{l}\right)^{2} + \left(\delta\beta_{T}\right)^{2} + 4 \left(\delta P\right)^{2}} \quad . \tag{30}$$

The factors of four multiplying the square of the density and vapor pressure uncertainties are from the additional uncertainty due to the dependence on the temperature derivatives of these variables. Uncertainties calculated with Eq. (30) are shown in Table 1.3-5 and included as dotted lines in Fig. 1.3-8. Average values for a given temperature range are given in Table 1.3-5. In Fig. 1.3-8, the calculated uncertainties are smoothed curves which correspond to the tabulated uncertainties at the limits of the temperature intervals. The uncertainties increase with increasing temperature from 10% at the melting point to 85% at the critical temperature. These estimates are in accord with estimates given by Fink and Leibowitz.⁽⁷⁾ They are sufficiently large to include the deviations between various recommendations except for the 19% deviation at 371 K of the values given by Bystrov et al. and Shpil'rain et al.

The uncertainties in the instantaneous volumetric thermal-expansion coefficient for sodium vapor have been calculated from the uncertainties in the vapor density and thermalpressure coefficient using the equation

$$\left(\delta\alpha_{P}\right)_{g} = \sqrt{4\left(\delta\rho_{g}\right)^{2} + \left(\delta\gamma_{V}\right)^{2}}$$
 (31)

Uncertainties have been included as dotted lines in Fig. 1.3-9 and in Table 1.3-6. In Fig. 1.3-9, the uncertainties have been smoothed by linear interpolation between values at the limiting temperatures in Table 1.3-6. Uncertainties are 50% at low temperature due to the large low temperature uncertainty in the vapor density. These large uncertainties at low temperature are a result of the large uncertainties in the enthalpy of vaporization at low temperatures. Above 1600 K, the estimated uncertainties increase with temperature to 55% at the critical point. Comparison of these uncertainties with deviations between recommended values from this assessment and that of Fink and Leibowitz⁽⁷⁾ shows that the deviations are significantly less than the estimated uncertainties except above 2500 K. These estimated uncertainties are similar to those estimated by Fink and Leibowitz.

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Fig. 1.3-1 Liquid Sodium and Sodium Vapor Densities



Fig. 1.3-2 Comparison of Recommended Density of Liquid Sodium with Values from Other Assessments



Fig. 1.3-3 Deviations of the Recommended Values for the Density of Liquid Sodium from Values from Other Assessments



Fig 1.3-4 Comparison of Recommended Values for the Density of Sodium Vapor with Values from Other Assessments



Fig. 1.3-5 Deviations of Recommended Vapor Density Values from Values from Other Assessments



Fig 1.3-6 Comparison of Recommended Values for the Density of Sodium Vapor with Values from the SASS Approximation Equation



Fig 1.3-7 Deviations of the SASS Equation for Sodium Vapor Density from the Recommended Values



Fig. 1.3-8 Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient of Liquid Sodium



Fig. 1.3-9 Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient for Sodium Vapor



Fig. 1.3-10 Comparison of Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient of Liquid Sodium with Values from Other Assessments



Fig. 1.3-11 Percent Deviations of the Recommended Thermal-Expansion Coefficient for Liquid Sodium from Values from Other Assessments



Fig. 1.3-12. The Thermal-Pressure Coefficient (γ_V) and the Temperature Derivative of the Vapor Pressure along the Saturation Curve (γ_{σ})



Fig. 1.3-13 Comparison of the Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient of Sodium Vapor with Values from Fink and Leibowitz⁷



Fig. 1.3-14 Percent Deviations of the Recommended Values of the Thermal-Expansion Coefficient of Sodium Vapor from Values from Fink and Leibowitz7