1.5   CRITICAL PARAMETERS

Summary

Recommended values for the critical parameters: critical temperature, critical pressure, and critical density are given in Table 1.5-1. Estimates of uncertainty (approximately 2 σ) are included with each value.

Table 1.5-1   Recommended Values of Critical Parameters

T_C (K)	P_C (MPa)	ρ_C (kg $\cdot$ m^{-3})
2503.7 ± 12	25.64 ± 0.4	219 ± 20

The recommended value for the critical pressure, 25.64 MPa, is from experiments by Bhise and Bonilla[1,2] who measured the vapor pressure from 1255 to 2499.4 K using a pressure tube method. Experimental error in the range of the critical point was 0.7%. The critical pressure is the only critical parameter of sodium for which experimental data are available.

The critical temperature, 2503.7 K, was obtained from the recommended equation for the vapor pressure of saturated sodium. It is the temperature at which the vapor pressure, calculated by Eq. (1), equals the critical pressure, 25.64 MPa. The recommended equation for the vapor pressure of sodium, given by Browning and Potter,[3] is

$$\ln P = 11.9463 - 12633.73/T - 0.4972 \ln T \quad . \tag{1}$$

The critical density, 219 kg$\cdot$m^{-3}, was determined using 2503.7 K for the critical temperature and the fits to the experimental density data from the melting point to 2200 K given by Shpil'rain et al.[4] and by Bystrov et al.[5]

Discussion

Recommended values for critical parameters given in various assessments since 1968 are shown in Table 1.5-2. Note that the critical density of 207 kg$\cdot$m^{-3} given by Bystrov et al.[5] is not consistent with their choice of 2503 K for the critical temperature and the equation given by Bystrov et al. for the density as a function of temperature.

Table 1.5-2　Critical Parameters Recommended in Assessments

T_C (K)	P_C (MPa)	ρ_C (kg · m⁻³)	Author	Year	Ref.
2573 ± 60	34.15 ± 4	206 ± 16	Achener	1968	6
2500	37	180	Vargaftik	1975	7
2503.3	25.64 ± 0.02	—	Bhise & Bonilla	1976	1, 2
2508.7 ± 12.5	25.64 ± 0.02	214.1 ± 0.9	Das Gupta	1977	8
2509.46 ± 24	25.64 ± 0.02	214.1 ± 1	Fink & Leibowitz	1979	9
2508	25.64	230	Thurnay	1982	10
2485 ± 15	24.8 ± 0.5	300 ± 50	Binder	1984	11
2630 ± 50	34 ± 4	205	Petiot & Seiler	1984	12
2497 ± 18	25.22 ± 0.06	211 ± 2	Ohse et al.	1985	13
2505	—	218	Shpil'rain et al.	1985	4
2503.7 ± 12	25.64	—	Browning & Potter	1985	3
2503 ± 50	25.6 ± 1.5	207 ± 30	Bystrov et al.	1990	5

Following the determination of the critical pressure by measurements by Bhise and Bonilla,[1,2] their value of 25.46 MPa was recommended in most assessments and was used for determining the critical temperature. However, Ohse et al.[13] recommended 25.22 MPa for the critical pressure. This is an average of the critical pressures from experiments by Bhise and Bonilla and by Binder.[11] Binder used a flexible bellows technique with a linear transducer to obtain measurements of PVT at high temperature and pressure. He extrapolated his results on superheated sodium to obtain values for the critical parameters and to estimate the vapor pressure on the saturation curve. Binder gives 24.8 ± 0.5 MPa for the critical pressure at a critical temperature of 2485 ± 15 K. The lower critical pressure is consistent with the lower critical temperature. Freyland and Hensel[14] determined properties of potassium at high pressure and high temperature using the same technique as that used by Binder. In the analysis of vapor pressure data and critical parameters for potassium, Browning and Potter[3] found that the critical parameters, determined by Freyland and Hensel from their superheated sample, were inconsistent with critical parameters

determined experimentally by others and inconsistent with the available vapor pressure data for potassium along the saturation curve. Comparison of Binder's extrapolated saturated vapor pressures with other vapor pressure measurements for sodium shows poor agreement. They are consistently high relative to other measurements. Consequently, the determination of the critical pressure by Bhise and Bonilla is recommended rather than that of Binder or the average of the two given by Ohse et al.

Petiot and Seiler[12] recommend a critical temperature of 2630 ± 50 K from their analysis of vapor pressure and vapor density measurements to 2250 K. This temperature is more than 100 K higher than the recommended critical temperature obtained from the vapor pressure equation of Browning and Potter[3] (Eq. [1]) and the critical pressure of Bhise and Bonilla.[1,2] If the critical temperature suggested by Petiot and Seiler is used in the recommended vapor pressure equation, the corresponding pressure is 32 MPa which is within the uncertainty for the critical pressure of 34 ± 4 MPa suggested by Petiot and Seiler.[12]   However, these high critical pressures are inconsistent with the measurements of Bhise and Bonilla. If the critical pressure given by Bhise and Bonilla is used in the vapor pressure equation given by Petiot and Seiler, a critical temperature of 2480 K is obtained. This temperature is within the 50 K uncertainty of the critical temperature suggested by Browning and Potter and recommended here. Thus, the vapor pressure curve of Petiot and Seiler[12] is consistent with that of Browning and Potter[3] but the critical temperature selected by Petiot and Seiler is not consistent with the experimentally determined critical pressure of Bhise and Bonilla.

Fink and Leibowitz[9] recommended 214 kg·m^{-3} for the critical density at the critical temperature 2509.46 K. This value is based on application of a correlation for alkali metals to low temperature density data (up to 1640 K). The correlation derived by Bhise and Bonilla[1] is

$$\frac{\rho_l}{\rho_C} - 1 = 0.9799513 + 2.761335 \left(1 - \frac{T}{T_C} \right) \tag{2}$$

$$for \ \frac{T}{T_C} \leq 0.78 \quad .$$

Bhise and Bonilla derived this correlation to estimate the critical densities of alkali metals from the reduced density data for rubidium. Its validity is based on the close agreement between the saturated reduced densities as functions of the reduced temperatures of cesium and rubidium. Application of the correlation in Eq. (2) assumes that the reduced densities of all alkali metals have the same behavior as that of rubidium. Bhise and Bonilla[1] applied this correlation to five density data of Ewing et al.[15,16] from 1131 to 1639 and obtained 213 kg·m⁻³ for the critical density at the critical temperature 2503.3 K.

More recently Shpil'rain et al.[4] fit all the density data from the melting point to 2201 K to a polynomial equation. Application of the correlation given in Eq. (2) to densities given by Shpil'rain et al. from the melting point to 1300 K using 2503.7 K for the critical temperature gives a nearly constant value of 214 kg·m⁻³ for the critical density. Above 1300 K, critical densities calculated by application of Eq. (2) decrease significantly with temperature. At 1953 K, (T/T_C = 0.78), application of Eq. (2) would give 203 kg·m⁻³ for the density at the critical temperature 2503.7 K. The polynomial equation given by Shpil'rain et al.[4] and the equation recommended by Bystrov et al.[5] are consistent with a critical density near 219 kg·m⁻³ for a critical temperature of 2503.7 K.

Because the polynomial equation given by Shpil'rain et al.[4] is not a proper form for extrapolation to the critical point, the recommended densities of Shpil'rain et al. in the range of experimental data (371 to 2201 K) were refit by a nonlinear least squares procedure using an equation suggested by Hornung[17] that has proper behavior at the critical point:

$$\rho_l = \rho_C + f\left(1 - \frac{T}{T_C}\right) + g\left(1 - \frac{T}{T_C}\right)^h . \tag{3}$$

The parameter h in Eq. (3) was constrained to be between 0.4 and 0.5 based on the behavior of alkali metals in the critical region.[18] Nonlinear least squares fits were performed with this constraint on h and with g and f free parameters using critical densities equal to 214 kg·m⁻³ and 219 kg·m⁻³. Examination of the X^2 deviation for the liquid densities in the temperature range from the melting point to 2200 K showed that the best fits were obtained with the critical density equal to 219 kg·m⁻³ rather than 214 kg·m⁻³. Thus, 219 kg·m⁻³ has been selected for the critical density of sodium at 2503.7 K.

The recommended value for the critical density is higher than the $214\,kg\cdot m^{-3}$ suggested by Fink and Leibowitz.[9] This higher value for the critical density is consistent with the lower value of 2503.7 K for the critical temperature compared to the 2509.46 K recommended by Fink and Leibowitz. It is also consistent with the critical density suggested by Shpil'rain et al.[4] from analysis of the available data on the density of sodium.

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