

THERMODYNAMIC AND TRANSPORT PROPERTIES OF SODIUM LIQUID AND VAPOR

Reactor Engineering Division

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Thermodynamic and Transport Properties of Sodium Liquid and Vapor

by

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THERMODYNAMIC AND TRANSPORT PROPERTIES OF SODIUM LIQUID AND VAPOR

by

J. K. Fink and L. Leibowitz

ABSTRACT

The data on thermodynamic and transport properties of sodium have been reviewed to obtain thermodynamically consistent equations for the thermodynamic and transport properties of saturated sodium liquid and vapor. The recently published Russian recommendations and results of equation of state calculations on thermophysical properties of sodium have been included in this critical assessment. Thermodynamic properties of sodium liquid and vapor that have been assessed include: enthalpy, heat capacity at constant pressure, heat capacity at constant volume, vapor pressure, boiling point, enthalpy of vaporization, density, thermal expansion, adiabatic and isothermal compressibility, speed of sound, critical parameters, and surface tension. Transport properties of liquid sodium that have been assessed include: viscosity and thermal conductivity. For each property, recommended values and their uncertainties are graphed and tabulated as functions of temperature. Detailed discussions of the analyses and determinations of the recommended equations include comparisons with recommendations given in other assessments and explanations of consistency requirements. The rationale and methods used in determining the uncertainties in the recommended values are also discussed.

INTRODUCTION

A complete review of the thermophysical properties of sodium was published in 1985 in the IUPAC Handbook of Thermodynamic and Transport Properties of Alkali Metals.⁽¹⁾ In that handbook, separate research groups reviewed data on each property for all the alkali metals. Consequently, resulting recommendations of related thermodynamic and transport properties were not necessarily consistent. Consistent assessments of sodium properties were completed by Thurnay in 1981⁽²⁾ and by ourselves in 1979.^(3,4) We have performed the present thermodynamically consistent assessment to include new information available since these past reviews.^(2,3,4) Russian recommendations which include new Russian experimental data and theoretical calculations are now available in the open literature.⁽⁵⁾ Data on sodium enthalpy and heat capacity have been recently evaluated and new equations developed.^(6,7) New data on vapor pressure,⁽⁸⁾ critical parameters,^(8,9) and surface tension⁽¹⁰⁾ and new theoretical research relating to the thermal conductivity of alkali metals⁽¹¹⁾ have been included in this assessment.

The goals of this review were: (1) to obtain consistent equations for the thermodynamic and transport properties of sodium liquid and vapor that have proper physical behavior throughout the temperature range from the melting point to the critical point and (2) to assess the uncertainty of these equations as a function of temperature. With the exception of data related to the thermal conductivity, previously assessed data have not been reanalyzed. We have relied on existing statistical fits to experimental data and have examined new data and theories with respect to existing assessments. New equations that give correct physical behavior at limits such as the critical point have been derived to replace polynomial fits that are appropriate only for the limited temperature range of the experimental data. Care has been taken in deriving more than one equation for the entire temperature range so that there is continuity not only for the property being represented but also for the derivatives that are required for calculations off the saturation curve to subcooled or superheated properties.

This report has been organized according property. Thermodynamic properties of sodium liquid and vapor are given in Section 1. Transport properties of sodium liquid are in Section 2. Six subsections under thermodynamic properties cover: (1) enthalpy and heat

capacity, (2) vapor pressure, boiling point, and enthalpy of vaporization, (3) density and thermal expansion, (4) compressibility and speed of sound, (5) critical parameters, and (6) surface tension. Thermal conductivity and viscosity are the two subsections under transport properties. For ease of use as a reference report, each subsection is complete. All equations, graphs, tables, and references needed for each property are given in the subsection on that property so that the reader only interested in one property (e.g. compressibility) need only read the subsection on that property (compressibility). The subsections for each property are divided into three parts: summary, discussion, and uncertainty. The summary consists of the recommended equations and tabulated values. It is given first for each property so that the reader interested only in this information does not need to read the entire subsection on the property. Next, a detailed discussion of the analysis and comparisons with other assessments is given. The uncertainty part gives the basis for determining the uncertainties in the recommended property values.

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1. THERMODYNAMIC PROPERTIES

1.1 ENTHALPY AND HEAT CAPACITY

1.1.1 ENTHALPY

Summary

Recommended values for the enthalpy increments of liquid sodium and sodium vapor relative to the solid at 298.15 K are given in Table 1.1-1 in $\text{kJ}\cdot\text{kg}^{-1}$. CODATA⁽¹⁾ values for the enthalpy of liquid sodium along the saturation curve are recommended for the temperature range 371 to 2000 K. The equation, given by Cordfunke and Konings,⁽²⁾ for the CODATA values for the enthalpy of liquid sodium in $\text{kJ}\cdot\text{kg}^{-1}$, is

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

for 371 K \leq T \leq 2000 K.

Above 2000 K, the law of rectilinear diameters was used to extrapolate the average of the liquid and vapor enthalpies to the critical point. The enthalpy of liquid (vapor) sodium relative to the solid at 298.15 K is the average enthalpy minus (plus) one half the enthalpy of vaporization. In $\text{kJ}\cdot\text{kg}^{-1}$, the average enthalpy is given by

$$H(\text{AVG}, T) - H(s, 298.15) = E + FT \quad (2)$$

for 2000 K \leq T \leq 2503.7 K ,

where

$$E = 2128.4 ,$$

$$F = 0.86496 .$$

Table 1.1-1 Sodium Enthalpy Increment, $H(T) - H(s, 298.15 \text{ K})$

| Temperature (K) | Liquid (kJ · kg ⁻¹) | Vapor (kJ · kg ⁻¹) |
|--------------------|------------------------------------|-----------------------------------|
| 371. | 207. | 4739. |
| 400. | 247. | 4757. |
| 500. | 382. | 4817. |
| 600. | 514. | 4872. |
| 700. | 642. | 4921. |
| 800. | 769. | 4966. |
| 900. | 895. | 5007. |
| 1000. | 1020. | 5044. |
| 1100. | 1146. | 5079. |
| 1200. | 1273. | 5111. |
| 1300. | 1402. | 5140. |
| 1400. | 1534. | 5168. |
| 1500. | 1671. | 5193. |
| 1600. | 1812. | 5217. |
| 1700. | 1959. | 5238. |
| 1800. | 2113. | 5256. |
| 1900. | 2274. | 5268. |
| 2000. | 2444. | 5273. |
| 2100. | 2625. | 5265. |
| 2200. | 2822. | 5241. |
| 2300. | 3047. | 5188. |
| 2400. | 3331. | 5078. |
| 2500. | 3965. | 4617. |
| 2503.7 | 4294. | 4294. |

The enthalpy of vaporization, ΔH_g , in kJ·kg⁻¹, is given by

$$\Delta H_g = 393.37 \left(1 - \frac{T}{T_C} \right) + 4398.6 \left(1 - \frac{T}{T_C} \right)^{0.29302} \quad (3)$$

for $371 \text{ K} \leq T \leq 2503.7 \text{ K}$,

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

The enthalpy of sodium vapor (total vapor over the saturated liquid) was calculated from the sum of the enthalpy of the liquid along the saturation curve and the enthalpy of vaporization given in Eq. (3). Thus, below 2000 K, the enthalpy of the vapor is given by the

sum of Eq. (1) and Eq. (3). Above 2000 K, the enthalpy of the vapor is Eq. (2) plus one half Eq. (3).

Recommended values for the enthalpies of liquid sodium and sodium vapor and the average enthalpy are shown in Fig. 1.1-1. Uncertainty bands have been included up to 2400 K. Above 2400 K, uncertainties in the values for the enthalpies of the liquid and vapor increase rapidly to 12% at 2500 K. Uncertainties for the recommended liquid and vapor enthalpies at a number of temperatures are given in Tables 1.1-2 and 1.1-3, respectively.

Discussion

Liquid — Recommended values for the enthalpy of liquid sodium along the saturation curve are given in $\text{kJ}\cdot\text{kg}^{-1}$ in Table 1.1-1 and in $\text{J}\cdot\text{mol}^{-1}$ in Table 1.1-4. The CODATA recommended value for the molecular weight of the liquid (22.98977 grams/mole) was used to convert from $\text{J}\cdot\text{mol}^{-1}$ to $\text{kJ}\cdot\text{kg}^{-1}$. The recommended values for the enthalpy of liquid sodium from 371 to 2000 K are from the assessment by CODATA.⁽¹⁾ The CODATA values are identical with values tabulated by Glushko et al.⁽³⁾ CODATA values have been recommended in the books by Bystrov et al.⁽⁴⁾ and by Cordfunke and Konings.⁽²⁾ Bystrov et al. state that the CODATA values "...are based primarily on values of enthalpy along the saturation curve, determined by the mixing method in calorimeters of different types."⁽⁴⁾ In the CODATA assessment, the different sets of data were weighted according to the experimental accuracy. Highest weights were given to data of Ginnings et al.,⁽⁵⁾ Shpil'rain et al.,⁽⁶⁾ Fredrickson and Chasanov,⁽⁷⁾ and Martin.⁽⁸⁾ Data from other measurements were included in the CODATA assessment but at a lesser weight. The CODATA equation has been selected rather than the values from the JANAF Tables⁽⁹⁾ or the SGTE equation⁽¹⁰⁾ (equation recommended by the Scientific Group Thermodata Europe) because the CODATA equation has a simpler form and has been recommended in other reputable reviews.^(2,4)

Equation (1), which reproduces the CODATA values for the enthalpy of liquid sodium, should not be extrapolated to the critical temperature (2503.7 K) because use of this equation above 2300 K leads to unphysical values of related thermodynamic properties; i.e., isothermal compressibility, thermal-expansion coefficient. Therefore, values for the enthalpy of liquid sodium above 2000 K were calculated from extrapolation of the average of the liquid and vapor enthalpies to the critical point using the law of rectilinear diameters. For $T \geq 2000$ K, the average enthalpy in $\text{kJ}\cdot\text{kg}^{-1}$ is defined in Eq. (2). The constants E and F in

Table 1.1-2 Estimated Uncertainty in the Recommended Values for Enthalpy of Liquid Sodium

| Temperature (K) | $H(l, T) - H(s, 298.15)$ (kJ · kg ⁻¹) | Uncertainty, $\left(\frac{\delta H_l}{H_l}\right)$ (%) |
|--|--|---|
| 371 1000 ^(a) 1600 ^(a) 2000 ^(a) | $-365.77 + 1.6582 T - 4.2375 \times 10^{-4} T^2$ $+ 1.4847 \times 10^{-7} T^3 + 2992.6 T^{-1}$ | 1. 1. 1.5 2. |
| 2050 2400 ^(a) 2500 ^(a) | $2128.4 + 0.86496 T - \frac{1}{2} \Delta H_g$ where $\Delta H_g = 393.37 \left(1 - \frac{T}{T_C}\right)$ $+ 4398.6 \left(1 - \frac{T}{T_C}\right)^{0.29302}$ | 10. 10. 12. |

^(a)Uncertainty is assumed to vary linearly with temperature between these temperatures.

$$1000 \text{ to } 1600 \text{ K,} \quad \left(\frac{\delta H_l}{H_l}\right) (\%) = 0.17 + 8.3 \times 10^{-4} T$$

$$1600 \text{ to } 2000 \text{ K,} \quad \left(\frac{\delta H_l}{H_l}\right) (\%) = -0.5 + 1.25 \times 10^{-3} T$$

$$2400 \text{ to } 2500 \text{ K,} \quad \left(\frac{\delta H_l}{H_l}\right) (\%) = -38 + 0.02 T$$

Table 1.1-3 Estimated Uncertainty in the Recommended Values for Enthalpy of Sodium Vapor

| Temperature (K) | $H(g, T) - H(s, 298.15)$ (kJ · kg ⁻¹) | Uncertainty, $\left(\frac{\delta H_g}{H_g}\right)^{(a)}$ (%) |
|-----------------|--|---|
| 371 | $H_l + \Delta H_g^{(b)}$ where $H_l = -365.77 + 1.6582 T - 4.2375$ $\times 10^{-4} T^2 + 1.4847 \times 10^{-7} T^3$ $+ 2992.6 T^{-1}$ | 1. |
| 1000 | | 1. |
| 1400 | | 1.5 |
| 1600 | | 2.8 |
| 1800 | | 4. |
| 2000 | | 4. |
| 2050 | $H_{AVG} + \frac{1}{2} \Delta H_g$ where $H_{AVG} = 2128.4 + 0.86496 T$ | 10. |
| 2400 | | 10. |
| 2500 | | 12. |

^(a)T < 2000 K,

$$(\delta H_g)^2 = (\delta H_l)^2 + (\delta \Delta H_g)^2$$

2000 < T < 2400 K,

$$(\delta H_g)^2 = (\delta H_{AVG})^2 + \left(\frac{\delta \Delta H_g}{4}\right)^2$$

2400 to 2500 K,

$$\left(\frac{\delta H_g}{H_g}\right) \text{ is assumed to vary linearly with}$$

$$\left(\frac{\delta H_g}{H_g}\right) (\%) = -38 + 0.02 T$$

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

Table 1.1-4 The Enthalpy and Heat Capacity of Solid and Liquid Sodium Per Mole of Sodium^(a)

| Temperature (K) | H(T) - H(s, 298.15) (J · mol ⁻¹) | C _p ^(b) (J · mol ⁻¹ · K ⁻¹) |
|--------------------|---|---|
| 298.15 | 0 | 28.230 |
| 300. | 52 | 28.262 |
| 371. | 2154 | 31.509 |
| 371. | 4752 | 31.799 |
| 400. | 5670 | 31.532 |
| 500. | 8779 | 30.659 |
| 600. | 11807 | 29.921 |
| 700. | 14769 | 29.353 |
| 800. | 17684 | 28.973 |
| 900. | 20570 | 28.787 |
| 1000. | 23448 | 28.799 |
| 1100. | 26337 | 29.012 |
| 1200. | 29257 | 29.427 |
| 1300. | 32229 | 30.045 |
| 1400. | 35273 | 30.866 |
| 1500. | 38409 | 31.891 |
| 1600. | 41658 | 33.120 |
| 1700. | 45040 | 34.553 |
| 1800. | 48575 | 36.190 |
| 1900. | 52285 | 38.032 |
| 2000. | 56188 | 40.078 |

^(a)Table is based on CODATA values from Cordfunke and Konings.⁽²⁾

^(b)C_p tabulated here is the derivative of the enthalpy along the saturation curve. It deviates from the values given in Table 1.1-5 by less than 0.3% below 1900 K, 0.39% at 1900 K, and 1.15% at 2000 K.

Eq. (2) were determined by matching the values of the liquid enthalpy and its first derivative with respect to temperature at 2000 K. This is preferred to determination of constants by a linear fit to the average enthalpy from 371 to 2000 K, because matching at 2000 K prevents discontinuities in related thermodynamic properties. Because the average enthalpy (shown in Fig. 1.1-1) is not exactly a straight line, greatest deviations between values calculated with Eq. (2) and the average enthalpy occur at low temperatures. At 400 K deviations are 1.1%, whereas above 1600 K, deviations are less than 0.03%. The enthalpies of liquid sodium and sodium vapor were calculated above 2000 K by, respectively, subtracting and adding one half of the enthalpy of vaporization (Eq. [3]) to the average enthalpy defined in Eq. (2).

The recommended values of the enthalpies of liquid sodium along the saturation curve are in good agreement with values from the JANAF Tables,⁽⁹⁾ values calculated from the equation recommended by the Scientific Group Thermodata Europe (SGTE),⁽¹⁰⁾ and values from two assessments by Fink and Leibowitz,^(11,12) as shown in Fig. 1.1-2. Deviations from recommended values, expressed as a percent defined as

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

are shown in Fig. 1.1-3. Lines have been included as a guide between the points at which the percent deviations were calculated. The recommended values agree within 0.4% with values to 1600 K given in the JANAF Tables.⁽⁹⁾ Maximum deviations from the two assessments by Fink and Leibowitz are about 1%. Better agreement is found below 1600 K with the 1979 assessment⁽¹¹⁾ (F&L 79 in Fig. 1.1-3) than with the one from the IUPAC handbook,⁽¹²⁾ edited by Ohse (F&L-Ohse), because the latter assessment included data that was given little weight in the CODATA assessment. Comparison with values calculated using the equation recommended by SGTE gave the largest deviations. Values from the six-term SGTE equation deviated from the CODATA values by 1.3% at 2000 K and from the recommended equations by 1.5% at 2200 K.

Vapor — The enthalpy of the vapor over saturated liquid sodium has been calculated as the sum of the enthalpy of liquid sodium on the saturation curve and the enthalpy of vaporization. Below 2000 K, this is the sum of the liquid enthalpy from the CODATA equation, Eq. (1), and the enthalpy of vaporization, Eq. (3). Above 2000 K, the enthalpy of

sodium vapor is given by the sum of the average of the liquid and vapor enthalpies, Eq. (2), plus one half of the enthalpy of vaporization, Eq. (3). Values are tabulated in $\text{kJ}\cdot\text{kg}^{-1}$ in Table 1.1-1.

The quasi-chemical method of Golden and Tokar⁽¹³⁾ has been used in the calculation of the enthalpy of vaporization up to 1600 K. This quasi-chemical approach assumed that the vapor is composed of monomers, dimers, and tetramers. The equilibrium constants of Stone et al.⁽¹⁴⁾ for the monomer, dimer, and tetramer were used in the determination of the enthalpy of vaporization up to 1600 K. These calculated enthalpies of vaporization were fit to an equation, Eq. (3), which has proper behavior at the critical temperature. Thus, Eq. (3) represents the enthalpy of vaporization for the entire liquid range.

In recent equation of state calculations by Vargaftik and Voljak⁽¹⁵⁾ and by Bystrov et al.,⁽⁴⁾ the vapor was assumed to be composed of monomers, dimers, and positive ions. The equations obtained by the quasi-chemical method would be equivalent to these equations of state using virial expansions with the equilibrium constants replaced by group integrals if identical components of the gas had been assumed. Assuming different components led to different diatomic fractions and different average molecular weights as a function of temperature. Note that different assumptions in the formulation of the equations of state by Vargaftik and Voljak⁽¹⁵⁾ and by Bystrov et al.⁽⁴⁾ also led to differences in the diatomic fractions and molecular weights as a function of temperature. Consequently, comparisons for the vapor should be made with respect to mass not mole because the mass is the same for the different formulations.

Recommended values of the enthalpy of sodium vapor and those given by Vargaftik and Voljak,⁽¹⁵⁾ by Bystrov et al.,⁽⁴⁾ and by Fink and Leibowitz⁽¹¹⁾ are shown in Fig. 1.1-4. Comparison of the recommended values for sodium vapor enthalpy with values calculated by Vargaftik and Voljak, and by Bystrov et al. using equations of state show good agreement. Good agreement was also obtained with values from Fink and Leibowitz,⁽¹¹⁾ which were calculated using the quasi-chemical method for the heat of vaporization below 1644 K and an extrapolation to the critical point above 1644 K. Deviations from the recommended values, expressed as percents defined as in Eq. (4), are shown in Fig. 1.1-5. Lines have been included between the calculated points to guide the eye. This graph shows that deviations of enthalpies calculated by Vargaftik and Voljak and those tabulated by Bystrov et al. are within 1.2%.

Enthalpies given by Fink and Leibowitz⁽¹¹⁾ differ by 1.02% or less up to 2400 K and by 3% at 2500 K. The larger deviations as the critical point is reached are expected because of differences in the critical temperature in the two assessments. Fink and Leibowitz⁽¹¹⁾ used 2504.9 K for the critical temperature. The critical temperature in this analysis is 2503.7 K.

Uncertainty

The uncertainties in the recommended CODATA values for the enthalpy of liquid sodium below 2000 K have been estimated from uncertainties given by Bystrov et al.⁽⁴⁾ and from deviations of other recommended equations. The uncertainties in the CODATA values for enthalpy of sodium are: 0.3% at 298 K, 0.5% at 1000 K, and 1.5% at 2000 K. Comparison of the deviations from other assessments with the recommended values for liquid sodium enthalpy (Fig. 1.1-3) indicate that deviations on the order of 1% occur below 1000 K because of deviations in different data used in the different analyses. Thus, an estimated uncertainty of 1% below 1000 K is consistent with deviations from available data. The uncertainty at 1600 K is estimated as 1.5% and that at 2000 K is estimated as 2%. Uncertainties are assumed to increase linearly with temperature from 1000 to 1600 K and from 1600 to 2000 K. These linear equations are given in Table 1.1-2.

Uncertainties for the liquid above 2000 K 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 quantity (δH) is given by

$$(\delta H)^2 = \sum \left(\frac{\partial H}{\partial x_i} \right)^2 (\delta x_i)^2 \quad , \quad (5)$$

where δx_i are the uncertainties in the dependent parameters. Thus, above 2000 K, the uncertainty in the liquid enthalpy (δH) is a function of the uncertainty in the average enthalpy (δH_{AVG}) and the uncertainty in the enthalpy of vaporization ($\delta \Delta H_g$):

$$(\delta H)^2 = (\delta H_{AVG})^2 + \frac{1}{4}(\delta \Delta H_g)^2 \quad . \quad (6)$$

The uncertainty in the liquid enthalpy varies from about 10% in the 2000 to 2400 K range to 12% at 2500 K. Between 2400 and 2500 K, calculated uncertainties in enthalpy are approximated by a linear equation in temperature that is given in Table 1.1-2.

For temperatures below 2000 K, the uncertainty in the vapor enthalpy (δH_g) is the square root of the sum of the squares of the uncertainties in the liquid enthalpy and in the enthalpy of vaporization:

$$\delta H_g = \sqrt{(\delta H_l)^2 + (\delta \Delta H_g)^2} . \quad (7)$$

Above 2000 K, the uncertainty in the vapor enthalpy (δH_g) is identical to the uncertainty in the liquid enthalpy and is given by Eq. (6). Calculated uncertainties in the enthalpy of sodium vapor are 1% from 371 to 1000 K. They increase to 1.5% at 1400 K. From 1400 to 2000 K, calculated uncertainties are tabulated every 200 K in Table 1.1-3. Comparison of calculated uncertainties with deviations of other assessments from the recommended values for the enthalpy of sodium vapor (graphed in Fig. 1.1-5) shows that most assessments are within the 1% uncertainty below 1000 K. Deviations from recommendations are significantly less than the estimated uncertainties above 2000 K.

1.1.2 HEAT CAPACITY

Summary

Recommended values for the heat capacities at constant pressure and the heat capacities at constant volume for the liquid and vapor in $\text{kJ}\cdot\text{kg}^{-1}$ are given in Tables 1.1-5 and Table 1.1-6. Values in $\text{kJ}\cdot\text{mol}^{-1}$ for the heat capacity at constant pressure have been included in Table 1.1-4. Liquid heat capacities are shown in Fig. 1.1-6; vapor heat capacities are shown in Fig. 1.1-7. Estimates of the uncertainties in the tabulated values are given in Tables 1.1-7 through 1.1-10.

Heat Capacity at Constant Pressure, C_p — The heat capacities at constant pressure of liquid sodium and sodium vapor have been calculated from the heat capacity along the saturation curve (C_σ) using the thermodynamic relation

$$C_p = C_\sigma + \left(\frac{T \alpha_p \gamma_\sigma}{\rho} \right) , \quad (8)$$

Table 1.1-5 Heat Capacity of Liquid Sodium

| Temperature (K) | C_p (kJ · kg ⁻¹ · K ⁻¹) | C_v (kJ · kg ⁻¹ · K ⁻¹) |
|--------------------|---|---|
| 371. | 1.383 | 1.262 |
| 400. | 1.372 | 1.241 |
| 500. | 1.334 | 1.170 |
| 600. | 1.301 | 1.104 |
| 700. | 1.277 | 1.045 |
| 800. | 1.260 | 0.994 |
| 900. | 1.252 | 0.951 |
| 1000. | 1.252 | 0.914 |
| 1100. | 1.261 | 0.885 |
| 1200. | 1.279 | 0.862 |
| 1300. | 1.305 | 0.844 |
| 1400. | 1.340 | 0.830 |
| 1500. | 1.384 | 0.819 |
| 1600. | 1.437 | 0.811 |
| 1700. | 1.500 | 0.803 |
| 1800. | 1.574 | 0.795 |
| 1900. | 1.661 | 0.784 |
| 2000. | 1.764 | 0.768 |
| 2100. | 1.926 | 0.768 |
| 2200. | 2.190 | 0.791 |
| 2300. | 2.690 | 0.872 |
| 2400. | 4.012 | 1.172 |
| 2469. | 8.274 | 2.463 |
| 2500. | 39.279 | 16.371 |

Table 1.1-6 Heat Capacity of Sodium Vapor

| Temperature (K) | C_p (kJ · kg ⁻¹ · K ⁻¹) | C_v (kJ · kg ⁻¹ · K ⁻¹) |
|--------------------|---|---|
| 400. | 0.86 | 0.49 |
| 500. | 1.25 | 0.84 |
| 600. | 1.80 | 1.31 |
| 700. | 2.28 | 1.71 |
| 800. | 2.59 | 1.93 |
| 900. | 2.72 | 1.98 |
| 1000. | 2.70 | 1.92 |
| 1100. | 2.62 | 1.81 |
| 1200. | 2.51 | 1.68 |
| 1300. | 2.43 | 1.58 |
| 1400. | 2.39 | 1.51 |
| 1500. | 2.36 | 1.44 |
| 1600. | 2.34 | 1.39 |
| 1700. | 2.41 | 1.38 |
| 1800. | 2.46 | 1.36 |
| 1900. | 2.53 | 1.33 |
| 2000. | 2.66 | 1.30 |
| 2100. | 2.91 | 1.30 |
| 2200. | 3.40 | 1.34 |
| 2300. | 4.47 | 1.44 |
| 2400. | 8.03 | 1.76 |
| 2500. | 417.03 | 17.03 |

Table 1.1-7 Estimated Uncertainties in the Recommended Values for Heat Capacity at Constant Pressure of Liquid Sodium

| Temperature (K) | C_P (kJ · kg ⁻¹ · K ⁻¹) | Uncertainty, $\left(\frac{\delta C_P}{C_P}\right)$ (%) |
|-----------------|---|---|
| 371 ≤ T ≤ 1000 | $C_P = C_\sigma + \left(\frac{T \alpha_P \gamma_\sigma}{\rho}\right)$ | 2 |
| 1000 < T ≤ 1600 | | 3 |
| 1600 < T ≤ 2000 | | 20 |
| 2000 < T ≤ 2200 | | 30 |
| 2200 < T ≤ 2400 | | 35 |
| 2400 < T ≤ 2503 | | 50 |

Table 1.1-8 Estimated Uncertainties in the Recommended Values for the Heat Capacity at Constant Volume of Liquid Sodium

| Temperature (K) | C_V (kJ · kg ⁻¹ · K ⁻¹) | Uncertainty, $\left(\frac{\delta C_V}{C_V}\right)$ (%) |
|-----------------|---|---|
| 371 ≤ T ≤ 1000 | $C_V = C_P \left(\frac{\beta_S}{\beta_T}\right)$ | 5 |
| 1000 < T ≤ 1600 | | 10 |
| 1600 < T ≤ 2000 | | 40 |
| 2000 < T ≤ 2200 | | 65 |
| 2200 < T ≤ 2400 | | 80 |
| 2400 < T ≤ 2503 | | 90 |

Table 1.1-9 Estimated Uncertainties in the Recommended Values for the Heat Capacity at Constant Pressure of Sodium Vapor

| Temperature (K) | C_P ($\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) | Uncertainty, $\left(\frac{\delta C_P}{C_P}\right)$ (%) |
|-----------------------|---|--|
| $371 \leq T \leq 500$ | $C_P = C_\sigma + \left(\frac{T \alpha_P \gamma_\sigma}{\rho_g}\right)$ | 50 |
| $500 < T \leq 1000$ | | 20 |
| $1000 < T \leq 1600$ | | 15 |
| $1600 < T \leq 2000$ | | 35 |
| $2000 < T \leq 2200$ | | 50 |
| $2200 < T \leq 2400$ | | 60 |
| $2400 < T \leq 2503$ | | 65 |

where α_p is the thermal-expansion coefficient, γ_σ is the partial derivative of the pressure with respect to temperature along the saturation curve, and ρ is the density. These thermodynamic properties are defined in the discussion section.

Heat Capacity at Constant Volume, C_V

Liquid — The heat capacity at constant volume of saturated liquid sodium was calculated from the heat capacity at constant pressure and the adiabatic and isothermal compressibilities (β_S, β_T) using the thermodynamic relation

$$C_V = C_P \left(\frac{\beta_S}{\beta_T}\right) . \quad (9)$$

Table 1.1-10 Estimated Uncertainties in the Recommended Values for the Heat Capacity at Constant Volume of Sodium Vapor

| Temperature (K) | C_p (kJ · kg ⁻¹ · K ⁻¹) | Uncertainty, $\left(\frac{\delta C_V}{C_V}\right)$ (%) |
|--------------------|---|---|
| 371 ≤ T ≤ 500 | $C_V = C_P - \left(\frac{T \alpha_P \gamma_V}{\rho_g}\right)$ | 75 |
| 500 < T ≤ 1000 | | 30 |
| 1000 < T ≤ 1600 | | 20 |
| 1600 < T ≤ 2000 | | 35 |
| 2000 < T ≤ 2200 | | 45 |
| 2200 < T ≤ 2400 | | 55 |
| 2400 < T ≤ 2503 | | 65 |

Vapor — The heat capacity at constant volume of saturated sodium vapor was calculated using the thermodynamic relation

$$C_V = C_P - \left(\frac{T \alpha_P \gamma_V}{\rho_g}\right), \quad (10)$$

where C_p , α_p , and ρ_g are, respectively, the heat capacity at constant pressure, the thermal-expansion coefficient, and the density for sodium vapor, and γ_v is the thermal-pressure coefficient. Equations for these thermodynamic properties are given below in the discussion of heat capacity.

Discussion

Heat Capacity at Constant Pressure, C_p — The liquid and vapor heat capacities at constant pressure were calculated from the thermodynamic relation given in Eq. (8). The heat capacity along the saturation curve, C_s , is defined as

$$C_{\sigma} = T \left(\frac{\partial S}{\partial T} \right)_{\sigma} . \quad (11)$$

It is related to the partial derivative of the enthalpy along the saturation curve by

$$C_{\sigma} = \left(\frac{\partial H}{\partial T} \right)_{\sigma} - \left(\frac{\gamma_{\sigma}}{\rho} \right) , \quad (12)$$

where

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

In Eqs. (8, 11-13) P is the vapor pressure, ρ is the liquid (vapor) density, and H is the liquid (vapor) enthalpy, given above. The vapor pressure, P , is given by an equation derived by Browning and Potter:⁽¹⁶⁾

$$\ln P = a + \frac{b}{T} + c \ln T . \quad (14)$$

Then γ_{σ} the temperature derivative of the pressure along the saturation curve is

$$\gamma_{\sigma} = \left(-\frac{b}{T^2} + \frac{c}{T} \right) \exp \left(a + \frac{b}{T} + c \ln T \right) , \quad (15)$$

and the coefficients in Eqs. (14, 15) for P in MPa and T in kelvins are defined as

$$\begin{aligned} a &= 11.9463 , \\ b &= -12633.7 , \\ c &= -0.4672 . \end{aligned}$$

C_p Liquid— For saturated liquid sodium, the thermal-expansion coefficient (α_p) was calculated from the thermodynamic relation

$$\alpha_p = \alpha_{\sigma} + \beta_T \gamma_{\sigma} , \quad (16)$$

where β_T is the isothermal compressibility and α_{σ} is the coefficient of thermal expansion along the saturation curve defined as

$$\alpha_{\sigma} = - \left(\frac{1}{\rho_l} \right) \left(\frac{\partial \rho_l}{\partial T} \right)_{\sigma} . \quad (17)$$

The liquid density ρ_l is given by

$$\rho = \rho_C + f \left(1 - \frac{T}{T_C} \right) + g \left(1 - \frac{T}{T_C} \right)^h , \quad (18)$$

where the parameters for density in $\text{kg}\cdot\text{m}^{-3}$ and temperature (T) in kelvins are

$$\begin{aligned} \rho_C &= 219., \\ f &= 275.32, \\ g &= 511.58, \\ h &= 0.5, \end{aligned}$$

and ρ_C is the density at the critical temperature, $219 \text{ kg}\cdot\text{m}^{-3}$.

The isothermal compressibility (β_T) is defined by the thermodynamic relation

$$\beta_T = \left[\frac{\beta_S C_{\sigma} + \left(\frac{T}{\rho_l} \right) \alpha_{\sigma} (\alpha_{\sigma} + \beta_S \gamma_{\sigma})}{C_{\sigma} - \left(\frac{T}{\rho_l} \right) \gamma_{\sigma} (\alpha_{\sigma} + \beta_S \gamma_{\sigma})} \right] , \quad (19)$$

where β_S is the adiabatic compressibility given by

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

with

$$\theta = \left[\frac{(T - T_m)}{(T_C - T_m)} \right] ,$$

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

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

and

$$b = 3.2682 ,$$

$$T_m = 371 \text{ K} ,$$

$$T_C = 2503.7 \text{ K} .$$

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

$$\beta_s = \left(\frac{1}{\rho v^2} \right) , \quad (21)$$

where the speed of sound in $\text{m}\cdot\text{s}^{-1}$ is given by the quadratic equation determined from the fit to the available data by Fink and Leibowitz:⁽¹¹⁾

$$v = 2660.7 - 0.37667 T - 9.0356 \times 10^{-5} T^2 \quad (22)$$

for 371 K \leq T \leq 1773 K .

At high temperatures, the heat capacity at constant pressure for liquid sodium differs from the heat capacity along the saturation curve (C_σ) and from the partial derivative of the enthalpy along the saturation curve. From Eqs. (11, 12), the heat capacity at constant pressure is related to the partial derivative with respect to temperature of the enthalpy along the saturation curve ($\partial H/\partial T)_\sigma$ by

$$C_p = \left(\frac{\partial H}{\partial T} \right)_\sigma + \left(\frac{\gamma_\sigma}{\rho} \right) (T \alpha_p - 1) . \quad (23)$$

The heat capacity at constant pressure (C_p), the heat capacity along the saturation curve (C_σ), and the partial derivative, with respect to temperature of the enthalpy along the saturation curve, are shown for liquid sodium in Fig. 1.1-8. At about 1900 K, $T \alpha_p$ becomes greater than unity and the heat capacity at constant pressure becomes greater than the partial derivative of the enthalpy along the saturation curve. Deviations of C_σ and $(\partial H/\partial T)_\sigma$ from C_p increase as the critical temperature is approached, as shown by the deviation plot in Fig. 1.1-9.

Values of C_p tabulated by CODATA,⁽¹⁾ are just the first term in Eq. (23); i.e., the derivative of the enthalpy along the saturation curve. Cordfunke and Konings,⁽²⁾ and Bystrov et al.⁽⁴⁾ tabulate the CODATA values with no correction at high temperatures. The JANAF Tables⁽⁹⁾ give heat capacities only to 1600 K. Up to this temperature there is no significant difference between the heat capacity at constant pressure and the temperature derivative of the enthalpy along the saturation curve. Heat capacities at constant pressure were given by Fink and Leibowitz⁽¹¹⁾ to the critical point using the appropriate thermodynamic relations. The values recommended in this assessment are compared to those from Fink and Leibowitz, the CODATA values, and the JANAF values in Fig. 1.1-10. Deviations defined as

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

are shown in Fig. 1.1-11. Deviations of the CODATA values from those recommended are less than 0.3% up to 1900 K, 0.39 % at 1900 K, and 1.15% at 2000 K. Deviations of heat capacities given in the JANAF tables are within 1.8%. Values recommended by Fink and Leibowitz deviate from current recommendations by less than 0.8% up to 1400 K. Figure 1.1-11 shows that above 1300 K, percent deviations increase with temperature to 3% at 1900 K, 4% at 2200 K, and 8% at 2400 K. At 2500 K, deviations are 46%. These large deviations are related to the increase in C_p as the critical temperature is reached and the different critical temperatures in the two assessments. The critical temperature in the Fink and Leibowitz assessment was 2509.4 K, whereas in this assessment the critical temperature is 2503.7 K.

C_p Vapor — The heat capacity at constant pressure for sodium vapor was calculated from Eq. (8) with the thermodynamic parameters for the vapor defined by Eqs. (11-15). The thermal-expansion coefficient for sodium vapor was calculated from the relation

$$(\alpha_p)_g = \left[\frac{(\alpha_\sigma)_g}{1 - \left(\frac{\gamma_\sigma}{\gamma_v} \right)} \right], \quad (25)$$

where the vapor coefficient of thermal expansion along the saturation curve $(\alpha_\sigma)_g$ is defined as

$$(\alpha_{\sigma})_g = - \left(\frac{1}{\rho_g} \right) \left(\frac{\partial \rho_g}{\partial T} \right)_{\sigma} . \quad (26)$$

The vapor density was calculated from the enthalpy of vaporization, the derivative of the pressure, and the liquid density using the relation

$$\rho_g = \left(\frac{\Delta H_g}{T\gamma_{\sigma}} + \frac{1}{\rho_l} \right)^{-1} . \quad (27)$$

In Eq. (25), γ_v is the thermal-pressure coefficient. Below 1600 K, the thermal-pressure coefficient was calculated using the quasi-chemical approximation.⁽¹³⁾ Values calculated via the quasi-chemical approximation, shown in Fig. 1.1-12, 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

$$\gamma_v = \left(-\frac{b}{T^2} + \frac{c}{T} + d + 2eT \right) \exp \left(a + \frac{b}{T} + c \ln T + dT + eT^2 \right) \quad (28)$$

for 371 K ≤ T ≤ 1600 K ,

where

$$\begin{aligned} a &= 8.35307 , \\ b &= -12905.6 , \\ c &= -0.45824 , \\ d &= 2.0949 \times 10^{-3} , \\ e &= -5.0786 \times 10^{-7} . \end{aligned}$$

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:⁽¹¹⁾

$$\gamma_v = \gamma_v^c + A \left(1 - \frac{T}{T_c} \right)^{\frac{1}{2}} + B \left(1 - \frac{T}{T_c} \right)$$

for 1600 K ≤ T ≤ 2500 K ,

where

$$\begin{aligned}\gamma_V^C &= \gamma_\sigma^C = 4.6893 \times 10^{-2} , \\ A &= -2.5696 \times 10^{-3} , \\ B &= 3.5628 \times 10^{-5} , \\ T_C &= 2503.7 \text{ K} .\end{aligned}$$

The superscript or subscript C in Eq. (29) denotes the value at the critical temperature (T_C). The parameters A and B in Eq. (29) 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. 1.1-12. The derivative of the vapor pressure (γ_σ) has been included in the figure.

In Fig. 1.1-13, the recommended values for the heat capacity at constant pressure for sodium vapor above the saturated liquid are compared with values from quasi-chemical calculations by Fink and Leibowitz,⁽¹¹⁾ values from equation of state calculations by Bystrov et al.,⁽⁴⁾ and values from equation of state calculations of Vargaftik and Voljak.⁽¹⁵⁾ At 400 K, the recommended heat capacity is lower than the values given by both the Fink and Leibowitz calculation and that of Vargaftik and Voljak. Between 500 and 700 K, recommended values are above those given by these two calculations. Below 1600 K, values from the calculations of Bystrov et al. are consistently low relative to the recommended values and the other two sets of calculations, as shown in the deviation plots in Fig. 1.1-14. The deviations from the recommended values are defined as in Eq. (24) for liquid heat capacities. The similarity in shape of the deviations over some temperature ranges indicate the possibility of systematic error due to the choice of functional forms for the equations used in the calculation of vapor heat capacities. Deviations with respect to the other calculations are generally on the order of 10% except at low and high temperatures. Agreement on the order of 6% or less was found with values recommended by Fink and Leibowitz for the 700 to 1600 K temperature range. For temperatures up to 2200 K, agreement was on the order of or less than 10%. However, at 2500 K, values deviated by 56% due to different values in the critical temperature and the increase in heat capacity as the critical temperature is approached. The large deviations of the low temperature values given by Fink and Leibowitz and those recommended arise from differences in the derivative of the vapor enthalpies at low temperatures, shown in Fig. 1.1-15. The significant differences at low temperatures arise from differences in the contribution to the

derivative from the enthalpy of vaporization. Although both calculations used the quasi-chemical method to obtain values for the enthalpy of vaporization below 1600 K, Fink and Leibowitz⁽¹¹⁾ obtained the derivative by numerical differentiation, whereas here the functional fit was differentiated. Use of a functional form to represent the thermal-pressure coefficient rather than the values from the quasi-chemical approximation also increased the differences between these calculations.

C_V Liquid — The recommended values for the heat capacity at constant volume of liquid sodium are shown in Fig. 1.1-16 along with values recommended in the assessment by Fink and Leibowitz.⁽¹¹⁾ Figure 1.1-16 shows that differences in the recommended values from the two assessments increase with temperature. This is due to the different critical temperatures in the two assessments and increases in deviations of dependent parameters with temperature in the two assessments. Deviations are within 2% up to 1200 K. At 1800 K, recommended values differ by 20%. Differences are on the order of 50% at temperatures equal or greater than 2200 K.

C_V Vapor — Recommended values for the heat capacity at constant volume for sodium vapor are shown in Fig. 1.1-17 along with values recommended in the assessments by Fink and Leibowitz,⁽¹¹⁾ by Bystrov et al.⁽⁴⁾ and by Vargaftik and Voljak.⁽¹⁵⁾ Deviations of these other assessments from the recommended values defined as

$$Deviations = \left(\frac{[C_V(Other) - C_V(Recommended)] 100\%}{C_V(Recommended)} \right) \quad (30)$$

are shown in Fig. 1.1-18. Trends are similar to those for C_p vapor as expected because the two heat capacities are related. However maximum deviations are greater for C_V . As for C_p , values from the equation of state calculation of Bystrov et al. below 1600 K are lower than recommended values and also lower than values from other calculations. The deviations at low temperature from values given by Fink and Leibowitz arise from the same source (derivative of enthalpy of vaporization and thermal-pressure coefficient) as for C_p . Fink and Leibowitz values deviate by +35% at 400 K but by -21% at 500 K. Between 600 and 1600 K, they are within 6%. Between 1600 and 2300 K, they are within 8% but increase to 23% at 2400 K. At 2500 K, Fink and Leibowitz's recommended value deviates by only 5%. Deviations of

Vargaftik and Voljak's values are generally within 5% except for low temperatures where they are as high as 21%. Bystrov's values deviate by as much as 14%.

Ratios of the heat capacity at constant pressure to the heat capacity at constant volume for the vapor are shown in Fig. 1.1-19. Better agreement exists between the different recommendations for the ratio than for the individual heat capacities.

Uncertainties

Because the functional forms of the thermodynamic relations used to calculate the heat capacities are so complex and the dependent parameters are not independent of each other, the square of the uncertainties cannot be simply calculated from the square of the uncertainties of the dependent parameters as was done for enthalpy (Eq. [5]). Consequently, a number of factors were considered in estimating the heat capacity uncertainties. These included: (1) uncertainty estimates given in other assessments, (2) deviations between recommended values from different assessments, (3) calculation of uncertainties from uncertainties assuming no dependence between parameters, and (4) sensitivity of calculated properties to the uncertainties of measured properties which includes calculations of error propagation.

C_p *Liquid* — Bystrov et al.⁽⁴⁾ give the uncertainties for the CODATA heat capacities at constant pressure as 0.1% at 298 K, 3% at 1000 K, and 8% at 2000 K. At low temperatures, recommended values of the heat capacity at constant pressure are identical to the CODATA values, which are just the derivative of the enthalpy increment along the saturation curve. Thus, the main uncertainty in the heat capacity at constant pressure is due to the uncertainty in this derivative. Below 1600 K, the uncertainty was approximated as twice the uncertainty in the enthalpy increment along the saturation curve. At higher temperatures, other uncertainties begin to have some affect but contribute little unless they are large. Equations (8-23) indicate that the heat capacity at constant pressure is a function of the derivatives of enthalpy, pressure, and density and also functions of density and speed of sound. Dependence on the speed of sound in sodium enters through the thermal-expansion coefficient which is a function of the compressibility. From examination of the propagation of errors in these basic properties, errors due to the thermal expansion coefficient and the compressibility were found to have little effect on the value of the heat capacity at constant pressure. Thus above 1600 K, the uncertainty in the heat capacity at constant pressure was approximated as

$$\delta C_p = \sqrt{(2 \delta H)^2 + (2 \delta P)^2 + (\delta \rho)^2} \quad (31)$$

A factor of two times the uncertainty in enthalpy increment and vapor pressure were used because the heat capacity is dependent upon the temperature derivatives of these properties and the error in the derivative is usually greater than the error in the function. For simplicity, single values are given for the percent uncertainties for each temperature interval in Table 1.1-7. The value chosen is the largest calculated uncertainty in each temperature interval. For temperatures above 2400 K, an uncertainty of 50% is estimated based not on Eq. (31) but on the deviations between the 2500 K heat capacities calculated in this assessment and the 1979 assessment by Fink and Leibowitz.⁽¹¹⁾ Uncertainty bands are shown as dotted lines in the graph of the heat capacity at constant pressure for liquid sodium in Fig. 1.1-20. The estimated uncertainties given in Table 1.1-7 are similar to those given by Fink and Leibowitz and by Bystrov et al. up to 1000 K. However, at higher temperatures, they are larger than those given by Bystrov et al. but similar to those given by Fink and Leibowitz. The Fink and Leibowitz estimates are 27% for 1644 to 2200 K, 36% for 2200 to 2400 K and 80% above 2400 K.

C_v Liquid — The uncertainties of the recommended values for the heat capacity at constant volume for liquid sodium are given in Table 1.1-8. They were calculated from the uncertainties in the dependent parameters: adiabatic compressibility, isothermal compressibility, and heat capacity at constant pressure. Employing the approximation that the errors from these parameters are independent and using unity to approximate the contributions from the partial derivatives that multiply the square of each uncertainty in the sum gives the relation

$$\delta C_v = \sqrt{(\delta C_p)^2 + (\delta \beta_s)^2 + (\delta \beta_T)^2} \quad (31)$$

In Table 1.1-8, uncertainties given for each temperature interval are the largest calculated in that interval rounded to the nearest 5%. In Fig. 1.1-21, the dotted lines are the uncertainty bands. Uncertainties calculated using Eq. (32) are in good agreement with estimates given by Fink and Leibowitz.⁽¹¹⁾

C_p Vapor — Examination of the propagation of uncertainties in the calculation of the heat capacity at constant pressure for the vapor indicated that uncertainties in the thermal-expansion coefficient could not be ignored as was the case for the liquid. The uncertainties in

the heat capacity at constant pressure for sodium vapor were calculated from the uncertainty in the heat capacity along the saturation curve, C_σ , and the uncertainty in the vapor thermal-expansion coefficient with the approximations that these uncertainties are independent and the partial derivatives of C_p with respect to C_σ and α_p are unity; thus,

$$\delta C_p = \sqrt{(\delta C_\sigma)^2 + (\delta \alpha_p)^2} . \quad (33)$$

The uncertainty in the heat capacity along the saturation curve, C_σ , was calculated from the square root of the sum of the squares of twice the uncertainties in the vapor enthalpy plus the uncertainty in the vapor density. Because the uncertainty in the vapor density is a function of the uncertainties in the liquid density, heat of vaporization, and the pressure, the uncertainty in the pressure was not explicitly included in the sum for the uncertainty in C_σ . The uncertainty in the thermal-expansion coefficient was calculated from uncertainties in the vapor density and the thermal-pressure coefficient, assuming these uncertainties are independent. Thus, both terms in Eq. (33) are functions of the uncertainty in the vapor density. The uncertainty in the vapor heat capacity at constant pressure is given as a function of temperature in Table 1.1-9 and shown as dotted uncertainty bands in Fig. 1.1-22. Throughout each interval, the highest uncertainty in the interval rounded to the nearest 5% was used. The high uncertainty at low temperatures arises from uncertainties in the thermal-pressure coefficient and the derivative of the vapor pressure at low temperatures. Estimated uncertainties given in Table 1.1-9 are higher than those of Bystrov et al. at all temperatures and higher than those given by Fink and Leibowitz⁽¹¹⁾ at low temperatures (below 500 K) but are similar to those of Fink and Leibowitz above 1000 K. Fink and Leibowitz give uncertainties of 16% below 1644 K, 36% from 1644 to 2000 K, 50% for 2000 to 2400 K and 100% above 2400 K. Bystrov et al. give uncertainties of 2% at 1000 K, 3% at 1400 K, and 24% at 1800 K.

C_v Vapor — The uncertainty in the heat capacity at constant volume for the vapor was calculated from uncertainties in the heat capacity at constant pressure, the vapor density, the vapor thermal-expansion coefficient, and the thermal-pressure coefficient using the relation

$$\delta C_v = \sqrt{(\delta C_p)^2 + (\delta \alpha_p)^2 + (\delta \rho)^2 + (\delta \gamma_v)^2} . \quad (34)$$

This relation assumes independence of these errors, which is an approximation, and ignores the contributions from the partial derivatives. Uncertainties are given in Table 1.1-10 for various

temperature intervals and shown in Fig. 1.1-23. Comparison with the uncertainties given by Fink and Leibowitz⁽¹¹⁾ gives similar conclusions as for those for the vapor heat capacity at constant pressure. Fink and Leibowitz estimate uncertainties of 28% below 1644 K, 40% from 1644 to 2000 K, 60% from 2000 to 2400 K, and 100% above 2400 K. Comparison of recommendations from various assessments indicate all lie within the uncertainty estimates given in Table 1.1-10.

Polynomial Approximation

The CODATA equation, which is the derivative of the enthalpy increment along the saturation curve, may be used as a polynomial approximation to the heat capacity at constant pressure; this equation is

$$C_p \approx + 1.6582 - 8.4790 \times 10^{-4} T + 4.4541 \times 10^{-7} T^2 - 2992.6 T^{-2} \quad (35)$$

Up to 1900 K, deviations of values calculated with this polynomial expression from the recommended values are less than 0.3%. Deviations are 0.39% at 1900 K and 1.15% at 2000 K. Above 2000 K, deviations increase as the critical temperature is approached, as shown in Figs. 1.1-8 and 1.1-9, which respectively compare the derivative along the saturation curve with C_o and C_p and give deviations from C_p . The deviation at 2400 K is 15.5%. At 2500 K, it is 32%.

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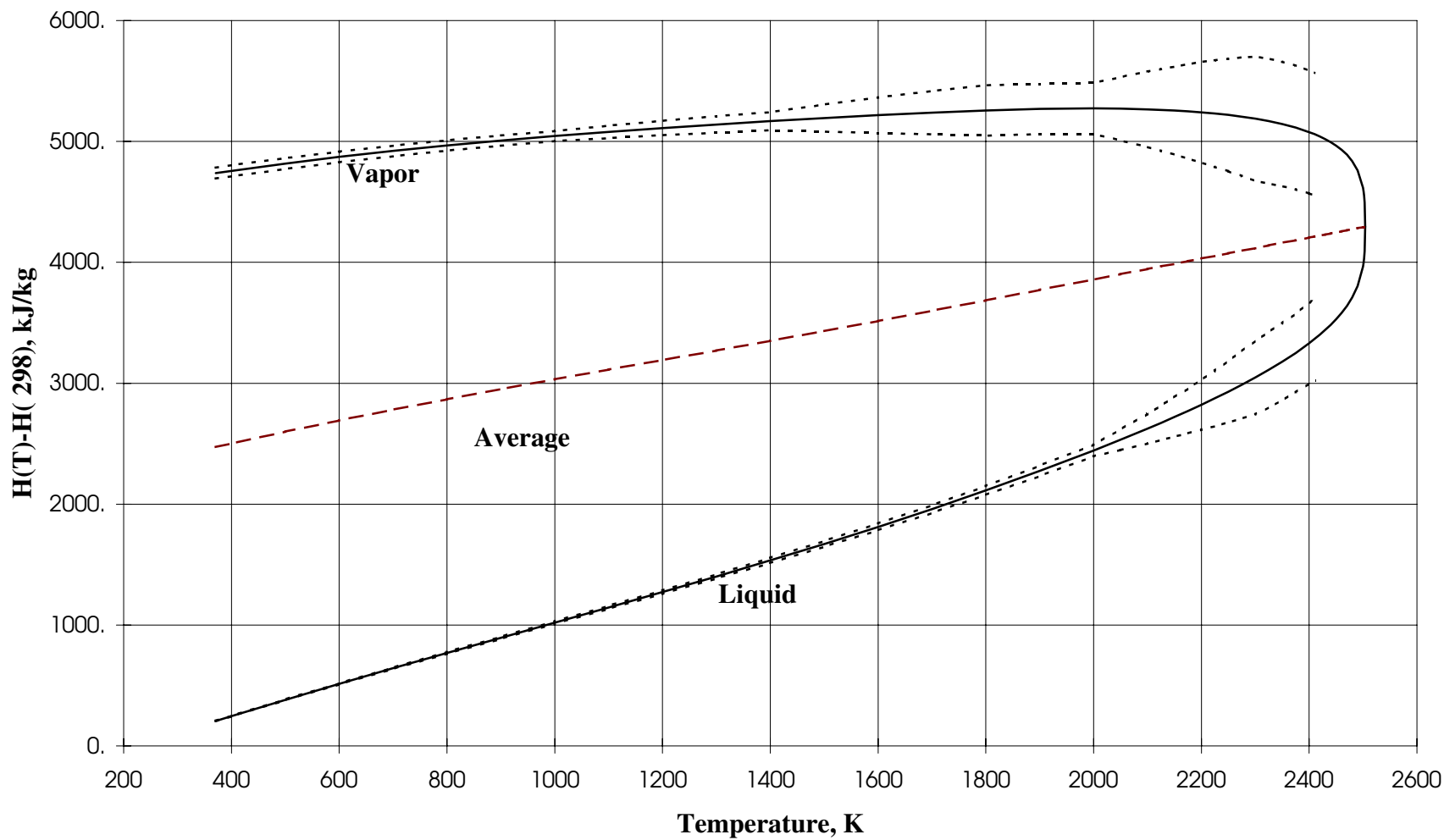


Fig. 1.1-1 Enthalpy Increments for Liquid and Vapor Sodium and the Average of the Liquid and Vapor Enthalpy Increments. Dotted Lines Give Uncertainties, Which Increase Discontinuously to 10% at 2000 K

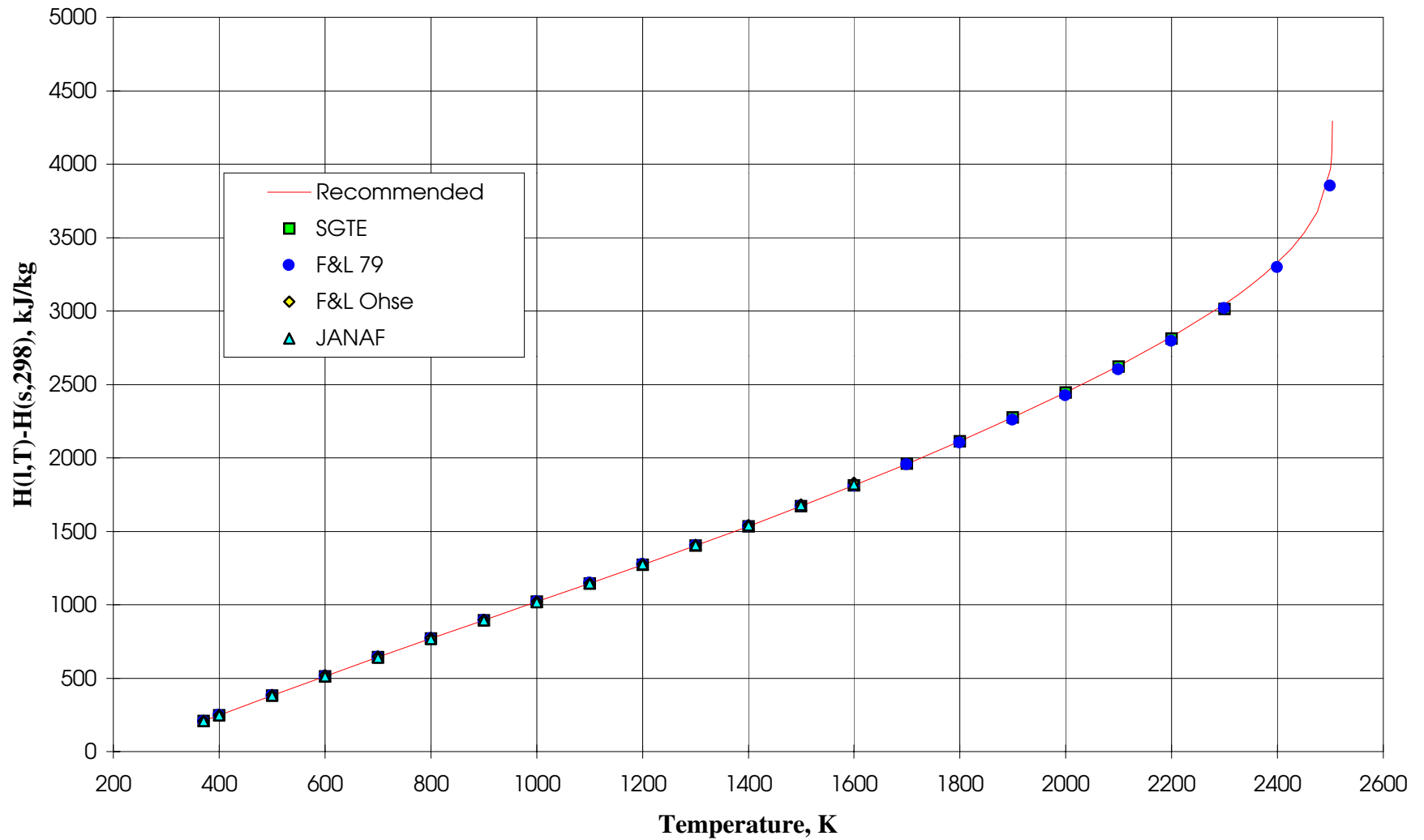


Fig. 1.1-2 Comparison of Recommended Values for the Enthalpy Increment of Liquid Sodium with Values from Other Assessments

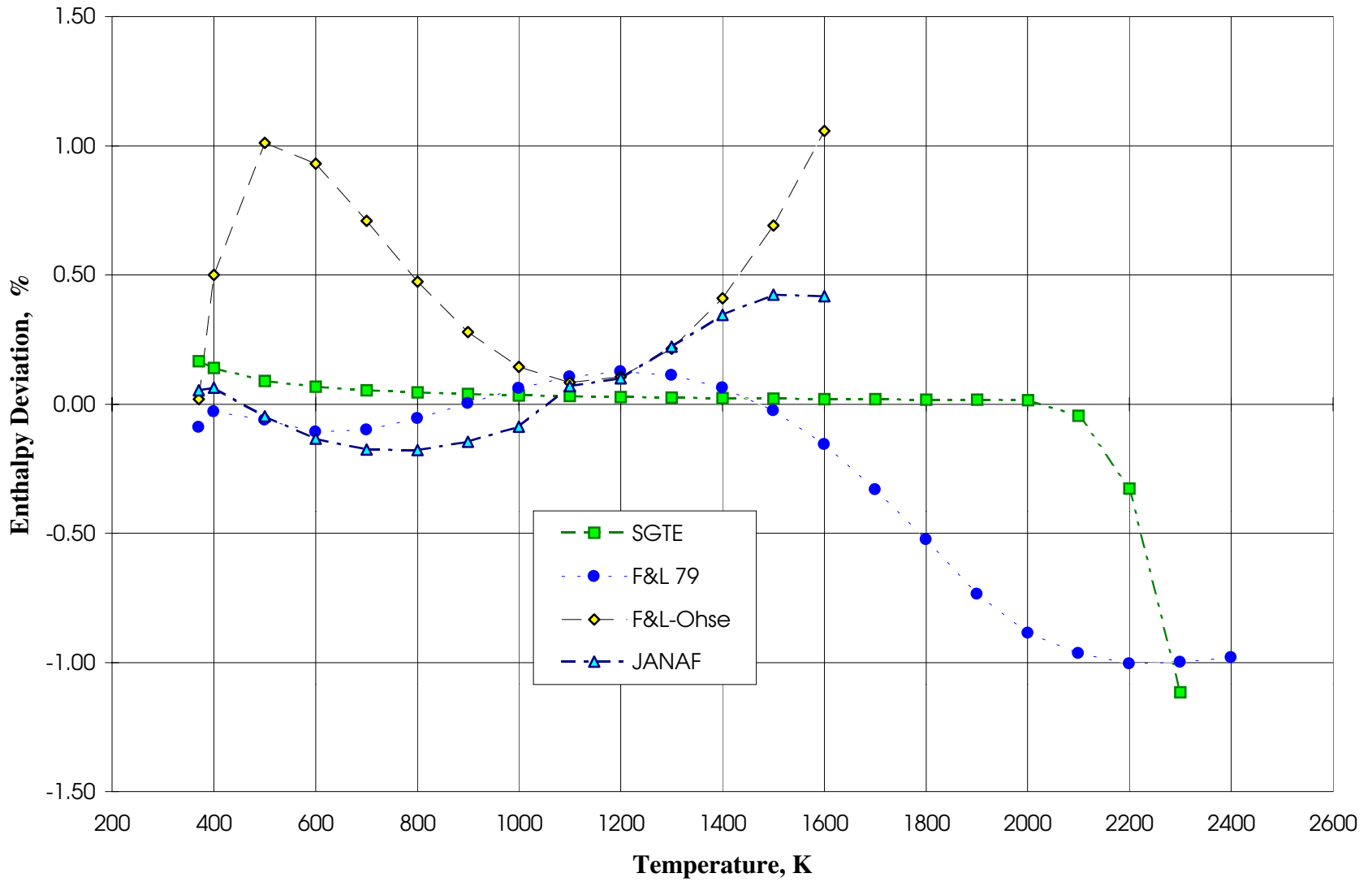


Fig. 1.1-3 Deviations of Values from Other Assessments from the Recommended Values for the Enthalpy of Liquid Sodium

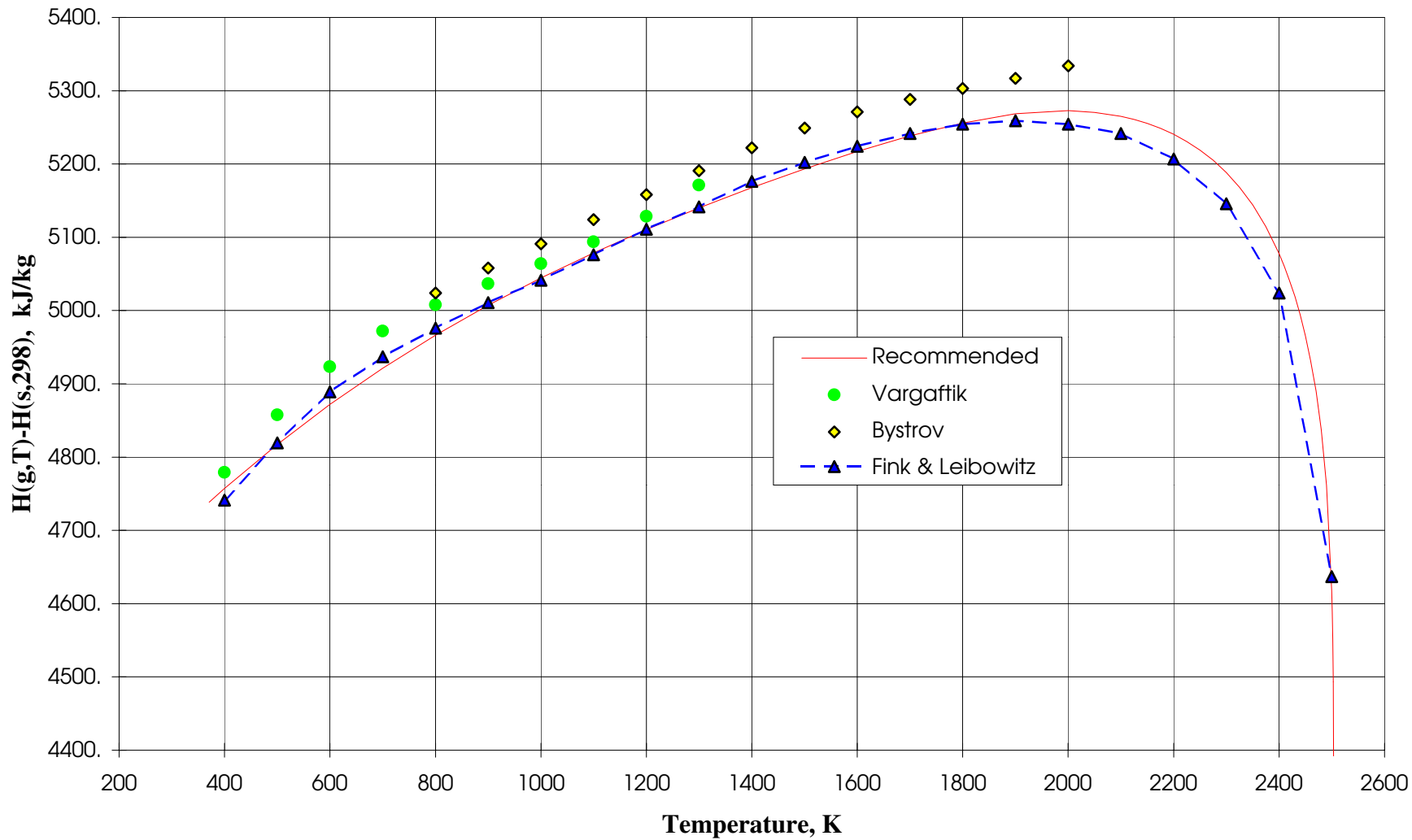


Fig. 1.1-4 Comparison of Recommended Values for the Enthalpy Increment of Sodium Vapor with Values from Other Assessments

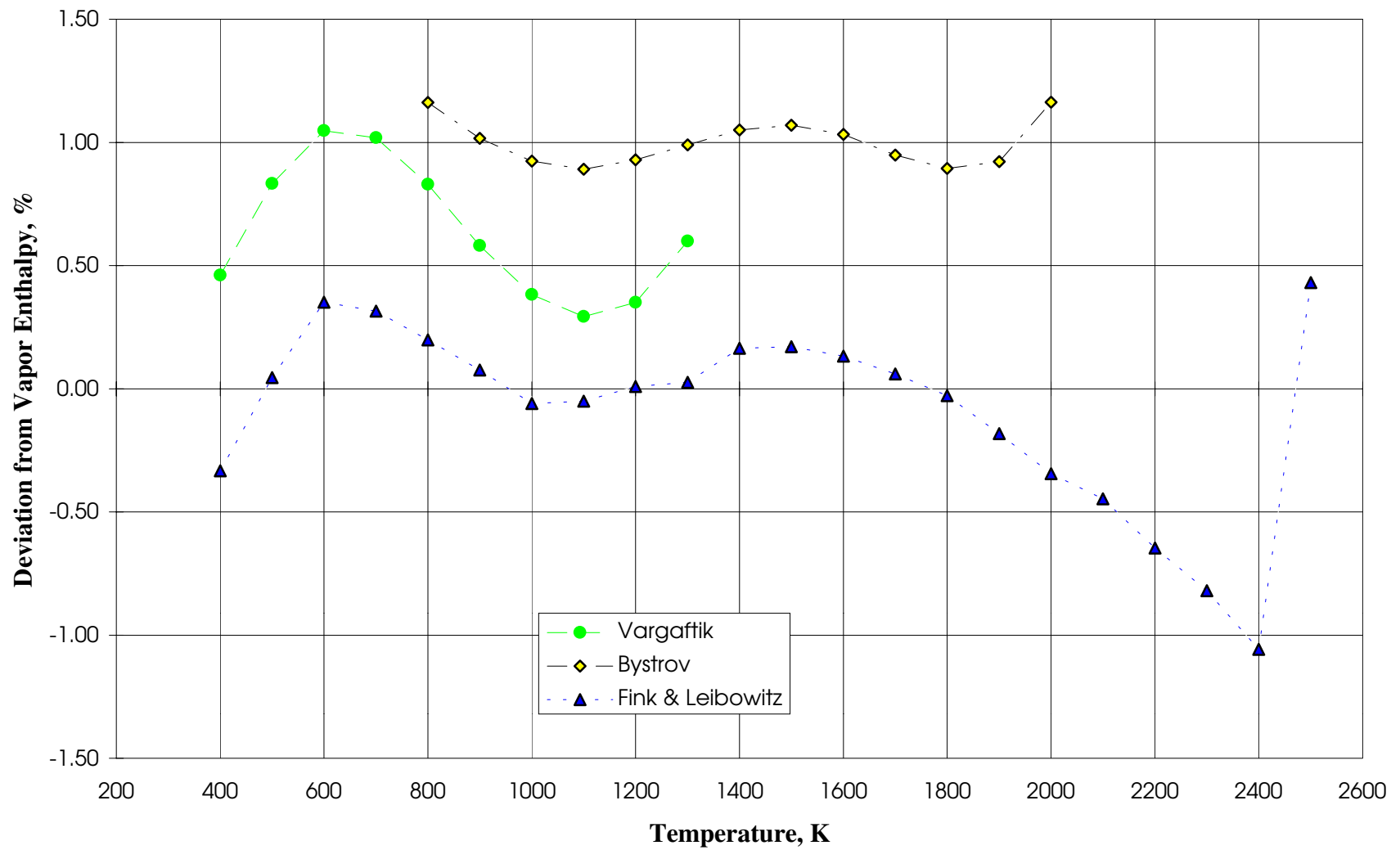


Fig. 1.1-5 Deviations of Values from Other Assessments from the Recommended Values for the Enthalpy of Sodium Vapor

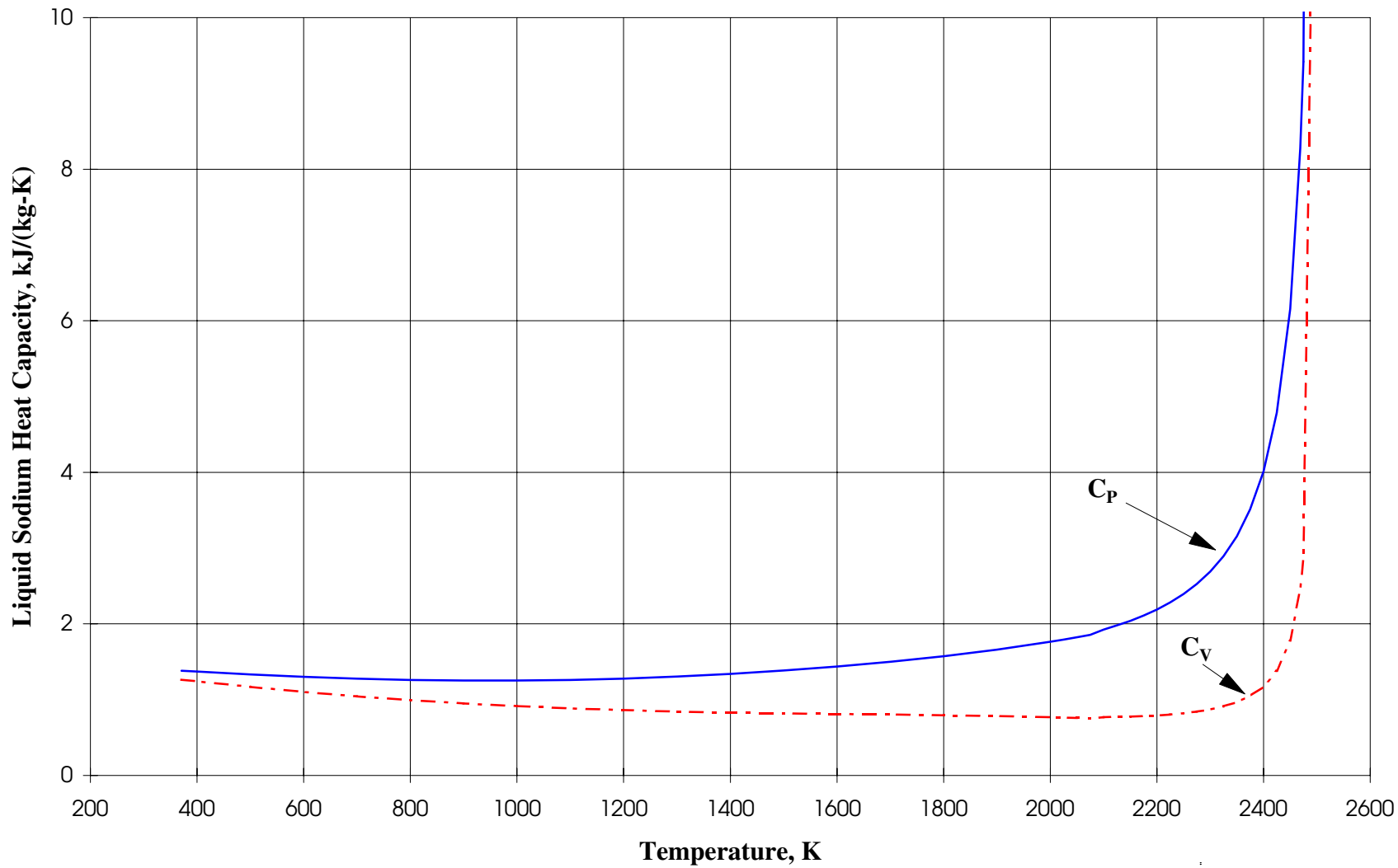


Fig. 1.1-6 Recommended Values for the Heat Capacity at Constant Pressure, C_p , and the Heat Capacity at Constant Volume, C_v , of Liquid Sodium

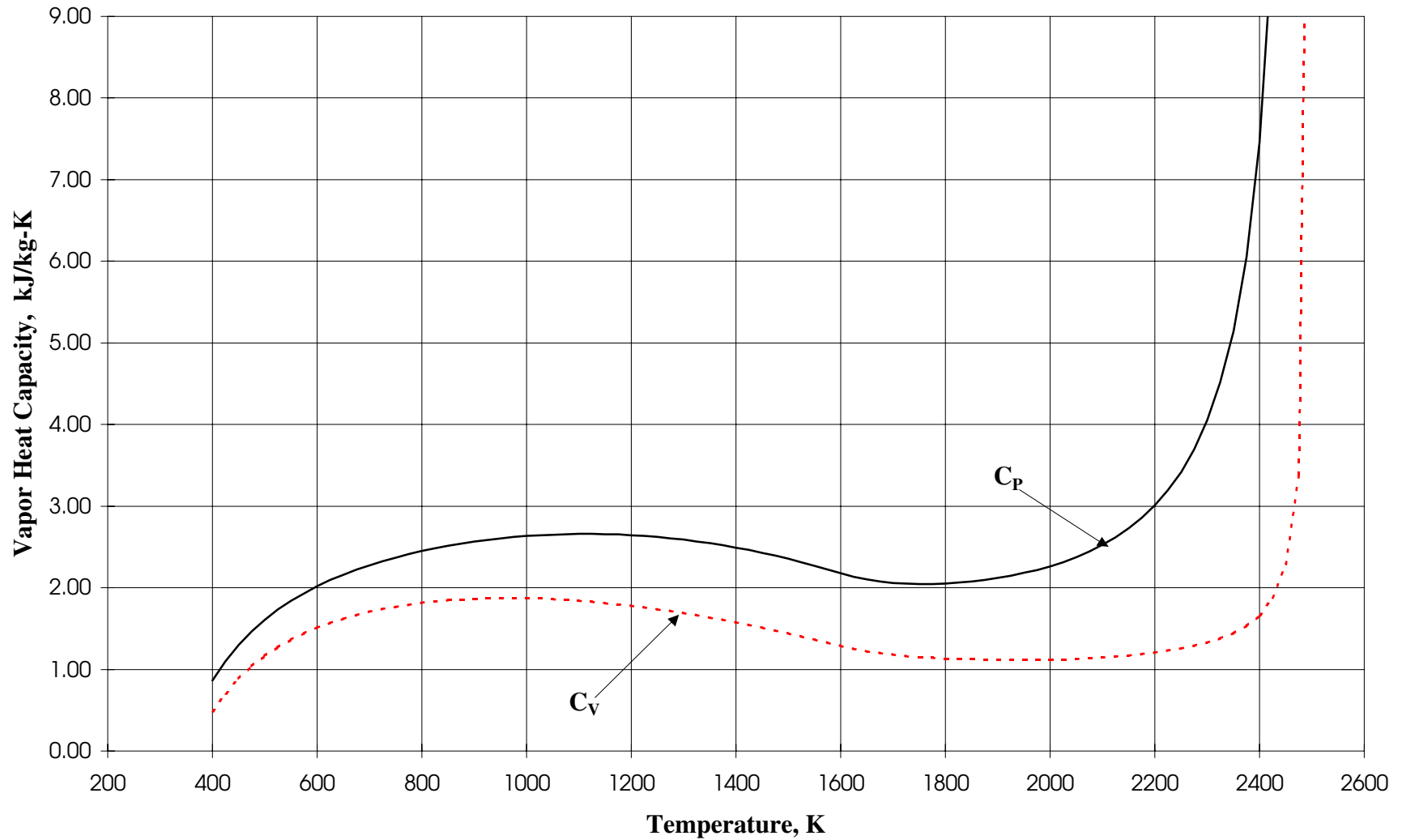


Fig. 1.1-7 Recommended Values of the Heat Capacity at Constant Pressure, C_p , and the Heat Capacity at constant Volume, C_v , of Sodium Vapor

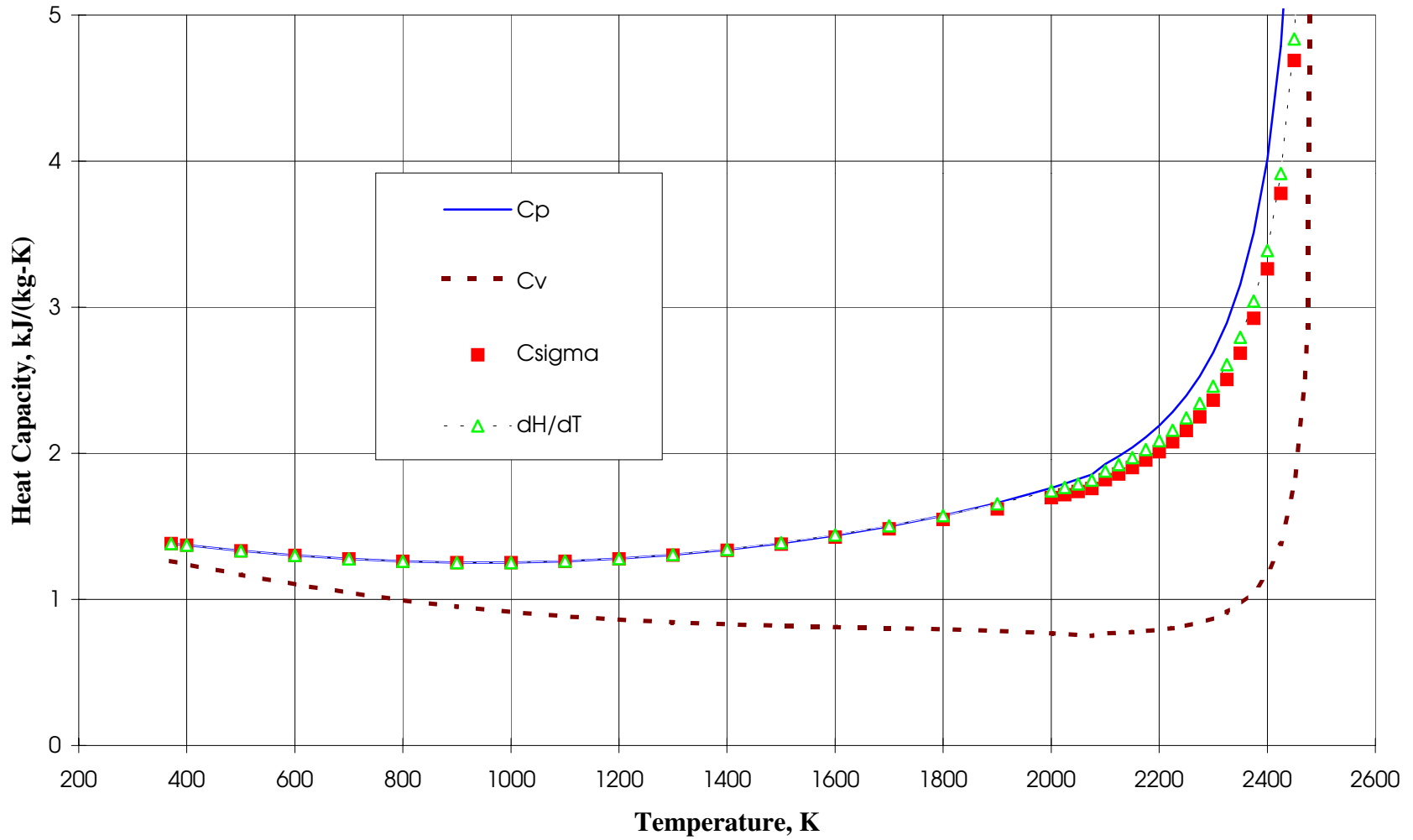


Fig. 1.1-8 Comparison of the Heat Capacity at Constant Pressure, Heat Capacity at Constant Volume, Heat Capacity Along the Saturation Curve, and the Temperature Derivative of the Saturation Enthalpy

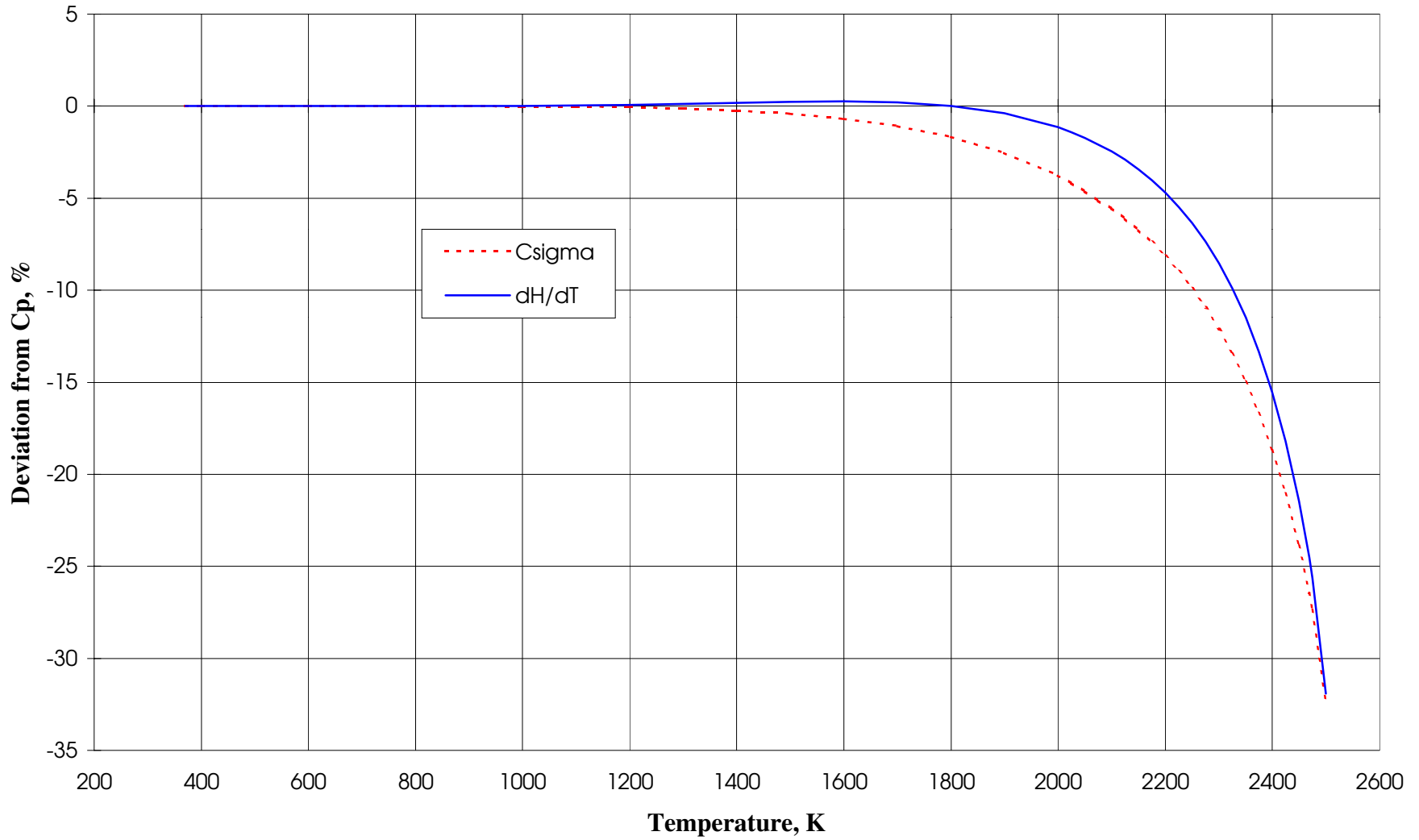


Fig. 1.1-9 Deviations of the Heat Capacity Along the Saturation Curve and the Temperature Derivative of the Saturation Enthalpy from the Heat Capacity at Constant Pressure

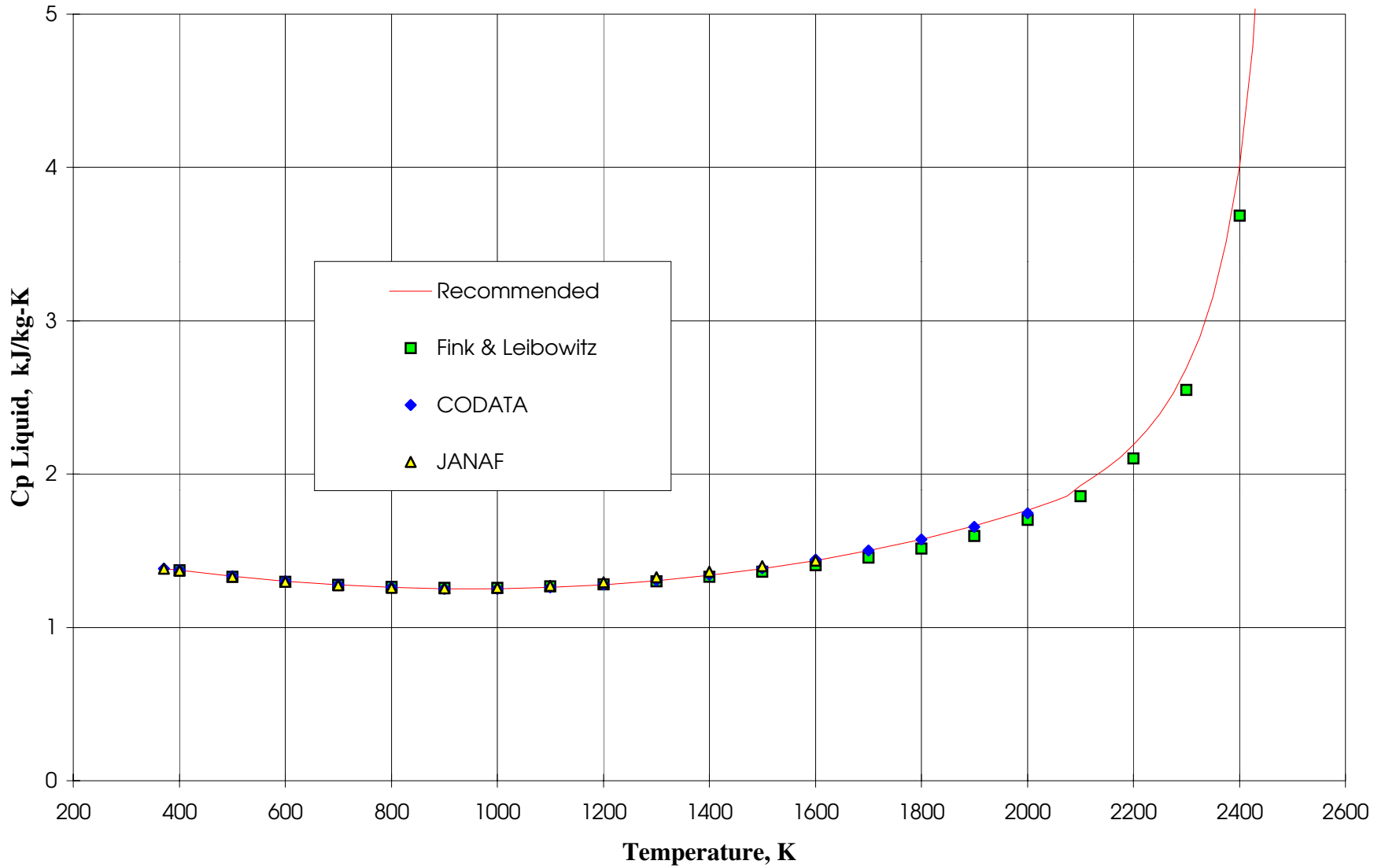


Fig. 1.1-10 Comparison of the Recommended Values for the Heat Capacity at Constant Pressure for Liquid Sodium with Values from Other Assessments

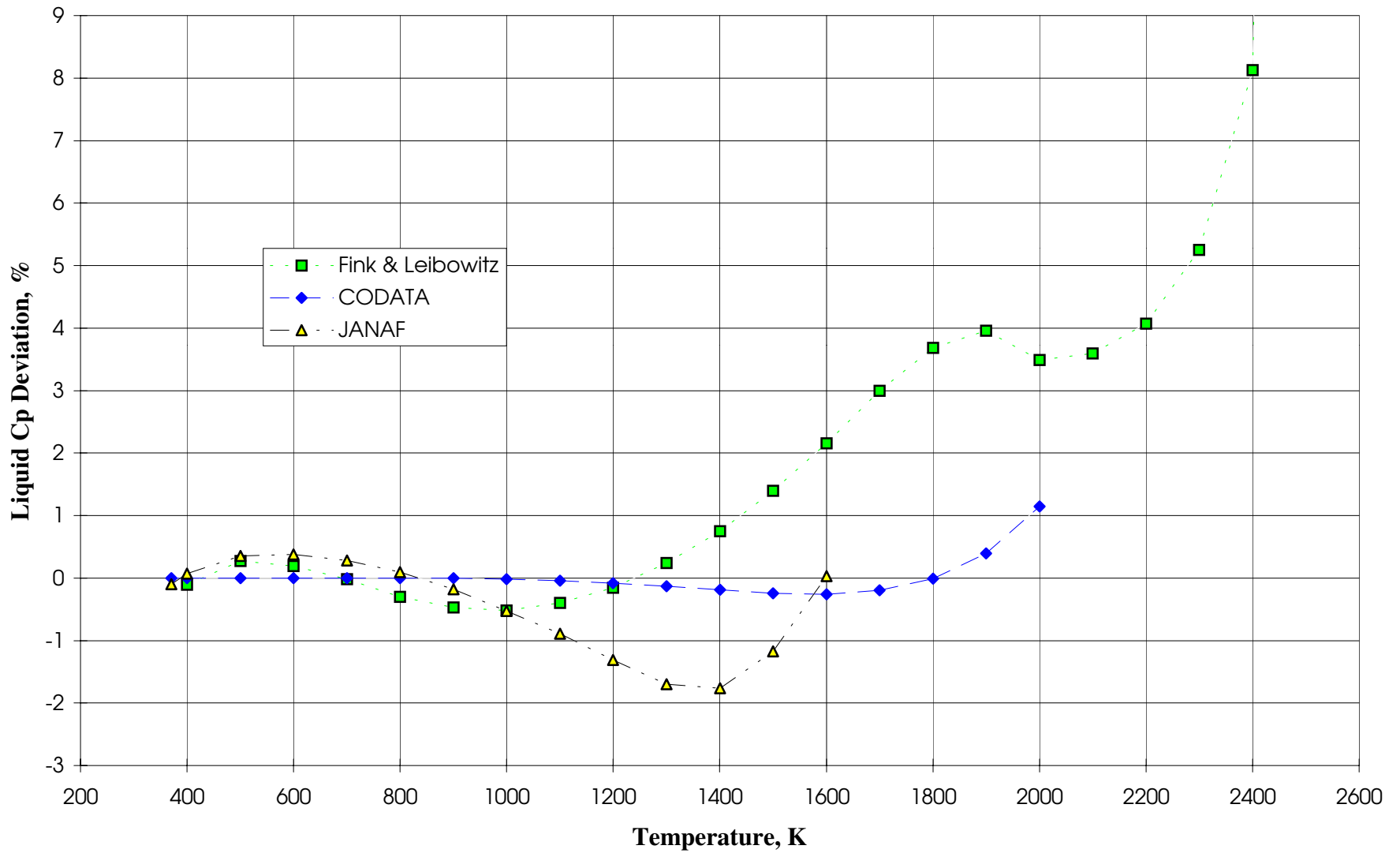


Fig. 1.1-11 Deviations of Values from Other Assessments from the Recommended Values for the Heat Capacity at Constant Pressure of Liquid Sodium

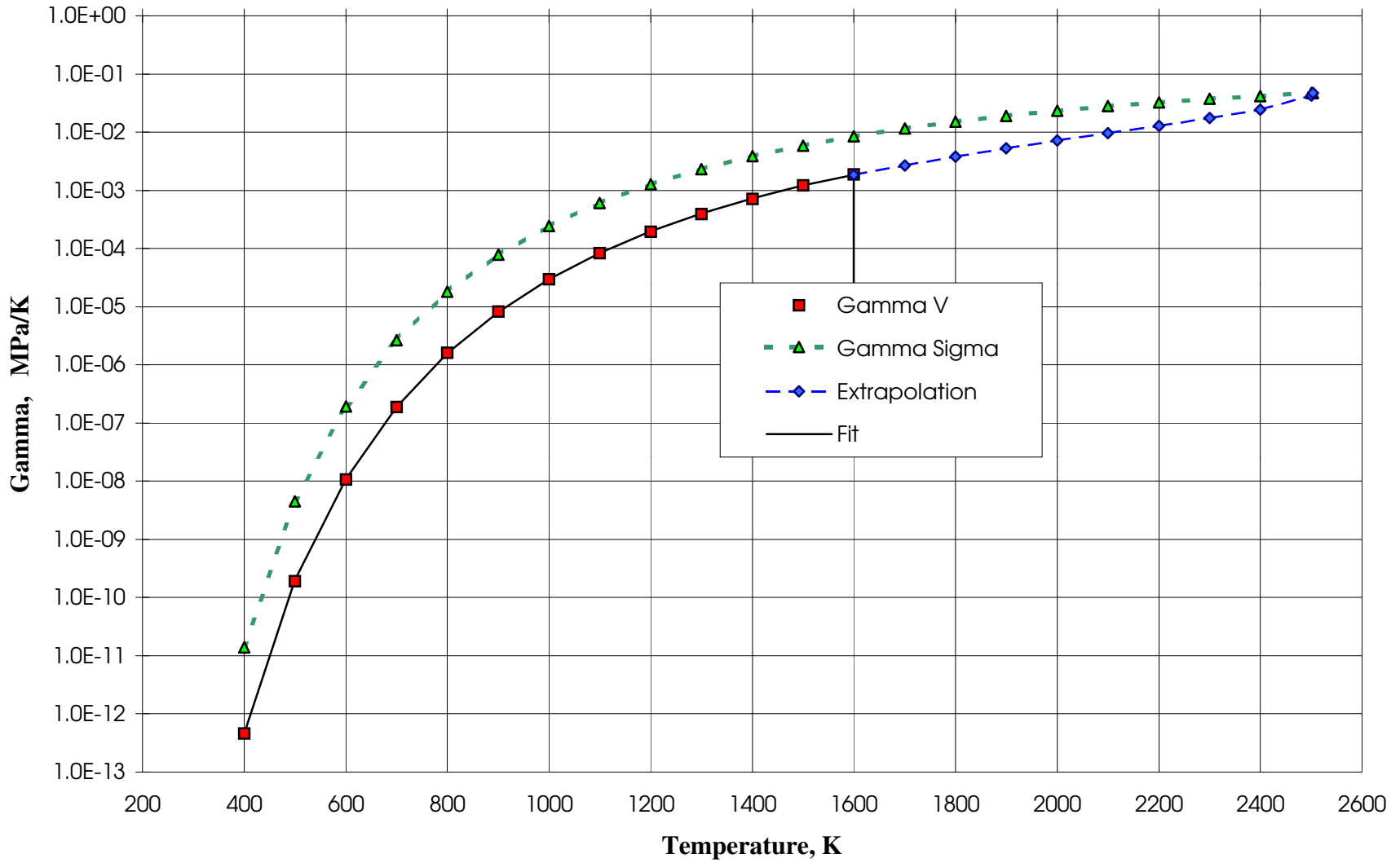


Fig. 1.1-12 Fit to Quasi-Chemical Values of the Thermal Pressure Coefficient, γ_V , and Extrapolation above 1600 K to Agree with γ_σ at the Critical Point

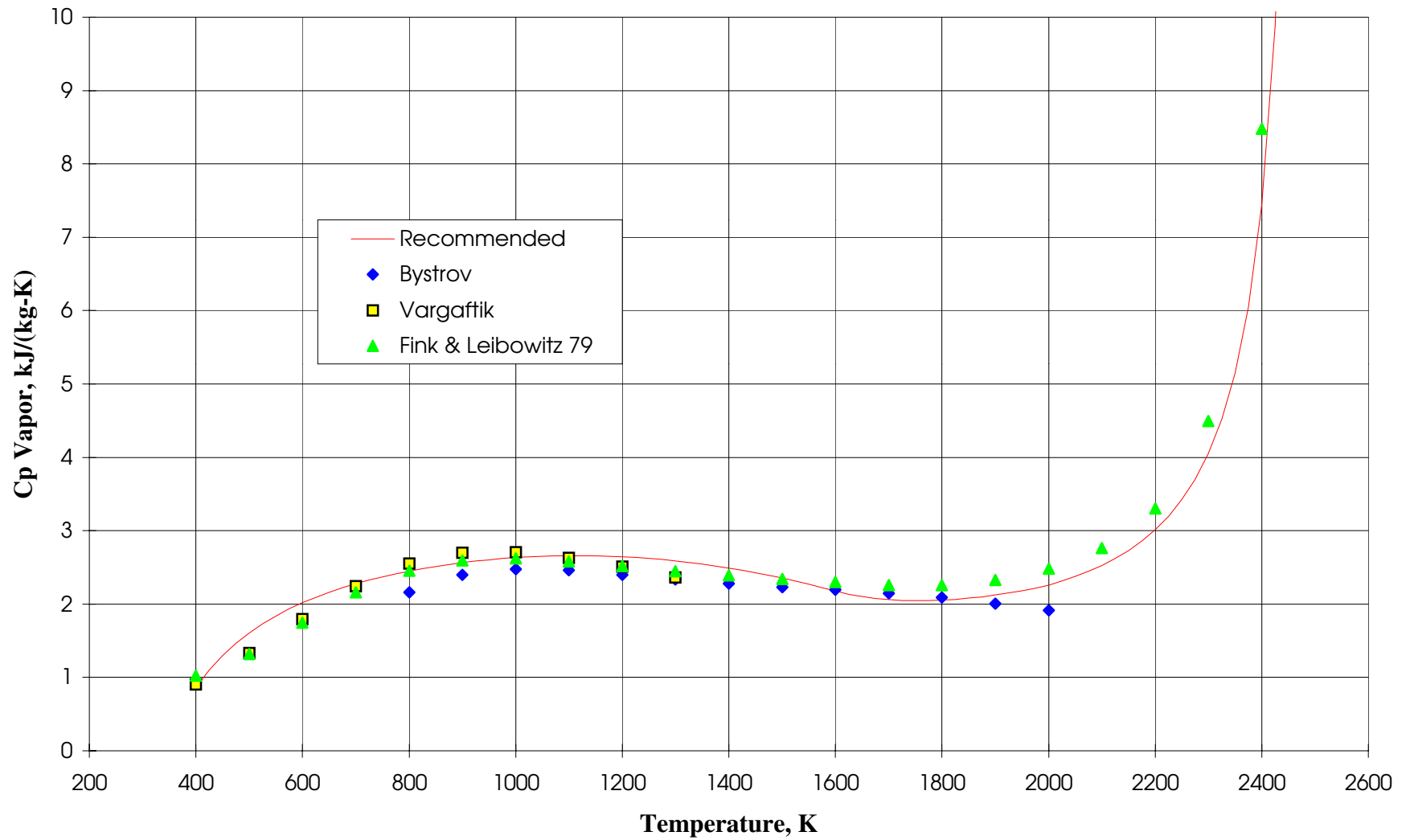


Fig. 1.1-13 Comparison of the Recommended Values for the Heat Capacity at Constant Pressure for Sodium Vapor with Values from Other Assessments

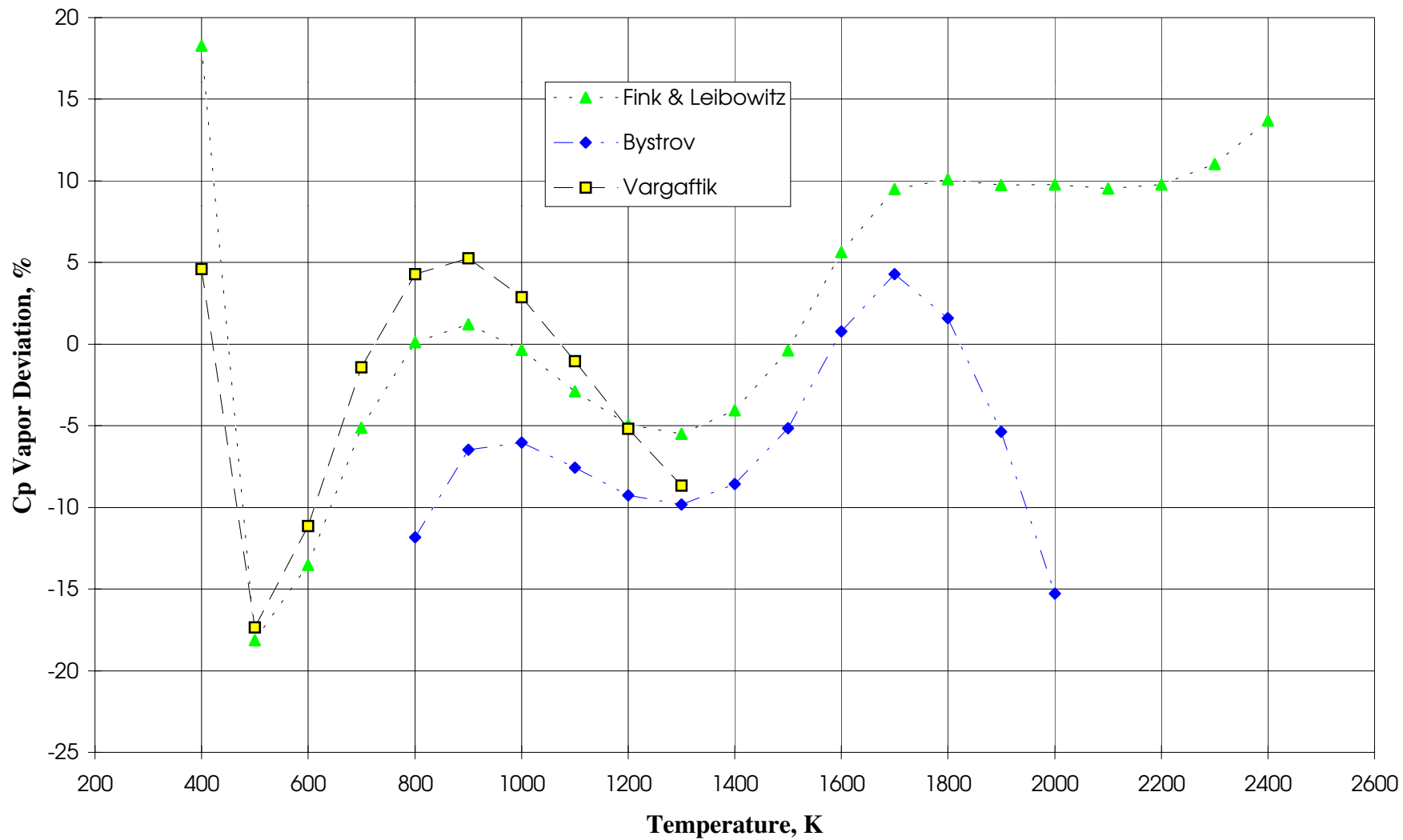


Fig. 1.1-14 Deviation of Values from Other Assessments from the Recommended Values for the Heat Capacity at Constant Pressure of Sodium Vapor

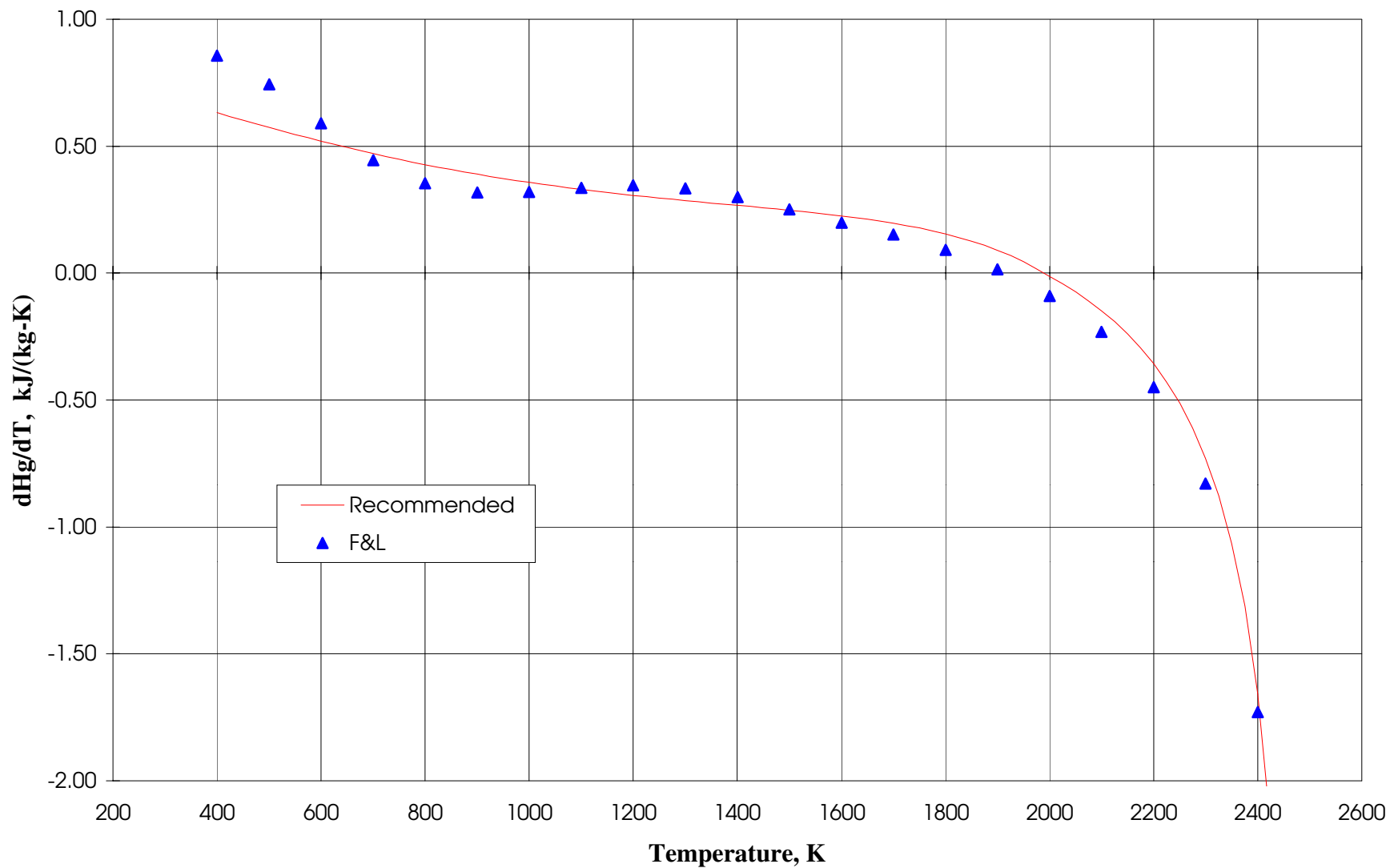


Fig. 1.1-15 Comparison of the Values for the Temperature Derivative of the Vapor Enthalpy from this Calculation with the Fink and Leibowitz¹¹ Values (F&L) Calculated Using the Quasi-Chemical Method

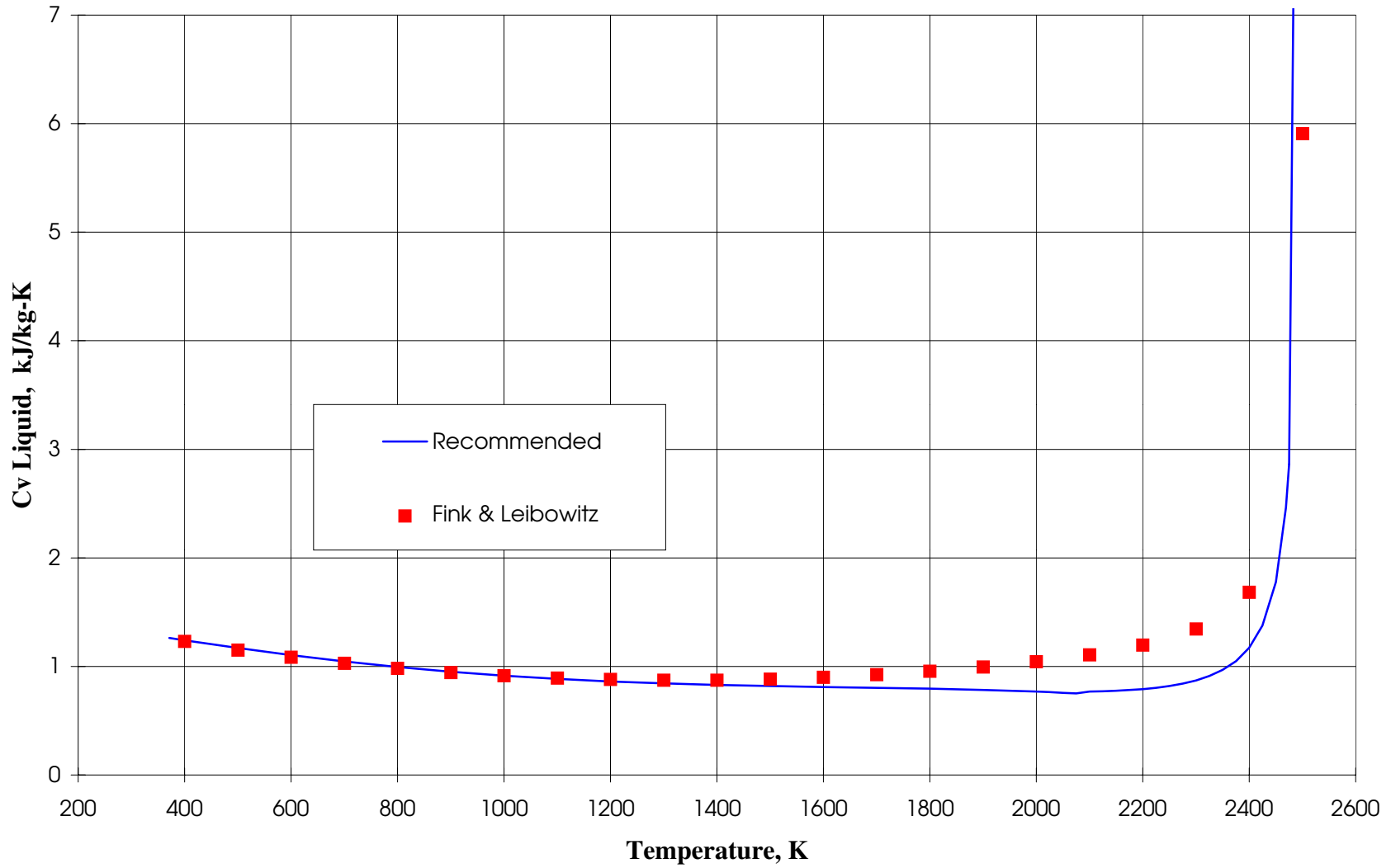


Fig 1.1-16 Comparison of the Recommended Values for the Heat Capacity at Constant Volume for Liquid Sodium with Values from Other Assessments

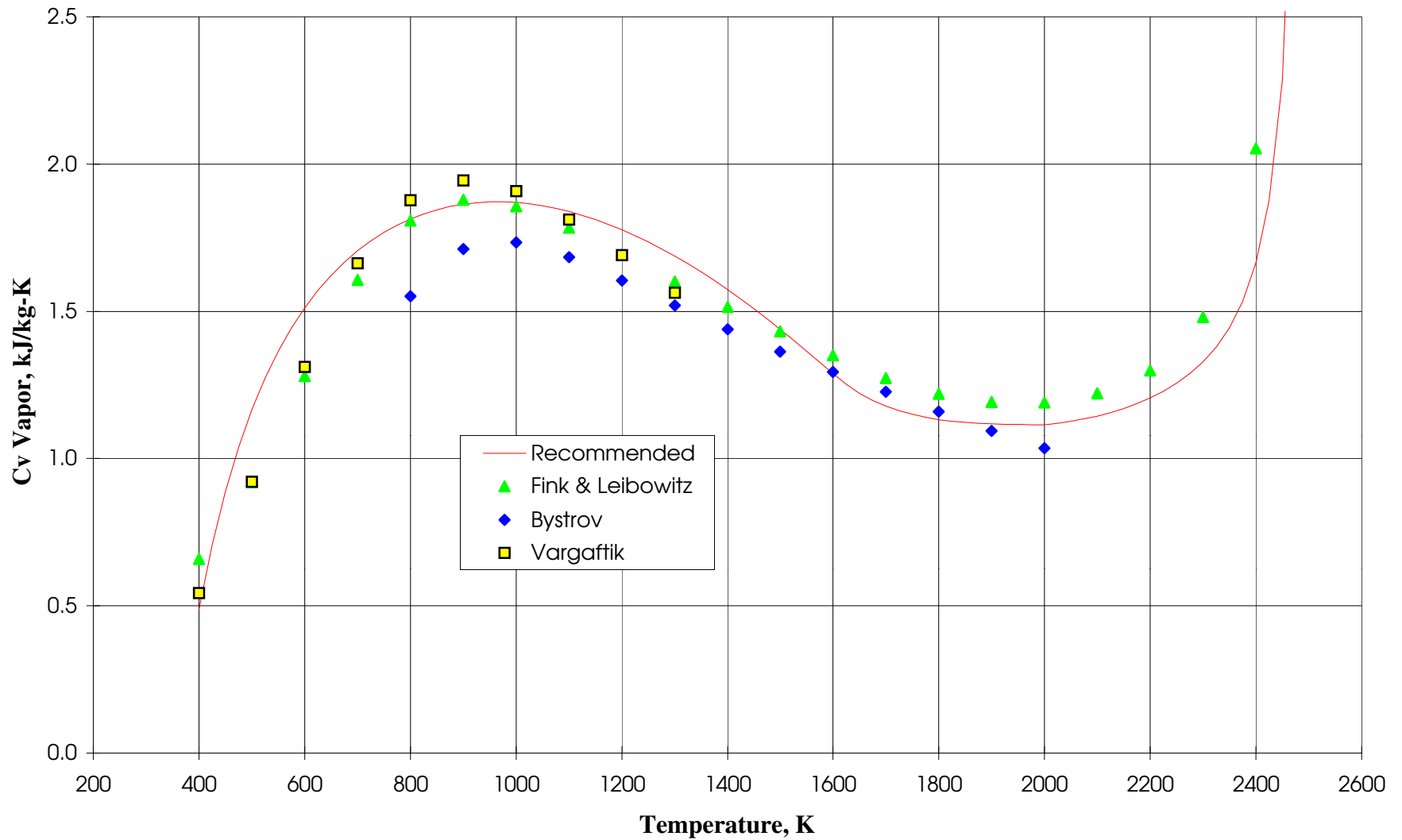


Fig. 1.1-17 Comparison of the Recommended Values for the Heat Capacity at Constant Volume for Sodium Vapor with Values from Other Assessments

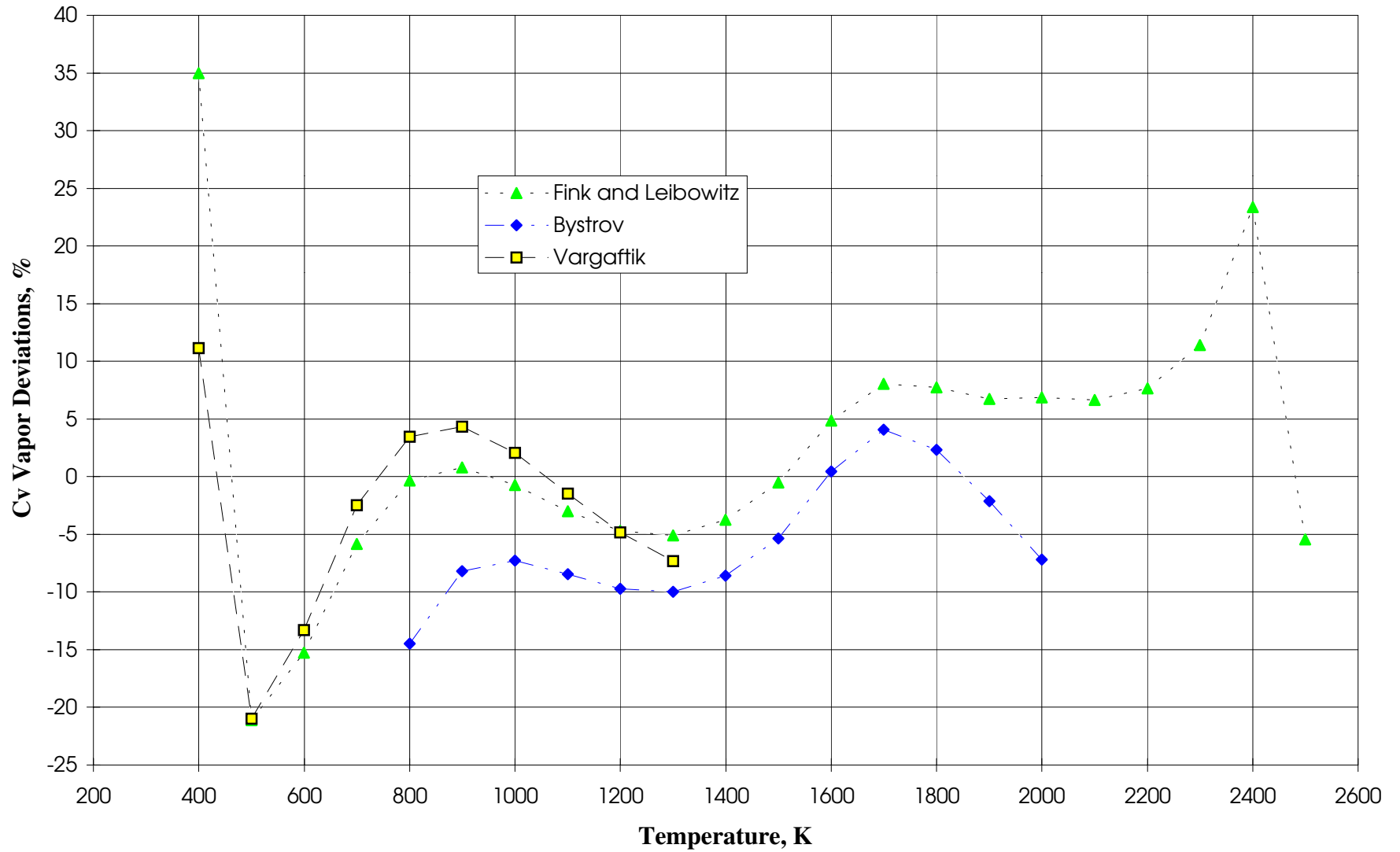


Fig. 1.1-18 Deviation of Values from Other Assessments from the Recommended Values for the Heat Capacity at Constant Volume of Sodium Vapor

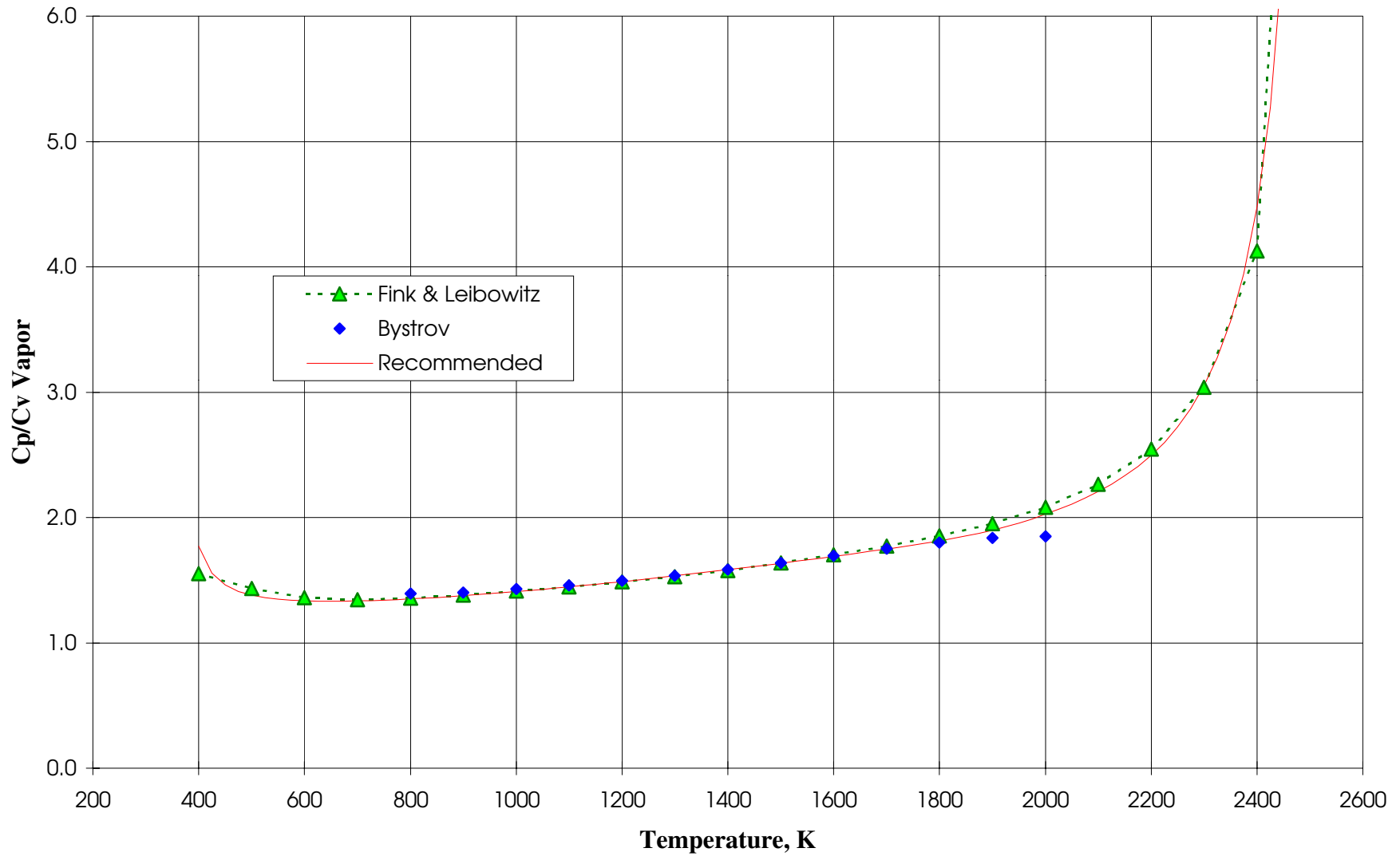


Fig. 1.1-19 Comparison of the Ratio of the Recommended Values for the Heat Capacity at Constant Pressure and Constant Volume for Sodium Vapor with Values of the Ratio from Other Assessments

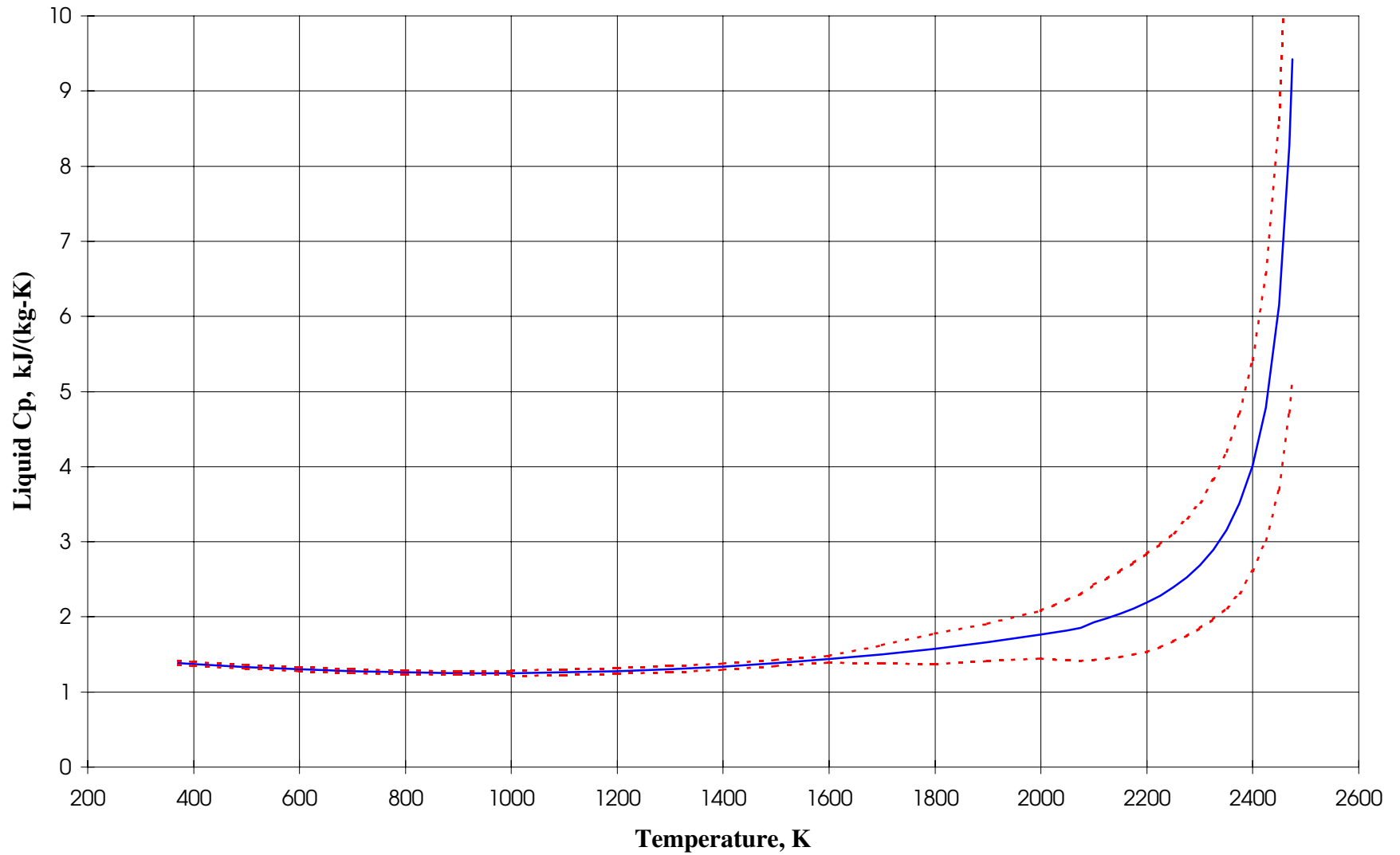


Fig. 1.1-20 The Heat Capacity at Constant Pressure for Liquid Sodium with Estimated Uncertainties (dotted lines)

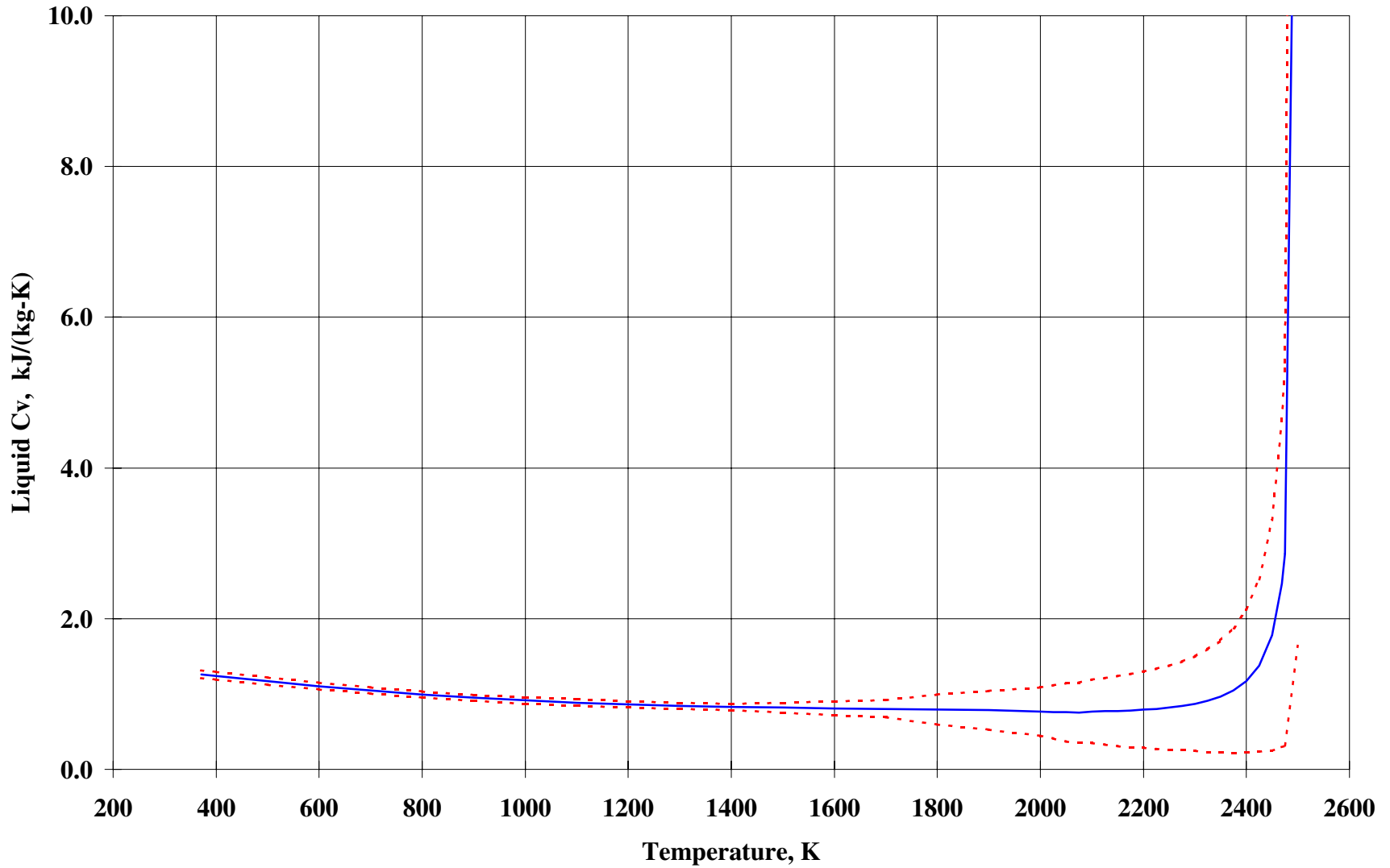


Fig. 1.1-21 The Heat Capacity at Constant Volume for Liquid Sodium with Estimated Uncertainties (dotted lines)

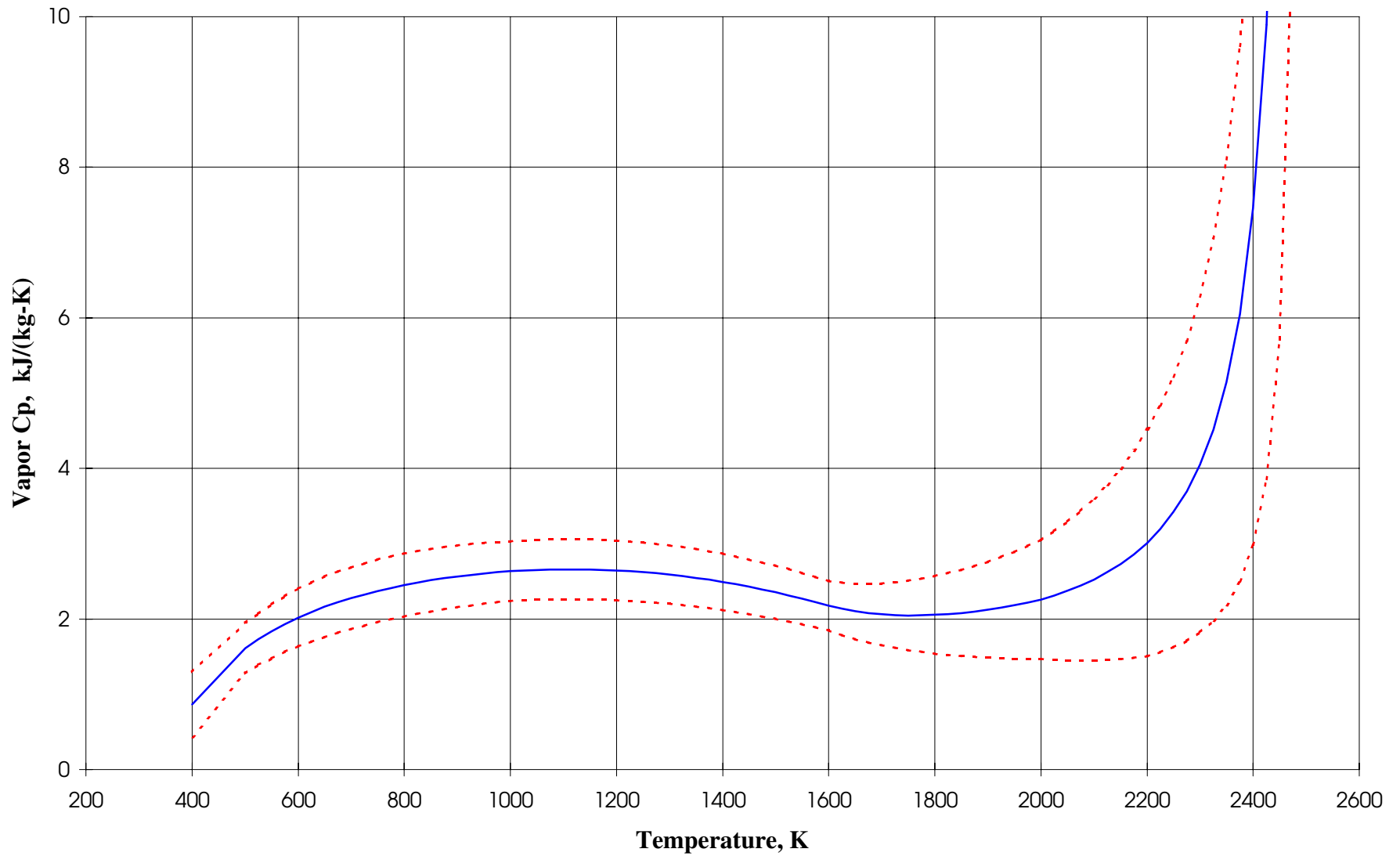


Fig. 1.1-22 The Heat Capacity at Constant Pressure for Sodium Vapor with Estimated Uncertainties (dotted lines)

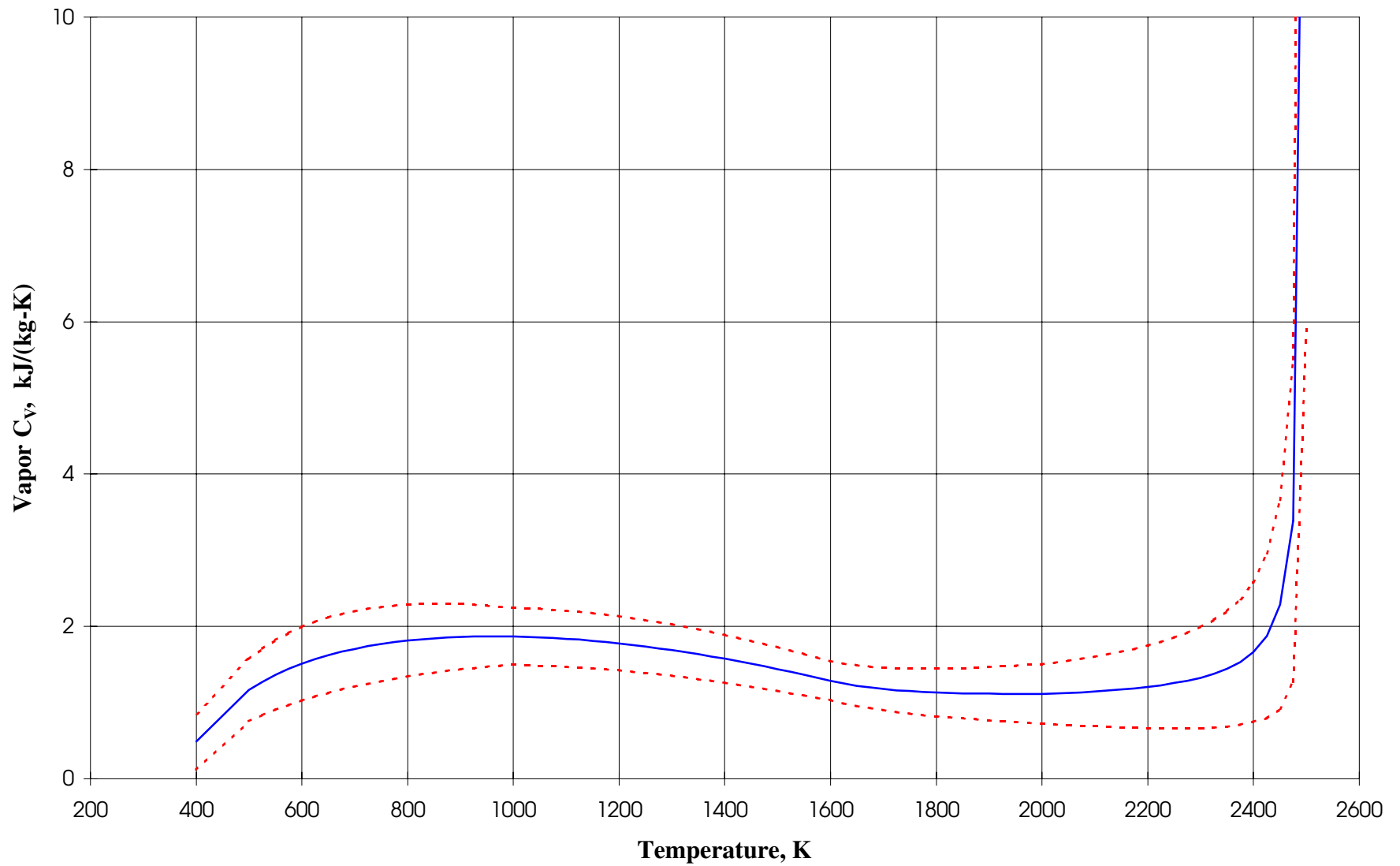


Fig. 1.1-23 The Heat Capacity at Constant Volume for Sodium Vapor with Estimated Uncertainties (dotted lines)

1.2 VAPOR PRESSURE, BOILING POINT, AND ENTHALPY OF VAPORIZATION

1.2.1 VAPOR PRESSURE

Summary

Recommended values for the vapor pressure of sodium are given in Table 1.2-1 as a function of temperature. They are calculated from an equation given by Browning and Potter.⁽¹⁾ The equation from Browning and Potter has been recommended because their analysis (1) is based on a careful assessment of the available experimental data, (2) is consistent with recommended values for the critical pressure, (3) is in good agreement with recommendations from other recent assessments, and (4) provides a simple three-term equation for the entire temperature range. This equation for the natural logarithm of the vapor pressure over saturated liquid sodium (liquid sodium in equilibrium with its vapor) is

$$\ln P = 11.9463 - 12633.73/T - 0.4672 \ln T , \quad (1)$$

where P is in MPa and T is in K. This recommended equation is based on Browning and Potter's analysis of the available data⁽²⁻¹⁰⁾ in the 864 to 2499 K temperature range. It gives a temperature of 2503.7 K for the critical pressure of 25.64 MPa.⁽⁸⁾ Figures 1.2-1 and 1.2-2 show the recommended values of the vapor pressure over saturated liquid sodium as a function of temperature and the natural logarithm of the vapor pressure as a function of inverse temperature. Uncertainty bands have been included in Fig. 1.2-1. Estimates of the uncertainties as a function of temperature are given in Table 1.2-2.

Discussion

The recommended equation for the vapor pressure of saturated sodium is one of two equations from the analysis by Browning and Potter.⁽¹⁾ It is based on their analysis of nine sets of data from 864 to 2499 K, as shown in Table 1.2-3. The other equation given by Browning and Potter is a fit to the experimental data from 864 to 2361 K. This equation, preferred by Browning and Potter and given as Eq. (6) in Reference 1, is:

$$\ln P = 11.2916 \pm 0.5077 - (12532.694 \pm 87.141)/T - (0.3869 \pm 0.0600) \ln T , \quad (2)$$

where P is in MPa and T is in K. Browning and Potter recommended this equation, which fit data only to 2361 K, rather than their fit to all the available data to the critical pressure because the Bhise and Bonilla⁽⁸⁾ data above 2361 K were based on temperatures determined indirectly rather than

Table 1.2-1 Vapor Pressure of Saturated Sodium

| Temperature (K) | Pressure (MPa) | Pressure (atm) |
|--------------------|----------------------------|-------------------------|
| 400 | $(1.80 \times 10^{-10})^*$ | (1.78×10^{-9}) |
| 500 | (8.99×10^{-8}) | (8.87×10^{-7}) |
| 600 | (5.57×10^{-6}) | (5.49×10^{-5}) |
| 700 | (1.05×10^{-4}) | (1.04×10^{-3}) |
| 800 | (9.41×10^{-4}) | (9.28×10^{-3}) |
| 900 | 5.147×10^{-3} | 5.080×10^{-2} |
| 1000 | 1.995×10^{-2} | 0.1969 |
| 1100 | 6.016×10^{-2} | 0.5937 |
| 1200 | 0.1504 | 1.485 |
| 1300 | 0.3257 | 3.214 |
| 1400 | 0.6298 | 6.216 |
| 1500 | 1.113 | 10.98 |
| 1600 | 1.828 | 18.04 |
| 1700 | 2.828 | 27.91 |
| 1800 | 4.161 | 41.06 |
| 1900 | 5.870 | 57.93 |
| 2000 | 7.991 | 78.86 |
| 2100 | 10.55 | 104.1 |
| 2200 | 13.57 | 133.9 |
| 2300 | 17.06 | 168.4 |
| 2400 | 21.03 | 207.5 |
| 2500 | (25.47) | (251.3) |
| 2503.7 | (25.64) | (253.1) |

*Parentheses indicate extrapolated beyond range of experimental data.

Table 1.2-2 Estimated Uncertainty in Values of Sodium Vapor Pressure
Calculated from Eq. (1)

| Temperature Range (K) | Vapor Pressure (P, MPa) | Uncertainty (%) |
|-----------------------|---|-----------------|
| 400 - 600 | $\ln P = 11.9463 - 12633.73/T - 0.4672 \ln T$ | 25 - 9 |
| 600 - 864 | | 6 - 4 |
| 864 - 1500 | | 3 |
| 1500 - 2000 | | 4 |
| 2000 - 2500 | | 5 |

Table 1.2-3 Vapor Pressure Data Fit by Browning and Potter

| Author | Date | Temperature Range (K) | Ref. |
|---------------------|------|-----------------------|------|
| Bohdansky et al. | 1967 | 1116 - 1390 | 2 |
| Schins et al. | 1971 | 1116 - 1390 | 3 |
| Achener & Jouthas | 1966 | 882 - 1228 | 4 |
| Bowles & Rosenblum | 1965 | 1072 - 2154 | 5 |
| Makanski et al. | 1955 | 893 - 1408 | 6 |
| Stone et al. | 1966 | 1140 - 1665 | 7 |
| Bhise & Bonilla | 1976 | 1255 - 2499 | 8 |
| Sowa | 1963 | 1173 - 1663 | 9 |
| Vinogradov & Voljak | 1966 | 864 - 1160 | 10 |

from thermocouple measurements. Both equations give temperatures of about 2503 K for the critical pressure of 25.64 MPa. Vapor pressures calculated with the two equations given by Browning and Potter are almost identical. Greatest deviations are 1.5% near the critical temperature, as shown in Fig. 1.2-3. Figure 1.2-3 shows deviations of other equations from the recommended equation, Eq. (1), expressed as a percent. The deviation is defined as

$$\frac{[P(CALC) - P(Eq. 1)] 100\%}{P(Eq. 1)}$$

The equation based on the fit to the data set that includes the high temperature Bhise and Bonilla data (Eq. [10] in Reference 1) has been selected rather than the one for the lower temperature range because the vapor pressures in the region of the critical point are required for the calculation of other thermodynamic properties and for calculations under severe accident conditions.

Comparisons have been made of the vapor pressure calculated from the recommended equation with equations recommended by Bystrov et al.,⁽¹¹⁾ Vargaftik and Voljak,⁽¹²⁾ Fink and Leibowitz,⁽¹³⁻¹⁵⁾ and Thurnay.⁽¹⁶⁾ For the temperature range of 864 to 2500 K, agreement was excellent as shown in the graph of vapor pressures in Fig. 1.2-4. Differences between vapor pressures calculated from the recommended equation (Eq. [1]) and those calculated with other equations, expressed as a percent are shown in Fig. 1.2-3.

Recently, Binder⁽¹⁷⁾ reported high temperature vapor pressures as well as values for critical parameters based on his experimental PVT measurements at high pressure and temperature. He obtained the critical parameters and the vapor pressure on the saturation curve by extrapolation of his results for superheated sodium. He gives 2485 ± 15 K for the critical temperature and 24.8 ± 0.5 MPa for the critical pressure. The critical vapor pressure measured by Bhise and Bonilla using a pressure tube method is 25.64 MPa. This measured value is higher than the extrapolated value given by Binder. The lower critical temperature given by Binder is consistent with his lower critical pressure. Freyland and Hensel⁽¹⁸⁾ determined high temperature/pressure properties of potassium using the same technique used by Binder. In their analysis of the potassium vapor pressure data and critical parameters, Browning and Potter⁽¹⁾ found that the critical temperature and pressure determined by Freyland and Hensel from their superheated sample were inconsistent with critical parameters determined experimentally by others and also inconsistent with the equation that fit available vapor pressure data for potassium. Comparison of values for the vapor pressure calculated with the linear equation of Binder with values from the recommended equation (Browning and Potter's Eq. [10]) and from recommended equations from other assessments indicates that the values from Binder's extrapolation are consistently high. Binder's values and those of the recommended equation as well as values from other assessments are shown in Fig. 1.2-4. Differences from the

recommended equation expressed as a percent are shown in Fig. 1.2-5. These comparisons indicate that the vapor pressure equation and critical parameters suggested by Binder are inconsistent with other sodium data. Consequently, the equation recommended for the vapor pressure of sodium does not include the Binder data.

The pressure of 25.64 MPa at the critical point was determined experimentally by Bhise and Bonilla.⁽⁸⁾ The recommended equation from Browning and Potter's analysis of the vapor pressure data in the temperature range of 864 to 2499 K gives a critical temperature of 2503.7 K for the critical pressure of 25.64 MPa. Bhise and Bonilla⁽⁸⁾ had fit their high temperature data, $T > 2350$ K, to a linear equation and obtained a critical temperature of 2507.6 K for the critical pressure 25.64 MPa. Das Gupta et al.⁽¹⁹⁾ reanalyzed the experimental data of Bhise and Bonilla. They retained 25.64 MPa for the critical pressure and suggested 2508.7 ± 12.5 K for the critical temperature. Browning and Potter⁽¹⁾ also analyzed the Bhise and Bonilla high temperature data using a three-term equation and obtained 2507.1 K for the critical temperature, which is almost identical to the Bhise and Bonilla value. However, when their high temperature data are included with other available vapor pressure data, critical temperatures around 2503 K are obtained. Bystrov et al.⁽¹¹⁾ recommend 2503 K for the critical temperature.

Some assessments of the critical temperature of sodium suggest a value 100 to 200 K higher than the value implied from the pressure measurements of Bhise and Bonilla.⁽⁸⁾ Petiot and Seiler⁽²⁰⁾ recommend a critical temperature of 2630 ± 50 K based on their analysis of vapor pressure and vapor density measurements to 2250 K. However, this value for the critical temperature is not consistent with the measured critical pressure of 25.64 MPa. The vapor pressure curve of Petiot and Seiler gives 2480 K as the temperature at which the vapor pressure equals 25.64 MPa, which is within the 50 K uncertainty of the temperature given by Browning and Potter's equation for that pressure. If the critical pressure of 34 ± 4 MPa, suggested by Petiot and Seiler, is used in the equations of Browning and Potter, a temperature of about 2660 K is obtained; this temperature is close to that given by Petiot and Seiler. Thus, the vapor pressure equations given by Petiot and Seiler and by Browning and Potter are consistent. The analyses differ in their choice of critical temperature. The higher critical temperature is not consistent with the measured critical vapor pressure of Bhise and Bonilla.⁽⁸⁾ This is the only measured critical parameter. Thus, Browning and Potter's selection of

25.64 MPa for the critical pressure and the corresponding critical temperature of around 2503 K is reasonable in terms of experimental data presently available.

Uncertainty

The uncertainties in the recommended values, shown in Table 1.2-2, arise from three sources: (1) the statistical fit by Browning and Potter to the experimental data; (2) uncertainties due to differences between recommended equations by various analyses; and (3) experimental errors. These sources of error are discussed below in the order given. These discussions are followed by an estimate of the uncertainties as a function of temperature from all three sources of error.

Equation (3) gives the uncertainties for each of the coefficients in Eq. (1). These uncertainties were obtained from the statistical least squares fit by Browning and Potter of the data shown in Table 1.2-3:

$$\ln P = 11.9463 \pm 0.5127 - (12633.73 \pm 90.524)/T - (0.4672 \pm 0.0616) \ln T \quad (3)$$

In Eq. (3), pressure (P) is in MPa and temperature (T) is in K.

Comparison of the vapor pressures obtained from Eq. (1) with vapor pressures calculated using another equation recommended by Browning and Potter⁽¹⁾ and equations recommended by other analysts,⁽¹¹⁻¹⁶⁾ show differences on the order of 0.03% to 3% for the temperature range 864 to 2503.7 K. The greatest deviations between the recommended equations occur near the low temperature 864 K.

Because Browning and Potter included no low temperature data in their database, Eq. (1) is strictly valid only for the temperature range 864 to 2503.7 K. Values calculated using this equation below 864 K are extrapolations and, therefore, may have larger errors than values calculated above 864 K. Comparison of extrapolated values with values from other equations show good agreement with the values given by equations recommended by Bystrov et al.⁽¹¹⁾ and by Vargaftik and Voljak.⁽¹²⁾ However, values of the vapor pressure obtained by extrapolation of Eq. (1) to 400 K differ by 24% from values calculated using the equation recommended in the assessment of sodium properties for LMFBR safety.⁽¹³⁻¹⁵⁾ However, values at higher temperatures are in good agreement. The equation recommended in the LMFBR safety analysis was based on a fit to the high temperature data of Bhise and Bonilla,⁽⁸⁾ the intermediate temperature data of Stone et al.,⁽⁷⁾ and the low temperature data (melting point to 1155 K) of Ditchburn and Gilmour.⁽¹⁷⁾ Both the Bhise and Bonilla data⁽⁸⁾ and that of Stone et al.⁽⁷⁾ were included in the assessment by Browning and Potter.

However, the Ditchburn and Gilmour data were not included in the Browning and Potter analysis nor in the analyses for the equations recommended by Bystrov et al.⁽¹¹⁾ and by Vargaftik and Voljak.⁽¹²⁾ The large deviation at 400 K between the equation recommended for LMFBR safety analysis⁽¹³⁻¹⁵⁾ and Eq. (1) is most likely due to inclusion of the low-temperature data of Ditchburn and Gilmour in the LMFBR safety analysis.

Bystrov et al.⁽¹¹⁾ have examined the errors in the experimental data above 1000 K. They report experimental errors of 1% for the temperature range 1000 to 1500 K, 2-3% up to 2000 K, and 4-5% at the higher temperatures.

Uncertainties in the recommended values have been estimated from the error in the statistical analysis, the error in the experimental data (given by Bystrov et al.⁽¹¹⁾), and the deviations between recommended equations. In the calculation of uncertainties, the errors from these sources have been assumed to be independent so that the overall uncertainty is the square root of the sum of the squares of the statistical, experimental, and fitting uncertainties. Estimated uncertainties are tabulated as a function of temperature in Table 1.2-2. The recommended equation derived from data for the temperature range 864 to 2499 K, but suggested for the entire temperature range, is included in Table 1.2-2. The uncertainties expressed as a percent are large for the low temperatures due to the large percent deviation in the vapor pressures calculated using different equations. Because the vapor pressure is so low at these low temperatures, the difference in vapor pressure between the equations is very small (4×10^{-12} MPa at 400 K) even though the percent deviation is large.

Polynomial Approximation

In some applications such as the SASS code,⁽²²⁾ the equation for the vapor pressure must be inverted, so that temperature (T) is expressed as a function of saturation pressure (P). Because the recommended equation cannot be inverted, the recommended values for the natural logarithm of the vapor pressure have been fit to a polynomial of the form used in the SASS code.⁽²²⁾

$$\ln P = A - \frac{B}{T} - \frac{C}{T^2} \quad (4)$$

Then T , is related to P by

$$T = \frac{2C}{-B + \sqrt{B^2 + 4AC} - 4C \ln P} . \quad (5)$$

Approximating the natural logarithm of the pressure ($\ln P$) with the polynomial given in Eq. (4) creates systematic errors due to differences in the functional forms. If the fit to Eq. (4) is done by minimizing χ^2 , then the coefficients in Eq. (4) are given by

$$\begin{aligned} A &= 7.8270 , \\ B &= 11275 , \\ C &= 4.6192 \times 10^5 . \end{aligned}$$

Deviations of Eq. (4) from Eq. (1) expressed as a percent given by

$$Deviation = \left(\frac{[Eq. (4) - Eq. (1)] 100\%}{Eq. (1)} \right) \quad (6)$$

vary for this fit from a minimum of 0.03% to 1.7%, as shown by the "xhisq" curve in Fig. 1.2-6. In Fig. 1.2-6, lines have been included to guide the eye between the points where the deviations were calculated. This fit gives a χ^2 of 0.0003. Minimizing the absolute value of the deviation defined in Eq. (6) gives a larger χ^2 (0.001) but does not give the large percent deviation at 1500 K. The fit based on minimization of the absolute value of Eq. (6) has the coefficients

$$\begin{aligned} A &= 7.8130 , \\ B &= 11209 , \\ C &= 5.2490 \times 10^5 . \end{aligned}$$

This fit, labeled abs(diff) in Fig. 1.2-6 is preferred because it has no large percent deviations at any points. Percent deviations are greatest at the two extremes (0.49% at 864 K and 0.25% at 2503.7 K). From the χ^2 for the two fits, shown in Fig. 1.2-7, it is clear that the larger χ^2 for this fit is due to the contributions to χ^2 from the two low temperature points (864 and 900 K). All other points have contributions similar to those for the χ^2 minimization. The lines in Fig. 1.2-7 are guides for the eye between the points.

1.2.2 BOILING POINT

Recommendation

The recommended value for the boiling point of saturated liquid sodium (liquid in equilibrium with its vapor) is 1154.7 ± 1.3 K. This is the temperature at which the vapor pressure, determined from Eq. (1), equals 1 atm (0.1013 MPa).

Discussion

Ohse et al.⁽²³⁾ list experiments designed to determine the boiling point of sodium. This list is given in Table 1.2-4, which also includes the boiling point, experimental method, and year of experiment. The boiling point of sodium determined from these experiments ranges from 1154.4 to 1156 K. Values for the boiling point of sodium given in recent assessments of vapor pressure and sodium property data are shown in Table 1.2-5 according to the year of assessment. Except for values given by Vargaftik⁽³⁴⁾ and by Cordfunke and Konings,⁽³⁶⁾ recommended boiling points are in the 1154 to 1156.5 K range.

The recommended value 1154.7 ± 1.3 K, from the equation given by Browning and Potter,⁽¹⁾ differs by 0.1 K from the value they give in their assessment. This is because Browning and Potter give the temperature at which the vapor pressure calculated via Eq. (2) is 1 atm, whereas the recommended value is based on Eq. (1). This difference is well within the 1.1 K uncertainty given by Browning and Potter. An uncertainty of 1.3 K is given for the recommended value so that the uncertainty includes the extremes in values from the experiments.

Table 1.2-4 Measured Boiling Point of Sodium*

| T_b, K | Measurement Method | Authors | Year | Ref. |
|-------------------------|---------------------------|---------------------|-------------|-------------|
| 1156 | Vapor Pressure | Heycock & Lamplough | 1912 | 24 |
| 1156 | Vapor Pressure | Ladenburg & Thiele | 1930 | 25 |
| 1154.5 | Vapor Pressure | Makansi et al. | 1955 | 6 |
| 1154.52 | Vapor Pressure | Bonilla et al. | 1962 | 26 |
| 1156 | Vapor Pressure | Sowa | 1963 | 9 |
| 1154.59 | Vapor Pressure | Bowles & Rosenblum | 1965 | 27 |
| 1150.15 | Vapor Pressure | Achener et al. | 1966 | 4 |
| 1154.6 | Vapor Pressure | Stone et al. | 1966 | 7 |
| 1156.0 | State Equilibrium | Vinogradov & Voljak | 1966 | 10 |
| 1154.4 | Vapor Pressure | Fischer | 1966 | 28 |
| 1156. | Vapor Pressure | Bohdansky & Shins | 1967 | 2 |
| 1155.5 | Vapor Pressure | Achener et al. | 1967 | 29 |
| 1155.12 | Heat Pipe | Schins et al. | 1971 | 3 |
| 1155.2 | Pressure Tube | Bhise & Bonilla | 1977 | 30 |
| 1154.6 | Vapor Pressure | Das Gupta | 1977 | 31 |

*Table is from Ohse et al.²²

Table 1.2-5 Boiling Points of Sodium Recommended in Assessments

| T_b, K | Author | Year | Ref. |
|------------------|---------------------|-------|-------|
| 1154.7 | Shpil'rain | 1970 | 32 |
| 1156 | Hultgren et al. | 1973 | 33 |
| 1151 | Vargaftik | 1978 | 34 |
| 1156.5 ± 1.1 | Fink & Leibowitz | 1979 | 13-15 |
| 1154 | Thurnay | 1981 | 16 |
| 1156 | Chase et al. | 1985* | 35 |
| 1154.5 ± 1.0 | Ohse et al. | 1985 | 22 |
| 1154.8 ± 1.1 | Browning & Potter | 1985 | 1 |
| 1158 | Cordfunke & Konings | 1990 | 36 |
| 1156.3 ± 1.0 | Bystrov et al. | 1990 | 11 |

*Data assessment done in 1962.

1.2.3 ENTHALPY OF VAPORIZATION

Summary

Recommended values for the enthalpy of vaporization of sodium, shown in Table 1.2-6, have been calculated from

$$\Delta H_g = 393.37 \left(1 - \frac{T}{T_C} \right) + 4398.6 \left(1 - \frac{T}{T_C} \right)^{0.29302} \quad (7)$$

for $371 K \leq T \leq 2503.7 K$,

where enthalpy of vaporization (ΔH_g) is in $\text{kJ}\cdot\text{kg}^{-1}$, temperature (T) is in kelvins, and $T_C = 2503.7 K$, the critical temperature. Equation (7) is a fit to values of the enthalpy of vaporization from 371 to 1600 K calculated using the quasi-chemical method developed by Golden and Tokar.⁽³⁷⁾ The form of equation used to fit these data gives the correct behavior at the critical point and is, therefore, suitable for extrapolation above 1600 K. Values calculated with Eq. (7) are in good agreement

Table 1.2-6 Enthalpy of Vaporization of Sodium

| Temperature (K) | $\text{kJ} \cdot \text{kg}^{-1}$ |
|-----------------|----------------------------------|
| 371 | 4532 |
| 400 | 4510 |
| 500 | 4435 |
| 600 | 4358 |
| 700 | 4279 |
| 800 | 4197 |
| 900 | 4112 |
| 1000 | 4025 |
| 1100 | 3933 |
| 1200 | 3838 |
| 1300 | 3738 |
| 1400 | 3633 |
| 1500 | 3523 |
| 1600 | 3405 |
| 1700 | 3279 |
| 1800 | 3143 |
| 1900 | 2994 |
| 2000 | 2829 |
| 2100 | 2640 |
| 2200 | 2418 |
| 2300 | 2141 |
| 2400 | 1747 |
| 2500 | 652 |
| 2503.7 | 0 |

with values recommended by Fink and Leibowitz,⁽¹³⁻¹⁵⁾ values recommended by Bystrov,⁽¹¹⁾ and values calculated with the equation recommended by Das Gupta.⁽³¹⁾

The recommended values of the enthalpy of vaporization are shown in Fig. 1.2-8. Uncertainty bands have been included up to 2400 K on the graph. Above 2400 K, the uncertainty in the critical temperature results in large uncertainties (30%) because the enthalpy of vaporization must be zero at the critical temperature. Uncertainties are given in Table 1.2-7 at a number of temperatures. Between the temperatures shown in Table 1.2-7, the uncertainties are assumed to vary linearly with temperature.

Table 1.2-7 Estimated Uncertainty in Values of the Enthalpy of Vaporization of Sodium Calculated from Eq. (7)

| Temperature (K) | Enthalpy of Vaporization (ΔH_g , $\text{kJ} \cdot \text{kg}^{-1}$) | Uncertainty (%) |
|-----------------|--|-----------------|
| 371 - 1000 | $\Delta H = 393.37 \left(1 - T/T_c\right) + 4398.6 \left(1 - T/T_c\right)^{0.29302}$ | 1 |
| 1400 | | 2 |
| 1800 | | 6.5 |
| 2000 | | 7.3 |
| 2400 | | 9.5 |

$$T_c = 2503.7\text{K}$$

Discussion

The quasi-chemical method⁽³⁷⁾ was used to calculate the enthalpy of vaporization from the melting point through 1600 K. The upper limit was chosen based on Padilla's⁽³⁸⁾ recommendation of 1644 K as the limit of validity of application of the quasi-chemical method to sodium. In the quasi-chemical method, the heat of vaporization is defined as

$$\Delta H_g = \left[\frac{N_1 \Delta H_1 + N_2 \Delta H_2 + N_4 \Delta H_4}{22.98977 (N_1 + 2N_2 + 4N_4)} \right], \quad (8)$$

where N_1 , N_2 , and N_4 are, respectively, the mole fractions of the monomer, dimer, and tetramer; and ΔH_i is the contribution to the enthalpy of vaporization for each species. The gram molecular mass of the monomer, 22.98977, is the value recommended by CODATA.⁽³⁹⁾ The contributions to the enthalpy of vaporization for the monomer, dimer, and tetramer in $\text{J} \cdot \text{mol}^{-1}$ are, respectively;

$$\begin{aligned} \Delta H_1 &= 107844 - 14.4203T + 7.05130 \times 10^{-3}T^2 \\ &\quad - 2.57107 \times 10^{-6}T^3 + 14184T^{-1}, \\ \Delta H_2 &= 2\Delta H_1 - 76584, \\ \Delta H_4 &= 4\Delta H_1 - 173544. \end{aligned} \quad (9)$$

The mole fractions of the monomer, dimer, and tetramer were calculated by solving the following set of equations:

$$\begin{aligned} N_1 + N_2 + N_4 &= 1 , \\ N_2 &= \alpha^2 P (N_1 + 2N_2 + 4N_4)^2 k_2 , \\ N_4 &= \alpha^4 P^3 (N_1 + 2N_2 + 4N_4)^4 k_4 , \end{aligned} \quad (10)$$

where α is the unassociated fraction of one mole of monomer

$$\alpha = \left(\frac{N_1}{N_1 + 2N_2 + 4N_4} \right) . \quad (11)$$

The equilibrium constants, k_2 and k_4 , were determined experimentally by Stone et al.⁽⁴⁰⁾ Their natural logarithms, as reported by Stone et al., are represented by

$$\begin{aligned} \ln k_2 &= -9.95845 + \left(\frac{16588.3}{T_R} \right) , \\ \ln k_4 &= -24.5912 + \left(\frac{37589.7}{T_R} \right) , \end{aligned} \quad (12)$$

where T_R is the temperature in Rankins. The pressure (P) in Eq. (10) is given by Eq. (1).

Values of the enthalpy of vaporization from 371 through 1600 K, calculated using Eqs. (8-12) were fit by Eq. (7), which has an appropriate form for proper behavior at the critical temperature. Thus, a single equation suitable for the entire liquid temperature range was obtained.

Figure 1.2-9 shows the recommended equation for the enthalpy of vaporization of sodium and values from 800 to 2000 K given by Bystrov et al.,⁽¹¹⁾ values from 400 to 2400 K recommended by Fink and Leibowitz,⁽¹³⁻¹⁵⁾ and values from 400 to 2400 K from the equation given by Das Gupta.⁽³¹⁾ Values from assessments by Bystrov et al., Fink and Leibowitz, and Das Gupta are in good agreement with each other and with values from the recommended equation. Values recommended by Fink and Leibowitz were calculated using the quasi-chemical method to 1644 K and using an empirical equation to extrapolate from 1644 K to the critical temperature of 2509.46 K. Values given by Bystrov et al. are from their equation of state for sodium vapor which assumed

that the vapor is composed of monomers, dimers, and positive ions. Das Gupta fit the enthalpy of vaporization data of Achener and Jouthas⁽⁴⁾ (867 to 1202 K) and values obtained by application of the Clausius-Clapeyron equation to the data of Stone et al.⁽⁷⁾ He recommended the equation

$$\Delta H_g = -1011.3 \left(1 - \frac{T}{T_C} \right) + 5689.1 \left(1 - \frac{T}{T_C} \right)^{0.4} \quad (13)$$

for the entire temperature range. In Eq. (10), ΔH_g is in $\text{kJ}\cdot\text{kg}^{-1}$, T is in K, and the critical temperature, T_C , is 2509.46 K.

Deviations from the recommended equation (Eq. [7]), expressed as percents, defined as

$$\frac{[\Delta H_g(\text{Other}) - \Delta H_g(\text{Eq. 7})]100\%}{\Delta H_g(\text{Eq. 7})},$$

are shown in Fig. 1.2-10. For temperatures equal or less than 2100 K, deviations are 2% or less. Deviations become large as the critical temperature is approached because the enthalpy of vaporization must be zero at the critical temperature and different values were selected for the critical temperature in the different assessments.

Uncertainty

Uncertainties based on experimental measurements are not available for the enthalpy of vaporization. Estimated uncertainties for the enthalpy of vaporization calculated with Eq. (7) are given in Table 1.2-7 for various temperatures. Uncertainties are assumed to increase linearly with temperature between the temperatures given in Table 1.2-7. These uncertainties have been estimated from errors given by Bystrov et al.⁽¹¹⁾ and from deviations in values calculated using equations from a number of recent data assessments.

Errors given by Bystrov et al. include inaccuracies in the equation of the saturation curve, errors due to nonideality of the vapor, and differences between Bystrov's recommended values and the data of Achener and Jouthas.⁽⁴⁾ Bystrov et al. give errors of 0.3% at 1000 K, 0.4% at 1400 K, and 6.5% at 1800 K. Estimated uncertainties given here for temperatures below 1800 K are greater than those given by Bystrov et al.⁽¹¹⁾ because deviations from the various accepted equations differ by 1% below 1000 K and by 2% at 1400 K.

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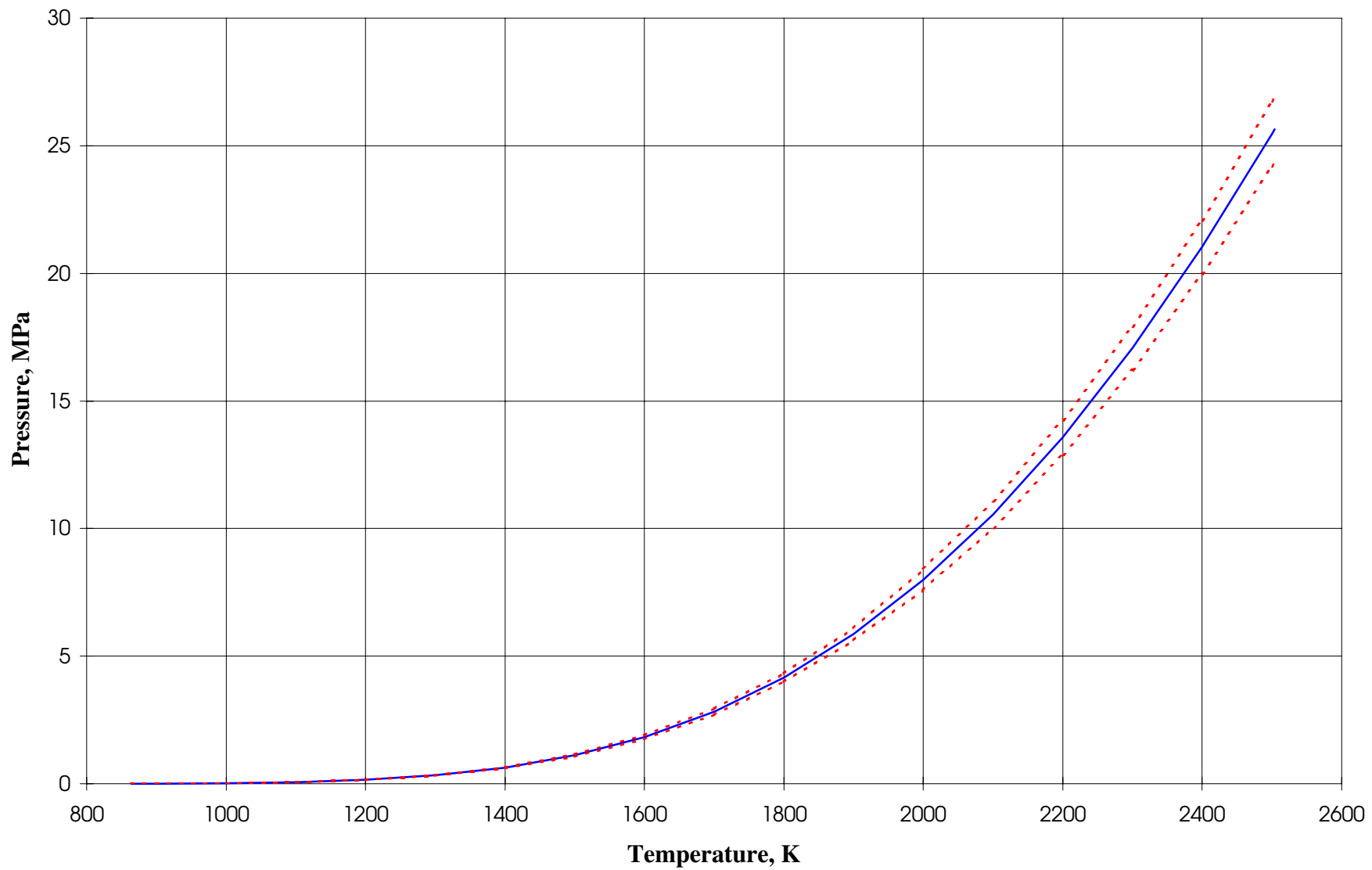


Fig. 1.2-1 The Vapor Pressure of Saturated Sodium

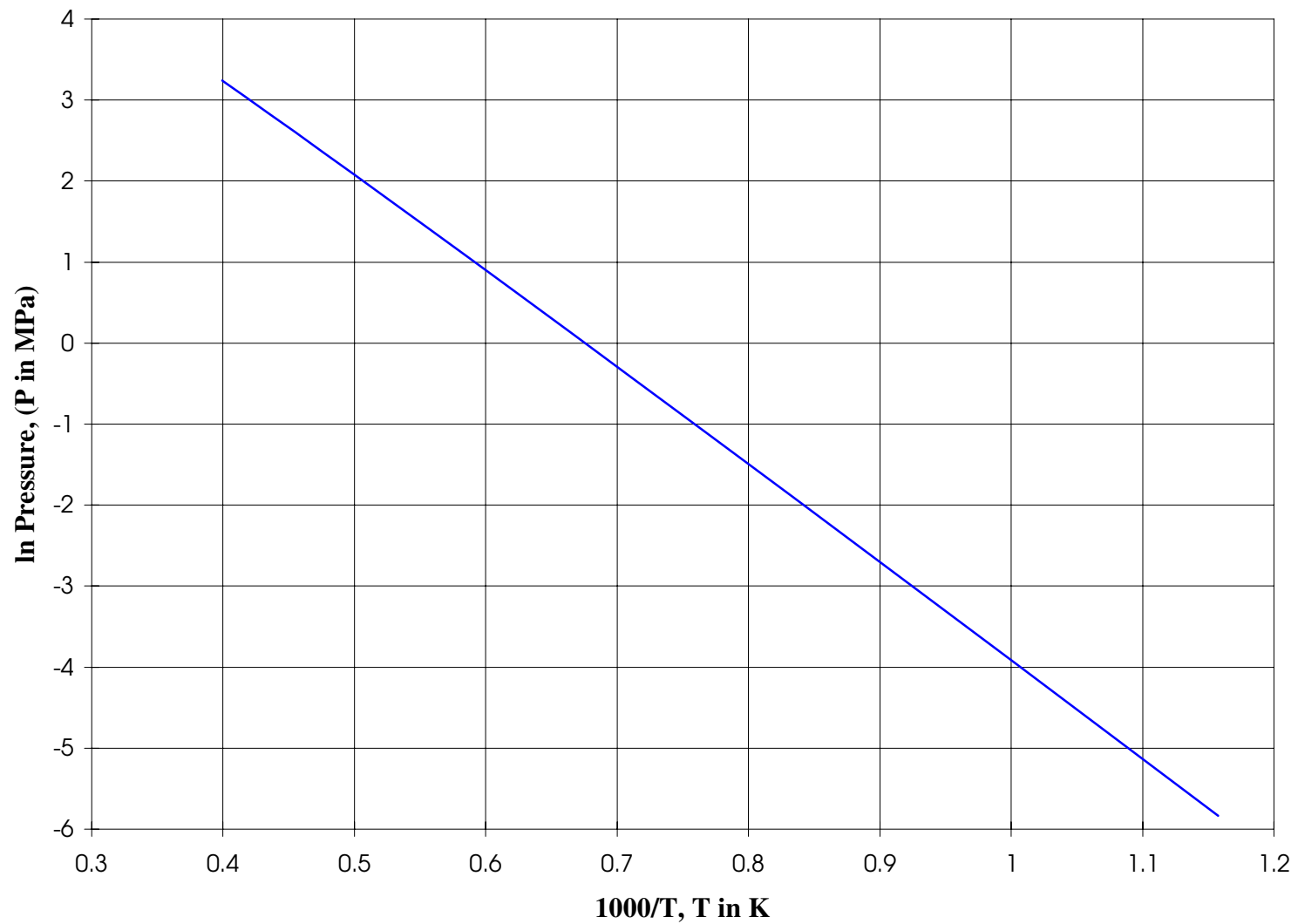


Fig. 1.2-2 The Natural Logarithm of Sodium Vapor Pressure as a Function of Inverse Temperature

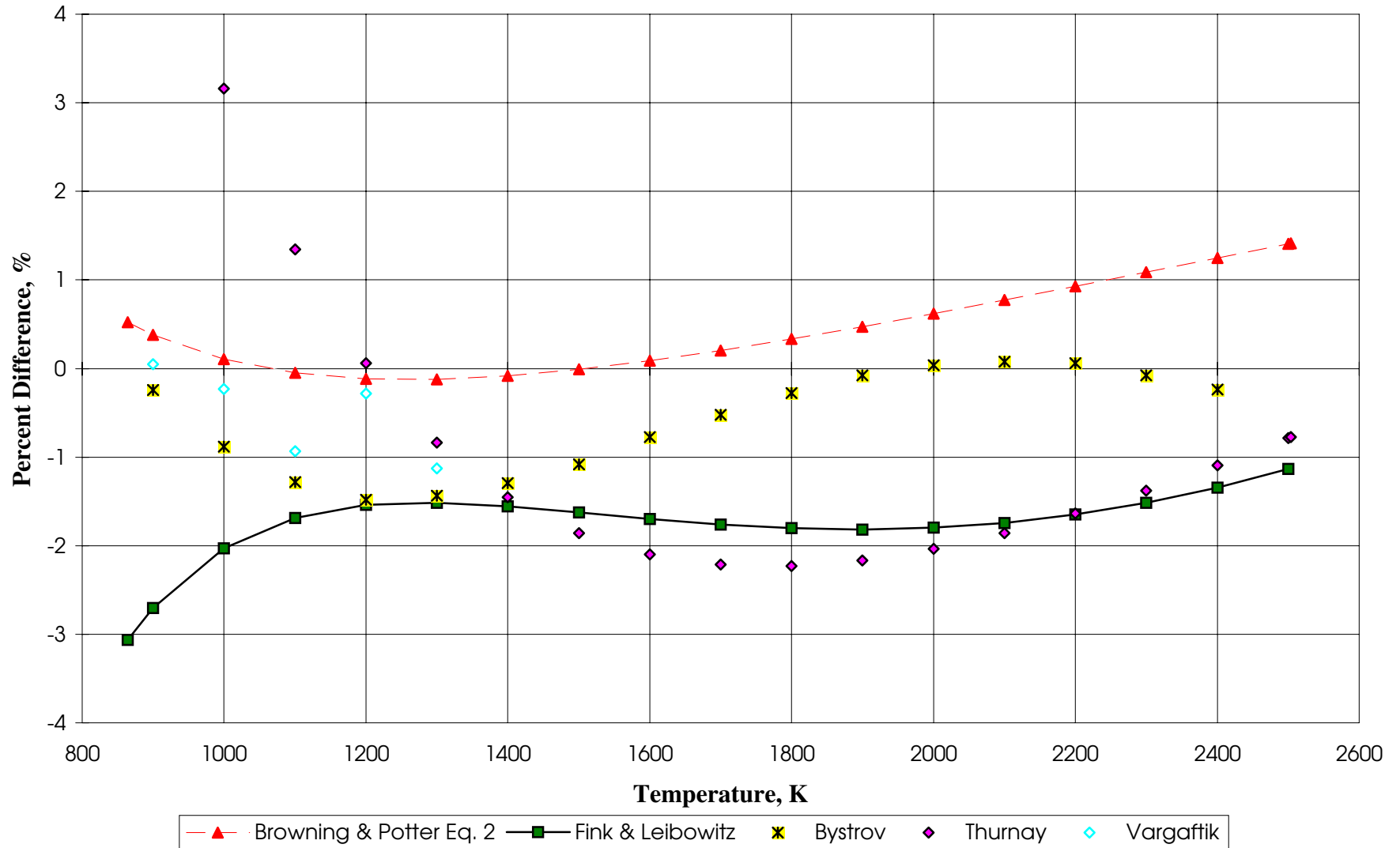


Fig. 1.2-3 Deviation of Other Vapor Pressure Equations from the Recommended Equation

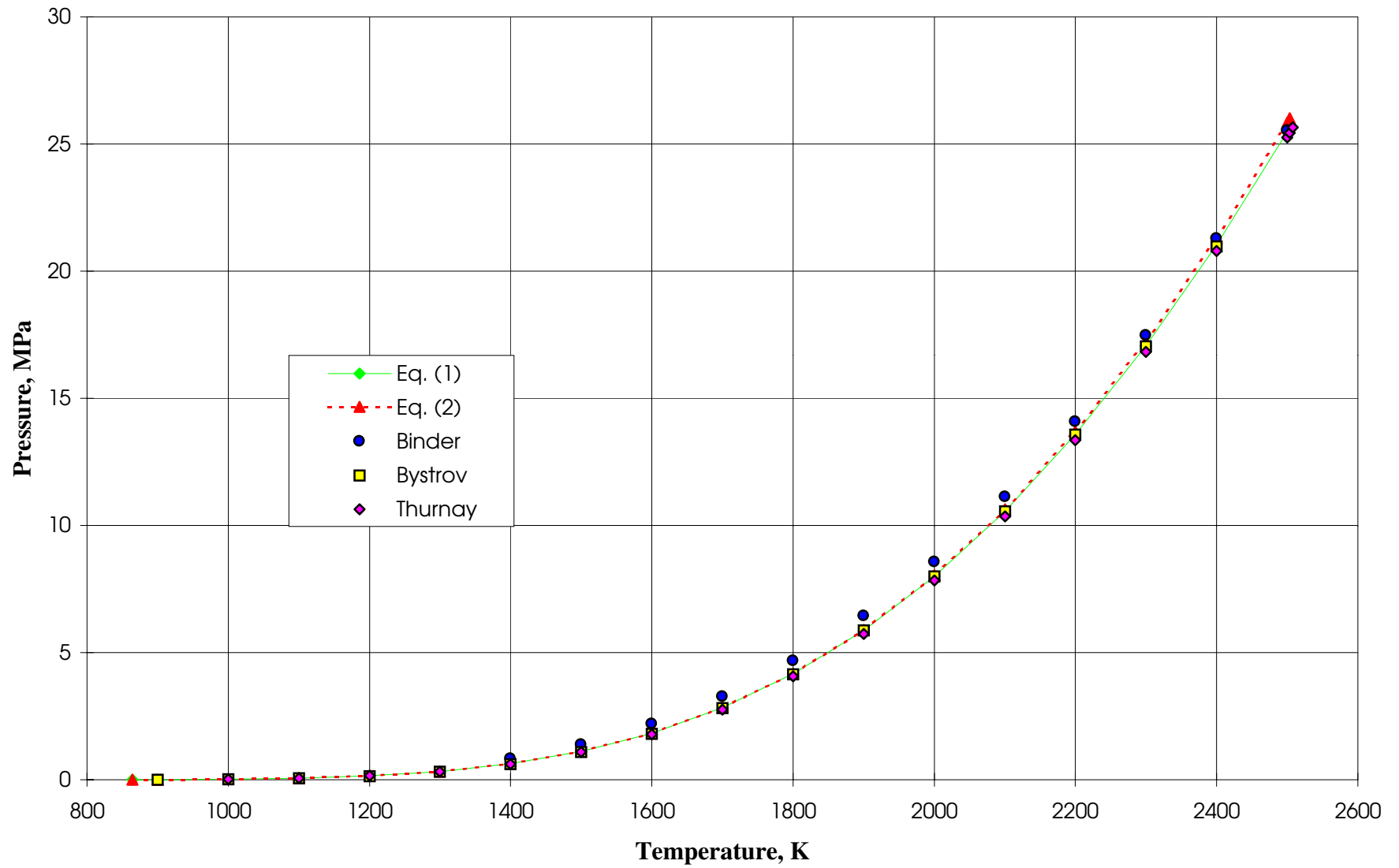


Fig. 1.2-4 Vapor Pressures Calculated from Various Recommended Equations

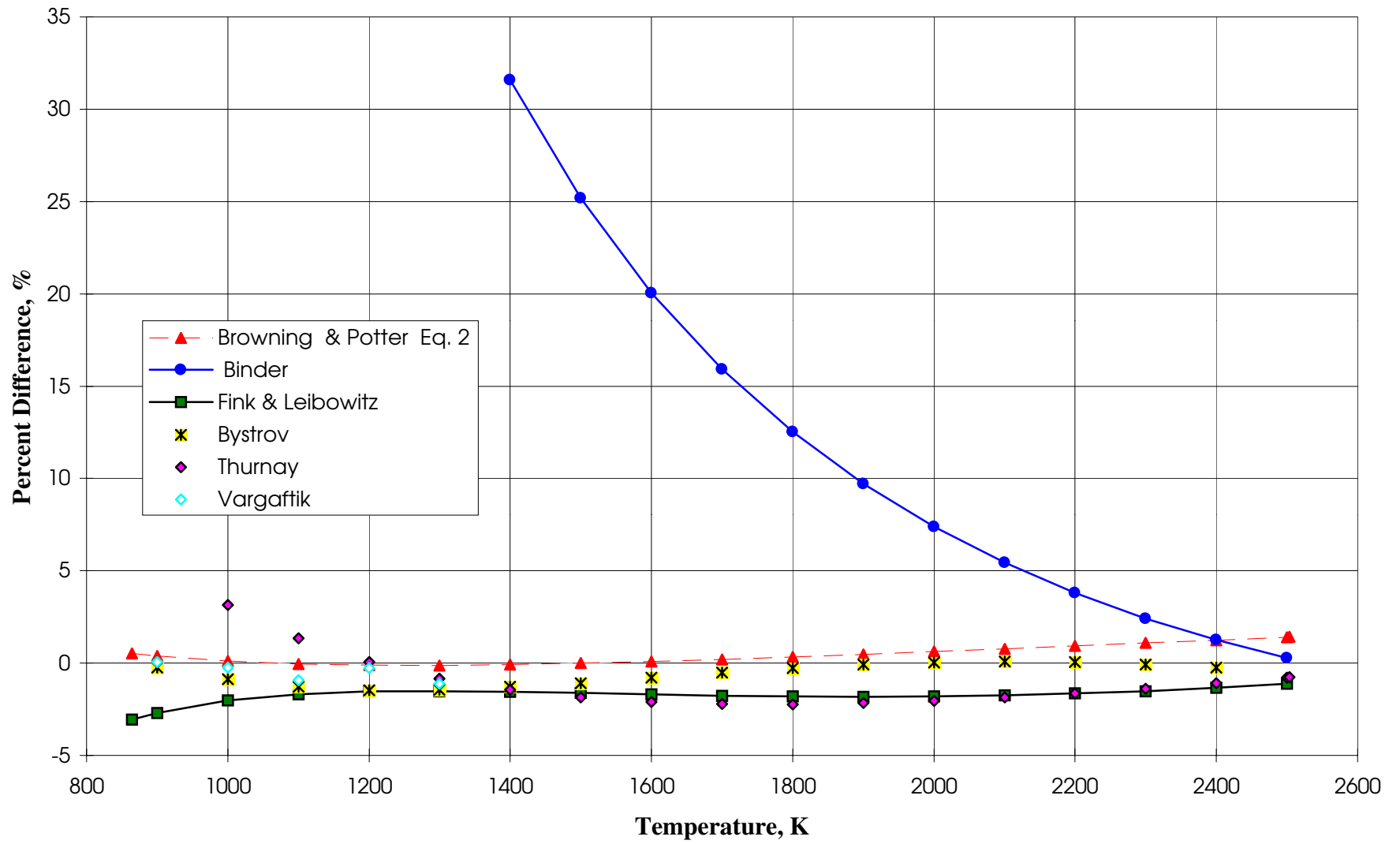


Fig. 1.2-5 Deviation of Binder's Vapor Pressure Equation from the Recommended Equation Compared with Deviations from Other Assessments

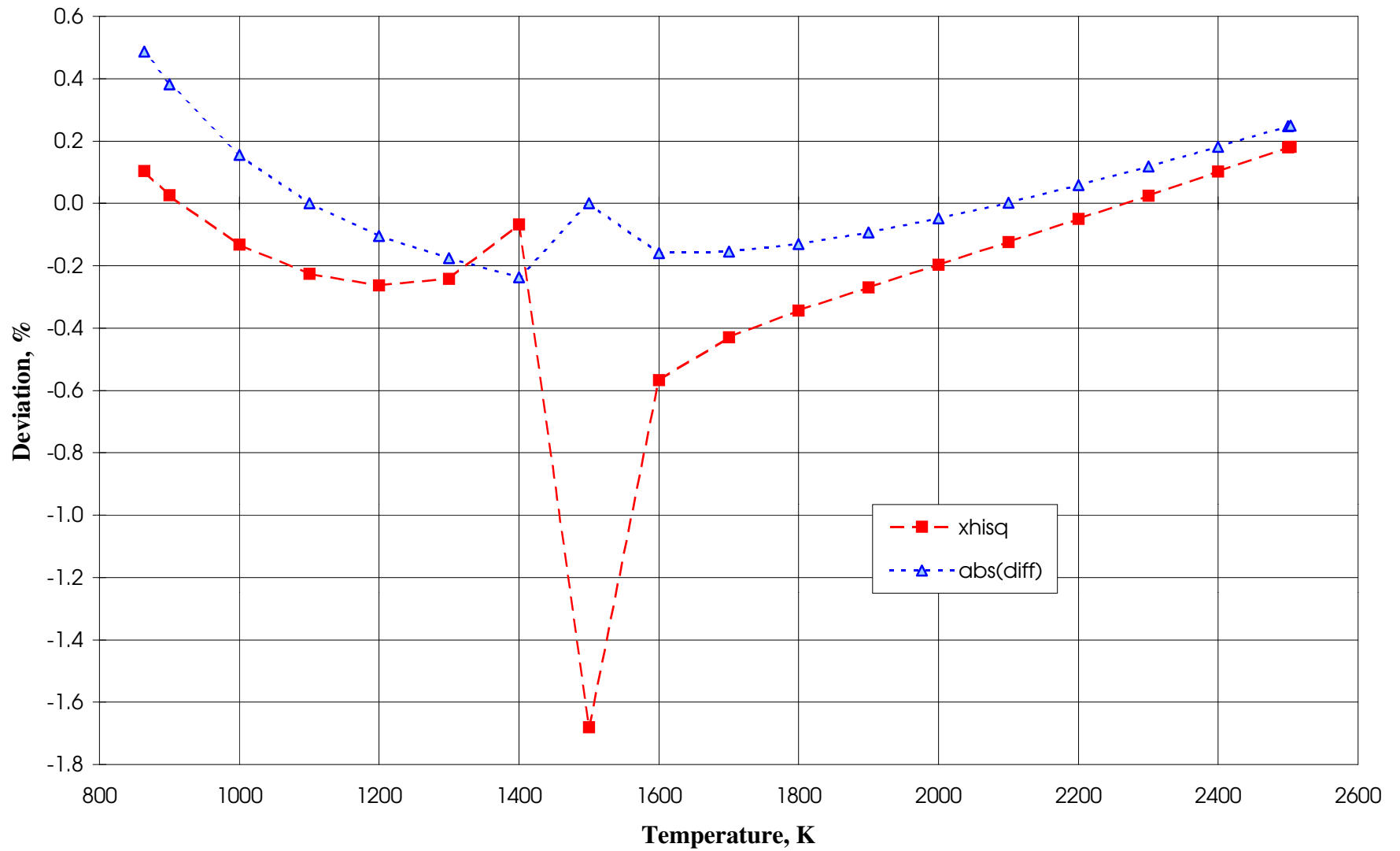
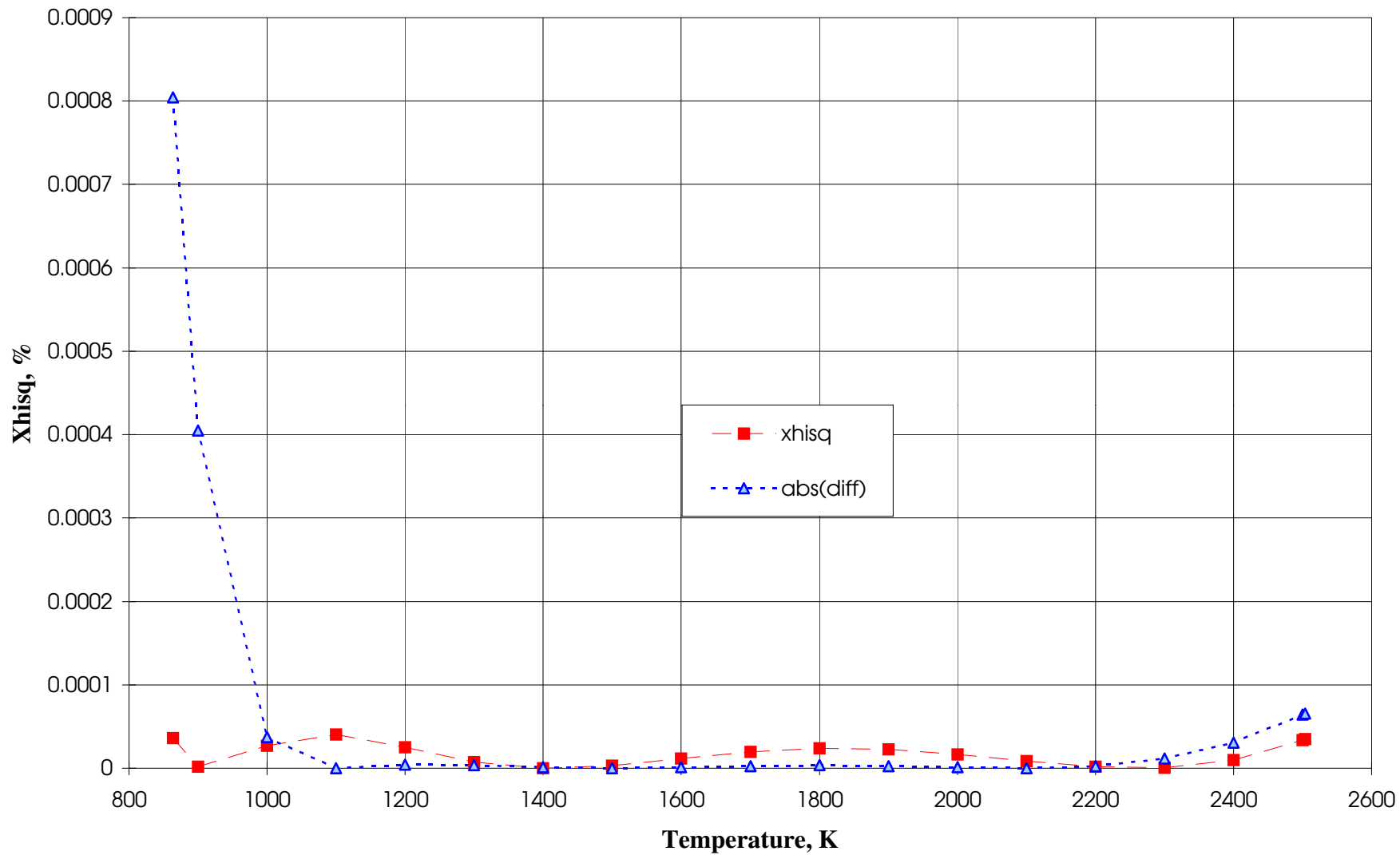


Fig. 1.2-6 Percent Deviation for Two Fits to $\ln P$ Using Eq.(4) "xhisq" Minimizes X^2 ; "abs(diff)" Minimizes the Absolute Value of the Deviation Defined in Eq. (6)



**Fig. 1.2-7 X^2 of Eq.(4) fits to $\ln P$ Using Two Minimization Techniques: "xhisq" Minimizes X^2 ;
 "abs(diff)" Minimizes the Absolute Value of the Deviation in Eq.(6)**

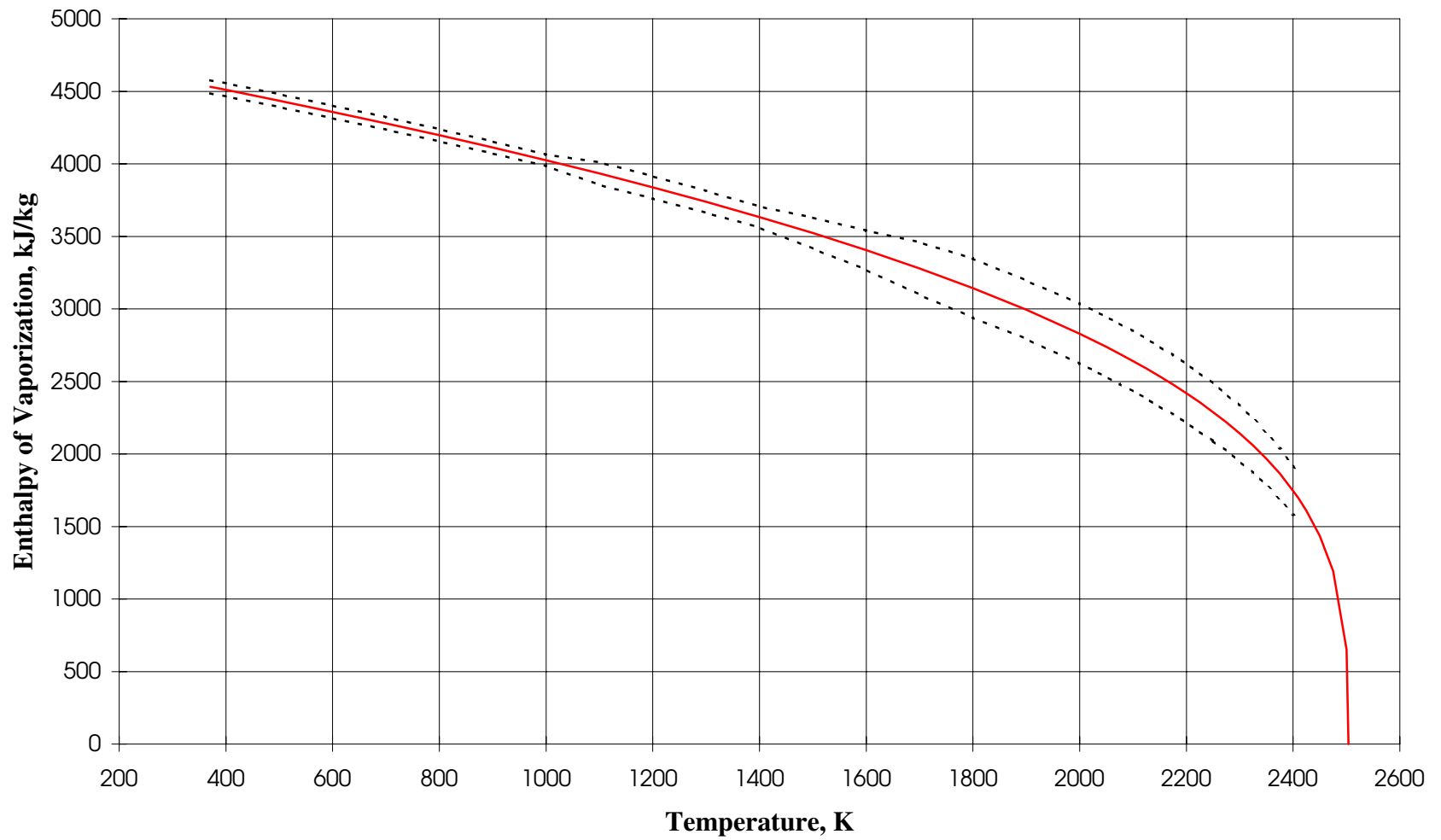


Fig. 1.2-8 Recommended Values of Enthalpy of Vaporization of Sodium (Dashed Lines Show the Estimated Uncertainty)

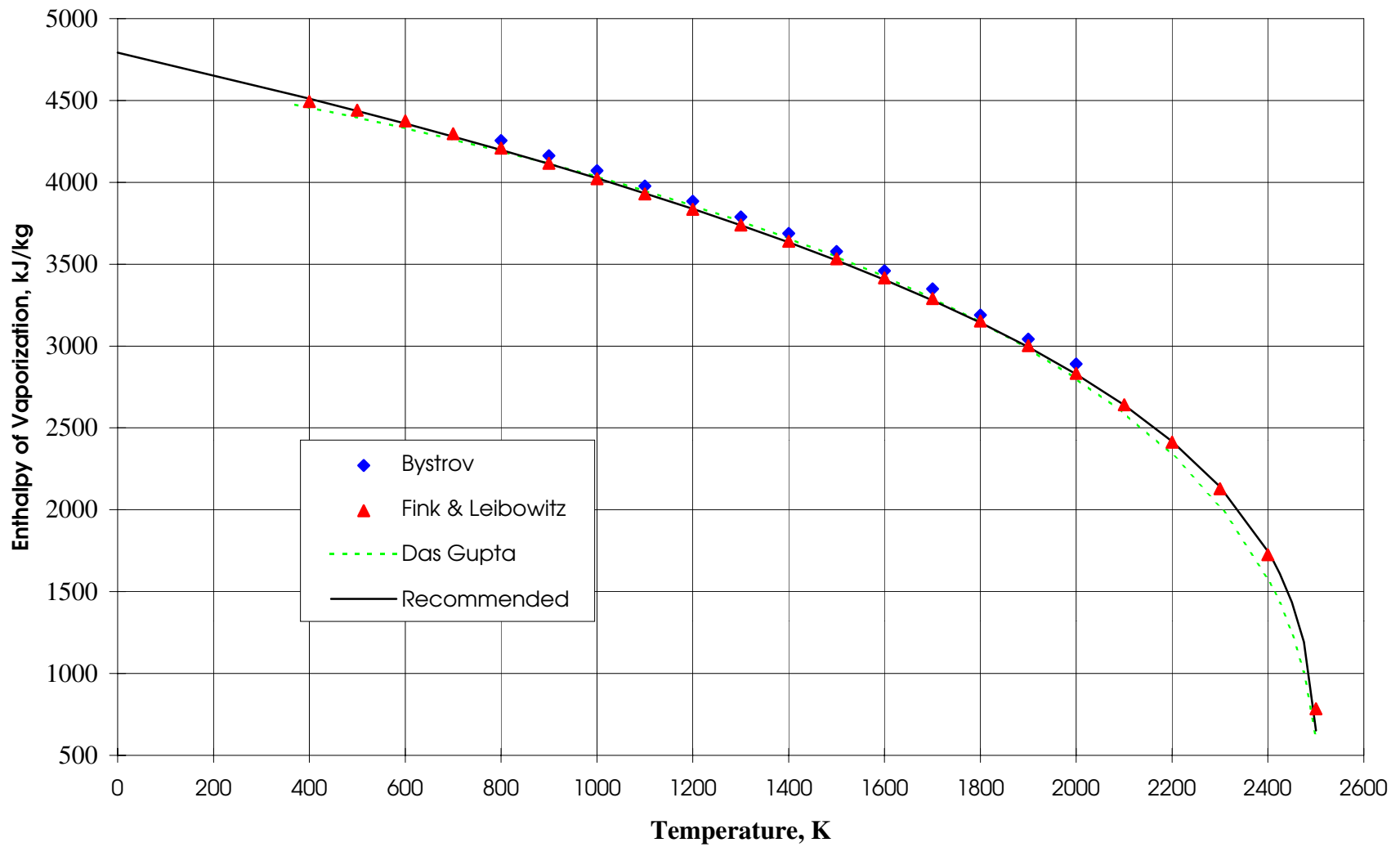


Fig. 1.2-9 Comparison of Recommended Equations for Enthalpy of Vaporization of Sodium with Values from Other Assessments

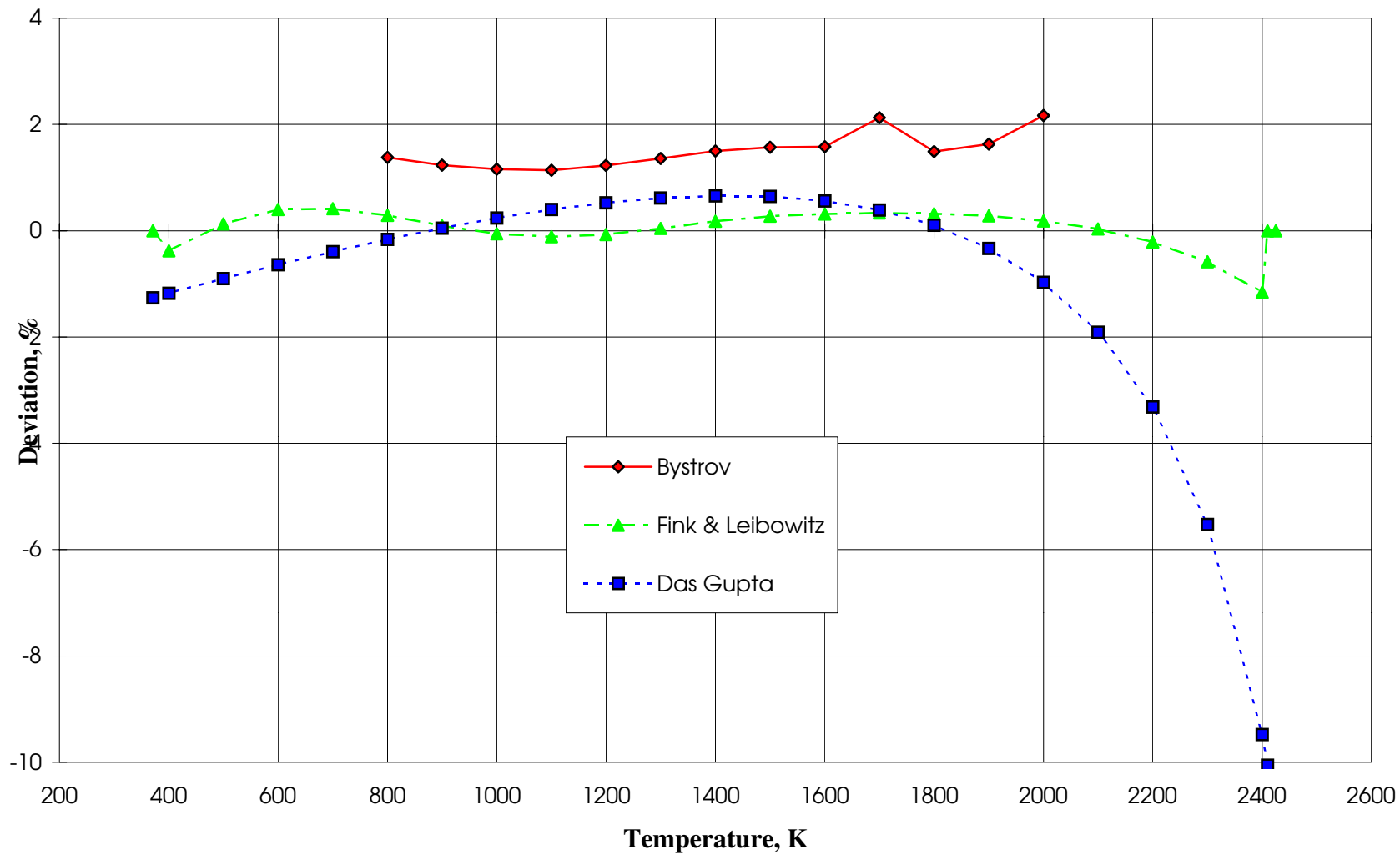


Fig. 1.2-10 Deviations of Values from Other Assessments from Recommended Values of the Enthalpy of Vaporization of Sodium

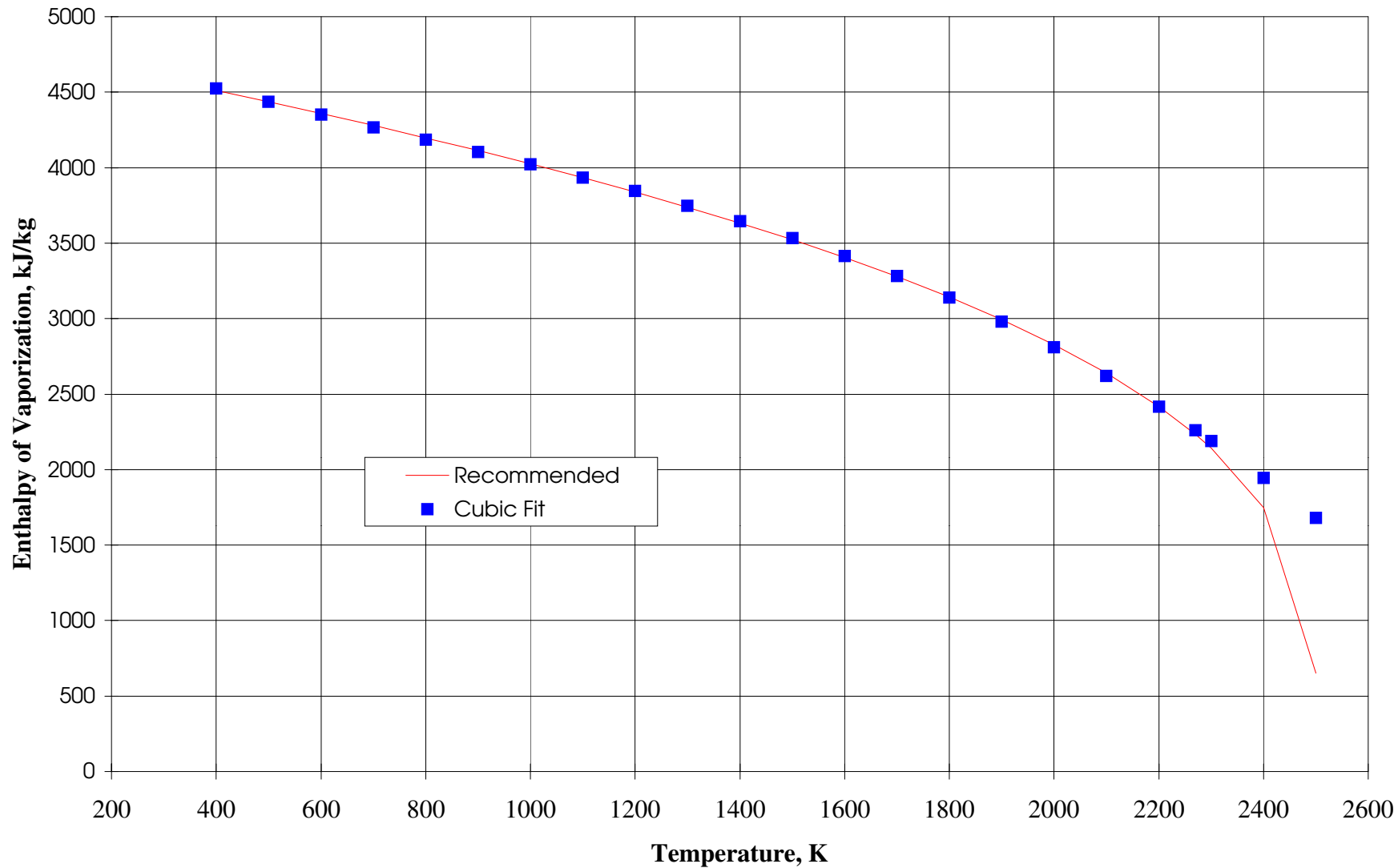


Fig. 1.2-11 Comparison of the Cubic Fit from the Recommended Values for the Enthalpy of Vaporization of Sodium

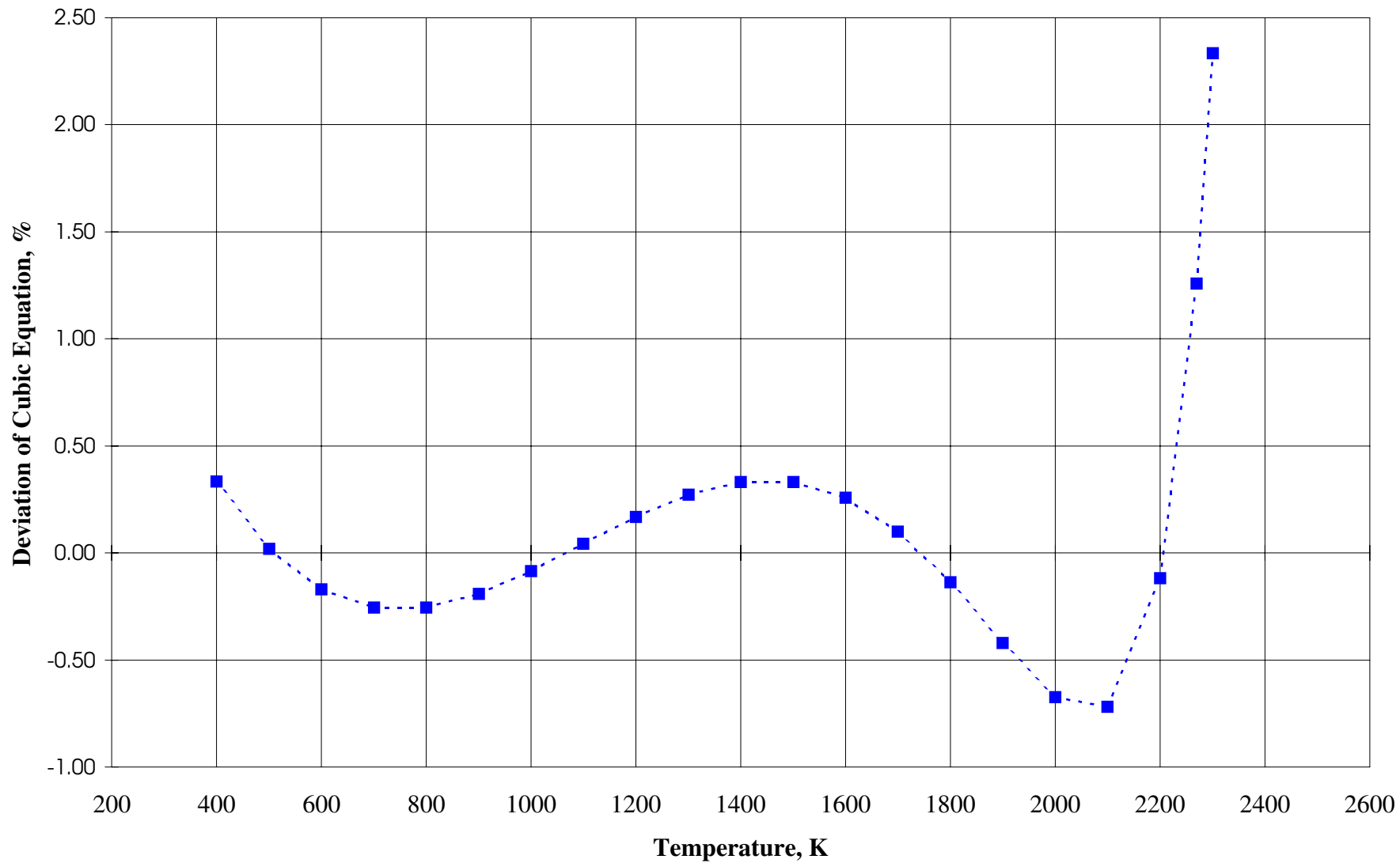


Fig. 1.2-12 Deviations of Values from the Cubic Fit from Recommended Values of the Enthalpy of Vaporization of Sodium

1.3 DENSITY AND THERMAL EXPANSION

1.3.1 DENSITY

Summary

Recommended values for the density of liquid sodium and sodium vapor are given in Table 1.3-1 in $\text{kg}\cdot\text{m}^{-3}$. The recommended equation for the density of liquid sodium in kg/m^3 along the saturation curve is

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

$$\text{for } 371 \text{ K} \leq T \leq 2503.7 \text{ ,}$$

where

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

and ρ_C and T_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_σ), and the liquid density (ρ_l) using the thermodynamic relation

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

Table 1.3-1 Sodium Density

| Temperature (K) | Liquid Density (kg · m ⁻³) | Vapor Density (kg · m ⁻³) |
|--------------------|---|--|
| 400. | 919. | 1.24 x 10 ⁻⁹ |
| 500. | 897. | 5.03 x 10 ⁻⁷ |
| 600. | 874. | 2.63 x 10 ⁻⁵ |
| 700. | 852. | 4.31 x 10 ⁻⁴ |
| 800. | 828. | 3.43 x 10 ⁻³ |
| 900. | 805. | 1.70 x 10 ⁻² |
| 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. |

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.

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

| Temperature (K) | ρ_l ($\text{kg} \cdot \text{m}^{-3}$) | Uncertainty, $\left(\frac{\delta\rho_l}{\rho_l} \right)$ (%) |
|-------------------------------|--|--|
| $371 \leq T \leq 700$ | | 0.3 |
| $700 < T \leq 1400$ | | 0.4 |
| $1500 \leq T \leq 2000^{(a)}$ | $\rho_l = 219 + 275.32 \left(1 - \frac{T}{T_C} \right) + 511.58 \left(1 - \frac{T}{T_C} \right)^{\frac{1}{2}}$ | 2.7 - 14 ^(a) |
| $2000 \leq T \leq 2200^{(a)}$ | | 14 - 19 ^(a) |
| $2200 \leq T \leq 2400^{(a)}$ | | 19 - 24 ^(a) |
| $2400 \leq T \leq 2503^{(a)}$ | | 24 - 26 ^(a) |

^(a)In the temperature range $1500 \text{ K} \leq T \leq 2503 \text{ K}$, 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

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

| Temperature (K) | ρ_g ($\text{kg} \cdot \text{m}^{-3}$) | Uncertainty, $\left(\frac{\delta\rho_g}{\rho_g} \right)$ (%) |
|-----------------------|---|--|
| $371 \leq T \leq 400$ | $\rho_g = \left(\frac{\Delta H_g}{T\gamma_\sigma} + \frac{1}{\rho_l} \right)^{-1}$ | 25 |
| $400 < T \leq 800$ | | 9 - 4 |
| $800 < T \leq 1300$ | | 3 |
| $1300 < T \leq 2000$ | | 5 - 15 |
| $2000 < T \leq 2200$ | | 16 - 20 |
| $2200 < T \leq 2400$ | | 20 - 24 |
| $2400 < T \leq 2503$ | | 24 - 27 |

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 $\text{kg} \cdot \text{m}^{-3}$ 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 X^2 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

$$\rho_l = \rho_C \left[1 + f \left(1 - \frac{T}{T_C} \right)^h + g(T_C - T)^2 \right], \quad (3)$$

which gives the correct behavior at the critical point. They used 2509.4 K for the critical temperature and 214 kg·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

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

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

$$\Delta H_g = 393.37 \left(1 - \frac{T}{T_c} \right) + 4398.6 \left(1 - \frac{T}{T_c} \right)^{0.29302} \quad (5)$$

$$\text{for } 371 \text{ K} \leq T \leq 2503.7 \text{ K} \quad ,$$

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 recommended 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_σ defined as

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

is given by

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

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

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

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

$$\begin{aligned} a &= 11.9463, \\ b &= -12633.73, \\ c &= -0.4672. \end{aligned}$$

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 ($1 \times 10^{-9} \text{ kg}\cdot\text{m}^{-3}$) at these temperatures, the actual deviations are on the order of $1 \times 10^{-10} \text{ kg}\cdot\text{m}^{-3}$.

Uncertainty

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% agreement 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

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

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

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

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 ($\delta\rho_l$). 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

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

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

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

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 ($\rho_c = 219$ kg·m⁻³, $T_c = 2503.7$ 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

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

where the polynomial coefficients are

$$\begin{aligned} a &= -85.768 , \\ b &= 24951 , \\ c &= 1.2406 \times 10^{-1} , \\ d &= -8.3368 \times 10^{-5} , \\ e &= 2.6214 \times 10^{-8} , \\ f &= -3.0733 \times 10^{-12} , \end{aligned}$$

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

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

where

$$\begin{aligned} A &= 7.8270 , \\ B &= 11275 , \\ C &= 4.6192 \times 10^5 . \end{aligned}$$

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

$$\alpha_p = \alpha_\sigma + \beta_T \gamma_\sigma \quad , \quad (15)$$

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

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

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

$$(\alpha_p)_g = \frac{(\alpha_\sigma)_g}{\left(1 - \frac{\gamma_\sigma}{\gamma_V} \right)} \quad , \quad (17)$$

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

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

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

| Temperature (K) | Liquid $\alpha_p \times 10^4$ (K ⁻¹) | Vapor $\alpha_p \times 10^3$ (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 1.3-5 Estimated Uncertainties in the Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient for Liquid Sodium

| Temperature (K) | α_P (K ⁻¹) | Uncertainty, $\left(\frac{\delta\alpha_P}{\alpha_P}\right)_l$ (%) |
|--------------------|---|--|
| 371 ≤ T ≤ 1000 | | 10 |
| 1000 < T ≤ 1600 | | 15 |
| 1600 < T ≤ 2000 | $\alpha_P = \alpha_\sigma + \beta_T \gamma_\sigma$ | 45 |
| 2000 < T ≤ 2200 | $\alpha_\sigma = -\frac{1}{\rho_l} \left(\frac{\partial\rho_l}{\partial T}\right)_\sigma$ | 60 |
| 2200 < T ≤ 2400 | | 75 |
| 2400 < T ≤ 2503 | | 85 |

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, $\left(\frac{\delta\alpha_P}{\alpha_P}\right)_g$ (%) |
|--------------------|---|--|
| 371 ≤ T ≤ 500 | | 50 |
| 500 < T ≤ 1600 | | 15 |
| 1600 < T ≤ 2000 | $\alpha_P = \frac{\alpha_\sigma}{\left(1 - \frac{\gamma_\sigma}{\gamma_V}\right)}$ | 30 |
| 2000 < T ≤ 2200 | | 40 |
| 2200 < T ≤ 2400 | | 50 |
| 2400 < T ≤ 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

$$\beta_T = \left[\frac{\beta_S C_\sigma + \left(\frac{T}{\rho_l} \right) \alpha_\sigma (\alpha_\sigma + \beta_S \gamma_\sigma)}{C_\sigma - \left(\frac{T}{\rho_l} \right) \gamma_\sigma (\alpha_\sigma + \beta_S \gamma_\sigma)} \right] . \quad (19)$$

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

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

with

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

and

$$\begin{aligned} b &= 3.2682 , \\ T_m &= 371 \text{ K} , \\ T_C &= 2503.7 \text{ K} . \end{aligned}$$

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

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

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

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

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

$$v = 2660.7 - 0.37667 T - 9.0356 \times 10^{-5} T^2 \quad (22)$$

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 $\text{kJ}\cdot\text{kg}^{-1}$, is

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

$$\text{for } 371 \text{ K} \leq T \leq 2000 \text{ K} .$$

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 $\text{kJ}\cdot\text{kg}^{-1}$, the average enthalpy is given by

$$H(AVG, T) - H(s, 298.15) = E + FT \quad (25)$$

$$\text{for } 2000 \text{ K} \leq T \leq 2503.7 \text{ K} ,$$

where

$$E = 2128.4 ,$$

$$F = 0.86496 .$$

The enthalpy of vaporization, ΔH_g , in $\text{kJ}\cdot\text{kg}^{-1}$, 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

$$\text{Deviations} = \left(\frac{[\alpha_p(\text{Other}) - \alpha_p(\text{Recommended})] 100\%}{\alpha_p(\text{Recommended})} \right) .$$

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 (α_o), the temperature derivative of the pressure along the saturation curve (γ_o) 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

$$\gamma_v = \left(-\frac{b}{T^2} + \frac{c}{T} + d + 2eT \right) \exp\left(a + \frac{b}{T} + c \ln T + dT + eT^2 \right) \quad (27)$$

for $371 \text{ K} \leq T \leq 1600 \text{ K}$,

where

$$\begin{aligned}
 a &= 8.35307 , \\
 b &= -12905.6 , \\
 c &= -0.45824 , \\
 d &= 2.0949 \times 10^{-3} , \\
 e &= -5.0786 \times 10^{-7} .
 \end{aligned}$$

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⁾

$$\gamma_V = \gamma_V^C + A \left(1 - \frac{T}{T_C} \right)^{\frac{1}{2}} + B \left(1 - \frac{T}{T_C} \right) \quad (28)$$

for $1600 \text{ K} \leq T \leq 2500 \text{ K}$,

where

$$\begin{aligned}
 \gamma_V^C &= \gamma_\sigma^C = 4.6893 \times 10^{-2} , \\
 A &= -2.5696 \times 10^{-3} , \\
 B &= 3.5628 \times 10^{-5} , \\
 T_C &= 2503.7 \text{ K} .
 \end{aligned}$$

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_σ , 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:

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

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

$$(\delta\alpha_p)_l = \sqrt{4 (\delta\rho_l)^2 + (\delta\beta_T)^2 + 4 (\delta P)^2}. \quad (30)$$

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 thermal-pressure coefficient using the equation

$$(\delta\alpha_p)_g = \sqrt{4(\delta\rho_g)^2 + (\delta\gamma_v)^2} . \quad (31)$$

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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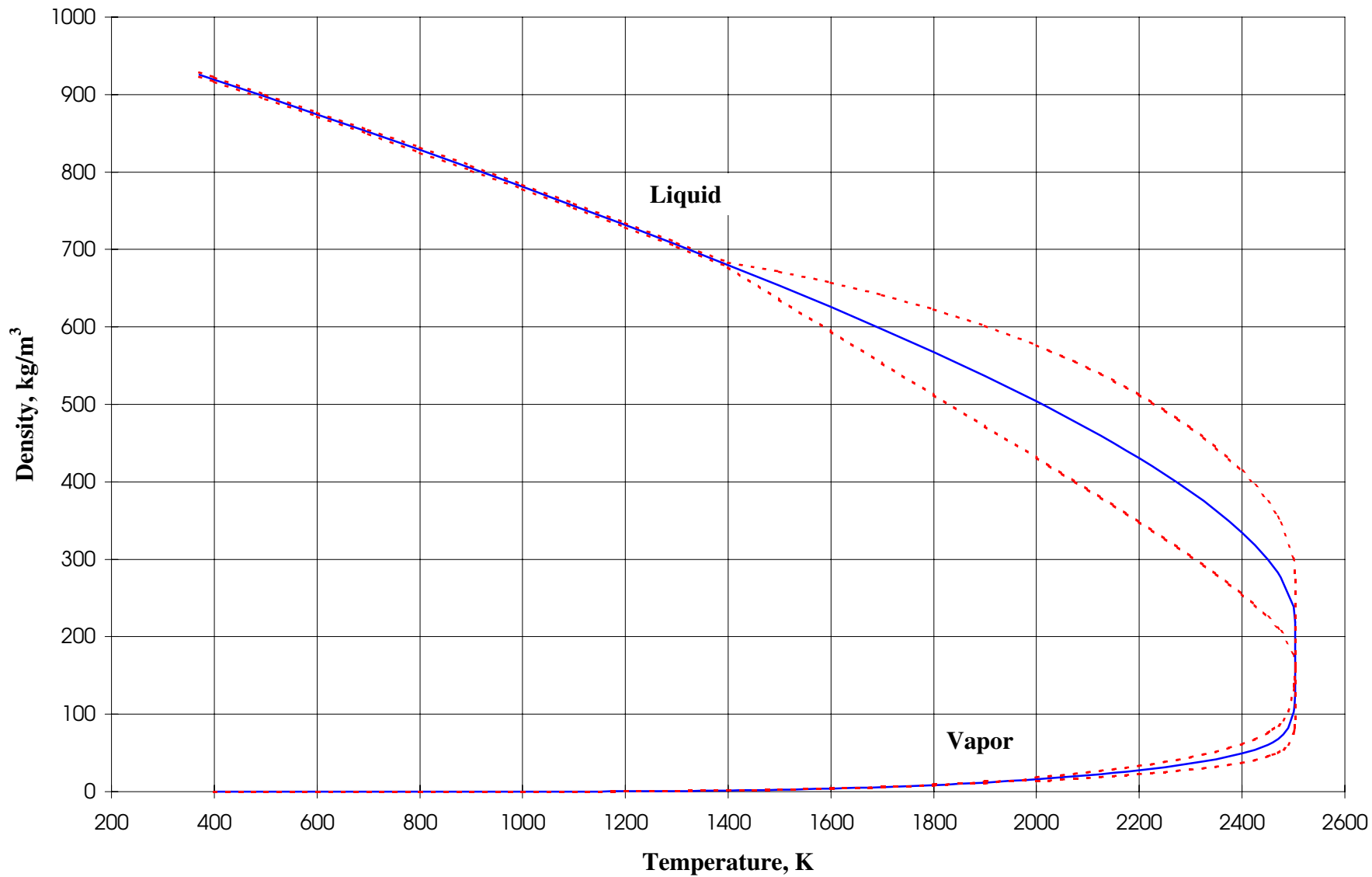


Fig. 1.3-1 Liquid Sodium and Sodium Vapor Densities

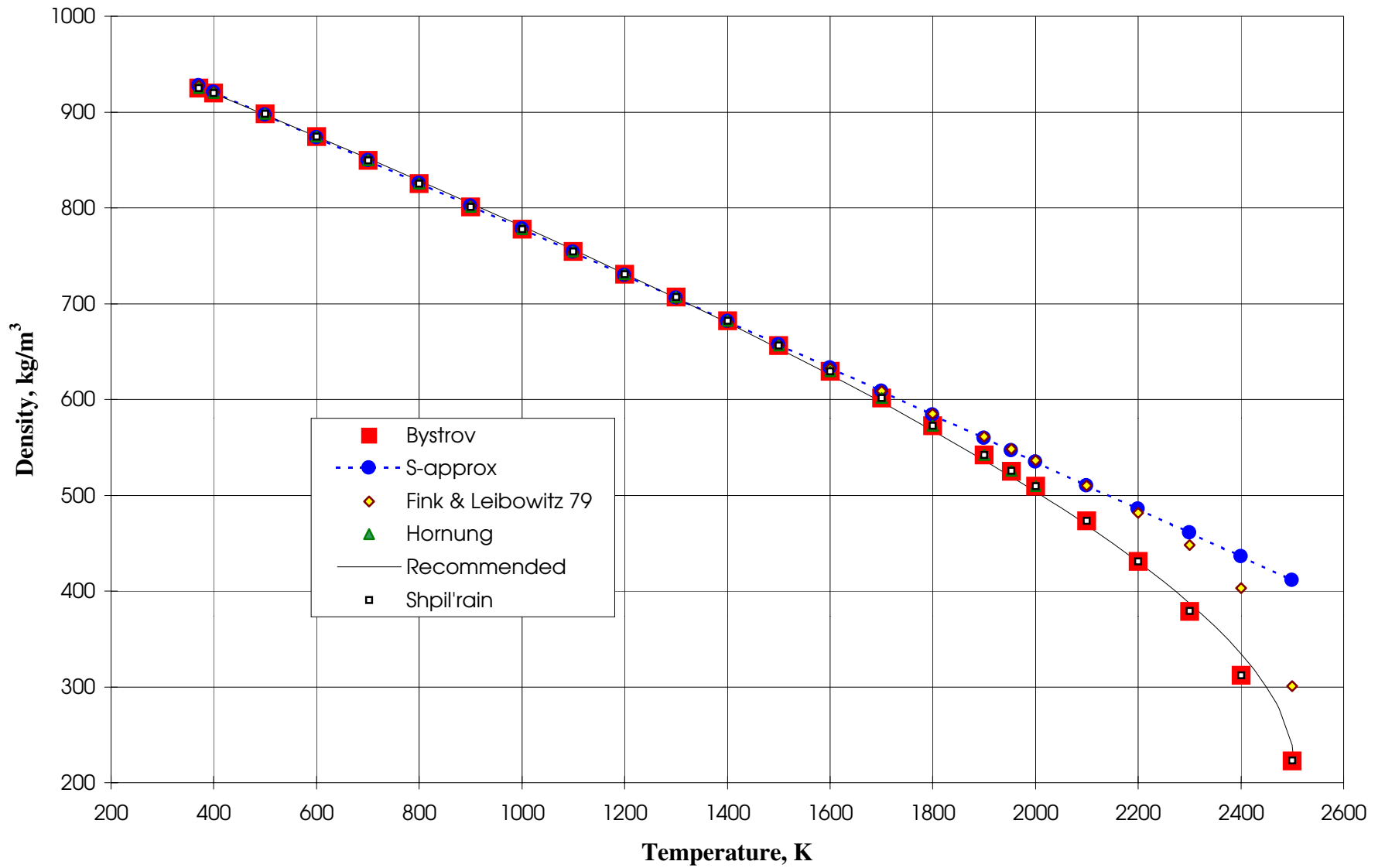


Fig. 1.3-2 Comparison of Recommended Density of Liquid Sodium with Values from Other Assessments

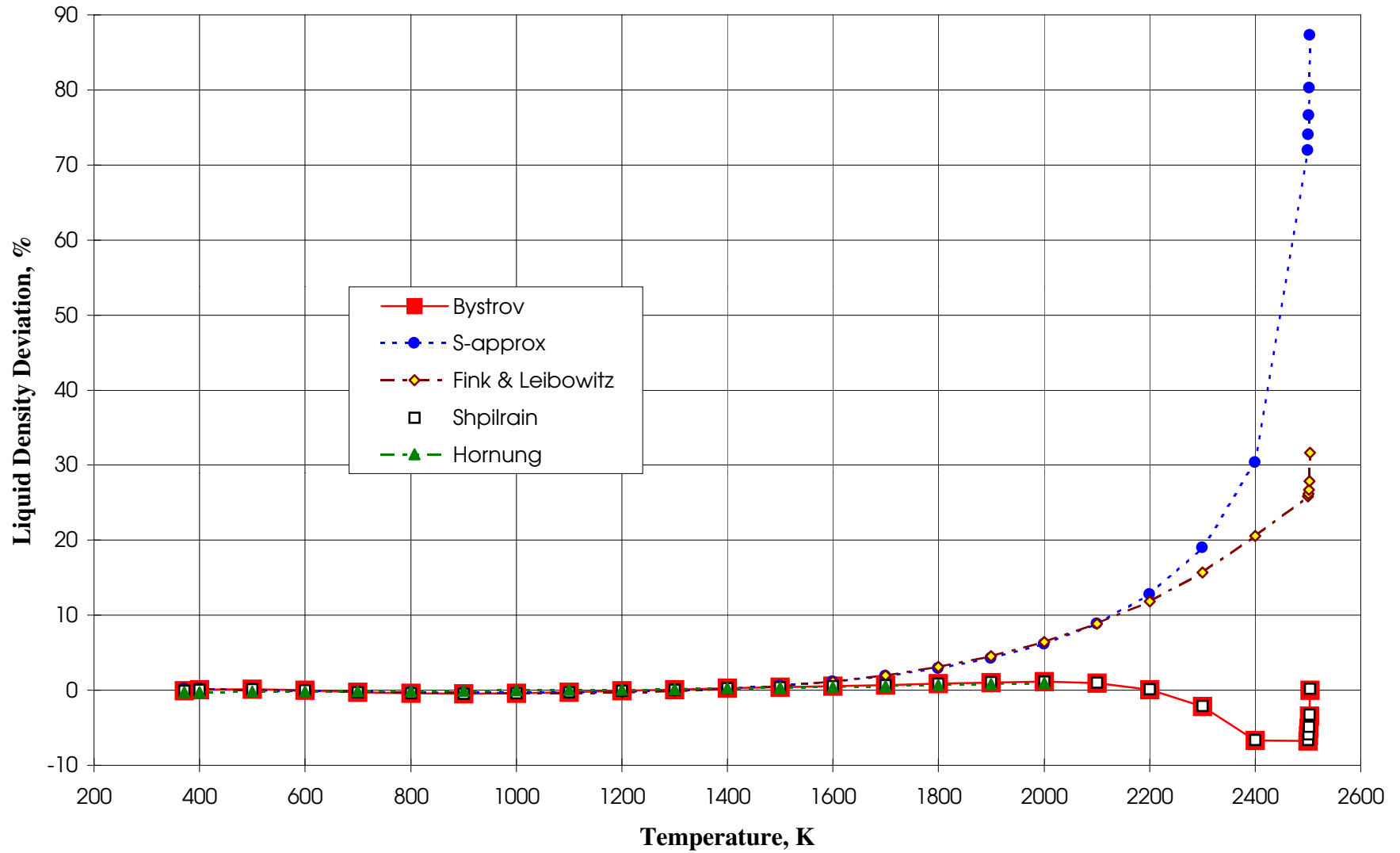


Fig. 1.3-3 Deviations of the Recommended Values for the Density of Liquid Sodium from Values from Other Assessments

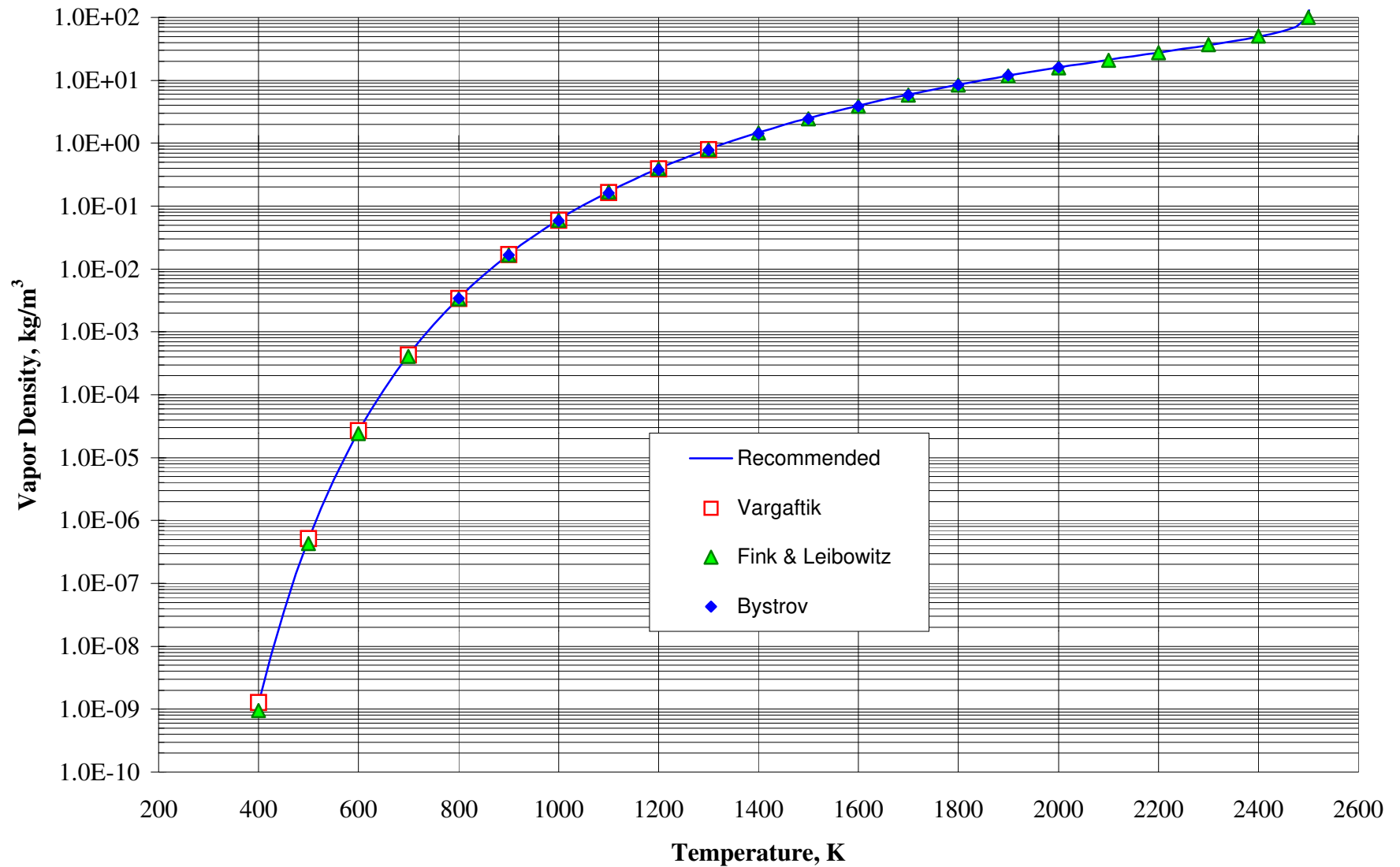


Fig 1.3-4 Comparison of Recommended Values for the Density of Sodium Vapor with Values from Other Assessments

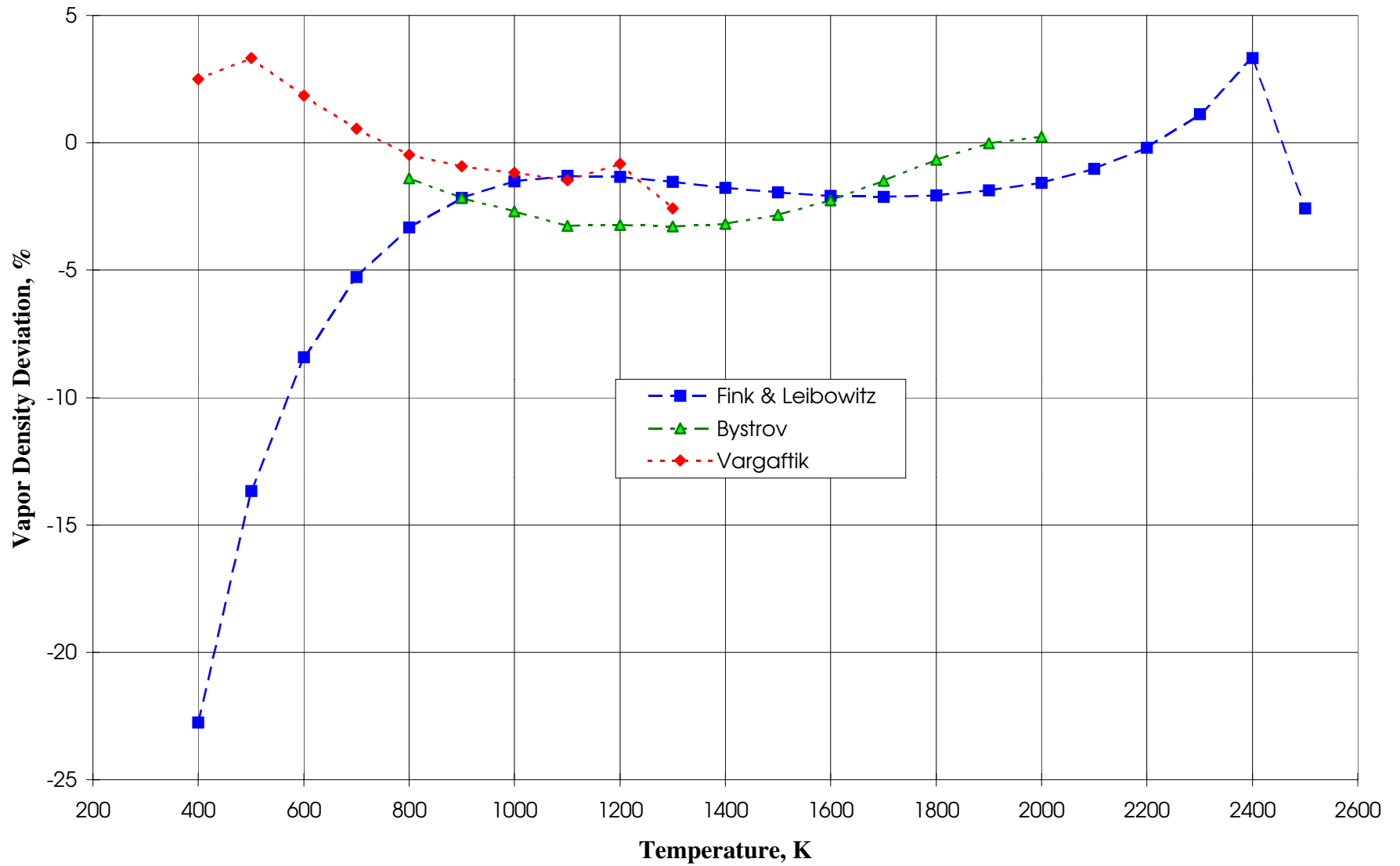


Fig. 1.3-5 Deviations of Recommended Vapor Density Values from Values from Other Assessments

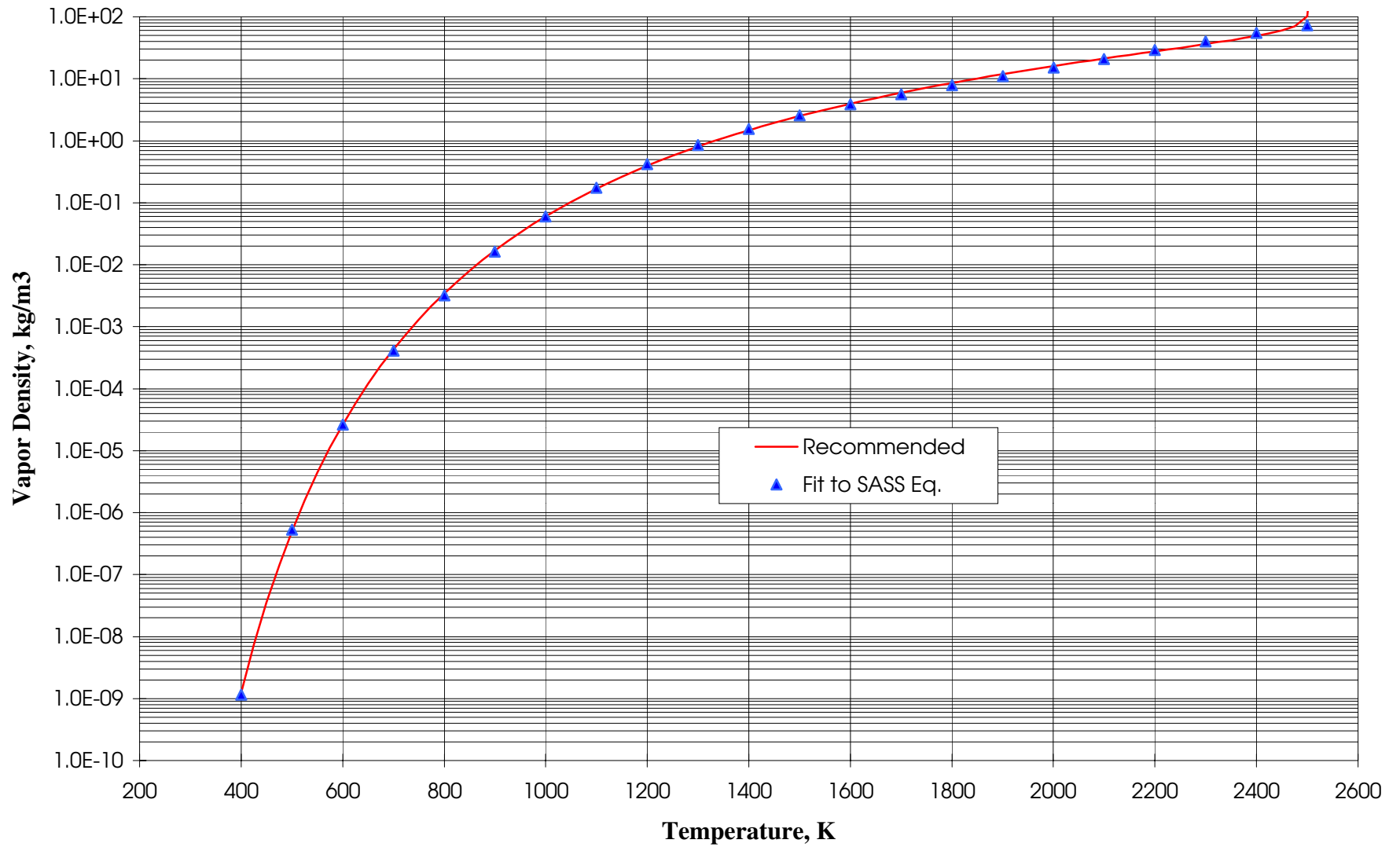


Fig 1.3-6 Comparison of Recommended Values for the Density of Sodium Vapor with Values from the SASS Approximation Equation

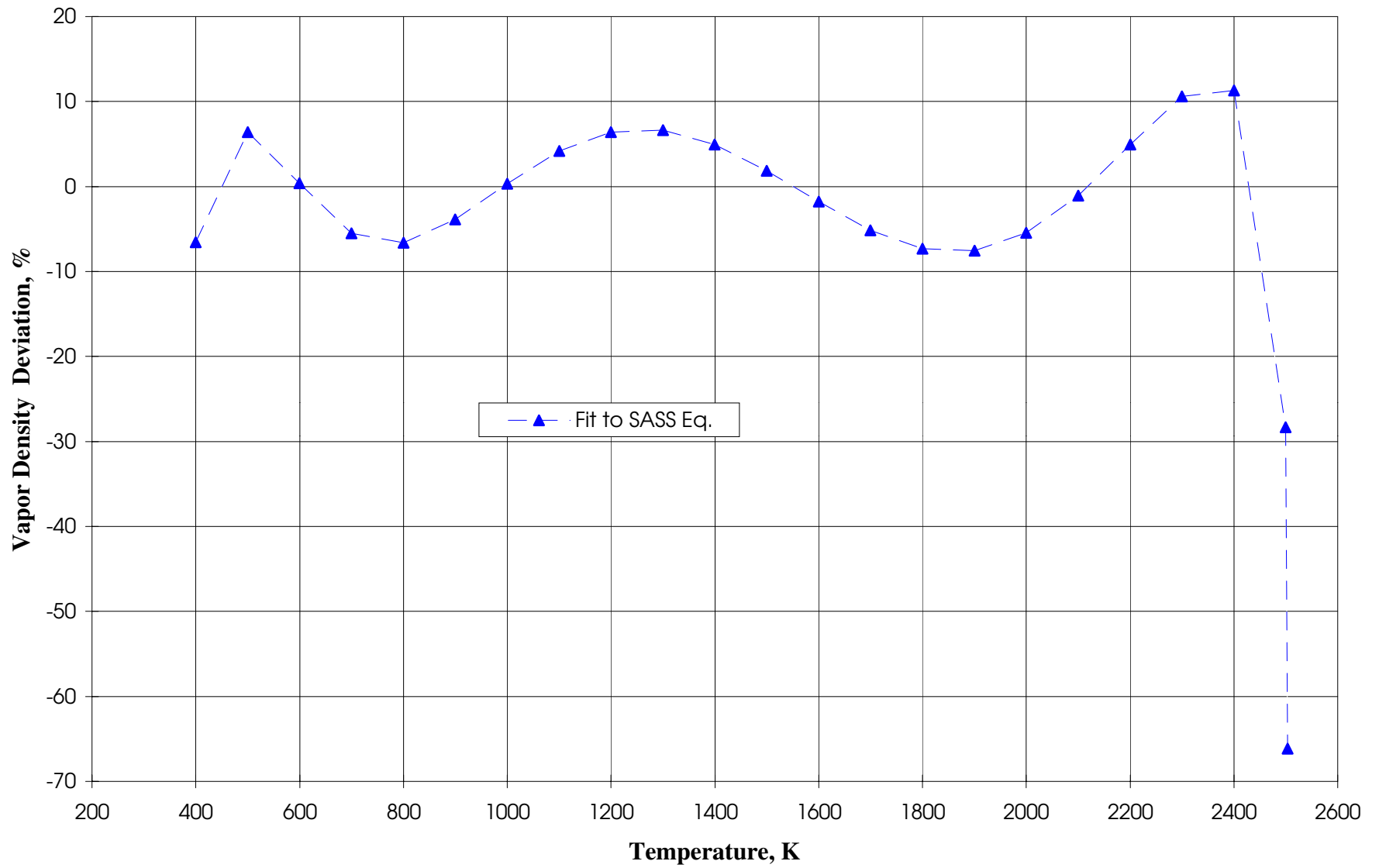


Fig 1.3-7 Deviations of the SASS Equation for Sodium Vapor Density from the Recommended Values

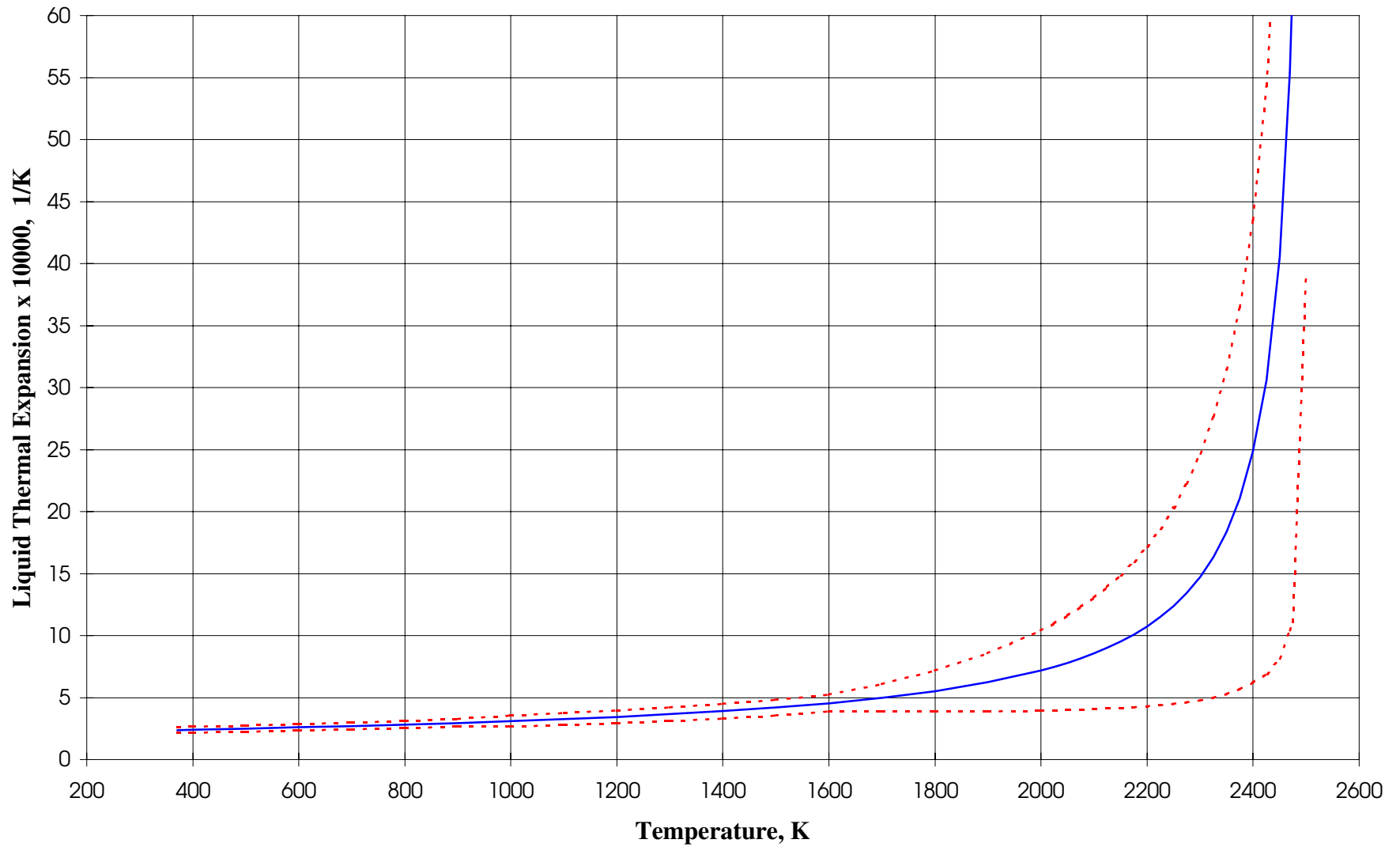


Fig. 1.3-8 Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient of Liquid Sodium

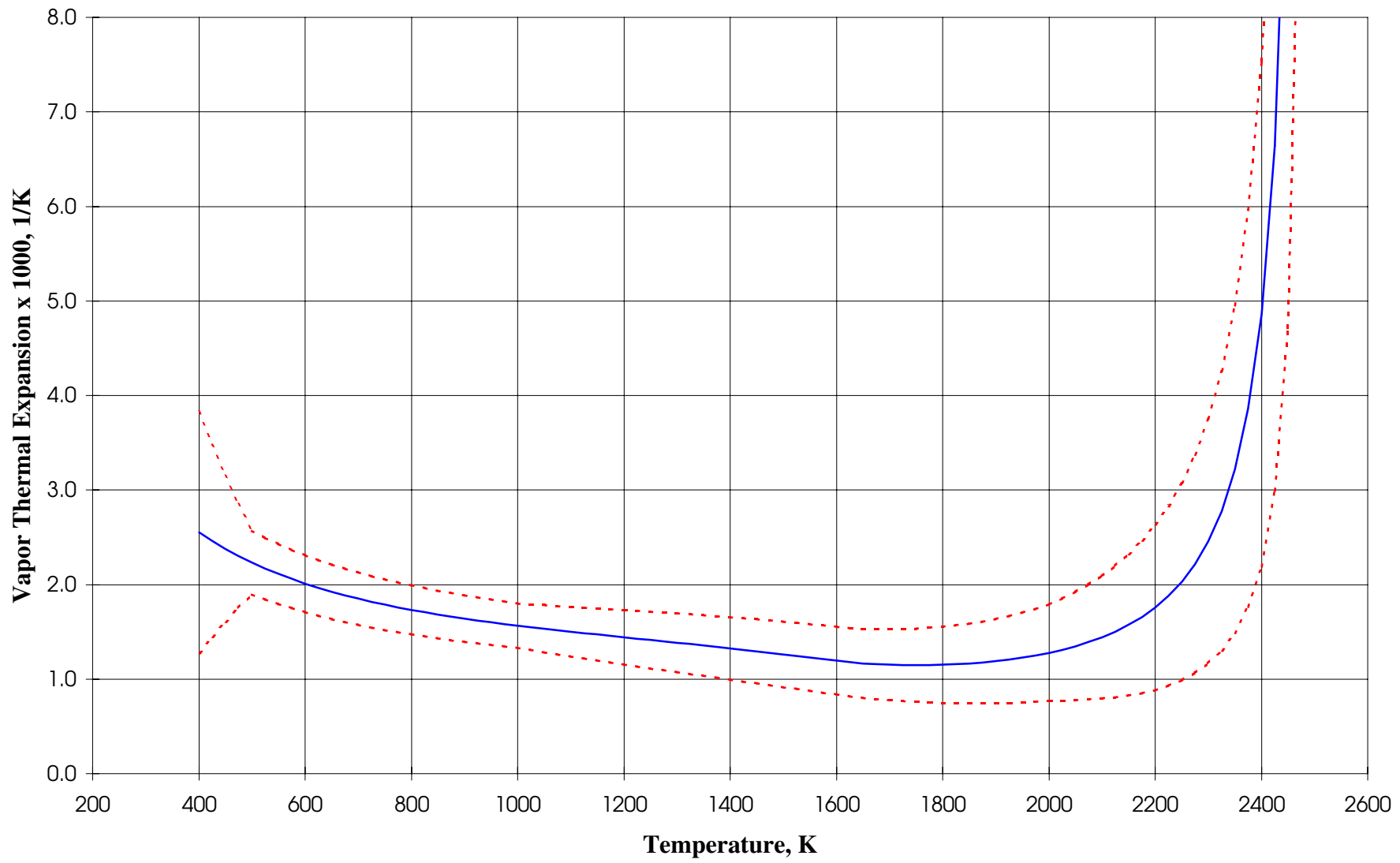


Fig. 1.3-9 Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient for Sodium Vapor

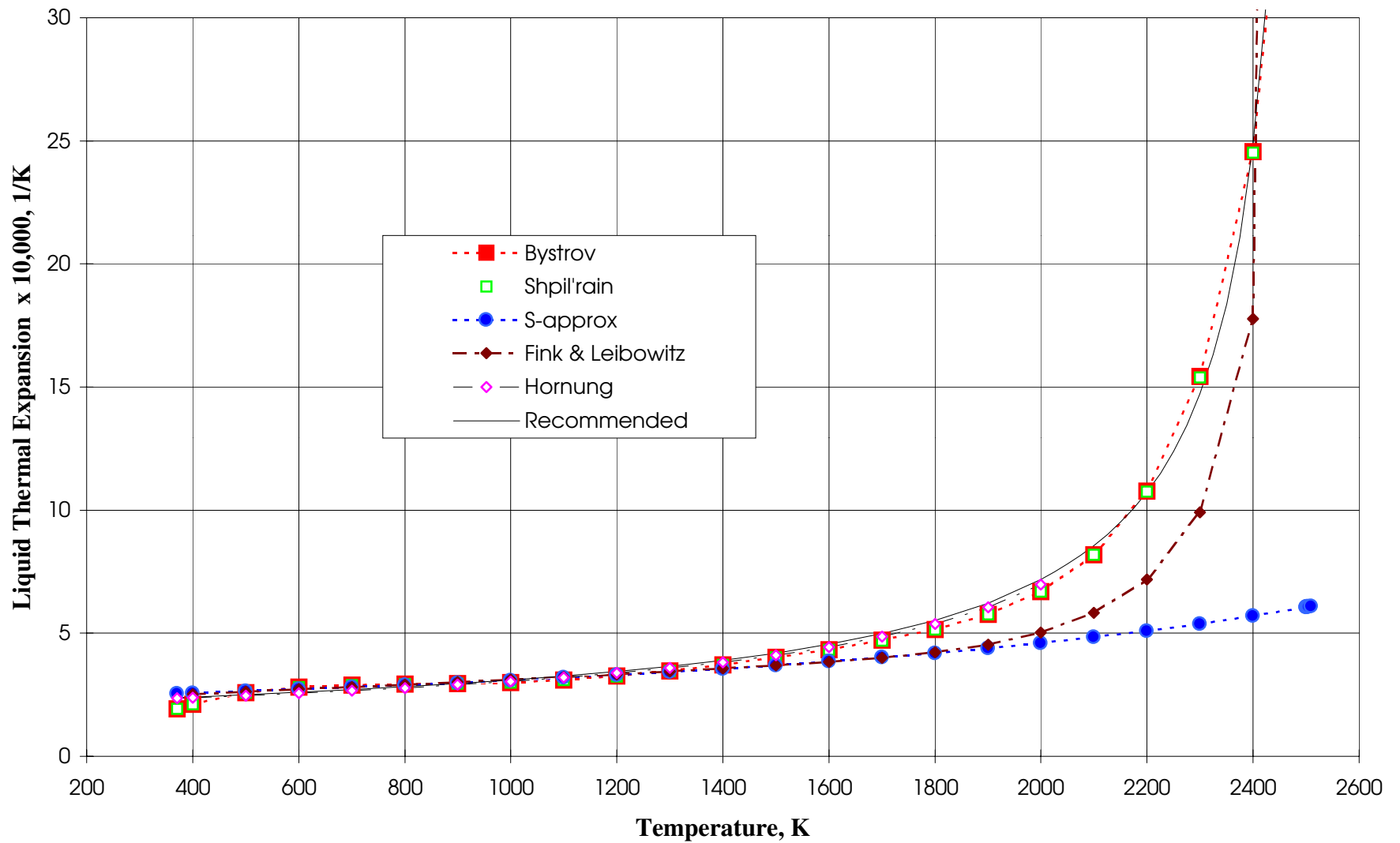


Fig. 1.3-10 Comparison of Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient of Liquid Sodium with Values from Other Assessments

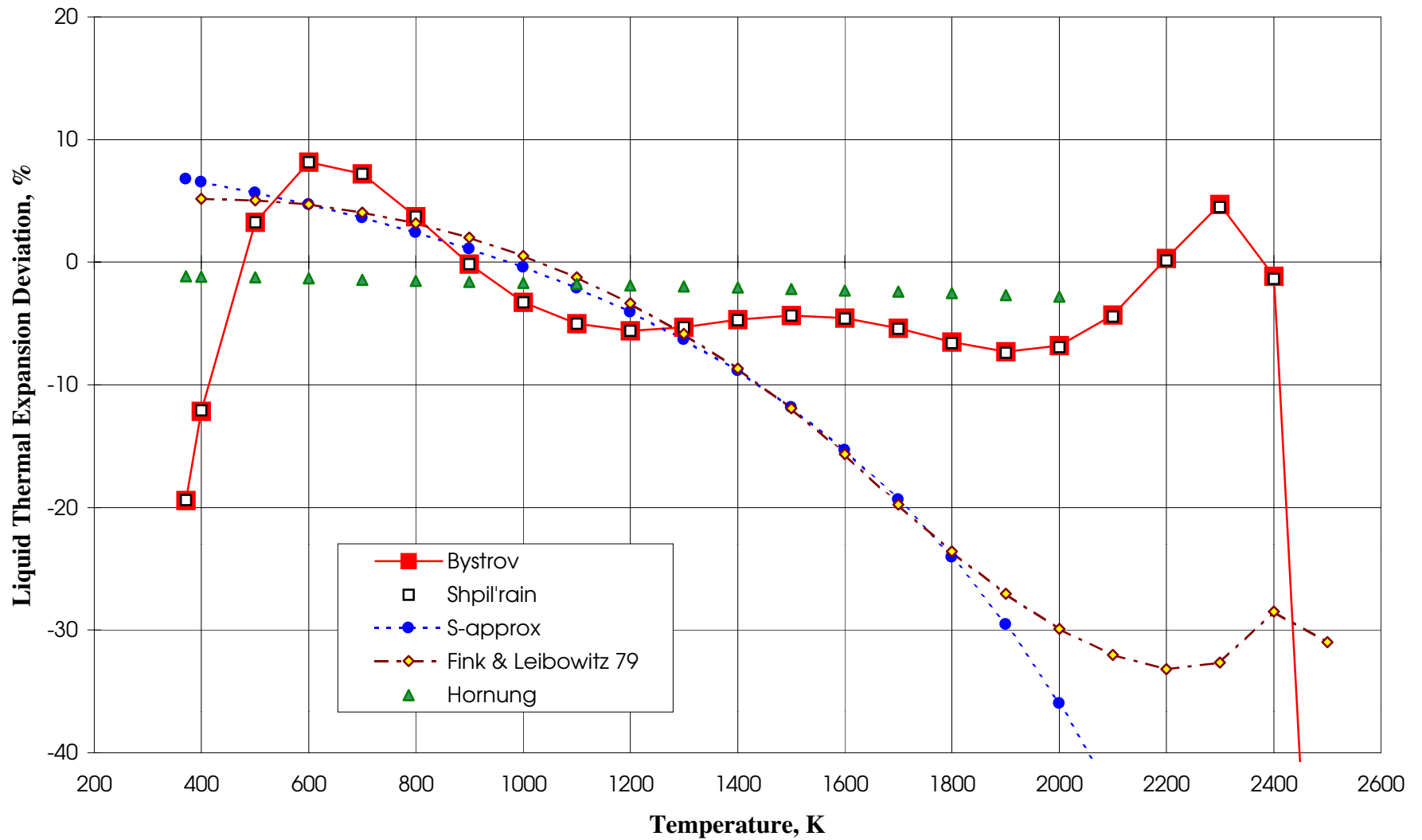


Fig. 1.3-11 Percent Deviations of the Recommended Thermal-Expansion Coefficient for Liquid Sodium from Values from Other Assessments

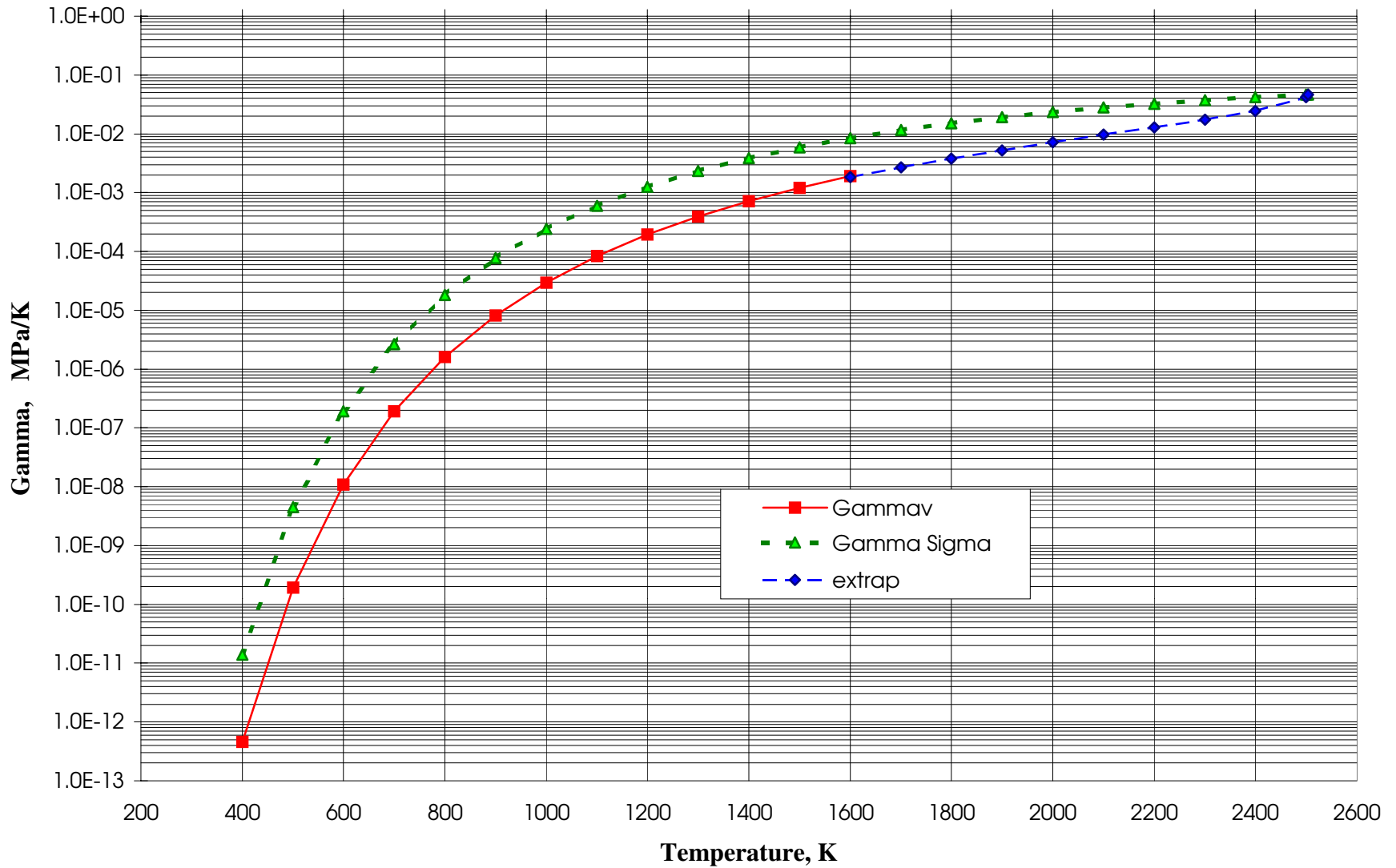


Fig. 1.3-12. The Thermal-Pressure Coefficient (γ_V) and the Temperature Derivative of the Vapor Pressure along the Saturation Curve (γ_σ)

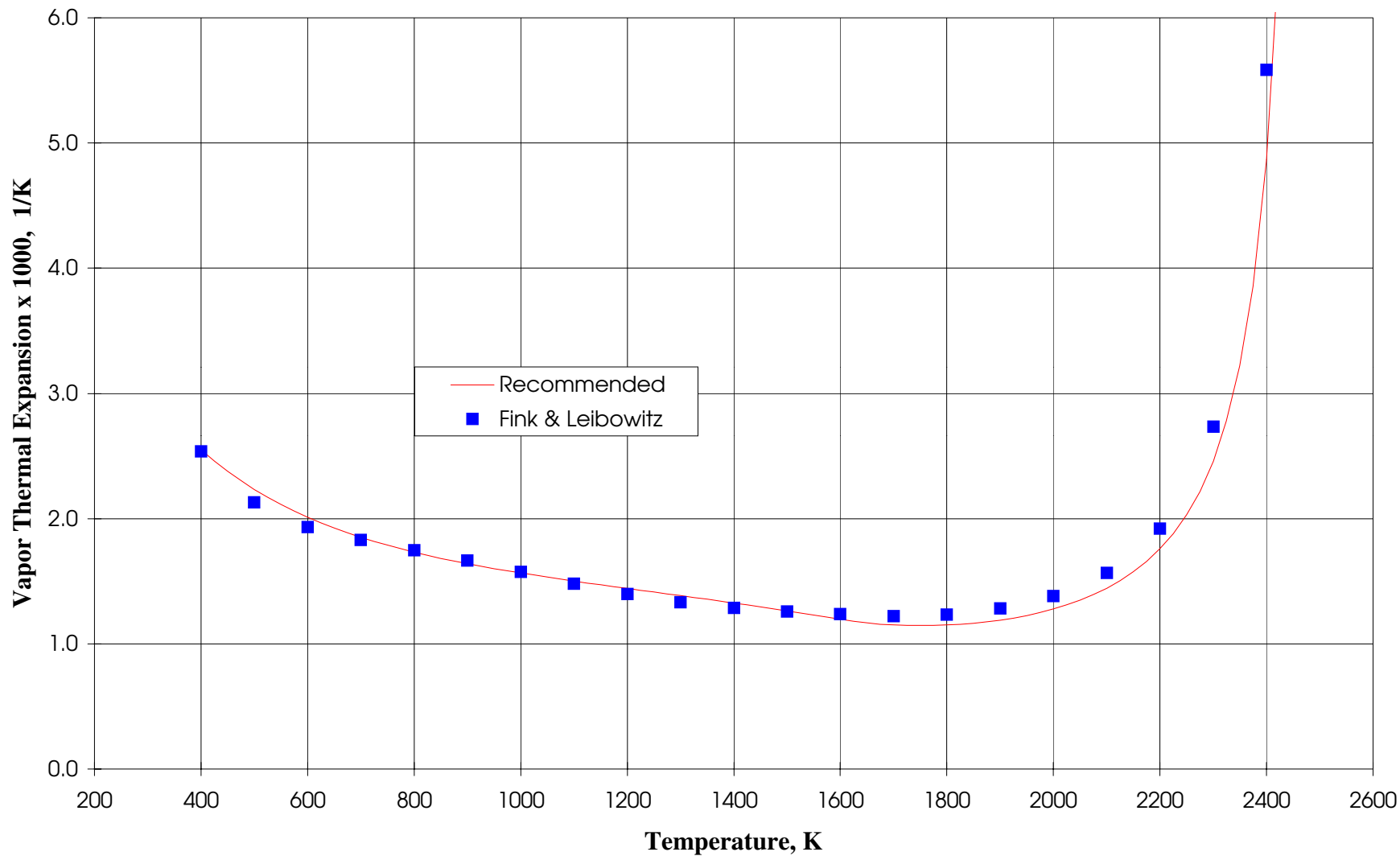


Fig. 1.3-13 Comparison of the Recommended Values for the Instantaneous Volumetric Thermal-Expansion Coefficient of Sodium Vapor with Values from Fink and Leibowitz⁷

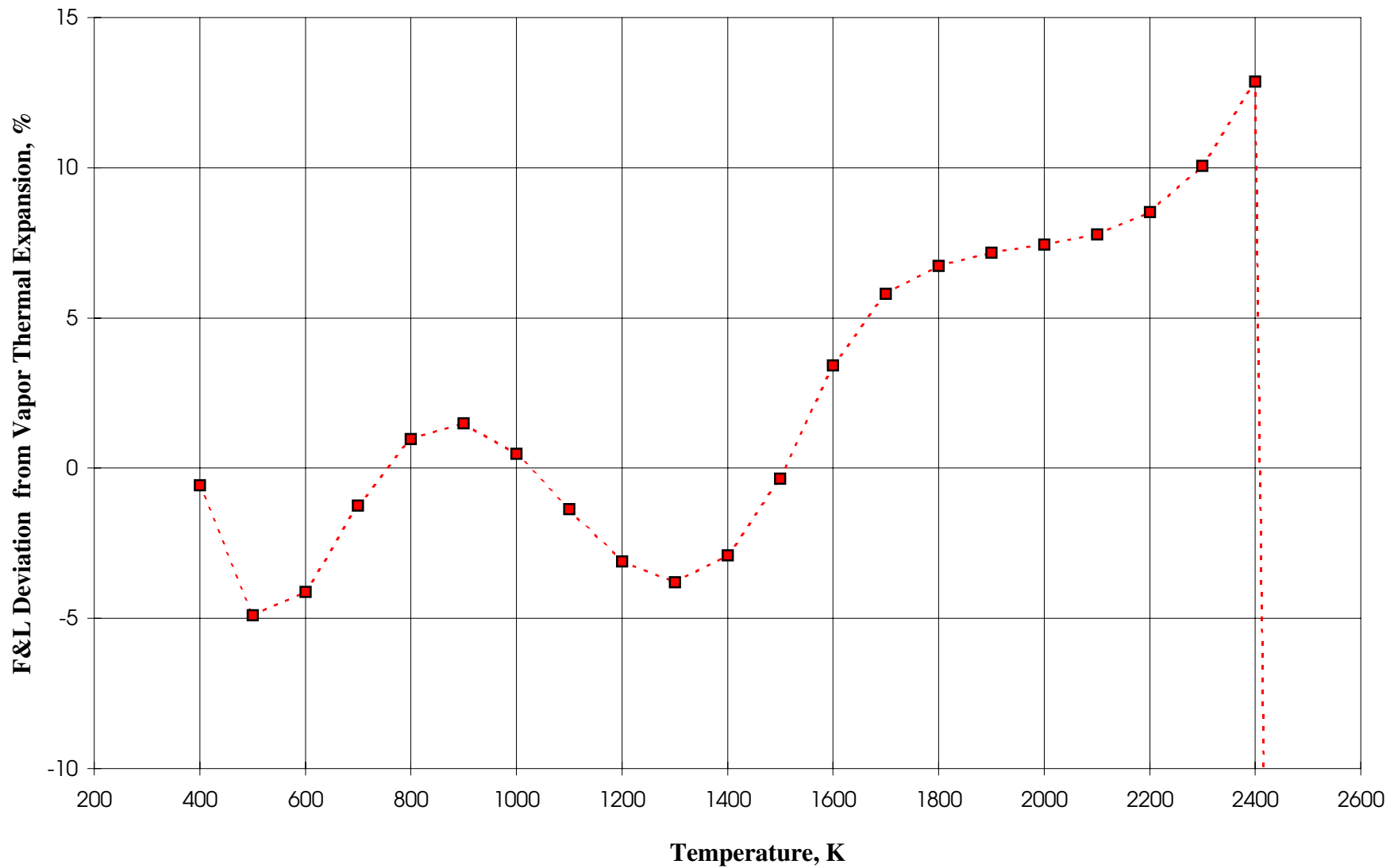


Fig. 1.3-14 Percent Deviations of the Recommended Values of the Thermal-Expansion Coefficient of Sodium Vapor from Values from Fink and Leibowitz7

1.4 COMPRESSIBILITY AND SPEED OF SOUND

1.4.1 ADIABATIC COMPRESSIBILITY

Summary

Recommended values for the adiabatic compressibility of liquid sodium and sodium vapor are given in Table 1.4-1 and graphed, respectively, in Figs. 1.4-1 and 1.4-2. The dashed lines in the graphs represent the uncertainties in the recommended values. Estimated uncertainties as a function of temperature are given in Tables 1.4-2 and 1.4-3.

For liquid sodium, the recommended values for the adiabatic compressibility, β_S , in MPa^{-1} are calculated from

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

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

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

the constant b is

$$b = 3.2682,$$

and the parameter θ is defined by

$$\theta = \frac{(T - T_m)}{(T_C - T_m)}. \quad (2)$$

T_m and T_C are, respectively, the temperatures at the melting point (371 K) and critical point (2503.7 K).

The adiabatic compressibility of sodium vapor was calculated from the heat capacity at constant volume (C_V), the heat capacity at constant pressure (C_P), and the isothermal compressibility (β_T) using the thermodynamic relation

$$\beta_S = \beta_T \left(\frac{C_V}{C_P} \right). \quad (3)$$

Table 1.4-1 Adiabatic Compressibility of Sodium

| Temperature (K) | Liquid $\beta_s \times 10^4$ (MPa ⁻¹) | Vapor β_s (MPa ⁻¹) |
|--------------------|---|--|
| 400 | 1.75 | 3.14×10^9 |
| 500 | 1.86 | 8.12×10^6 |
| 600 | 1.99 | 1.36×10^5 |
| 700 | 2.13 | 7.31×10^3 |
| 800 | 2.28 | 8.14×10^2 |
| 900 | 2.46 | 1.48×10^2 |
| 1000 | 2.66 | 3.78×10^1 |
| 1100 | 2.88 | 1.24×10^1 |
| 1200 | 3.14 | 4.90 |
| 1300 | 3.45 | 2.24 |
| 1400 | 3.81 | 1.14 |
| 1500 | 4.24 | 6.39×10^{-1} |
| 1600 | 4.77 | 3.83×10^{-1} |
| 1700 | 5.42 | 2.46×10^{-1} |
| 1800 | 6.27 | 1.67×10^{-1} |
| 1900 | 7.39 | 1.19×10^{-1} |
| 2000 | 8.87 | 8.79×10^{-2} |
| 2100 | 11.3 | 6.78×10^{-2} |
| 2200 | 15.2 | 5.44×10^{-2} |
| 2300 | 22.9 | 4.61×10^{-2} |
| 2400 | 45.6 | 4.45×10^{-2} |
| 2500 | 1291.31 | 3.74×10^{-1} |

Discussion

Adiabatic Compressibility of Liquid Sodium — The parameter b in Eq. (1) for the adiabatic compressibility (β_s) of liquid sodium was obtained by fitting the adiabatic compressibilities from the melting point to 1773 K. The adiabatic compressibilities in this temperature range were calculated from the liquid density (ρ_l) and speed of sound in liquid sodium (v) using the relation

$$\beta_s = \frac{1}{\rho_l v^2} . \quad (3)$$

Table 1.4-2 Estimated Uncertainties in the Recommended Values for Adiabatic Compressibility of Liquid Sodium

| Temperature (K) | β_S (MPa ⁻¹) | Uncertainty, $\left(\frac{\delta\beta_S}{\beta_S}\right)$ (%) |
|-----------------|--|---|
| 371 ≤ T ≤ 1400 | $\beta_S = 1.717 \times 10^{-4} \frac{\left(1 + \frac{\theta}{b}\right)}{(1 - \theta)}$ <p>where $b = 3.2682$,</p> $\theta = \frac{T - T_m}{T_c - T_m} ,$ $T_m = 371 \text{ K} ,$ $T_c = 2503.7 \text{ K} .$ | 2 |
| 1400 < T ≤ 2000 | | 25 |
| 2000 < T ≤ 2200 | | 37 |
| 2200 < T ≤ 2400 | | 49 |
| 2400 < T ≤ 2503 | | 55 |

Table 1.4-3 Estimated Uncertainties in the Recommended Values for the Adiabatic Compressibility of Sodium Vapor

| Temperature (K) | β_S (MPa ⁻¹) | Uncertainty, $\left(\frac{\delta\beta_S}{\beta_S}\right)$ (%) |
|-------------------|--|---|
| 371 ≤ T ≤ 500 | $\beta_S = \beta_T \left(\frac{C_V}{C_P}\right)$ | 50 |
| 500 < T ≤ 1000 | | 35 |
| 1000 < T ≤ 1600 | | 30 |
| 1600 < T ≤ 2000 | | 60 |
| 2000 < T ≤ 2200 | | 80 |
| 2200 < T ≤ 2503.7 | | 100 |

The liquid density (ρ_l) is given by

$$\rho_l = \rho_C + f \left(1 - \frac{T}{T_C} \right) + g \left(1 - \frac{T}{T_C} \right)^h, \quad (5)$$

where the parameters for density in $\text{kg}\cdot\text{m}^{-3}$ and temperature (T) in kelvins are

$$\begin{aligned} \rho_C &= 219., \\ f &= 275.32, \\ g &= 511.58, \\ h &= 0.5, \end{aligned}$$

and ρ_C , the density at the critical temperature, is $219 \text{ kg}\cdot\text{m}^{-3}$.

The recommended equation for the speed of sound (v) in $\text{m}\cdot\text{s}^{-1}$ is the quadratic equation determined by Fink and Leibowitz⁽¹⁾ who fit the available speed of sound data from the melting point to 1773 K; their equation is

$$v = 2660.7 - 0.37667 T - 9.0356 \times 10^{-5} T^2 \quad (6)$$

for 371 K \leq T \leq 1773 K .

In Fig. 1.4-3, recommended values for the adiabatic compressibility of liquid sodium are compared with values from assessments by Fink and Leibowitz,⁽¹⁾ Hornung,⁽²⁾ and Bystrov et al.⁽³⁾ Equations of similar form to Eqs. (1-6) were used by Fink and Leibowitz and by Hornung. Bystrov et al. used a linear equation to represent the speed of sound in sodium and a seven-term polynomial to represent the liquid density. They used Eq. (4) to calculate the adiabatic compressibility in the range of experimental data and to extrapolate to high temperatures. Values from all three assessments are in excellent agreement (within 2%) through 1600 K. Disagreement between the values calculated by Bystrov et al. and values from other assessments increases with increasing temperature above 1600 K. Deviations of values calculated in these assessments from the recommended values are shown in Fig. 1.4-4. The deviations shown in the graph in Fig. 1.4-4 were defined as

$$Deviations = \left(\frac{[\beta_S(Other) - \beta_S(Recommended)] 100\%}{\beta_S(Recommended)} \right) . \quad (7)$$

The increasing deviation with temperature of values calculated by Bystrov et al. arises from their choice of equations for the density and the adiabatic compressibility which do not have the correct physical behavior at the critical point. Extrapolation of these equations beyond the range of experimental data leads to large differences. Values calculated by Bystrov et al. are low by 63% at 2400 K and by 98% at 2500 K. Values calculated by Hornung and by Fink and Leibowitz are within 2% of the recommended values through 2000 K, the highest temperature calculated by Hornung. At 2400 K, values calculated by Fink and Leibowitz deviate by -5%. The magnitude of the deviation increases as the critical point is reached because of their selection of a different critical temperature and critical density than the one recommended in this assessment.

Adiabatic Compressibility of Sodium Vapor — The adiabatic compressibility of sodium vapor was calculated from the isothermal compressibility (β_T) and the heat capacities at constant pressure (C_p) and constant volume (C_v) using the thermodynamic relation given in Eq. (3). These thermodynamic properties are defined below in Eqs. (8-10). The isothermal compressibility (β_T) of sodium vapor was calculated from the instantaneous volumetric thermal-expansion coefficient (α_p) and the thermal-pressure coefficient (γ_v) using the thermodynamic relation

$$\beta_T = \frac{\alpha_p}{\gamma_v} . \quad (8)$$

The heat capacity at constant pressure of sodium vapor has been calculated from the heat capacity along the saturation curve (C_σ) using the thermodynamic relations

$$C_p = C_\sigma + \left(\frac{T\alpha_p\gamma_\sigma}{\rho_g} \right) , \quad (9)$$

where α_p is the thermal-expansion coefficient, γ_σ is the partial derivative of the pressure with respect to temperature along the saturation curve, and ρ_g is the vapor density. The heat capacity at constant volume of saturated sodium vapor was calculated using the thermodynamic relation

$$C_V = C_P - \left(\frac{T \alpha_p \gamma_V}{\rho_g} \right), \quad (10)$$

where C_P , α_p , ρ_g , and γ_V are, respectively, the heat capacity at constant pressure, the instantaneous volumetric thermal-expansion coefficient, the density of sodium vapor and the thermal-pressure coefficient.

The instantaneous volumetric thermal-expansion coefficient for sodium vapor $(\alpha_p)_g$

was calculated from the relation

$$(\alpha_p)_g = \frac{(\alpha_\sigma)_g}{\left(1 - \frac{\gamma_\sigma}{\gamma_V} \right)}, \quad (11)$$

where the coefficient of thermal expansion along the saturation curve $(\alpha_\sigma)_g$ for sodium vapor

is defined as

$$(\alpha_\sigma)_g = - \frac{1}{\rho_g} \left(\frac{\partial \rho_g}{\partial T} \right)_\sigma.$$

The vapor density (ρ_g) was calculated from the enthalpy of vaporization (ΔH_g) , the temperature derivative of the vapor pressure (γ_σ) , and the liquid density (ρ_l) using the relation

$$\rho_g = \left(\frac{\Delta H_g}{T \gamma_\sigma} + \frac{1}{\rho_l} \right)^{-1}, \quad (13)$$

where

$$\gamma_\sigma = \left(\frac{\partial P}{\partial T} \right)_\sigma. \quad (14)$$

The vapor pressure, P , is given by an equation derived by Browning and Potter:⁽⁴⁾

$$\ln P = a + \frac{b}{T} + c \ln T . \quad (15)$$

Then γ_σ , the temperature derivative of the pressure along the saturation curve, is

$$\gamma_\sigma = \left(-\frac{b}{T^2} + \frac{c}{T} \right) \exp\left(a + \frac{b}{T} + c \ln T \right) , \quad (16)$$

and the coefficients in Eqs. (15, 16) for P in MPa and T in kelvins are defined as

$$\begin{aligned} a &= 11.9463, \\ b &= -12633.73, \\ c &= -0.4672. \end{aligned}$$

The enthalpy of vaporization, ΔH_g , in $\text{kJ}\cdot\text{kg}^{-1}$, is given by

$$\Delta H_g = 393.37 \left(1 - \frac{T}{T_c} \right) + 4398.6 \left(1 - \frac{T}{T_c} \right)^{0.29302} \quad (17)$$

$$\text{for } 371 \text{ K} \leq T \leq 2503.7 \text{ K} ,$$

where T_c is the critical temperature, 2503.7 K, and T is the temperature in kelvins. The liquid density (ρ_l) used in the calculation of the vapor density in Eq. (13) is defined in Eq. (5).

The thermal-pressure coefficient (γ_v) used in Eqs. (8, 10, 11) is defined below in Eqs. (18, 19). Below 1600 K, the thermal-pressure coefficient was calculated using the quasi-chemical approximation.⁽⁵⁾ Values calculated via the quasi-chemical approximation 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 $\text{MPa}\cdot\text{K}^{-1}$ is

$$\gamma_V = \left(-\frac{b}{T^2} + \frac{c}{T} + d + 2eT \right) \exp\left(a + \frac{b}{T} + c \ln T + dT + eT^2 \right) \quad (18)$$

for 371 K ≤ T ≤ 1600 K ,

where

$$\begin{aligned} a &= 8.35307 , \\ b &= -12905.6 , \\ c &= -0.45824 , \\ d &= 2.0949 \times 10^{-3} , \\ e &= -5.0786 \times 10^{-7} . \end{aligned}$$

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:⁽¹⁾

$$\gamma_V = \gamma_V^C + A \left(1 - \frac{T}{T_C} \right)^{\frac{1}{2}} + B \left(1 - \frac{T}{T_C} \right) \quad (19)$$

for 1600 K ≤ T ≤ 2500 K ,

where

$$\begin{aligned} \gamma_V^C &= \gamma_\sigma^C = 4.6893 \times 10^{-2}, \\ A &= -2.5696 \times 10^{-3}, \\ B &= 3.5628 \times 10^{-5}, \\ T_C &= 2503.7 \text{ K} . \end{aligned}$$

The superscript *C* and subscript *C* in Eq. (19) denote the value at the critical temperature (T_C). The parameters *A* and *B* in Eq. (19) 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. 1.4-5. The derivative of the vapor pressure, γ_σ , has been included in the figure.

The heat capacity at constant pressure, C_p , defined in Eq. (9), is a function of the heat capacity along the saturation curve. The heat capacity along the saturation curve, C_σ , is defined as

$$C_\sigma = T \left(\frac{\partial S}{\partial T} \right)_\sigma . \quad (20)$$

It is related to the partial derivative of the enthalpy along the saturation curve by

$$C_\sigma = \left(\frac{\partial H}{\partial T} \right)_\sigma - \frac{\gamma_\sigma}{\rho_g} ,$$

where the enthalpy of the vapor along the saturation curve is the sum of the enthalpy of liquid sodium on the saturation curve and the enthalpy of vaporization;

$$H(g, T) - H(s, 298) = H(AVG, T) - H(s, 298) + \Delta H_g . \quad (22)$$

The enthalpy of vaporization, ΔH_g , is given in Eq. (17). Below 2000 K, the liquid enthalpy in $\text{kJ}\cdot\text{kg}^{-1}$, was calculated from the CODATA equation⁽⁶⁾ given by Cordfunke and Konings:⁽⁷⁾

$$\begin{aligned} H(AVG, T) - H(s, 298.15) = & - 365.77 + 1.6582 T - 4.2395 \times 10^{-4} T^2 \\ & + 1.4847 \times 10^{-7} T^3 + 2992.6 T^{-1} . \end{aligned} \quad (23)$$

Above 2000 K, the law of rectilinear diameters was used to extrapolate the average of the liquid and vapor enthalpies to the critical point. The enthalpy of sodium vapor relative to the solid at 298.15 K is the average enthalpy plus one half the enthalpy of vaporization. In $\text{kJ}\cdot\text{kg}^{-1}$, the average enthalpy is given by

$$H(AVG, T) - H(s, 298.15) = E + FT \quad (24)$$

$$\text{for } 2000 \text{ K} \leq T \leq 2503.7 \text{ K} ,$$

where

$$E = 2128.4 ,$$

$$F = 0.86496 .$$

Thus, the enthalpy of sodium vapor is

$$H(g, T) - H(s, 298.15) = E + FT + \frac{1}{2} \Delta H \quad (25)$$

for $2000 \text{ K} \leq T \leq 2503.7 \text{ K}$.

Values for the adiabatic compressibility of sodium vapor were available only in the assessment by Fink and Leibowitz.⁽¹⁾ Values from their assessment are compared with recommended values in Fig. 1.4-6. Deviations of values given by Fink and Leibowitz from values recommended in this assessment, defined as in Eq. (7), are within 10% for most of the temperature range, as shown in Fig. 1.4-7. Large deviations occur at both low and high temperatures. The low temperature deviations are due to differences in the thermal-pressure coefficient and enthalpy of vaporization at the low temperatures. Fink and Leibowitz calculated the thermal-pressure coefficient and the enthalpy of vaporization from the quasi-chemical approximation below 1600 K. In this assessment, values from the quasi-chemical approximation were fit with equations to provide mathematical functions for calculation for the entire temperature range. These differences led to differences near the melting point. The 25% deviation at 2400 K arises from differences in dependent parameters as the critical temperature is approached. Different values were chosen for the critical temperature in the two assessments. Fink and Leibowitz used 2509.4 K, whereas 2503.7 K has been selected for the critical temperature in this assessment.

Although values for the adiabatic and isothermal compressibilities of sodium vapor are not available from the assessment by Bystrov et al.,⁽³⁾ the ratio of the vapor heat capacities, which is related to the ratio of the vapor compressibilities, is given in their assessment. The thermodynamic relation between these two ratios is

$$\frac{\beta_T}{\beta_S} = \frac{C_P}{C_V} . \quad (26)$$

In Fig. 1.4-8, values for this ratio from the assessment of Fink and Leibowitz,⁽¹⁾ the assessment by Bystrov et al.,⁽²⁾ and this recommendation are compared. Percent deviations of the ratios from these assessments relative to the ratios calculated from the recommended values are shown in Fig. 1.4-9. For most of the temperature range, deviations are within 4%. Higher deviations were found with respect to the ratios from Fink and Leibowitz at 400 K and above 2400 K. At 2000 K, the ratio given by Bystrov et al. deviates by about 9%.

Uncertainty

The uncertainties in the recommended values for the adiabatic compressibilities of liquid sodium and sodium vapor have been calculated from 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 quantity $(\delta\beta_s)$ is given by

$$(\delta\beta_s)^2 = \sum \left(\frac{\partial\beta_s}{\partial x_i} \right)^2 (\delta x_i)^2, \quad (27)$$

where δx_i are the uncertainties in the dependent parameters.

Adiabatic Compressibility of Liquid Sodium — Differentiating Eq. (4) for the adiabatic compressibility of liquid sodium leads to Eq. (28) for the uncertainty

$$\delta\beta_s = \sqrt{(\delta\rho_l)^2 + 4(\delta v)^2}, \quad (28)$$

where $(\delta\rho_l)$ is the uncertainty in the liquid density and (δv) is the uncertainty in the speed of sound. Calculated uncertainties in the adiabatic compressibility of liquid sodium are 2% from 371 through 1400 K. They increase to 25% at 2000 K and to 55% at 2500 K. Calculated uncertainties are tabulated as a function of temperature in Table 1.4-2. Comparison of calculated uncertainties with deviations of other assessments from the recommended values (graphed in Fig. 1.4-4) shows that values from Fink and Leibowitz⁽¹⁾ and from Hornung⁽²⁾ are within 2% of the recommended values for the entire temperature range. However, values calculated by Bystrov et al.⁽³⁾ deviate by -10% at 1900 K and by -98% at 2500 K. These large deviations at the higher temperatures are consistent with the high calculated uncertainties. They arise from the use of polynomial equations for extrapolation of density and speed of sound to the critical temperature.

Adiabatic Compressibility of Sodium Vapor — Because the functional forms of the thermodynamic properties used to calculate the adiabatic compressibility of sodium vapor are so complex and these properties are not independent, the square of the uncertainties cannot be calculated from the square of the uncertainties of the dependent parameters. Consequently, the uncertainties in the calculated adiabatic compressibilities of sodium vapor were calculated from

the uncertainties in the fundamental properties used to calculate the dependent variables in Eq. (3). Uncertainties in the adiabatic compressibility of sodium vapor were calculated from the uncertainties in the thermal-pressure coefficient, the vapor enthalpy, and the enthalpy of vaporization using the approximation

$$\delta\beta_s = \sqrt{(\delta\gamma_v)^2 + (\delta H_g)^2 + (\delta\Delta H)^2} \quad . \quad (29)$$

Calculated uncertainties have been included as dashed lines in Fig. 1.4-2 and are tabulated as a function of temperature in Table 1.4-3. The maximum uncertainty in each temperature range has been included in the table. High uncertainties (50%) are calculated below 500 K. These are consistent with the large deviation between values calculated by Fink and Leibowitz and by the recommended equations (see Fig. 1.4-7). Uncertainties decrease to 35% from 500 to 1000 K, and 30% from 1000 to 1600 K. Above 1600 K, they increase with temperature. These estimated uncertainties are consistent with the estimated uncertainties given by Fink and Leibowitz.⁽¹⁾ However, they are considerably higher than deviations between values calculated by Fink and Leibowitz and by the recommended equations. These deviations are on the order of 3% for the 800 to 2100 K temperature range. They increase to 25% at 2400 K. Although no other values of adiabatic compressibility of the vapor are available for comparison, comparisons with ratios of isothermal compressibility to adiabatic compressibilities of Bystrov et al.⁽³⁾ indicate deviations are on the order of 3% for temperatures between 800 and 1900 K. At 2000 K, the deviation was -8.7%. Thus, uncertainties estimated using Eq. (29) appear to be conservative.

1.4.2 ISOTHERMAL COMPRESSIBILITY

Summary

Recommended values for the isothermal compressibility of liquid sodium and sodium vapor are given in Table 1.4-4 and graphed, respectively, in Figs. 1.4-10 and 1.4-11. The dashed lines in the graphs represent the uncertainties in the recommended values. Estimated uncertainties as a function of temperature are given in Tables 1.4-5 and 1.4-6.

Table 1.4-4 Isothermal Compressibility of Sodium

| Temperature (K) | Liquid $\beta_T \times 10^4$ (MPa ⁻¹) | Vapor β_T (MPa ⁻¹) |
|--------------------|---|--|
| 400 | 1.93 | 5.56×10^9 |
| 500 | 2.12 | 1.12×10^7 |
| 600 | 2.34 | 1.82×10^5 |
| 700 | 2.60 | 9.75×10^3 |
| 800 | 2.89 | 1.10×10^3 |
| 900 | 3.23 | 2.03×10^2 |
| 1000 | 3.64 | 5.32×10^1 |
| 1100 | 4.11 | 1.79×10^1 |
| 1200 | 4.66 | 7.30 |
| 1300 | 5.33 | 3.43 |
| 1400 | 6.15 | 1.81 |
| 1500 | 7.16 | 1.04 |
| 1600 | 8.44 | 6.48×10^{-1} |
| 1700 | 10.1 | 4.29×10^{-1} |
| 1800 | 12.4 | 3.03×10^{-1} |
| 1900 | 15.7 | 2.26×10^{-1} |
| 2000 | 20.6 | 1.78×10^{-1} |
| 2100 | 28.4 | 1.50×10^{-1} |
| 2200 | 42.1 | 1.36×10^{-1} |
| 2300 | 70.8 | 1.41×10^{-1} |
| 2400 | 156. | 1.99×10^{-1} |
| 2500 | 547. | 8.88 |

Table 1.4-5 Estimated Uncertainties in the Recommended Values for Isothermal Compressibility of Liquid Sodium

| Temperature (K) | β_T (MPa ⁻¹) | Uncertainty, $\left(\frac{\delta\beta_T}{\beta_T}\right)$ (%) |
|-------------------|---|---|
| 371 ≤ T ≤ 500 | $\beta_T = \frac{\beta_S C_\sigma + \left(\frac{T}{\rho_l}\right) \alpha_\sigma (\alpha_\sigma + \beta_S \gamma_\sigma)}{C_\sigma - \left(\frac{T}{\rho_l}\right) \gamma_\sigma (\alpha_\sigma + \beta_S \gamma_\sigma)}$ | 50 |
| 500 < T ≤ 1000 | | 35 |
| 1000 < T ≤ 1600 | | 30 |
| 1600 < T ≤ 2000 | | 60 |
| 2000 < T ≤ 2200 | | 80 |
| 2200 < T ≤ 2503.7 | | 100 |

Table 1.4-6 Estimated Uncertainties in the Recommended Values for the Isothermal Compressibility of Sodium Vapor

| Temperature (K) | β_T (MPa ⁻¹) | Uncertainty, $\left(\frac{\delta\beta_T}{\beta_T}\right)$ (%) |
|-------------------|---------------------------------------|---|
| 371 ≤ T ≤ 500 | $\beta_T = \frac{\alpha_p}{\gamma_v}$ | 50 |
| 500 < T ≤ 1600 | | 15 |
| 1600 < T ≤ 2000 | | 30 |
| 2000 < T ≤ 2200 | | 40 |
| 2200 < T ≤ 2400 | | 50 |
| 2400 < T ≤ 2503.7 | | 100 |

The isothermal compressibility (β_T) for liquid sodium was calculated from the thermodynamic relation

$$\beta_T = \frac{\beta_S C_\sigma + \left(\frac{T}{\rho_l}\right) \alpha_\sigma (\alpha_\sigma + \beta_S \gamma_\sigma)}{C_\sigma - \left(\frac{T}{\rho_l}\right) \gamma_\sigma (\alpha_\sigma + \beta_S \gamma_\sigma)}, \quad (30)$$

where β_S is the adiabatic compressibility, C_σ is the heat capacity along the saturation curve, α_σ is the thermal-expansion coefficient along the saturation curve, γ_σ is the temperature derivative of the vapor pressure along the saturation curve, and ρ_l is the liquid density.

The isothermal compressibility of sodium vapor was calculated from the instantaneous volumetric thermal-expansion coefficient of sodium vapor (α_p) and the thermal-pressure coefficient (γ_v) using the thermodynamic relation

$$\beta_T = \left(\frac{\alpha_p}{\gamma_v}\right). \quad (31)$$

Discussion

Isothermal Compressibility of Liquid Sodium — The isothermal compressibility of liquid sodium was calculated from the thermodynamic relation given in Eq. (30). The adiabatic compressibility (β_S) used in Eq. (30) is defined in Eqs. (1, 2, 4). The liquid density (ρ_l) is given in Eq. (5). The temperature derivative of the vapor pressure along the saturation curve (γ_σ) is given in Eq. (16). The thermal-expansion coefficient along the saturation curve (α_σ) is defined in terms of the liquid density in Eq. (32):

$$\alpha_\sigma = -\frac{1}{\rho_l} \left(\frac{\partial \rho_l}{\partial T}\right)_\sigma. \quad (32)$$

The heat capacity along the saturation curve (C_σ) is related to the partial derivative with respect to temperature of the liquid enthalpy increment along the saturation curve according to the thermodynamic relation

$$C_{\sigma} = \left(\frac{\partial H}{\partial T} \right)_{\sigma} - \frac{\gamma_{\sigma}}{\rho_l} . \quad (33)$$

Equation (23) is the recommended equation for the liquid enthalpy increment along the saturation curve below 2000 K. Above 2000 K, the liquid enthalpy is calculated from the average enthalpy (Eq. [24]) minus one half the enthalpy of vaporization (Eq. [17]); i.e.,

$$H(AVG, T) - H(s, 298.15) = E + FT - \frac{1}{2} \Delta H_g \quad (34)$$

for $2000 \text{ K} \leq T \leq 2503.7 \text{ K}$,

where

$$E = 2128.4 ,$$

$$F = 0.86496 .$$

Isothermal compressibilities for liquid sodium have been calculated by Bystrov et al.,⁽³⁾ Hornung,⁽²⁾ and Fink and Leibowitz.⁽¹⁾ In Fig. 1.4-12, values from these assessments are compared with recommended values. There is good agreement between recommendations from all assessments through 1300 K. Deviations of recommended values from values from other assessments defined as

$$Deviations = \left(\frac{[\beta_T(Other) - \beta_T(Recommended)] 100\%}{\beta_T(Recommended)} \right) , \quad (35)$$

are shown in Fig. 1.4-13. Above 1500 K, values from the other assessments are lower than the recommended values. From 1200 to 2400 K, values calculated by Bystrov et al. are closest to the recommended values. This may be because both calculations used the CODATA equation for the enthalpy of liquid sodium up to 2000 K.

Isothermal Compressibility of Sodium Vapor — The isothermal compressibility of sodium vapor was calculated from the instantaneous volumetric thermal-expansion coefficient for the vapor and the thermal-pressure coefficient using the thermodynamic relation given in Eq. (31). The vapor instantaneous volumetric thermal-expansion coefficient is defined in Eqs. (11-17). The thermal-pressure coefficient is given in Eqs. (18, 19).

In Fig. 1.4-14, the recommended values for the isothermal compressibility of sodium vapor are compared with values calculated by Fink and Leibowitz.⁽¹⁾ Values calculated by Fink and Leibowitz are higher than recommended values at all temperatures. Deviations defined in accord with Eq. (35) are shown in Fig. 1.4-15. Highest percent deviations are at the high and low temperatures. From 700 through 2100 K, deviations between these two calculations are within 6%. The high percent deviations at low temperatures arise from differences in the thermal-pressure coefficient in the two calculations, as discussed above.

Uncertainty

The uncertainties in the recommended values for the isothermal compressibilities of liquid sodium and sodium vapor have been calculated from uncertainties in the dependent parameters. If the dependent parameters (χ_i) are independent of each other, then the square of the uncertainty in the calculated quantity ($\delta\beta_T$) is given by

$$(\delta\beta_T)^2 = \sum \left(\frac{\partial\beta_T}{\partial\chi_i} \right)^2 (\delta\chi_i)^2, \quad (36)$$

where $\delta\chi_i$ are the uncertainties in the dependent parameters.

Isothermal Compressibility of Liquid Sodium — The isothermal compressibility, calculated using Eq. (30), is a function of thermodynamic variables which are functions of some of the same variables. For example, liquid density enters Eq. (30) not only explicitly but also through the adiabatic compressibility, the thermal-expansion coefficient along the saturation curve, and the heat capacity along the saturation curve. Vapor pressure enters both through the derivative along the saturation curve and through the heat capacity along the saturation curve. So the assumptions for application of Eq. (36) are not valid. Because of the complicated relationships between the dependent parameters, the uncertainty in the isothermal compressibility of liquid sodium has been approximated by

$$\delta\beta_T = \sqrt{(\delta\rho_l)^2 + (\delta\beta_s)^2 + (\delta C_o)^2}, \quad (37)$$

where $(\delta\rho_l)$ is the uncertainty in the liquid density, $(\delta\beta_s)$ is the uncertainty in the adiabatic compressibility, and (δC_o) is the uncertainty in the heat capacity along the saturation curve calculated from

$$\delta C_{\sigma} = \sqrt{4(\delta H_f)^2 + 4(\delta P)^2 + (\delta \rho_f)^2} . \quad (38)$$

The uncertainties calculated using Eqs. (37, 38) do not differ significantly from uncertainties calculated using other approximations such as calculation of uncertainties from the basic parameters (H , ΔH_g , P , v , ρ_f). Calculated uncertainties in the isothermal compressibility of liquid sodium are shown in Table 1.4-5. They range from 3% from 371 through 1000 K to 65% above 2400 K. Comparison of these estimated uncertainties with deviations of other assessments from the recommended values for the isothermal compressibility shows that the deviations are within the estimated uncertainties for most of the temperature range. Deviations are on the order of 3% or less from 371 through 1000 K. Between 1000 and 1600 K, all deviations are within 6% except for those from Fink and Leibowitz.⁽¹⁾ The percent deviation for values calculated by Fink and Leibowitz are 10% at 1500 K and 13% at 1600 K. The 30% deviation of values from Fink and Leibowitz are included in the 30% uncertainty from 1600 to 2000 K. The 45% and 60% uncertainties for the temperature ranges 2000 to 2200 K and 2200 to 2400 K are greater than any deviations between calculated values in the different assessments. However, deviations at 2500 K are greater than the 65% uncertainty given for temperatures greater than 2400 K. This is because the isothermal compressibility becomes very large as the critical point is approached and different values are selected for the critical temperature in the different assessments.

Isothermal Compressibility of Sodium Vapor— The uncertainties in the recommended values for the isothermal compressibility of sodium vapor were estimated using Eq. (36) and the thermodynamic relation for isothermal compressibility of sodium vapor given in Eq. (8). The uncertainties were estimated from the uncertainties in the instantaneous volumetric thermal-expansion coefficient for sodium vapor and the thermal-pressure coefficient according to

$$\delta \beta_T = \sqrt{(\delta \alpha_P)^2 + (\delta \gamma_V)^2} . \quad (39)$$

Uncertainties calculated with Eq. (39) are given for each temperature range in Table 1.4-6.

As for the adiabatic compressibilities, a high percent uncertainty (50%) is calculated for low temperatures (371 to 500 K). This is consistent with the large deviations between values from this calculation and values from Fink and Leibowitz⁽¹⁾ at low temperatures. At 400 K, the

deviation is 33%. The large percent deviation arises from the use of an equation to represent the thermal-pressure coefficient and the enthalpy of vaporization at low temperatures rather than use values from the quasi-chemical approximation. Uncertainties are 15% from 500 to 1600 K. Then they increase with increasing temperature to 100% at 2503 K. Calculated deviations between values given by Fink and Leibowitz and recommended values lie within the estimated uncertainties.

1.4.3 SPEED OF SOUND

Summary

Below 1773 K, the speed of sound (v) in liquid sodium in $\text{m}\cdot\text{s}^{-1}$ is given by the quadratic equation determined by Fink and Leibowitz⁽¹⁾ from fitting the data from 370 to 1270 K of Leibowitz et al.⁽⁸⁾ and data from 1010 to 1770 K from Chasanov et al.⁽⁹⁾

$$(4) \quad v = 2660.7 - 0.37667 T - 9.0356 \times 10^{-5} T^2 \quad (40)$$

for 371 K \leq T \leq 1773 K .

Above 1773 K, the speed of sound in liquid sodium is calculated from the liquid adiabatic compressibility (β_s) and the liquid density (ρ_l) using the thermodynamic relation

$$v = \frac{1}{\sqrt{\rho_l \beta_s}} \quad (41)$$

for 1773 K < T \leq 2503.7 K .

Recommended values for the speed of sound in liquid sodium are given in Table 1.4-7 and shown in Fig. 1.4-16. Estimated uncertainties in the recommended values have been included as dotted lines in Fig. 1.4-16 and are given in Table 1.4-8.

Discussion

The liquid density of sodium is given in Eq. (5). The adiabatic compressibility of liquid sodium is defined in Eqs. (1, 2). In Fig. 1.4-17, values for the speed of sound calculated from Eqs. (40, 41) are compared with values calculated by Fink and Leibowitz,⁽¹⁾ Bystrov et al.,⁽³⁾ and the extrapolation of the quadratic equation (Eq. [40]) to the critical point. This

Table 1.4-7 Speed of Sound in Liquid Sodium

| Temperature (K) | Speed of Sound (m · s⁻¹) |
|----------------------------|--|
| 400 | 2496 |
| 500 | 2450 |
| 600 | 2402 |
| 700 | 2353 |
| 800 | 2302 |
| 900 | 2249 |
| 1000 | 2194 |
| 1100 | 2137 |
| 1200 | 2079 |
| 1300 | 2018 |
| 1400 | 1956 |
| 1500 | 1892 |
| 1600 | 1827 |
| 1700 | 1759 |
| 1800 | 1676 |
| 1900 | 1587 |
| 2000 | 1487 |
| 2100 | 1372 |
| 2200 | 1235 |
| 2300 | 1060 |
| 2400 | 810 |
| 2500 | 180 |

Table 1.4-8 Estimated Uncertainties in the Recommended Values for Speed of Sound in Liquid Sodium

| Temperature (K) | v ($\text{m} \cdot \text{s}^{-1}$) | Uncertainty, $\left(\frac{\delta v}{v}\right)$ (%) |
|----------------------------|--|--|
| $371 \leq T \leq 1600$ | $v = 2660.7 - 0.37667 T - 9.0356 \times 10^{-5} T^2$ | 1 |
| $1600 < T \leq 1773^{(a)}$ | | 1.3 ^(a) |
| $1773 < T \leq 2000^{(a)}$ | $v = \frac{1}{\sqrt{\beta_S \rho_l}}$ | 10 ^(a) |
| $2000 < T \leq 2200^{(a)}$ | | 16 ^(a) |
| $2200 < T \leq 2400^{(a)}$ | | 22 ^(a) |
| $2400 < T \leq 2503^{(a)}$ | | 25 ^(a) |

^(a)From 1700 to 2503.7 K, the uncertainty is approximated by $\frac{\delta v}{v}$ (%) = $-48 + 0.029 T$

extrapolation is labeled "quad-ext" in the figure. Bystrov et al. represent the speed of sound with a linear equation, which they extrapolate to the critical point. Extrapolation of these polynomial representations of the speed of sound to the critical point do not give proper physical behavior for the speed of sound or for the adiabatic compressibility (calculated from the speed of sound) at the critical point. The extrapolation used here is identical to that used by Fink and Leibowitz.⁽¹⁾ It gives proper physical behavior at the critical point.

Deviations between recommended values and those of Bystrov et al. and Fink and Leibowitz, defined as

$$Deviations = \left(\frac{[v(Other) - v(Recommended)] 100\%}{v(Recommended)} \right), \quad (42)$$

are shown in Fig. 1.4-18. Values given by Fink and Leibowitz and those recommended here are identical through 1773 K. Above 1773 K, deviations increase with temperature due to differences in the density and critical temperature in the two assessments. Values given by Bystrov et al. agree within 1.3% through 1700 K. Above 1700 K, deviations increase with temperature, as shown in the figure. At 2400 K, deviations are 71%.

Uncertainty

Uncertainties in the recommended values for the speed of sound have been estimated from the deviations of the various assessments and the uncertainties given in these assessments. From 371 through 1600 K, the uncertainty is estimated as 1%. All recommended values are within this uncertainty in this temperature range. Above 1600 K, uncertainties increase with temperature according to the equation

$$\frac{\delta v}{v}(\%) = -48 + 0.029 T . \quad (43)$$

At 2500 K, uncertainties are estimated as 25%. This uncertainty is lower than the deviation between recommended values and those given by Bystrov et al. Because the equation used by Bystrov et al. does not have the proper behavior near the critical point, larger deviations than estimated uncertainties may be expected.

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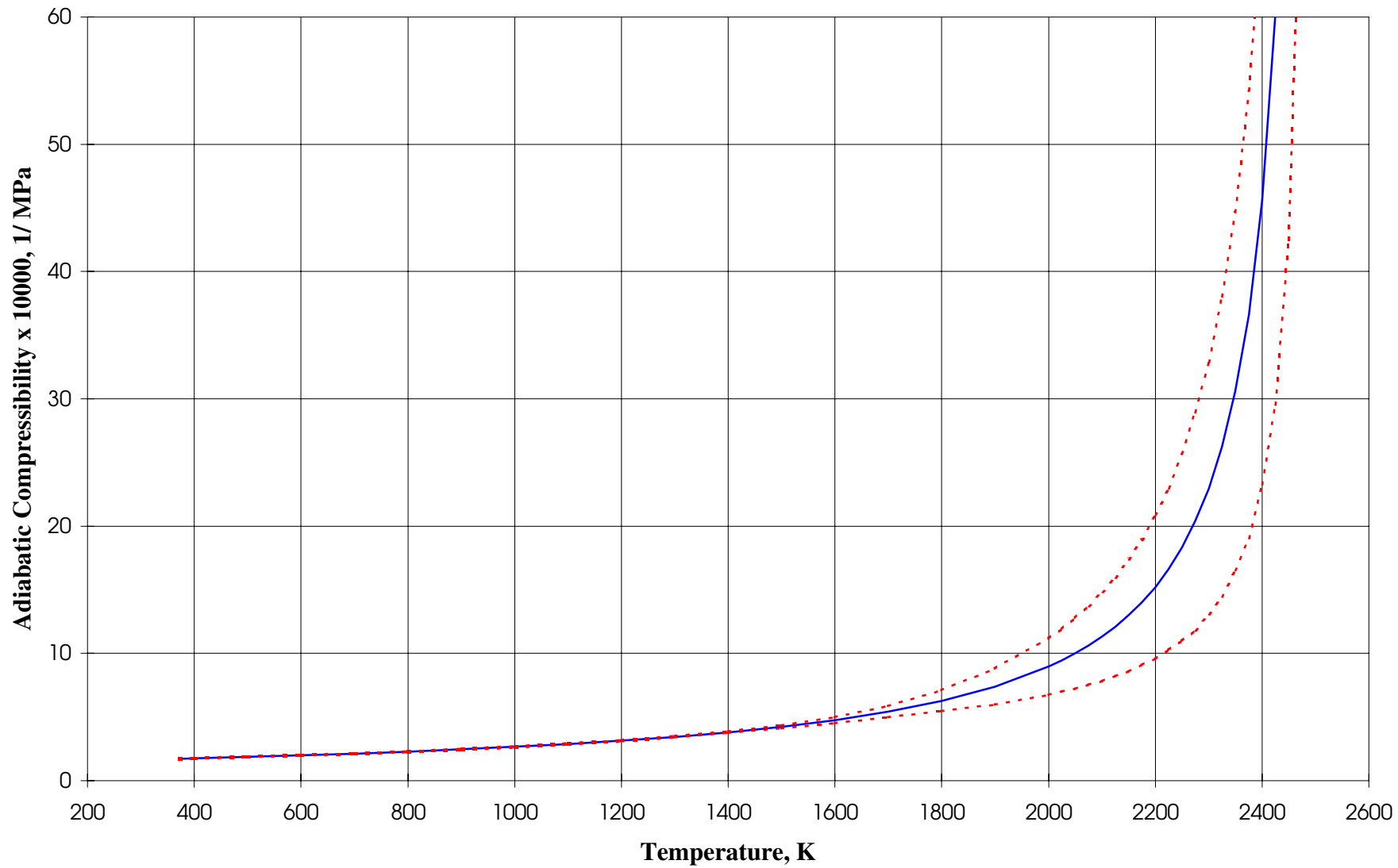


Fig. 1.4-1 Recommended Values for the Adiabatic Compressibility of Liquid Sodium

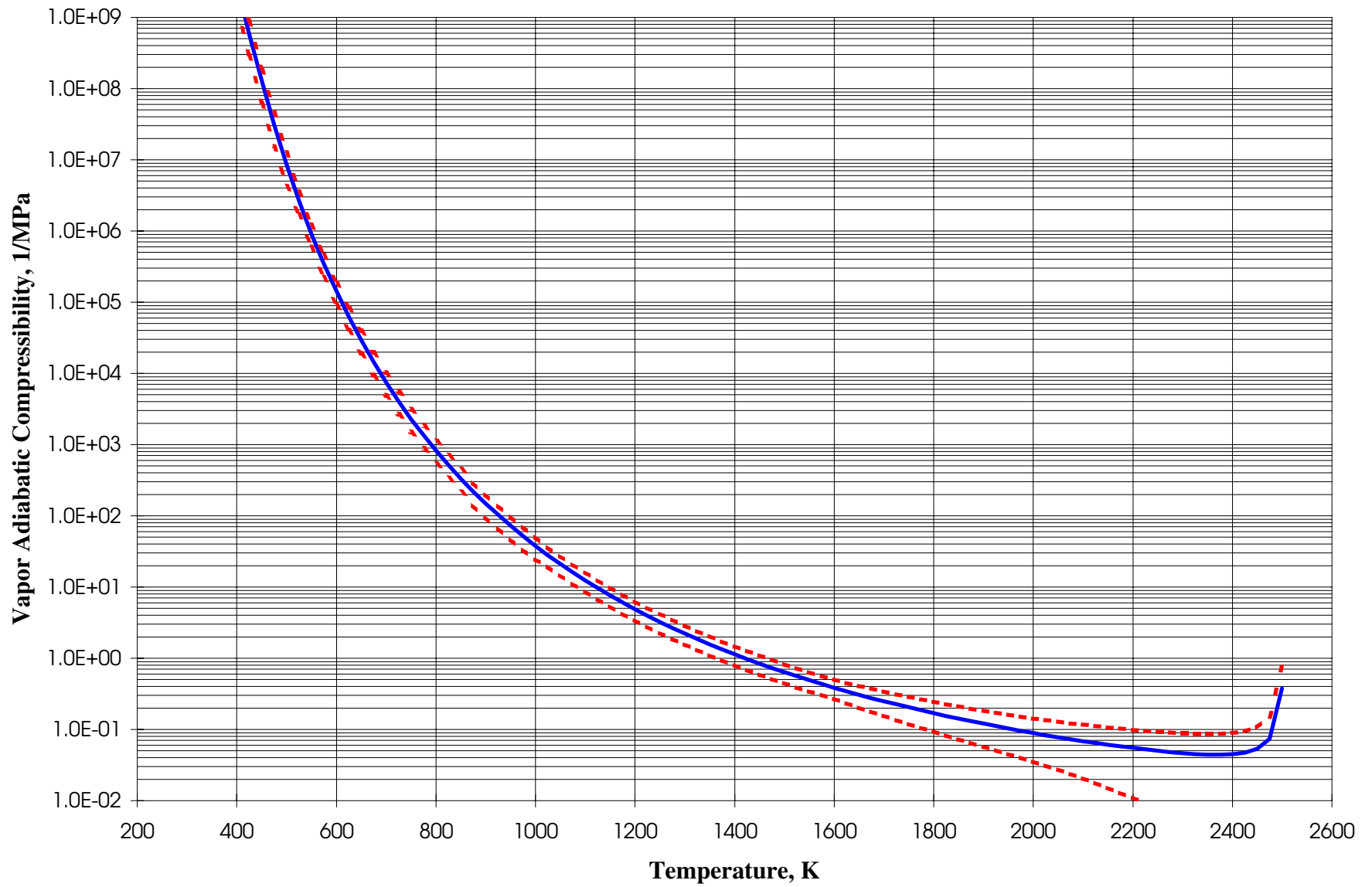


Fig.1.4-2 Recommended Values for the Adiabatic Compressibility of Sodium Vapor

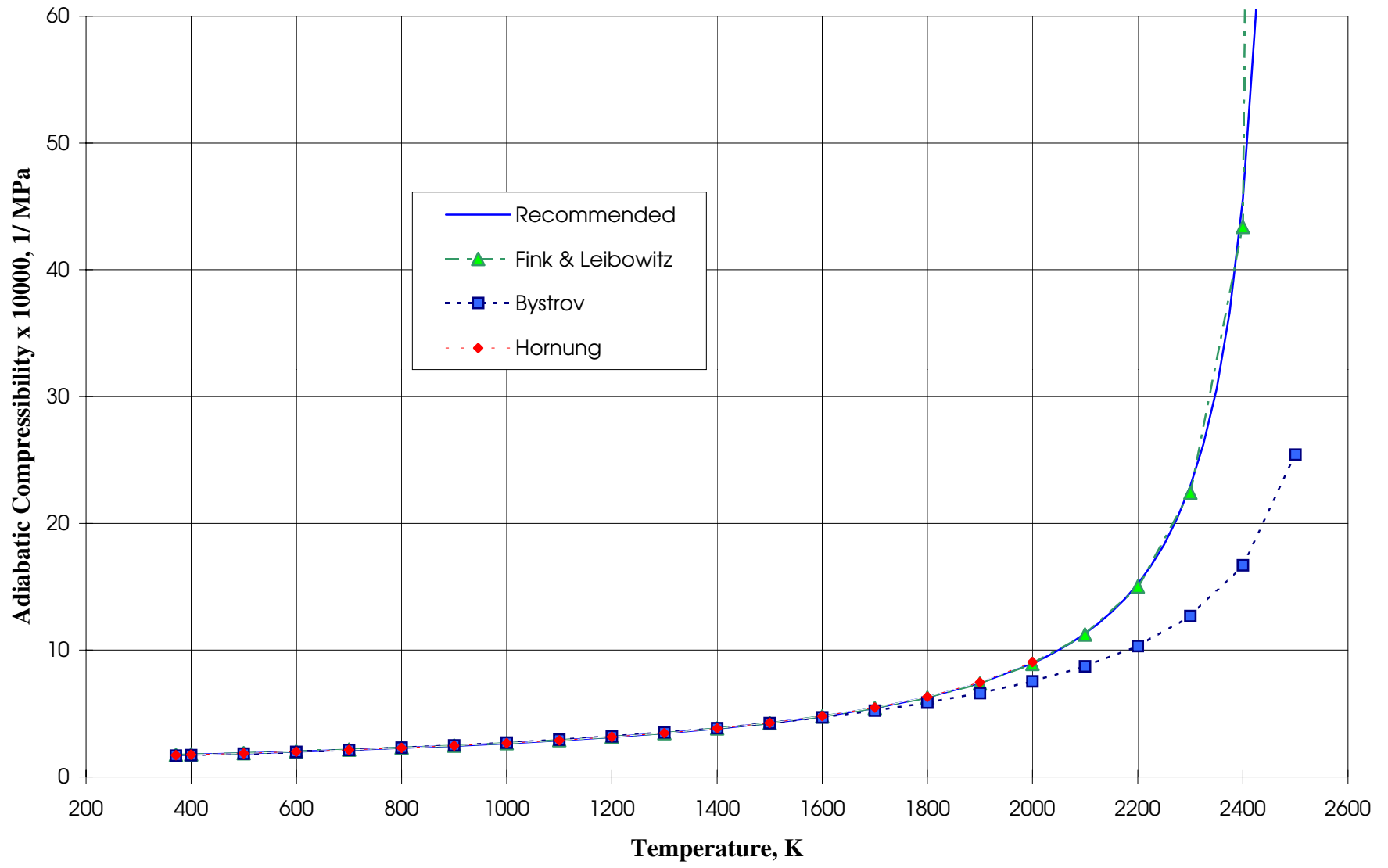


Fig. 1.4-3 Comparison of the Recommended Values for the Adiabatic Compressibility of Liquid Sodium with Values from Other Assessments

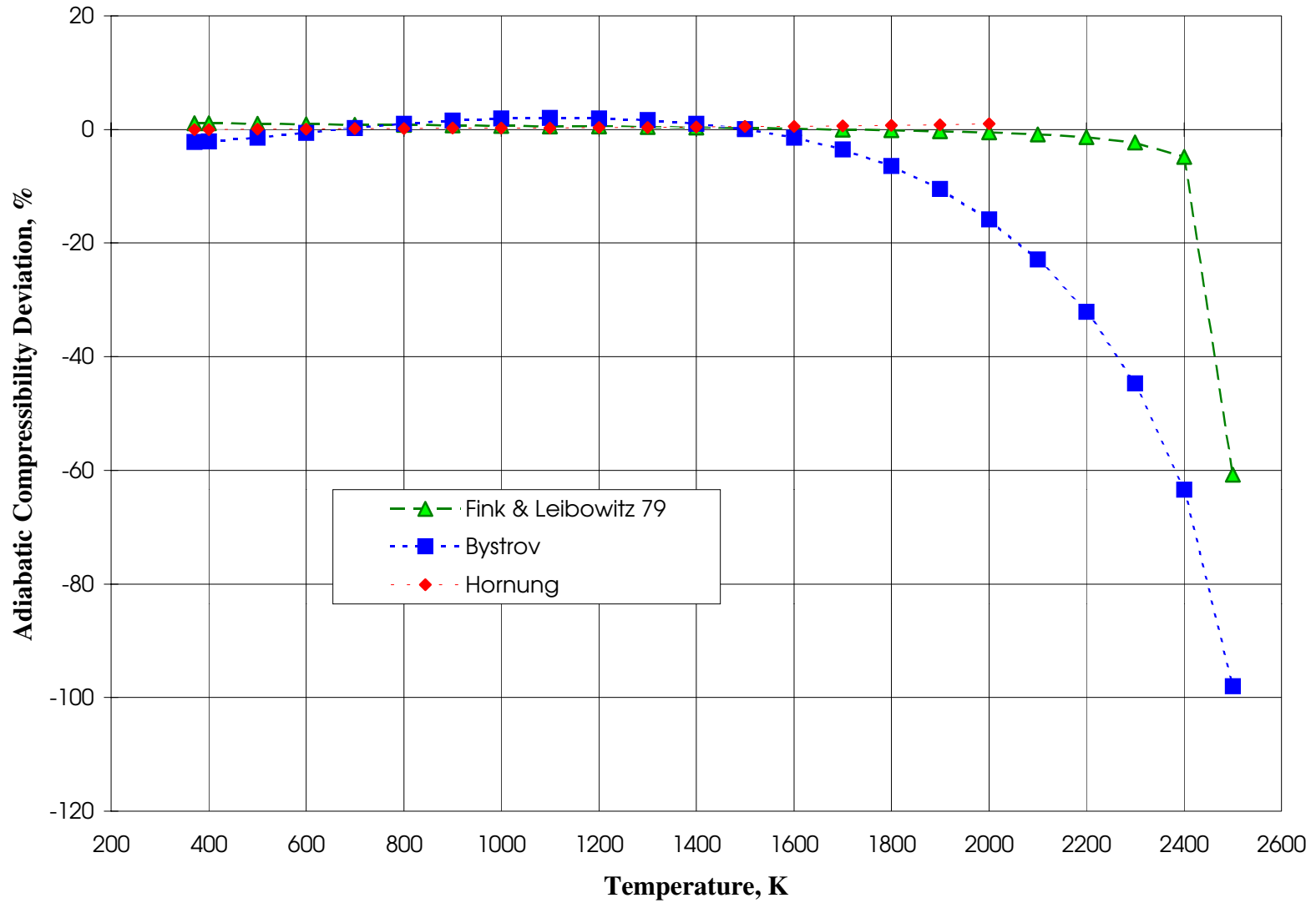


Fig. 1.4-4 Deviation of the Recommended Values for the Adiabatic Compressibility of Liquid Sodium from Values from Other Assessments

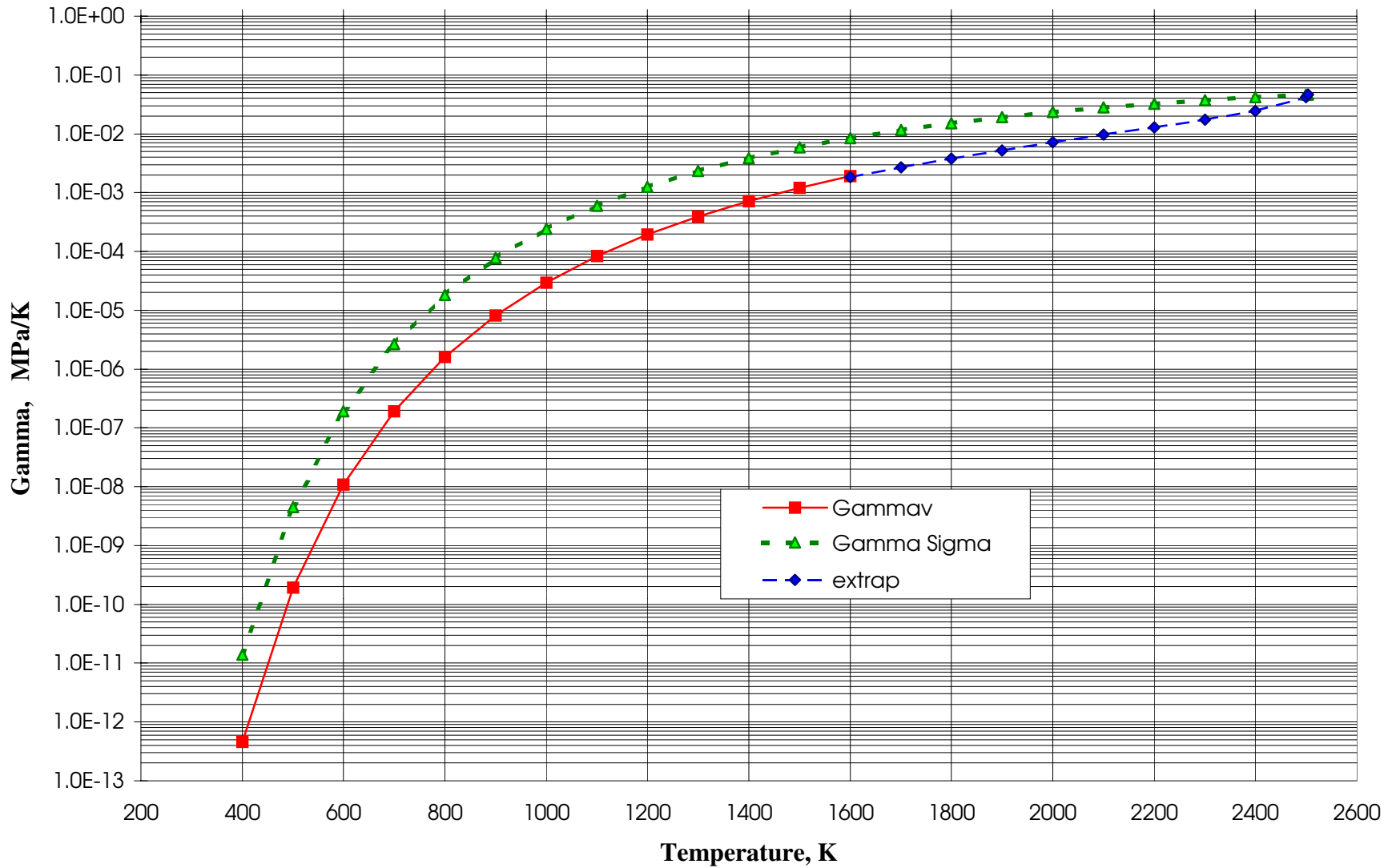


Fig. 1.4-5. The Thermal-Pressure Coefficient (γ_v) and the Temperature Derivative of the Vapor Pressure along the Saturation Curve (γ_σ)

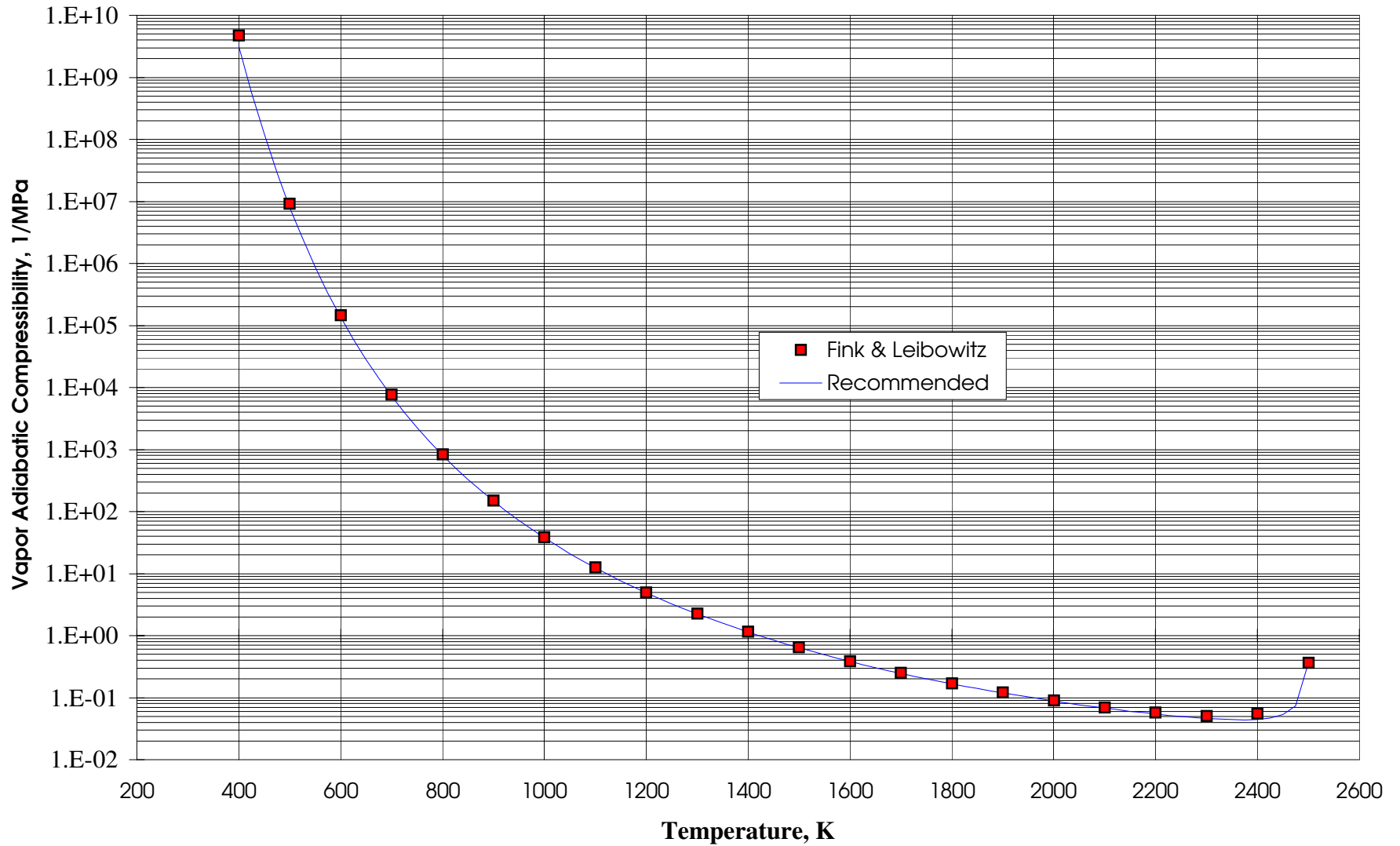


Fig. 1.4-6 Comparison of Recommended Values for the Adiabatic Compressibility of Sodium Vapor with Values from Fink and Leibowitz¹

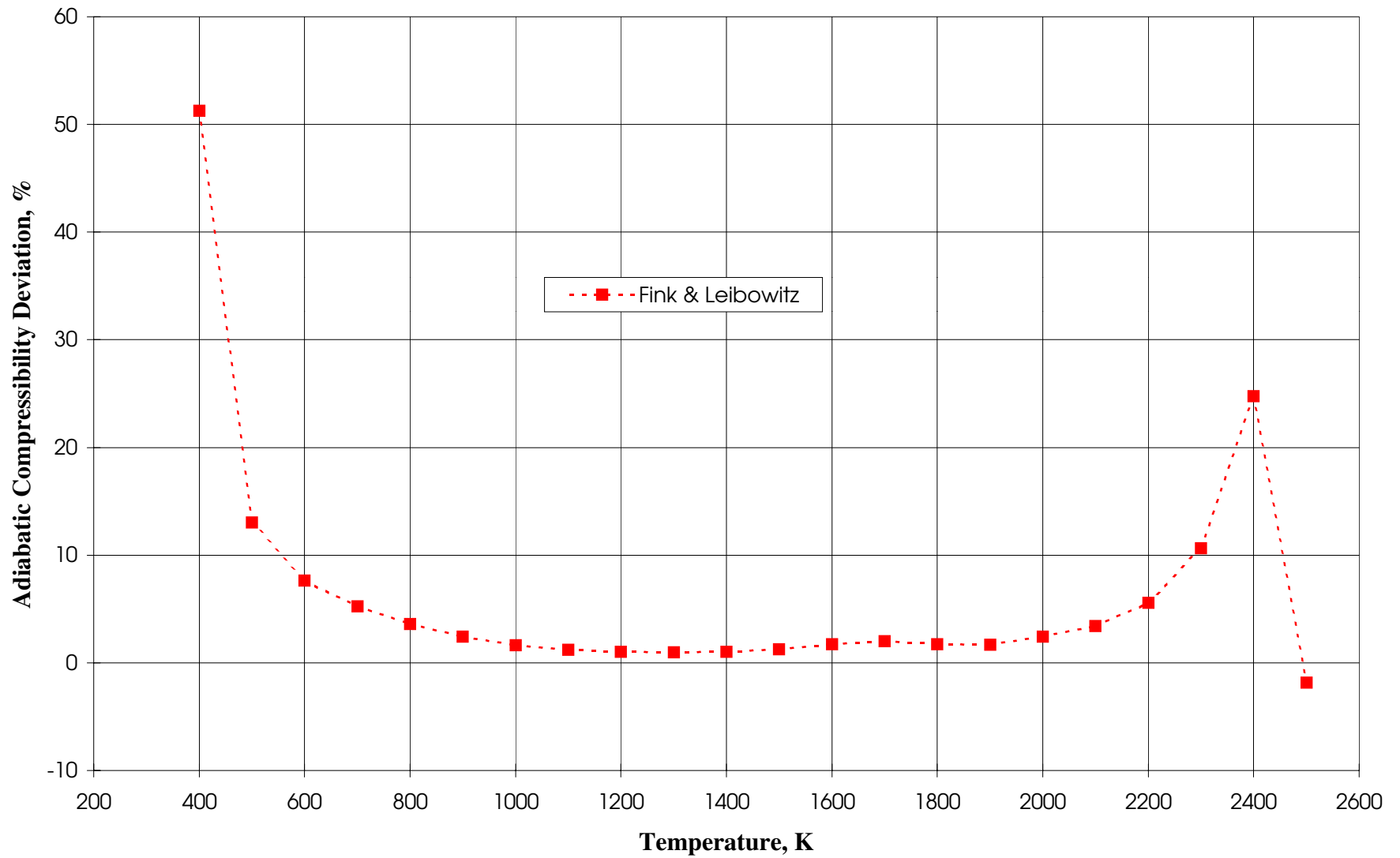


Fig. 1.4-7 Deviations of the Adiabatic Compressibility of sodium Vapor Calculated by Fink and Leibowitz¹ from Recommended Values

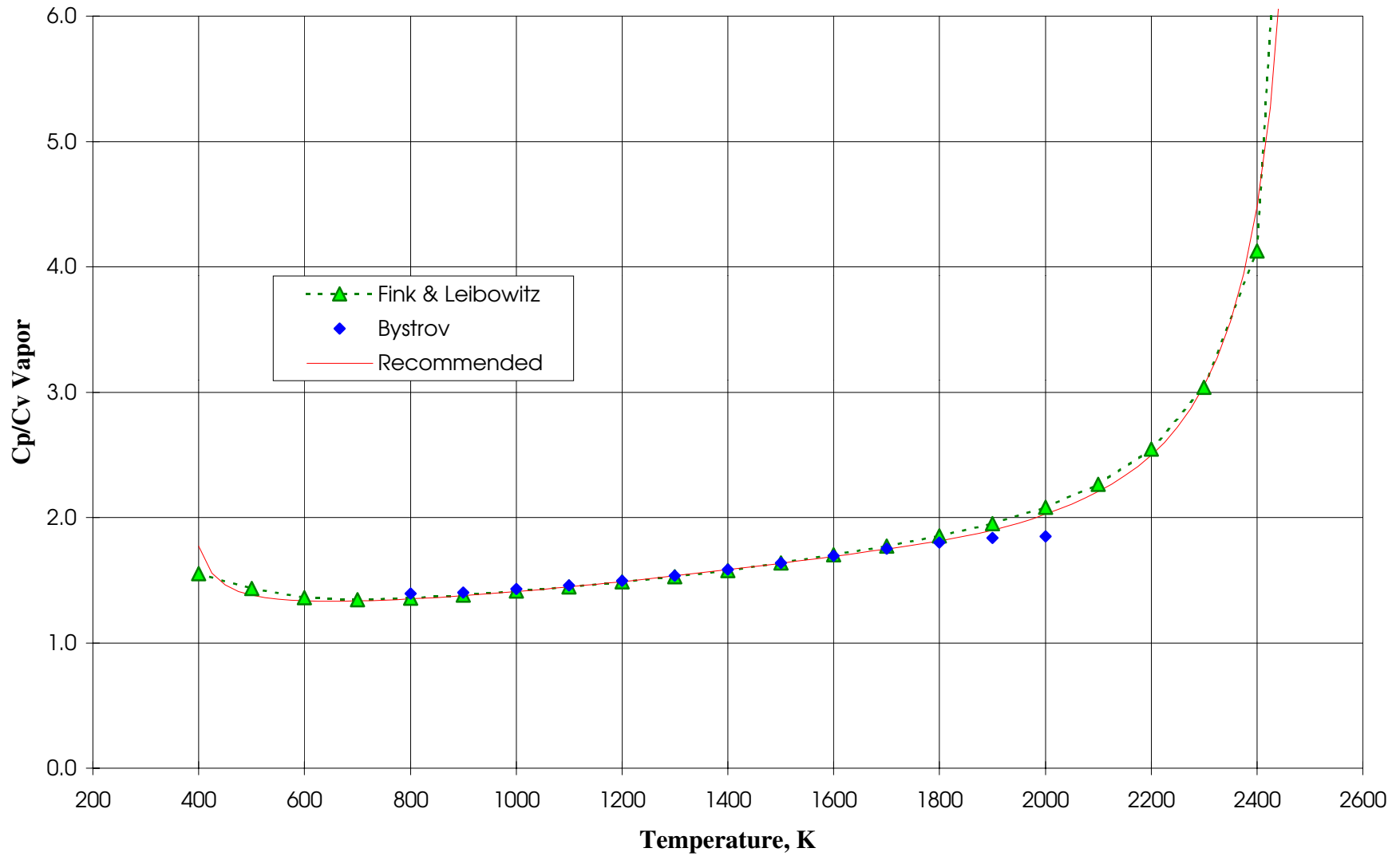


Fig. 1.4-8 Comparison of the Ratio of the Recommended Values for the Heat Capacity at Constant Pressure and Constant Volume for Sodium Vapor with Values of the Ratio from Other Assessments

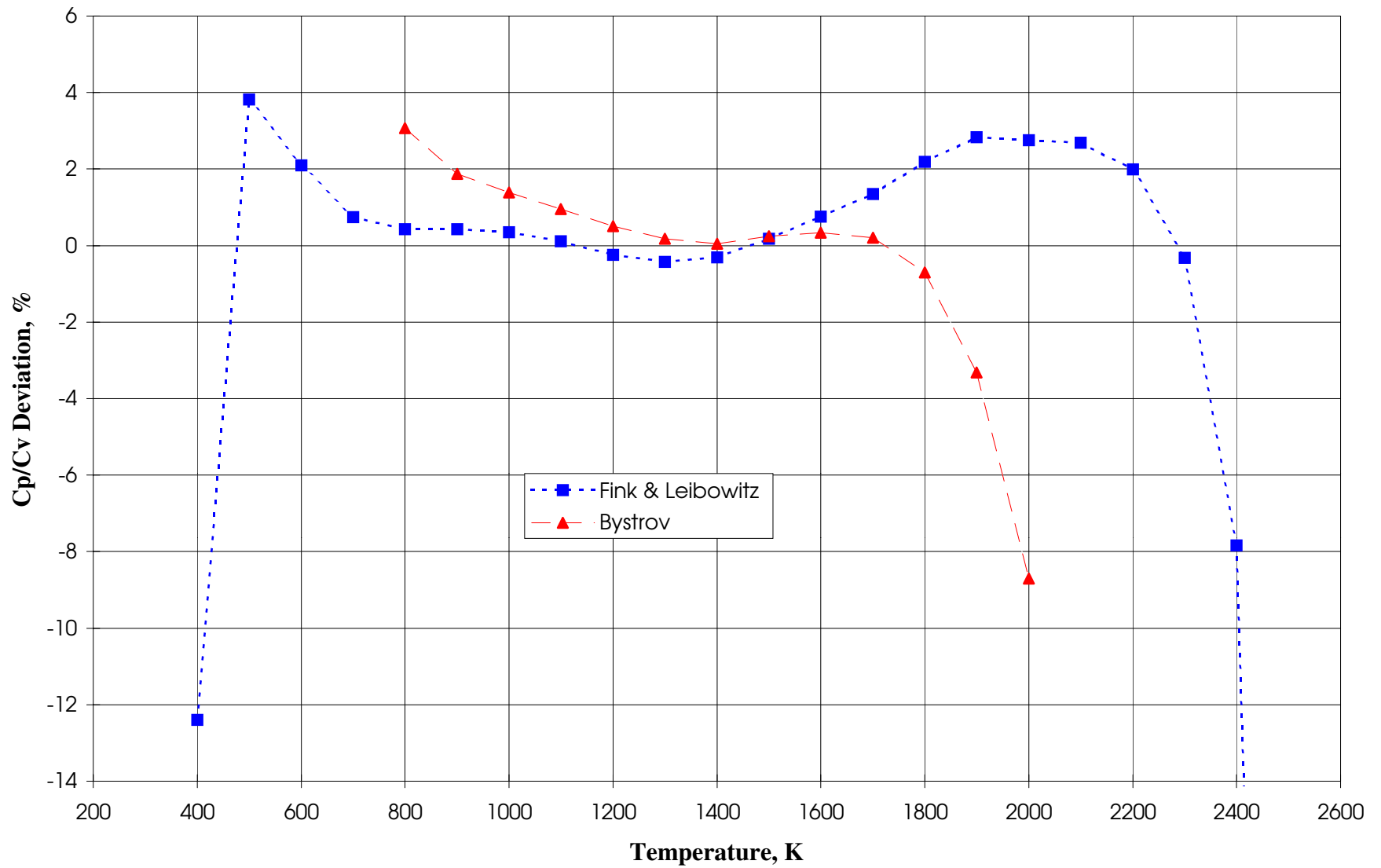


Fig. 1.4-9 Deviations of the Values of the Heat Capacity Ratios for Sodium Vapor Calculated by Fink and Leibowitz and by Bystrov et al. from Recommended Values

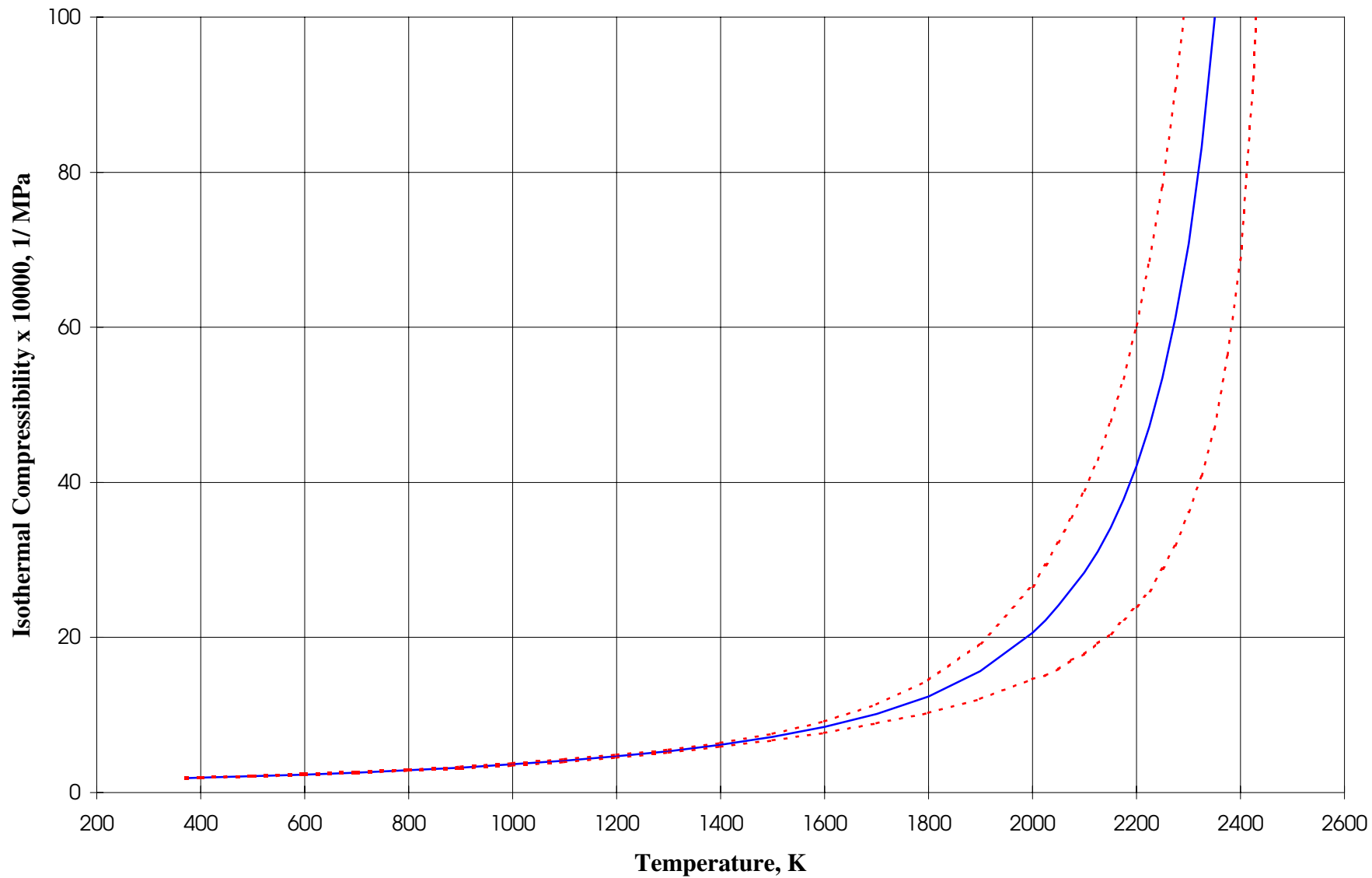


Fig. 1.4-10 Recommended Values for the Isothermal Compressibility of Liquid Sodium

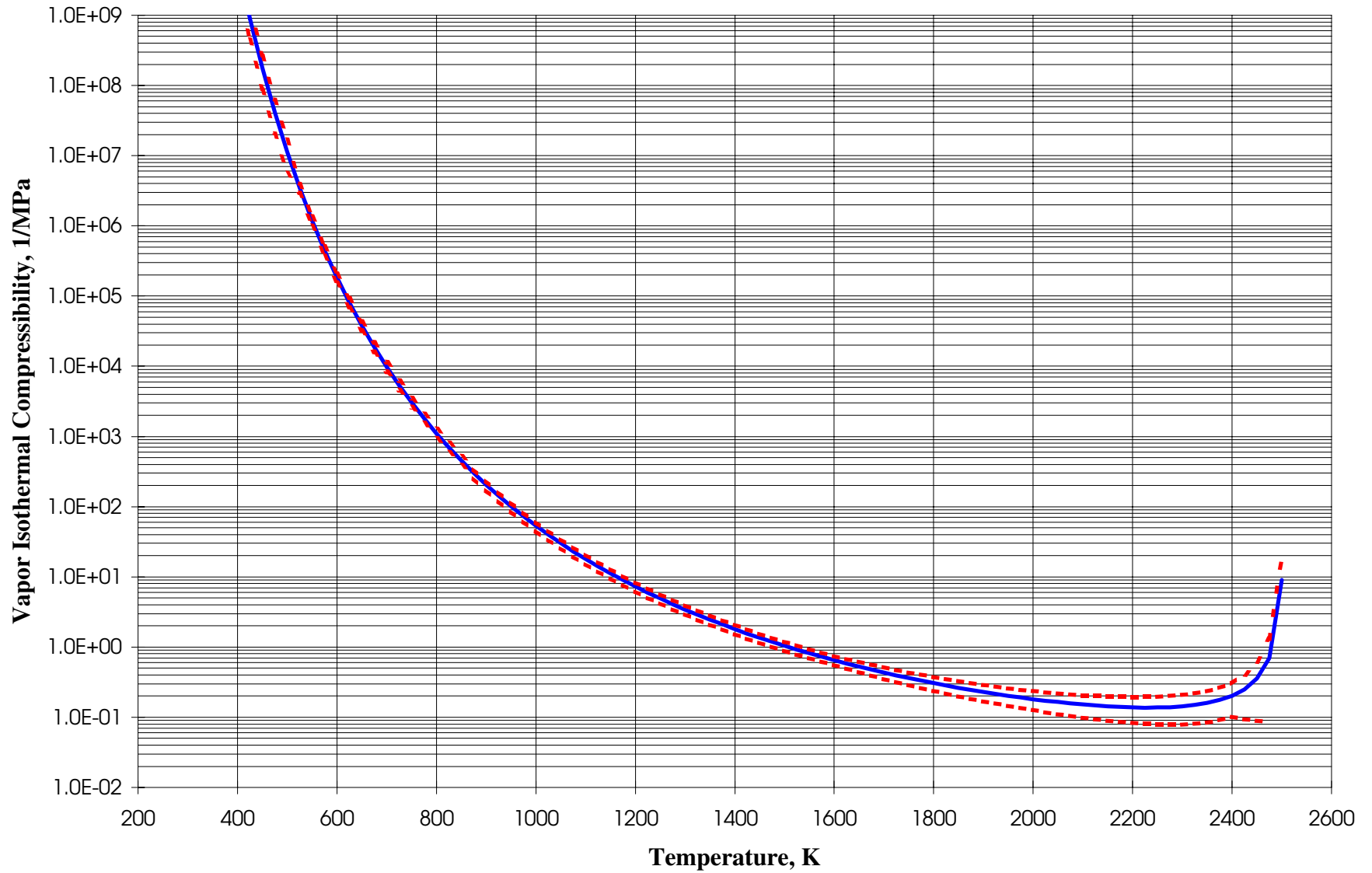


Fig. 1.4-11 Recommended Values for the Isothermal Compressibility of Sodium Vapor

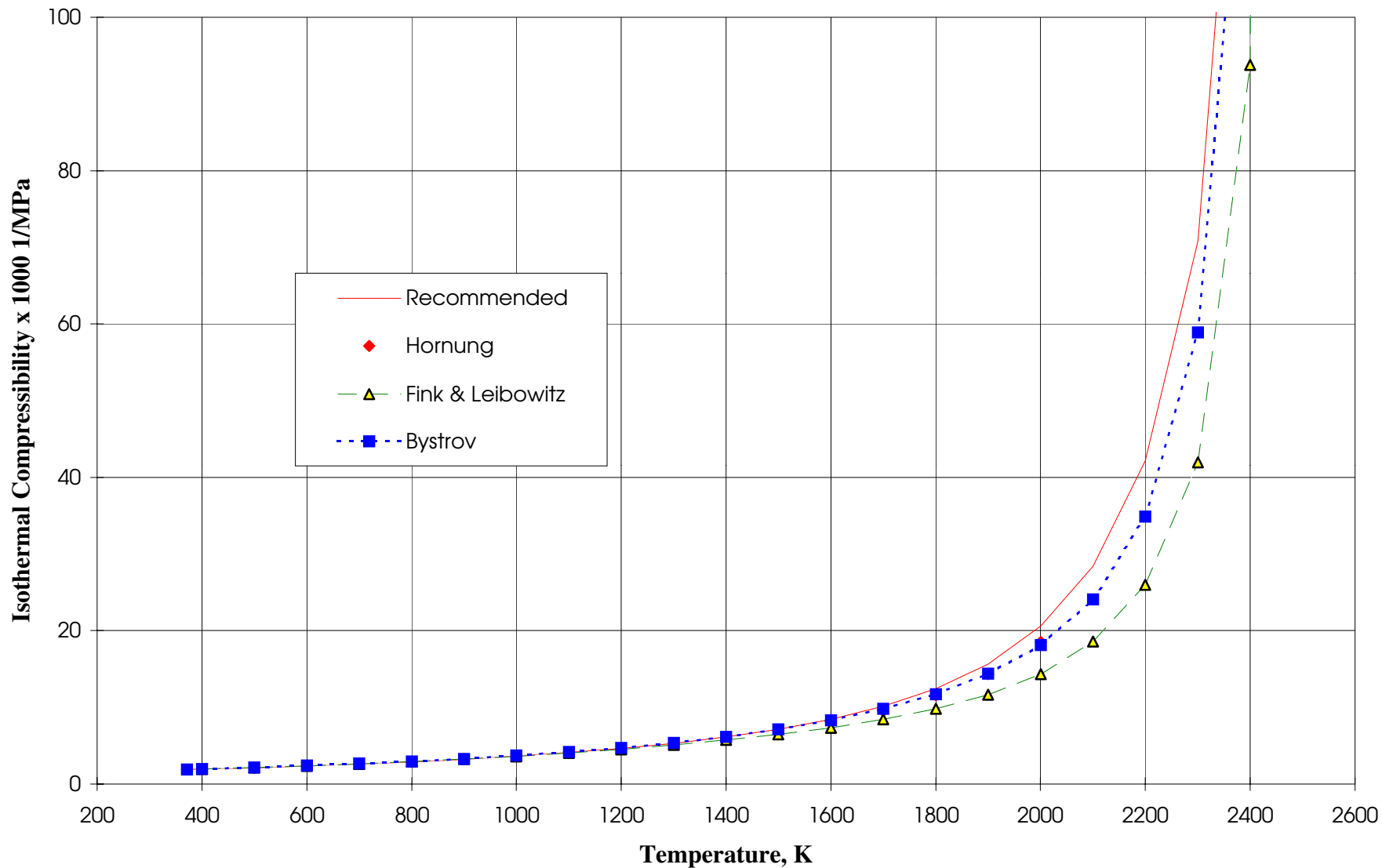


Fig. 1.4-12 Comparison of the Recommended Values for the Isothermal Compressibility of Liquid Sodium with Values from Other Assessments

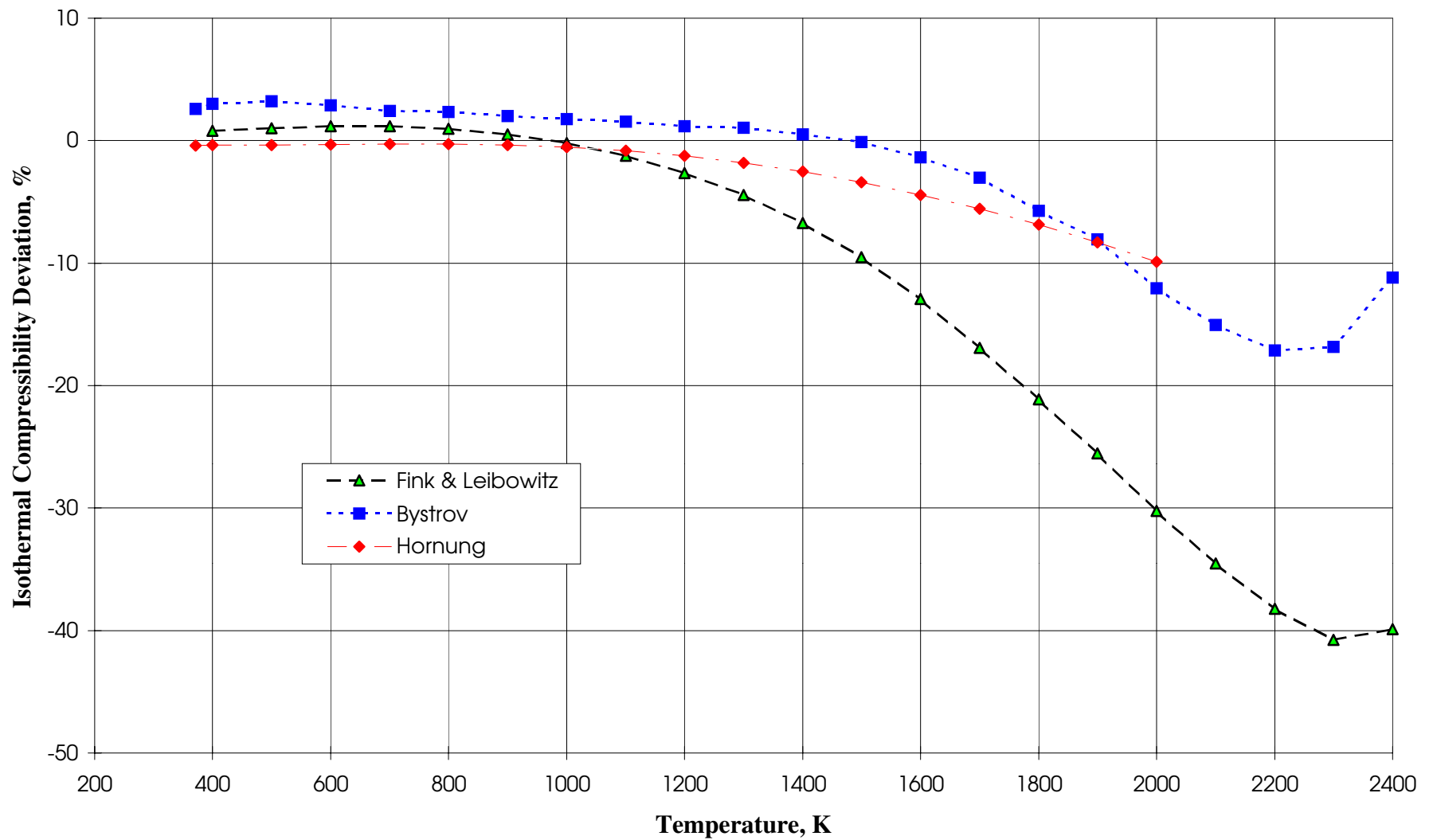


Fig. 1.4-13 Percent Deviations of the Recommended Values for the Isothermal Compressibility of Liquid Sodium from Values from Other Assessments

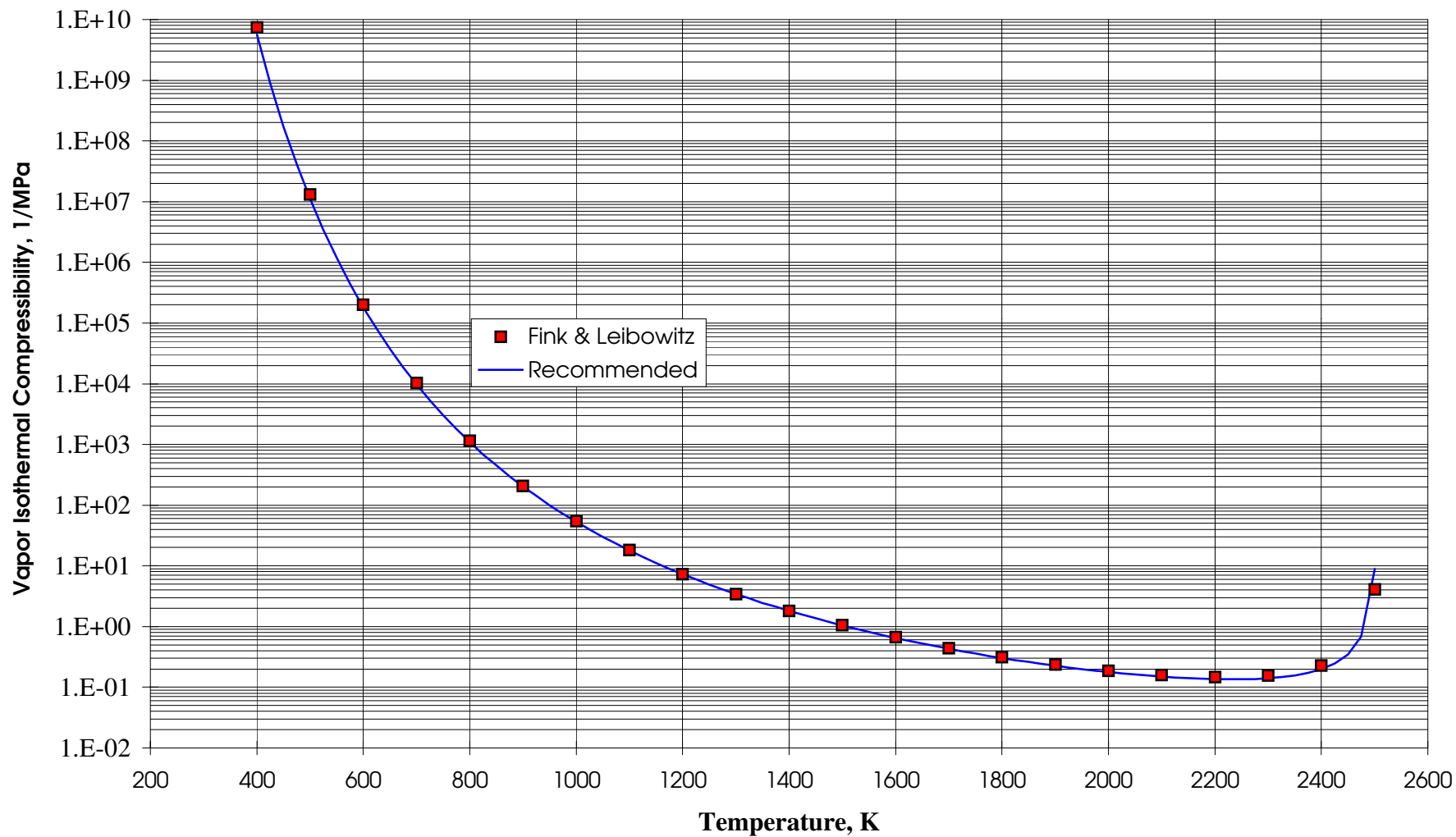


Fig. 1.4-14 Comparison of Recommended Values for the Isothermal Compressibility of Sodium Vapor with Values from Fink and Leibowitz¹

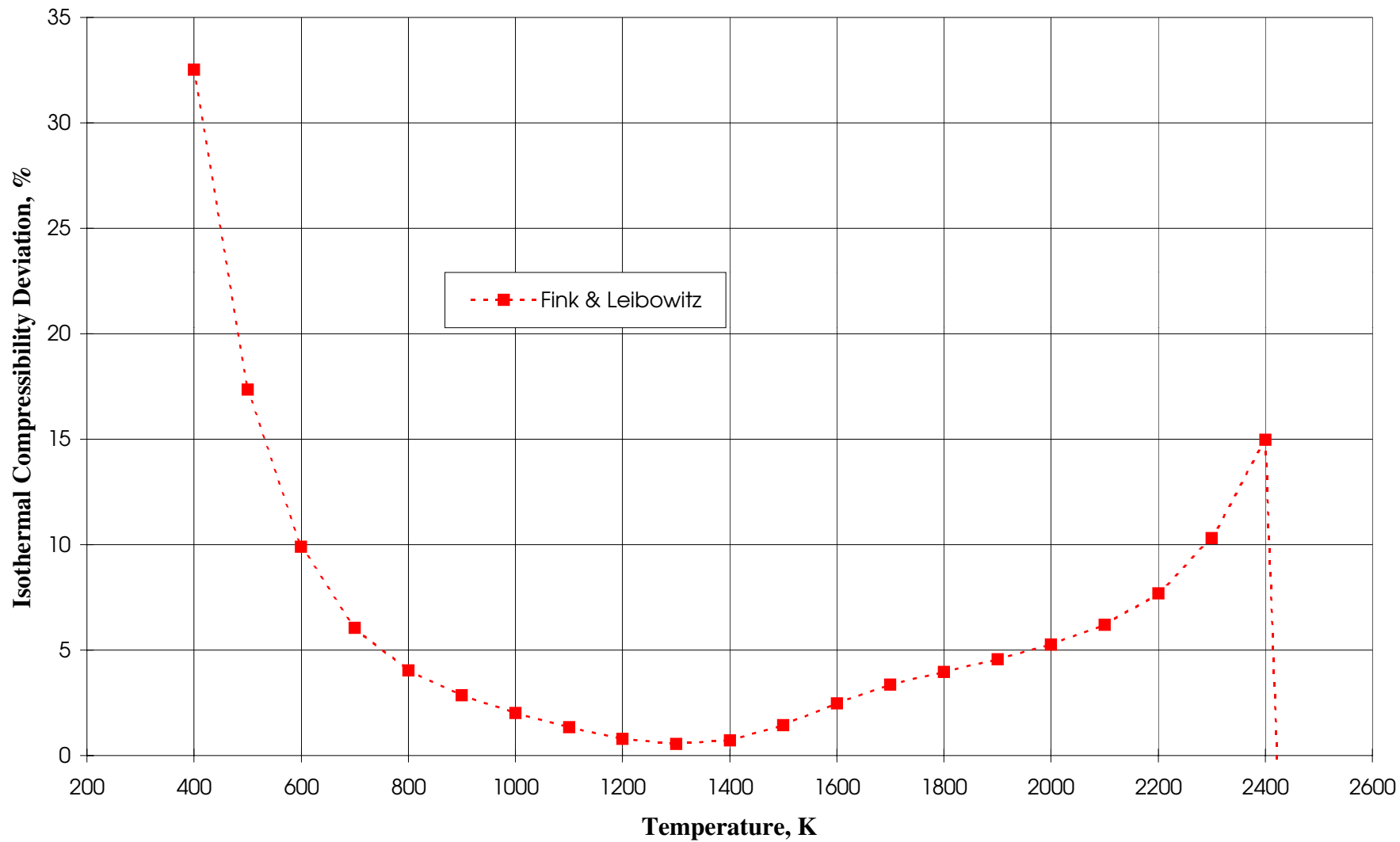


Fig. 1.4-15 Percent Deviations of the Recommended Values for the Isothermal Compressibility of Sodium Vapor from the Values from Fink and Leibowitz¹

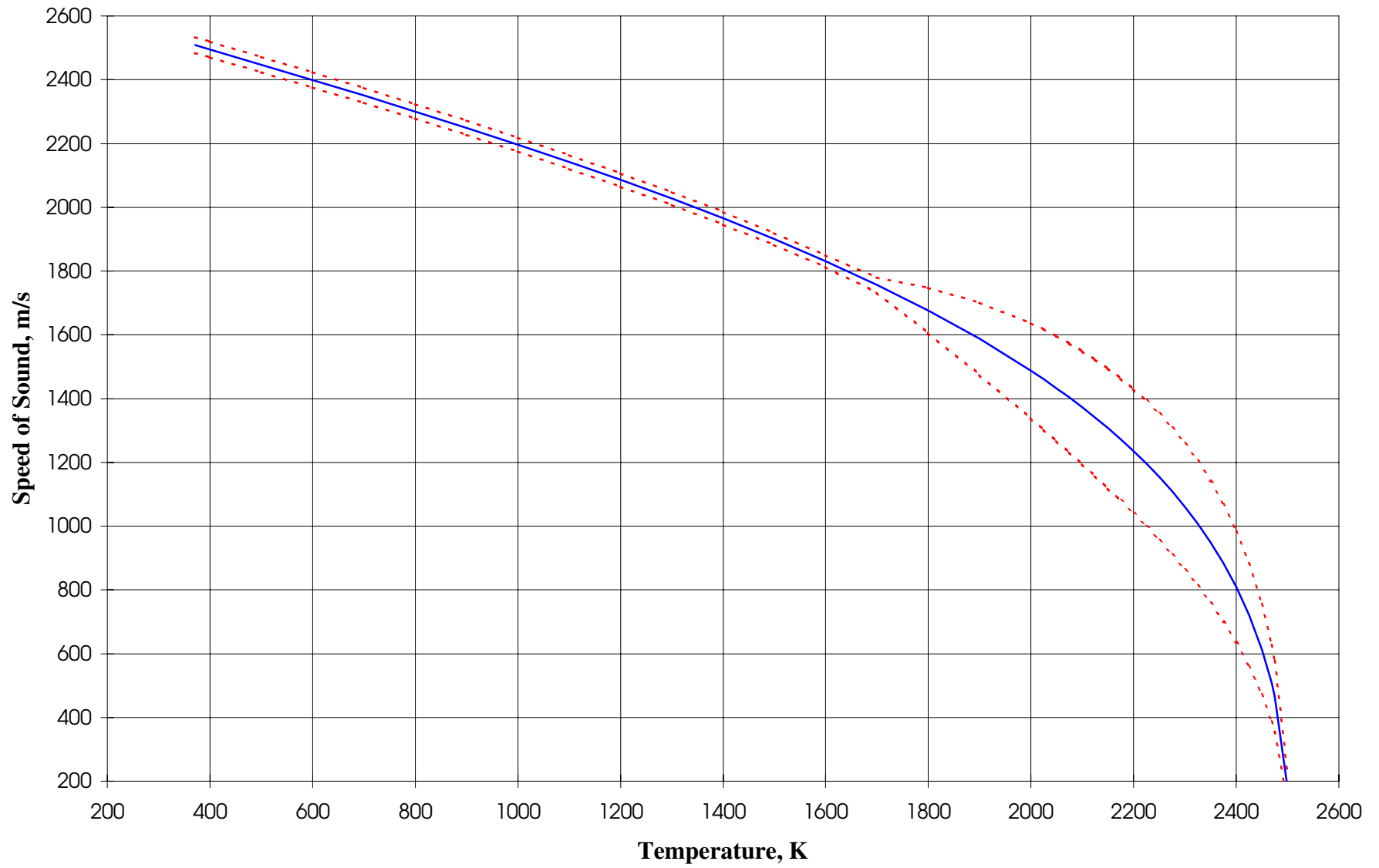


Fig. 1.4-16 Recommended Values for the Speed of Sound in Liquid Sodium

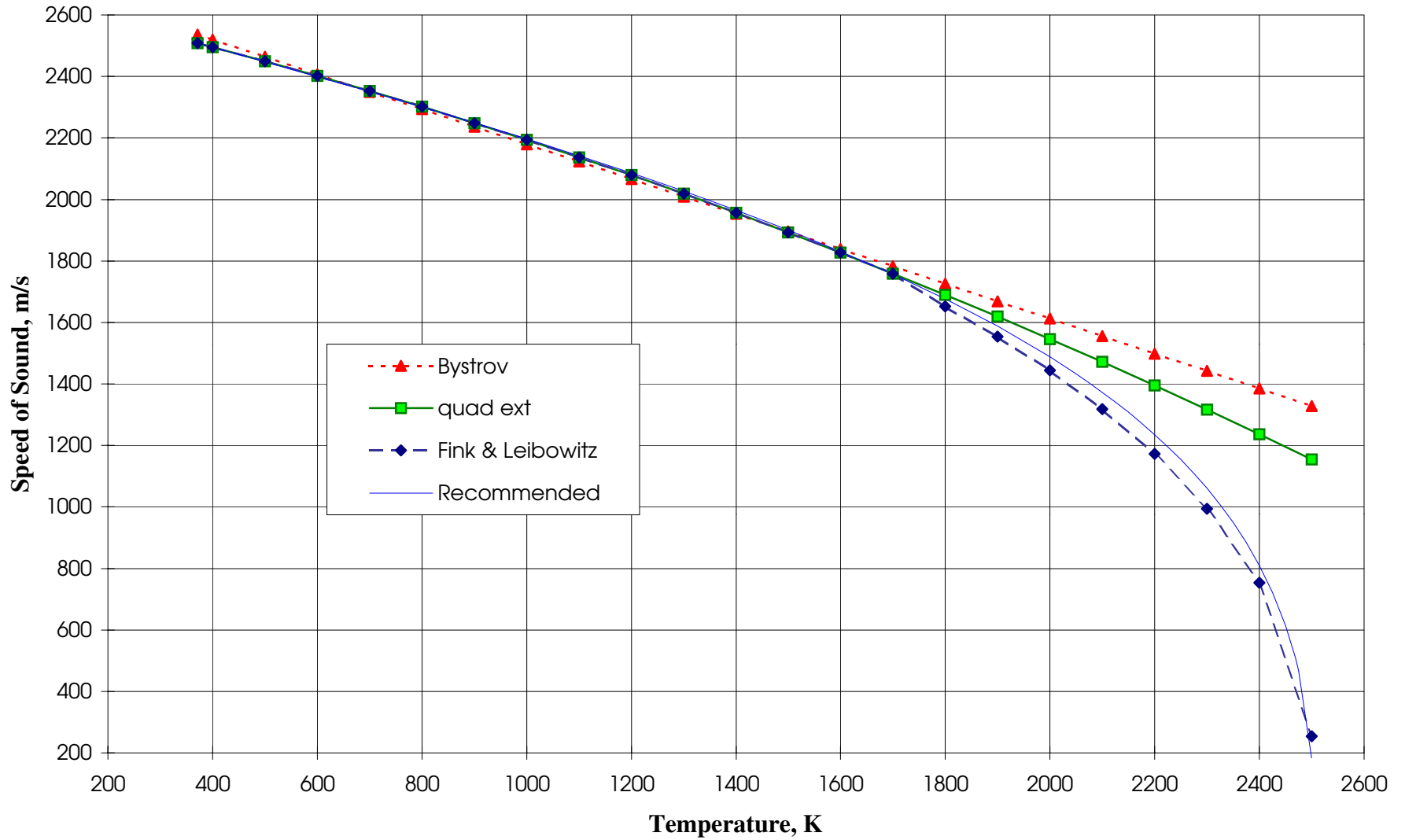


Fig. 1.4-17 Comparison of Recommended Values for the Speed of Sound in Liquid Sodium with Values from Other Assessments

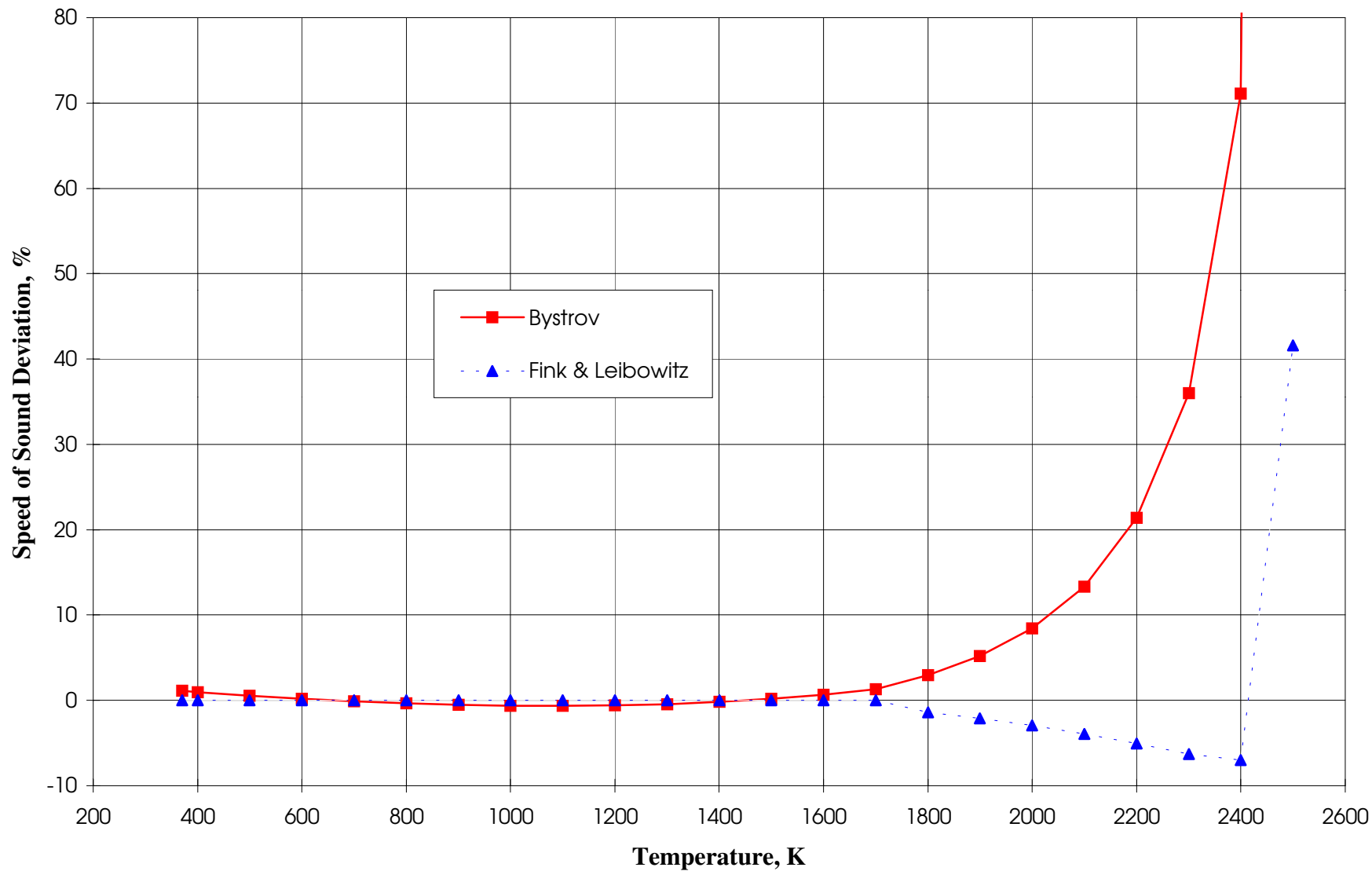


Fig. 1.4-18 Percent Deviations of the Recommended Values for the Speed of Sound in Liquid Sodium from Values from Other Assessments

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 2σ) are included with each value.

Table 1.5-1 Recommended Values of Critical Parameters

| T_c (K) | P_c (MPa) | ρ_c ($\text{kg} \cdot \text{m}^{-3}$) |
|-----------------|-----------------|---|
| 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

$$\ln P = 11.9463 - 12633.73/T - 0.4972 \ln T \quad (1)$$

The critical density, $219 \text{ kg} \cdot \text{m}^{-3}$, 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 $207 \text{ kg} \cdot \text{m}^{-3}$ 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 ($\text{kg} \cdot \text{m}^{-3}$) | 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 $214 \text{ kg}\cdot\text{m}^{-3}$ 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

$$\frac{\rho_l}{\rho_c} - 1 = 0.9799513 + 2.761335 \left(1 - \frac{T}{T_c} \right) \quad (2)$$

$$\text{for } \frac{T}{T_c} \leq 0.78 \quad .$$

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 $213 \text{ kg}\cdot\text{m}^{-3}$ 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 $214 \text{ kg}\cdot\text{m}^{-3}$ 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 $203 \text{ kg}\cdot\text{m}^{-3}$ 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 $219 \text{ kg}\cdot\text{m}^{-3}$ 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:

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

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 $214 \text{ kg}\cdot\text{m}^{-3}$ and $219 \text{ kg}\cdot\text{m}^{-3}$. 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 $219 \text{ kg}\cdot\text{m}^{-3}$ rather than $214 \text{ kg}\cdot\text{m}^{-3}$. Thus, $219 \text{ kg}\cdot\text{m}^{-3}$ has been selected for the critical density of sodium at 2503.7 K.

The recommended value for the critical density is higher than the $214 \text{ kg}\cdot\text{m}^{-3}$ 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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1.6 SURFACE TENSION

Summary

The recommended values for the surface tension of liquid sodium in $\text{mN}\cdot\text{m}^{-1}$, given in Table 1.6-1, are calculated from the Van der Waals equation:

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_C} \right)^n, \quad (1)$$

where

$$\begin{aligned} \sigma_0 &= 240.5, \\ n &= 1.126, \\ T_C &= 2503.7 \text{ K}. \end{aligned}$$

This equation is based on the analysis by Goldman⁽¹⁾ of the available data⁽²⁻¹⁶⁾ from 371 to 1600 K on the surface tension of liquid sodium. The standard deviation of the data from the recommended equation is 5.5%. Thus, the recommended uncertainty (± 2 standard deviations) is 11% in the range of experimental data. In the extrapolated region, the estimated uncertainty has been increased to 12%. Figure 1.6-1 shows the recommended values for the surface tension of sodium with the uncertainties as dashed lines. The uncertainties are given in Table 1.6-2.

Discussion

The recommended equation for the surface tension of sodium was obtained by adjusting the parameters σ_0 and n given by Goldman⁽¹⁾ for the recommended critical temperature, 2503.7 K. Goldman used 2509.4 K for the critical temperature in his analysis. The constants recommended by Goldman are:

$$\begin{aligned} \sigma_0 &= 240.7, \\ n &= 1.132, \\ T_C &= 2509.4 \text{ K}. \end{aligned}$$

Thus, the change in the critical temperature changes the constant σ_0 by 0.2 (0.08%) and the exponent n by 0.006 (0.5%). The recommended equation reproduces the values given by Goldman to within 0.07% up to 2000 K. Deviations increase as the critical temperature is approached because the surface tension must be zero at the critical temperature. Deviations of

Table 1.6-1 Surface Tension of Liquid Sodium

| Temperature (K) | Surface Tension (mN · m ⁻¹) |
|--------------------|--|
| 371 | 200.7 |
| 400 | 197.7 |
| 500 | 187.1 |
| 600 | 176.6 |
| 700 | 166.2 |
| 800 | 155.9 |
| 900 | 145.6 |
| 1000 | 135.4 |
| 1100 | 125.3 |
| 1200 | 115.3 |
| 1300 | 105.4 |
| 1400 | 95.6 |
| 1500 | 85.9 |
| 1600 | 76.3 |
| 1700 | 66.9 |
| 1800 | 57.6 |
| 1900 | 48.5 |
| 2000 | 39.5 |
| 2100 | 30.8 |
| 2200 | 22.4 |
| 2300 | 14.3 |
| 2400 | 6.7 |
| 2500 | 0.2 |
| 2503.7 | 0 |

the recommended values from those given by Goldman expressed as a percent are shown in Fig. 1.6-2. Deviations are 4% at 2400 K.

In his review of the data on the surface tension of liquid metals, Allen⁽¹⁷⁾ recommends using the equation given by Goldman for the surface tension of sodium. However, Allen states that although surface tension near the critical temperature is best described by a Van der Waals equation (Eq. [1]), near the melting temperature, the law of Eötvös gives a better value. The law of Eötvös states that

$$\sigma (Mv)^{2/3} = k (T_C - T) \quad , \quad (2)$$

Table 1.6-2 Uncertainties in the Recommended Values for the Surface Tension of Liquid Sodium

| Temperature (K) | σ (mN · m ⁻¹) | Uncertainty, $\left(\frac{\delta\sigma}{\sigma}\right)$ (%) |
|--------------------|---|--|
| 371 - 1600 | $\sigma = \sigma_o \left(1 - \frac{T}{T_c}\right)^n$ <i>where</i> $\sigma_o = 240.5$ $n = 1.126$ $T_c = 2503.7 \text{ K}$ | 11 |
| 1600 - 2503.7 | | 12 |

where M is the molecular weight, v is the specific volume, and T_c is the critical temperature. Allen recommends $197.9 \pm 1.8 \text{ mN}\cdot\text{m}^{-1}$ for the surface tension of sodium at its melting point. The recommended equation gives $200.7 \text{ mN}\cdot\text{m}^{-1}$ at the melting point. Because a single equation is desired for the entire temperature range, the equation given by Goldman adjusted for the critical temperature of 2503.7 K has been selected in accord with the recommendation of Allen.

The data analyzed by Goldman are listed in Table 1.6-3. Three sets of data not included in his nonlinear least squares fit are given at the end of the table. The data of Poindexter and Kernaghan⁽¹⁴⁾ were not included in the analysis because no information was reported on the possible contamination of the sample and their value for the surface tension at the melting point is high compared to values from other measurements. Achener's data⁽¹⁵⁾ were not included because the large oxygen content of the sodium in these experiments effected the surface tension. In his examination of measurements of the surface tension of alkali metals, Allen⁽¹⁷⁾ comments that oxygen impurities in sodium are surface-active. The apparent surface tension is lowered due to formation of an insoluble metal oxide film. Allen's graph of the available data shows that surface tensions measured by Achener are consistently lower than those of other experiments. The data

Table 1.6-3 Surface Tension Data Analyzed by Goldman

| Experimenter | Temperature Range (K) | No. of Points | Year | Ref. |
|---------------------------------------|-----------------------|---------------|------|------|
| Addison et al. | 402 - 453 | 6 | 1954 | 2 |
| Addison et al. | 383 - 492 | 27 | 1955 | 3 |
| Taylor | 411 - 723 | 30 | 1955 | 4 |
| Bradhurst and Buchanan | 373 - 523 | 3 | 1961 | 5 |
| Jordan and Lane | 473 | 1 | 1965 | 6 |
| Solov'ev and Makarova | 467 - 1206 | 26 | 1966 | 7 |
| Bhodansky and Schins | 890 - 1128 | 9 | 1967 | 8 |
| Longson and Thorley | 396 - 524 | 20 | 1967 | 9 |
| Germer and Mayer | 379 - 472 | 6 | 1968 | 10 |
| Roehlich, Tepper and Rankin | 414 - 1265 | 26 | 1968 | 11 |
| Todd and Turner | 402 - 777 | 11 | 1974 | 12 |
| Chowdhury, Binvignat-Toro and Bonilla | 905 - 1593 | 40 | 1982 | 13 |
| Poindexter and Kernaghan ^a | 376 - 517 | 27 | 1929 | 14 |
| Achener et al. ^a | 541 - 821 | 47 | 1969 | 15 |
| Kirlyanenko and Solov'ev ^a | 811 - 1399 | 27 | 1970 | 16 |

^aNot included in the least squares fit to the data.

by Kirlyanenko and Solov'ev⁽¹⁶⁾ were omitted because their results were not reproducible by the experimenters indicating a difficulty with their measurements. Allen⁽¹⁷⁾ cites a subsequent publication of data by Solov'ev and Kirlyanenko⁽¹⁸⁾ from the Russian literature in which their difficulty was apparently resolved. The data of Solov'ev and Kirlyanenko⁽¹⁸⁾ shown by Allen falls between that of Bohdansky and Schins⁽⁸⁾ and that of Solov'ev and Makarova.⁽⁷⁾

Bystrov et al.⁽¹⁹⁾ recommended a cubic equation for the surface tension of sodium from the melting point to 1700 K. It is based on analysis of the available data to 1700 K including 1984 data by Timrot and Reutov⁽²⁰⁾ published in the Russian literature. The deviation of the data from

the equation recommended by Bystrov et al. is 5%. The cubic equation recommended by Bystrov et al. gives $200.3 \text{ mN}\cdot\text{m}^{-1}$ for the surface tension at the melting point. This value is closer to the value from the recommended equation ($200.7 \text{ mN}\cdot\text{m}^{-1}$) than the value recommended by Allen ($197.8 \text{ mN}\cdot\text{m}^{-1}$). The equation given by Bystrov et al. is not recommended because its cubic form makes it unsuitable for application to the entire temperature range. Values given by this equation are compared with recommended values and those given by Goldman in Fig. 1.6-3. Deviations from recommended values defined as

$$\text{Deviations} = \frac{[\sigma(\text{Other}) - \sigma(\text{Eq. 1})] 100\%}{\sigma(\text{Eq. 1})} \quad (3)$$

are shown in Fig. 1.6-4. The curvature of the deviations of the values by Bystrov et al. is due to the systematic error caused by the use of the different functional form (cubic) to represent the surface tension. The maximum deviation of the values recommended by Bystrov et al. is 5.6% at 1500 K.

Uncertainty

The standard deviation of the data from the recommended equation is 5.5% for the temperature range 371 to 1600 K. Thus, the recommended uncertainty (2 standard deviations) is 11%. Goldman showed that all the data analyzed fall within this error band. Above 1600 K, the estimated uncertainty has been increased to 12%. Although no data are available in this higher temperature region, the error is limited because of the constraint that the surface tension becomes zero at the critical temperature.

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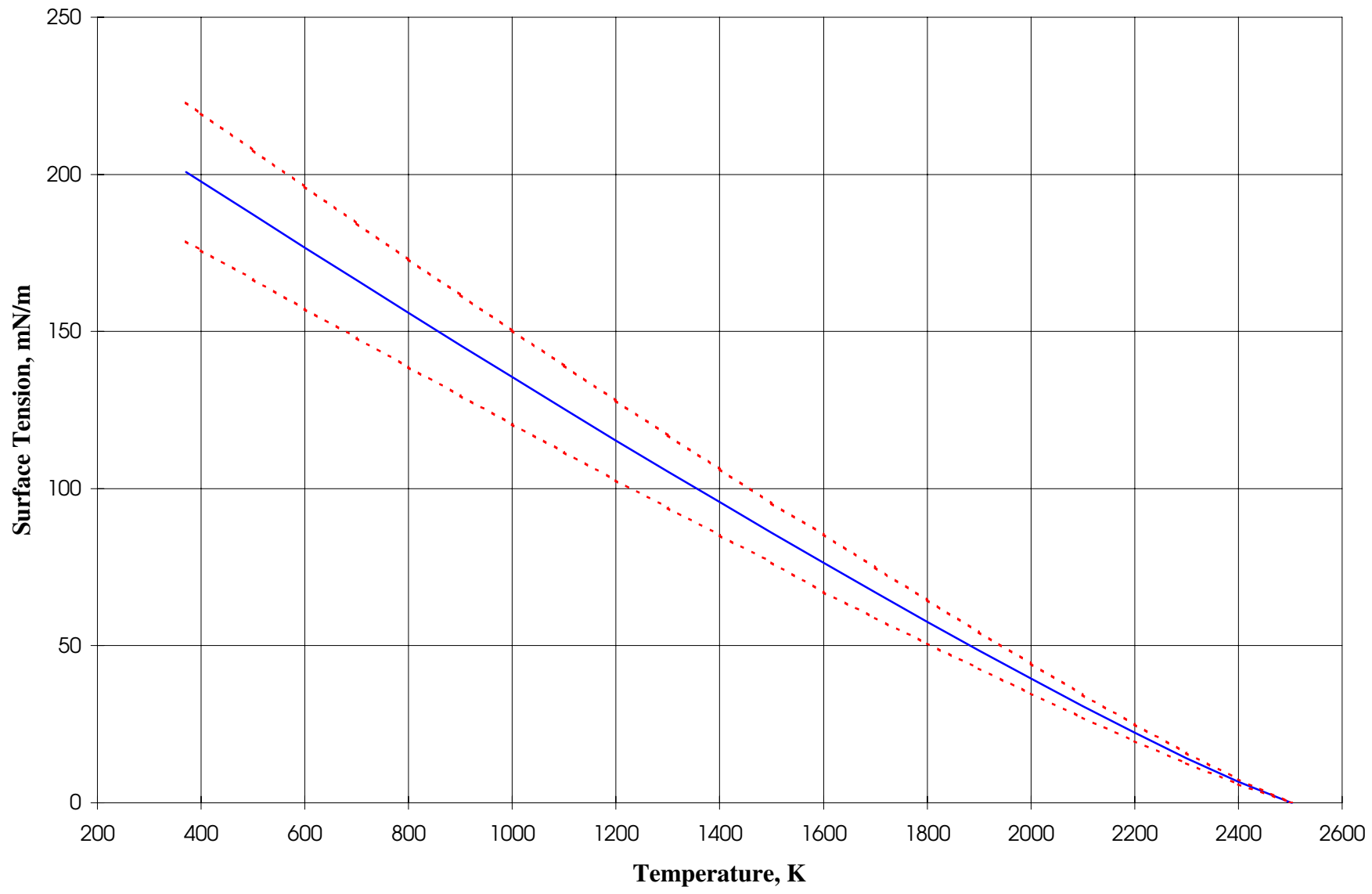


Fig. 1.6-1 Surface Tension of Liquid Sodium

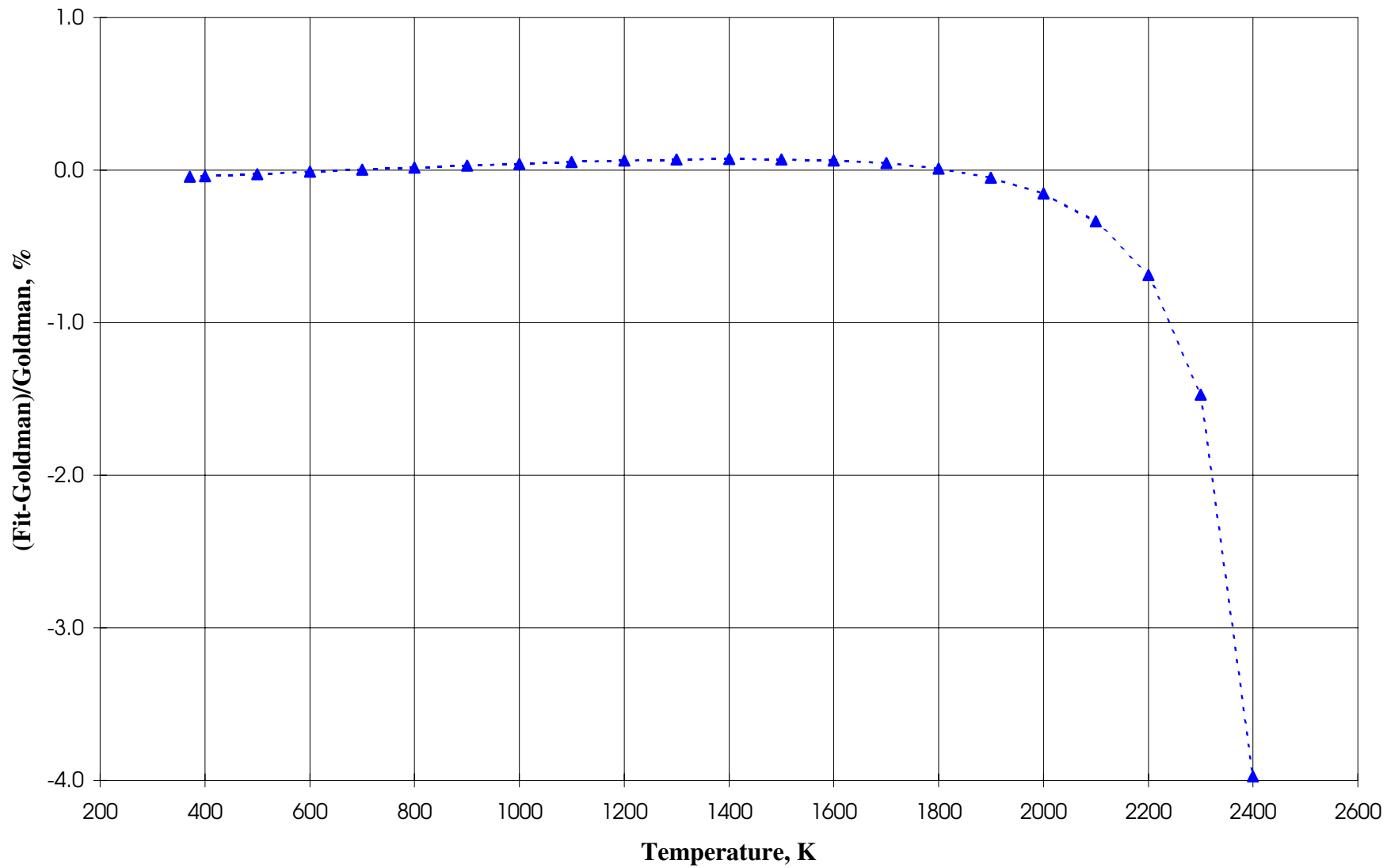


Fig. 1.6-2 Deviations of Recommended Values for the Surface Tension of Sodium from Values Given by Goldman

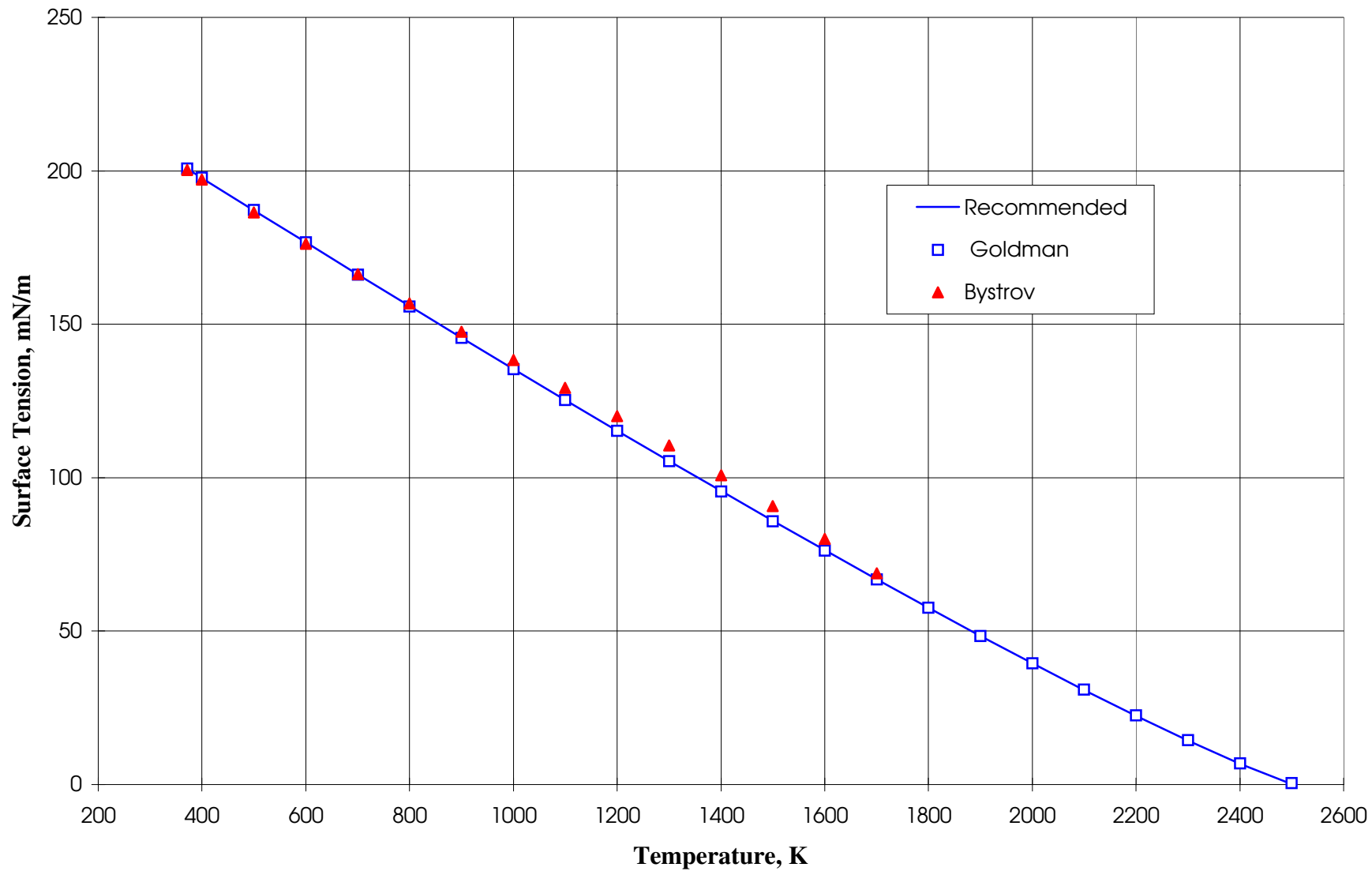


Fig. 1.6-3 Comparison of Recommended Values for the Surface Tension of Sodium with Values of Goldman and of Bystrov et al.

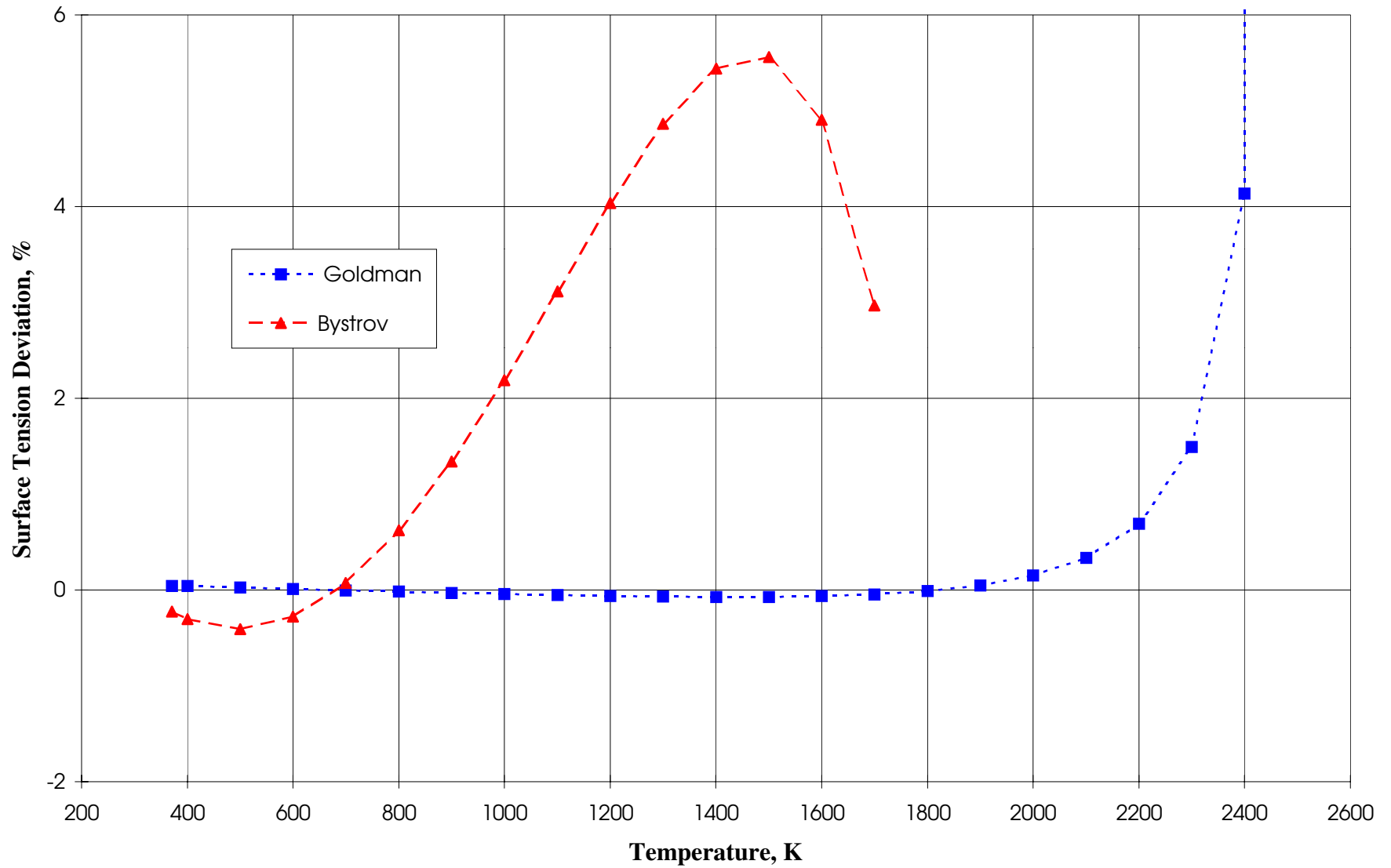


Fig. 1.6-4 Deviations of Other Assessments from the Recommended Values for the Surface Tension of Sodium

2. TRANSPORT PROPERTIES

2.1 THERMAL CONDUCTIVITY

Summary

The recommended values for the thermal conductivity of liquid sodium in $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, given in Table 2.1-1, were calculated with the polynomial

$$k = 124.67 - 0.11381T + 5.5226 \times 10^{-5}T^2 - 1.1842 \times 10^{-8}T^3 \quad . \quad (1)$$

This polynomial is a constrained least squares fit to thermal conductivities in the temperature range 371 to 1500 K that were calculated using the method recommended by Cook and Fritsch⁽¹⁾ for the calculation of thermal conductivity from electrical resistivity. This method includes the contribution to thermal conductivity from electron-electron scattering and a second order correction to the Sommerfeld value of the Lorentz function in the Wiedemann-Franz law. The fit was constrained to give agreement with the thermal conductivity of the vapor at the critical temperature. The vapor thermal conductivity at the critical point was obtained from extrapolation of sodium vapor thermal conductivities recommended by Vargaftik and Yargin⁽²⁾ in their review of experimental data and calculations of transport processes for alkali-metal vapors.

Figure 2.1-1 shows the recommended values for the thermal conductivity of sodium with the uncertainties as dashed lines. The uncertainties are given in Table 2.1-2.

Discussion

In this section, existing recommendations are compared with each other, with theory, and with experimental data to select the best method for calculation of the thermal conductivity of liquid sodium. Then, the details of the calculation are given including fits to related properties required in the calculation. Finally, an approximate equation is derived that represents the thermal conductivity in the range of experimental data and at higher temperatures to the critical temperature. Comparisons are made of this recommended equation with the calculated values and with values given in existing assessments.

Table 2.1-1 Thermal Conductivity of Liquid Sodium

| Temperature (K) | Thermal Conductivity (W · m ⁻¹ · K ⁻¹) |
|--------------------|--|
| 371 | 89.44 |
| 400 | 87.22 |
| 500 | 80.09 |
| 600 | 73.70 |
| 700 | 68.00 |
| 800 | 62.90 |
| 900 | 58.34 |
| 1000 | 54.24 |
| 1100 | 50.54 |
| 1200 | 47.16 |
| 1300 | 44.03 |
| 1400 | 41.08 |
| 1500 | 38.24 |
| 1600 | 35.44 |
| 1700 | 32.61 |
| 1800 | 29.68 |
| 1900 | 26.57 |
| 2000 | 23.21 |
| 2100 | 19.54 |
| 2200 | 15.48 |
| 2300 | 10.97 |
| 2400 | 5.92 |
| 2500 | 0.27 |
| 2503.7 | 0.05 |

Examination of Existing Recommendations — Examination of recommendations from various assessments of the thermal conductivity of liquid sodium indicates significant differences over the range of experimental data (371 to 1500 K). Figure 2.1-2 shows the recommendations from Cook and Fritsch,⁽¹⁾ Bystrov et al.,⁽³⁾ and Saksena et al.,⁽⁴⁾ CINDAS,⁽⁵⁾ and Fink and Leibowitz (F&L).⁽⁶⁾ Both the recommendations of Saksena et al. and those of Fink and Leibowitz are based on the CINDAS values. The Fink and Leibowitz approximation, shown in Fig. 2.1-2, is a polynomial fit to the CINDAS values and an extrapolation to the critical point using the method of Grosse.⁽⁷⁾ Saksena et al.⁽⁴⁾ represent the thermal conductivity in the liquid by an electronic

Table 2.1-2 Estimated Uncertainties in the Recommended Values for the Thermal Conductivity of Liquid Sodium

| Temperature (K) | k ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) | Uncertainty, $\left(\frac{\delta k}{k}\right)$ (%) |
|-------------------------------|---|---|
| $371 \leq T \leq 700$ | | 5 |
| $700 < T \leq 1100^{(a)}$ | $k = 124.67 - 0.11381T$ | 12 |
| $1100 \leq T \leq 1500^{(b)}$ | $+ 5.5226 \times 10^{-5}T^2 - 1.1842 \times 10^{-8}T^3$ | 15 |
| $T > 1500$ | | 15 |

$$^{(a)} \frac{\delta k}{k}(\%) = -7.25 + 0.0175 T$$

$$^{(b)} \frac{\delta k}{k}(\%) = 3.75 + 0.0075 T$$

contribution plus a contribution due to structural scattering. contribution from the electrical resistivity using the Lorentz constant. They assume the structural contribution has a $T^{4/7}$ dependence and determine the constant for the structural contribution by assuming the total thermal conductivity is given by the CINDAS values. Thus, their values for thermal conductivity are very close to the CINDAS recommendations. Recommendations by CINDAS and by Bystrov et al. are fits to combined sets of data of measurements of thermal conductivity and measurements of electrical resistivity converted to thermal conductivity using the Wiedemann-Franz law. Cook and Fritsch recommended values of thermal conductivity calculated from their fit to electrical conductivity converted to thermal conductivity using corrections to the Wiedemann-Franz law that

include higher order terms in the Lorentz constant and a contribution to thermal resistivity due to electron-electron scattering that is not present in electrical resistivity.

Selection of Method of Calculation — The method of Cook and Fritsch has been selected based on (1) the results of simultaneous measurements of thermal and electrical resistivities of alkali metals by Cook et al.,⁽⁸⁻¹⁵⁾ (2) review of the theoretical basis, and (3) comparison of the separate data from electrical and thermal conductivity measurements. These reasons are discussed in detail below.

Simultaneous measurement of the thermal and electrical resistivities of solid alkali metals and of liquid potassium, cesium, and rubidium by Cook et al.⁽⁸⁻¹⁵⁾ have shown that the thermal conductivity differs from the value obtained by application of the Wiedemann-Franz law:

$$k = \frac{L_0 T}{\rho} \quad , \quad (2)$$

where k is the thermal conductivity, ρ is the electrical resistivity, and L_0 is the Sommerfeld value of the Lorentz function:

$$L_0 = \frac{1}{3} \left(\frac{\pi k_B}{e} \right)^2 = 2.443 \times 10^{-8} \text{ W}\Omega\text{K}^{-2} \quad . \quad (3)$$

In their assessment of thermal conductivity of liquid alkali metals, Cook and Fritsch⁽¹⁾ examined contributions from many processes. They show that contributions from ionic conductivity and inelastic scattering of electrons are small and of opposite sign so that they cancel. However, they have included corrections to the Wiedemann-Franz law for second-order effects in the Lorentz function, $L(T)$, and a contribution due to electron-electron scattering. The correction due to second-order effects in the Lorentz function; i.e., off-diagonal matrix elements is

$$k = \frac{(L_0 - S^2)T}{\rho} \quad , \quad (4)$$

where S is the thermoelectric power. The electron-electron scattering contribution to the thermal resistivity (W_{ee}) is a linear function of temperature:

$$W_{ee} = BT . \quad (5)$$

For liquid sodium, Cook and Fritsch assume B is equal to the value obtained by Cook⁽⁸⁾ for solid sodium; i.e., $B = 1.1 \times 10^{-6} \text{ m}\cdot\text{W}^{-1}$.

Thus, Cook and Fritsch determined the thermal conductivity of alkali metals using the relation

$$k = \left[W_{ee} + \frac{\rho_e}{(L_0 - S^2)T} \right]^{-1} , \quad (6)$$

where W_{ee} is the thermal resistivity due to electron-electron scattering, ρ_e is the electrical resistivity, L_0 is the Sommerfeld value of the Lorentz function, and S is the thermoelectric power.

MacDonald and Geldart⁽¹⁶⁾ have calculated the electron-electron scattering contribution to the thermal resistivity of solid simple metals (including alkali metals) using an approximation to the scattering function based on the Landau Fermi-liquid theory and obtained reasonable agreement with values determined by Cook et al for the alkali metals. Theoretical calculations of the electron-electron scattering contribution, W_{ee} , for sodium by MacDonald and Geldart⁽¹⁶⁾ and by Lundmark⁽¹⁷⁾ give values of the linear constant B within the experimental uncertainty of values given by Cook.⁽⁸⁾ According to Lundmark,⁽¹⁷⁾ attribution of the deviations from the Wiedemann-Franz law to an electron-phonon contribution (which is small and goes as T^2) and an electron-electron scattering contribution (which is linear in temperature) is now commonly accepted.

In assessing the different recommendations for the thermal conductivity of liquid sodium, the data tabulated by CINDAS⁽⁵⁾ were examined to separate the thermal conductivity measurements from thermal conductivities calculated from electrical resistivity measurements via the Wiedemann-Franz law. Figure 2.1-3 gives a comparison of the thermal conductivity data from thermal conductivity measurements with recommendations by Cook and Fritsch (labeled Cook), CINDAS, and Bystrov et al. Data sets discussed in the CINDAS review⁽⁵⁾ that were clearly outliers have not been included in the figure. The recommended equation of

Bystrov et al. gives values that are consistently high compared to the thermal conductivity measurements. Therefore, the equation by Bystrov et al. is not included in further comparisons.

Figure 2.1-4 shows the thermal conductivities from thermal conductivity measurements (labeled "thermal") and the thermal conductivities calculated from electrical resistivity measurements (labeled "E CINDAS") as tabulated by CINDAS. The values of thermal conductivity calculated by CINDAS from electrical resistivity measurements via the Wiedemann-Franz law are consistently high relative to thermal conductivity measurements. The quadratic fit of just the values from electrical conductivity measurements (labeled "quadratic fit") shows a systematic deviation from thermal conductivity measurements at similar temperatures. Comparison of deviations of this quadratic equation with the thermal conductivity measurements results in residuals which are positive for all but 12 of the 141 points. Fitting the combined set of data from thermal conductivity and electrical resistivity measurements results in the CINDAS recommendation being high relative to the thermal conductivity measurements.

Figure 2.1-5 shows the electrical resistivity data tabulated by CINDAS converted to thermal conductivity using Eq. (6), which is the method suggested by Cook and Fritsch. These data, labeled "Electrical" in Fig. 2.1-5, are consistent with the measured thermal conductivities.

Thus, the method given by Cook and Fritsch is recommended for determining the thermal conductivity of liquid sodium from the melting point to 1500 K.

Calculation — Calculation of the thermal conductivity from the electrical resistivity using the method suggested by Cook and Fritsch requires the electrical resistivity as a function of temperature, the absolute thermoelectric power for sodium as a function of temperature, and the contribution due to electron-electron scattering. The electrical resistivities required in Eq. (6) were calculated using the equation recommended by Cook and Fritsch. Cook and Fritsch assessed and fit the electrical resistivity data for sodium in the temperature range 371 to 1500 K. Their recommended equation for electrical resistivity in $10^{-8} \Omega\text{m}$ is

$$\begin{aligned} \rho_e = & - 9.9141 + 8.2022 \times 10^{-2}T - 1.3215 \times 10^{-4}T^2 + 1.7212 \times 10^{-7}T^3 \\ & - 9.0265 \times 10^{-11}T^4 + 1.9553 \times 10^{-14}T^5, \end{aligned} \quad (7)$$

where temperature is in kelvins. Electrical resistivities calculated with this equation are in good agreement with values recommended by CINDAS⁽¹⁸⁾ and by Alekseev and Iakubov⁽¹⁹⁾ as shown in

Fig. 2.1-6. Deviations between values from these three assessments are less than the 2% uncertainty of the experimental data quoted by Alekseev and Iakubov.

Calculation of the thermal conductivity from the electrical resistivity using Eq. (6) requires the thermoelectric power for sodium (S) for the second order correction to the Lorentz constant, L_0 . Cook and Fritsch do not give an equation for the thermoelectric power for sodium but comment that experimental values disagree. Measurements of Seebeck coefficients in liquid sodium by Bressler and Anderson⁽²⁰⁾ show a linear increase in the absolute value from that at the melting point to $-16 \mu\text{V}\cdot\text{K}^{-1}$ at 700 K with a slight decrease in the absolute value to about $-14.5 \mu\text{V}\cdot\text{K}^{-1}$ at 873 K. Measurements by Bonilla et al.⁽²¹⁾ indicate that the absolute value of the thermoelectric power continues to increase above 700 K. Cook and Fritsch assumed a linear increase in absolute value from the melting point to $-16 \mu\text{V}\cdot\text{K}^{-1}$ at 700 K and an increase in absolute value to $-25 \mu\text{V}\cdot\text{K}^{-1}$ at 1170 K, in accord with the experimental results given by Bonilla et al.

The thermoelectric potentials for sodium relative to platinum that are given by Bonilla et al. for the temperature range 400 to 1173 K have been fit using the method of least squares to the quadratic equation

$$E (Pt/Na) = 1016.53 - 4.0791 T + 4.658 \times 10^{-3} T^2 \quad , \quad (8)$$

where the thermoelectric potential, E , is in μV and temperature, T , is in kelvins. The fit is shown in Fig. 2.1-7. The Seebeck coefficient of the thermoelectric power of sodium relative to platinum is the temperature derivative of the thermoelectric potential given by Bonilla et al. It is given in $\mu\text{V}\cdot\text{K}^{-1}$ by

$$-S(Na/Pt) = S(Pt/Na) = \frac{dE}{dT} = -4.0791 + 9.316 \times 10^{-3} T \quad . \quad (9)$$

The absolute thermoelectric power for sodium is equal to the sum of the thermoelectric power of sodium relative to platinum $S(\text{Na}/\text{Pt})$ and the absolute thermoelectric power of platinum. An equation for the absolute thermoelectric power for platinum was obtained by a linear least squares fit to the tabulated experimental values of the absolute thermoelectric power of platinum in the temperature range 400 to 1500 K given in Tables 4.2 and 4.3 of the New Series of Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology.⁽²²⁾ The equation obtained is

$$S(Pt) = -2.5809 - 0.01435T \quad , \quad (10)$$

where S is in $\mu\text{V}\cdot\text{K}^{-1}$ and T is in kelvins. Figure 2.1-8 shows graphs of the tabulated data in the temperature range 371 to 1500 K, the linear fit to these data, and three equations for the absolute thermoelectric power of platinum given in the Landolt-Bornstein handbook (labeled Eq. 31, 32, and 33 in the figure). These three equations fit individual sets of the tabulated experimental data. The linear fit obtained in this analysis is very close to Eq. (33) given in the Landolt-Bornstein handbook.

The absolute thermoelectric power for sodium was obtained by adding the thermoelectric power for sodium relative to platinum $S(\text{Na}/\text{Pt})$, the negative of the value given in Eq. (9), to the absolute thermoelectric power for platinum, given in Eq. (10). The equation obtained for the absolute thermoelectric power for sodium is

$$S(\text{Na}) = 1.4982 - 0.02367T \quad (11)$$

for $S(\text{Na})$ in $\mu\text{V}\cdot\text{K}^{-1}$ and T in kelvins. The negative of the thermoelectric power for sodium is shown in Fig. 2.1-9, along with the values given by Cook and Fritsch, the negative of the thermoelectric power for platinum, and the thermoelectric power of sodium relative to platinum obtained from differentiation of the thermoelectric potential given by Bonilla et al.

Calculation of the thermal conductivity of sodium using Eq. (6) requires the thermal resistivity due to electron-electron scattering (W_{ee}). Because no additional data are available since the analysis by Cook and Fritsch, their recommended equation, Eq. (5), has been used to calculate this contribution from the melting point to 1500 K.

Values of the thermal conductivity for sodium were calculated from 371 to 1500 K using Eq. (6) and Eqs. (3, 5, 7, 11) for the parameters given in Eq. (6). Results of this calculation as a function of temperature are shown in Figs. 2.1-4 and 2.1-5 with the label "Calculation." Results are in excellent agreement with those tabulated by Cook and Fritsch. In accord with Cook and Fritsch, calculations of thermal conductivity from resistivity using Eq. (6) have been made only to 1500 K because at higher temperature, (1) higher order terms in the Lorentz function than the L_0 and S^2 terms may be necessary and (2) the value of B may differ from the value for the solid.

To extrapolate thermal conductivity to the critical temperature, the method suggested by Grosse⁽⁷⁾ that was used by Fink and Leibowitz⁽⁷⁾ to extrapolate the CINDAS values⁽⁵⁾ was examined. It was not used because it is based on the Wiedemann-Franz law and extrapolation of the electrical resistivity. It has no means to include the electron-electron scattering contribution which increases linearly with temperature and becomes more pronounced at high temperatures. In addition, it includes no higher order corrections to the Lorentz function.

Recommended Equation for Entire Temperature Range — To obtain a simple expression for the thermal conductivity and to estimate values at higher temperatures, the calculated values in the temperature range 371 to 1500 K were fit by a least squares method to a cubic polynomial constrained at the critical point to give a value in accord with the thermal conductivity of the vapor. The value used for the thermal conductivity of sodium vapor at the critical temperature is from extrapolation of the values for the thermal conductivity of sodium vapor recommended by Vargaftik and Yargin.⁽²⁾ Vargaftik and Yargin have analyzed experimental data and calculations of viscosity and thermal conductivity of alkali metal vapors. From their analyses and calculations, they recommended values for the thermal conductivity of sodium vapor along the saturation curve from 700 to 1500 K. In this temperature range, the sodium vapor thermal conductivity increases from 0.032 to 0.050 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, as shown in Fig. 2.1-10. These recommended values were extrapolated to 0.052 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at the critical temperature, 2503.7 K. At the critical point, the thermal conductivity of the vapor and liquid become identical. Thus, the fit to the calculated values of the thermal conductivity of liquid sodium was constrained to be 0.052 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at the critical temperature, 2503.7 K. The resulting equation is Eq. (1), the recommended equation. It is shown in Fig. 2.1-11 along with the thermal conductivity of the vapor from 700 to 1500 K, the calculated thermal conductivities of liquid sodium from 371 to 1500 K, and the value of the thermal conductivity at the critical temperature. Deviations of this equation from the calculated values are within $\pm 3\%$.

In Fig. 2.1-12, values calculated with the recommended equation, Eq. (1), are compared with values from other assessments and calculated values. The recommended values show good agreement with the values calculated from Eq. (6) and with values tabulated by Cook and Fritsch. Values tabulated by Cook and Fritsch are within $\pm 2\%$ of the values from Eq. (1). Recommended values for temperatures from 1500 K to the critical temperature are consistent with values

recommended by Bystrov et al. At 2500 K, the recommended value ($0.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) is lower the value of Bystrov et al. ($1.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and significantly lower than the values near $6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ given by the extrapolation of the CINDAS values by Fink and Leibowitz (labeled "Fink & Leibowitz Extrap." in the figure), and the approximating polynomial given by Fink and Leibowitz. Deviations of the calculated values and values from other assessments from the recommended equation are shown in Fig. 2.1-13. The plotted deviations, expressed as a percent are defined by

$$\text{Deviations} = \frac{[k(\text{Other}) - k(\text{Recommended})] 100\%}{k(\text{Recommended})} \quad (12)$$

From the melting point to 2200 K, largest deviations are found with respect to values given in the assessment by Bystrov et al.; they differ by $\pm 13\%$. Large percent deviations are calculated near the critical point because the recommended equation approaches a lower value at 2503.7 K than do other calculations. The Fink and Leibowitz calculations are based on a higher critical temperature, 2509.4 K.

Uncertainty

The uncertainty in the recommended values have been estimated from the uncertainty in the electrical resistivity (2%), and the uncertainty in the thermal conductivities given by CINDAS (5 to 15%), and the deviations of values from different assessments, shown above. From the melting point to 700 K the uncertainty is estimated as 5%. Above 700 K, the uncertainty increases to 12% at 1100 K and to 15% at 1500 K. The uncertainties are assumed to increase linearly with temperature. Between 700 and 1100 K, the uncertainty is approximated by the linear equation

$$\frac{\delta k}{k}(\%) = -7.25 + 0.0175 T \quad (13)$$

for $700 \text{ K} \leq T \leq 1100 \text{ K}$.

Between 1100 and 1500 K, the uncertainty is approximated by

$$\frac{\delta k}{k}(\%) = 3.75 + 0.0075T \quad (13)$$

for $1100 \text{ K} \leq T \leq 1500 \text{ K}$.

Above 1500 K, uncertainties are estimated as 15%. Uncertainties are shown as dotted lines in Fig. 2.1-1 and are given in Table 2.1-2.

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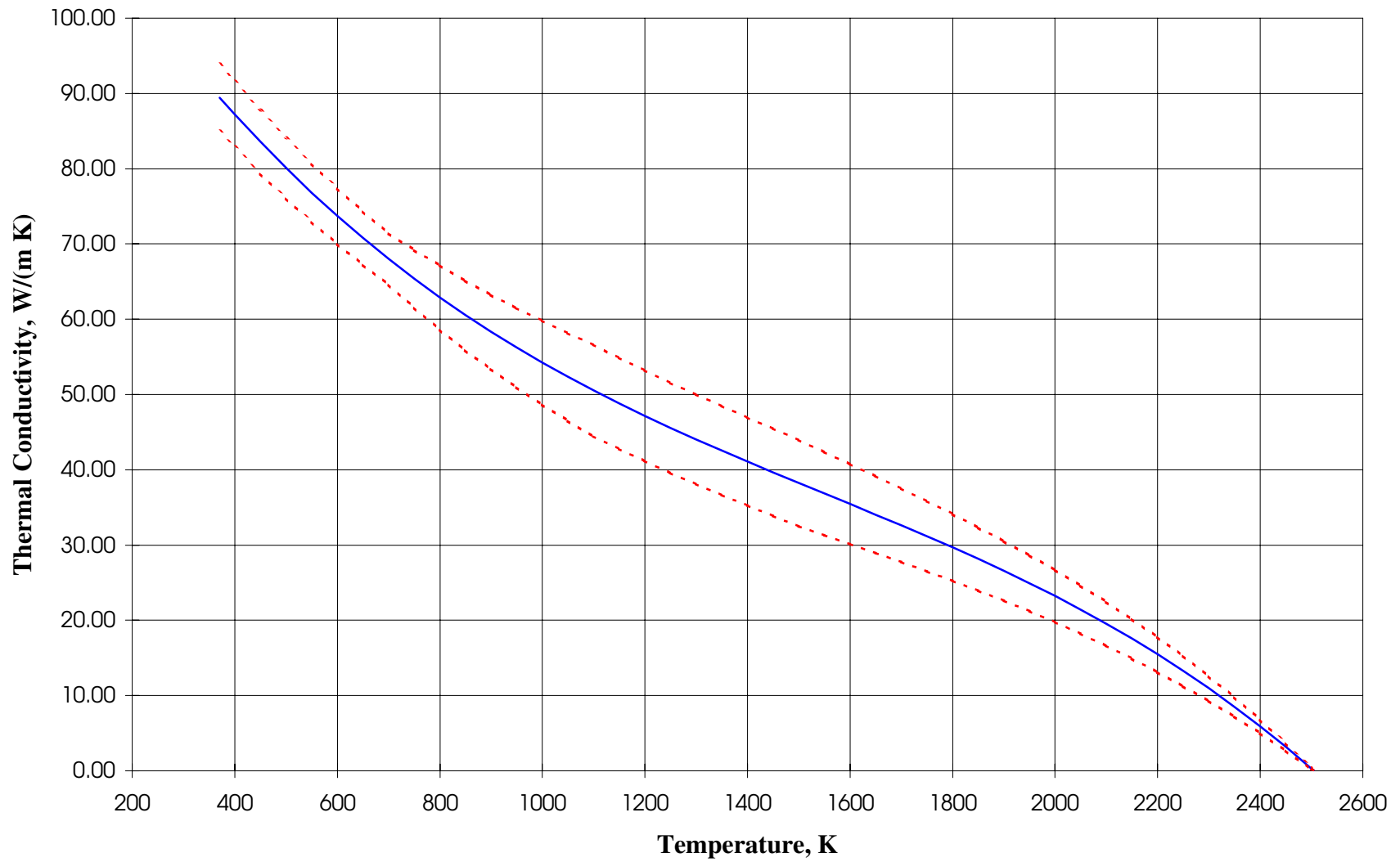


Fig. 2.1-1 Thermal Conductivity of Liquid Sodium

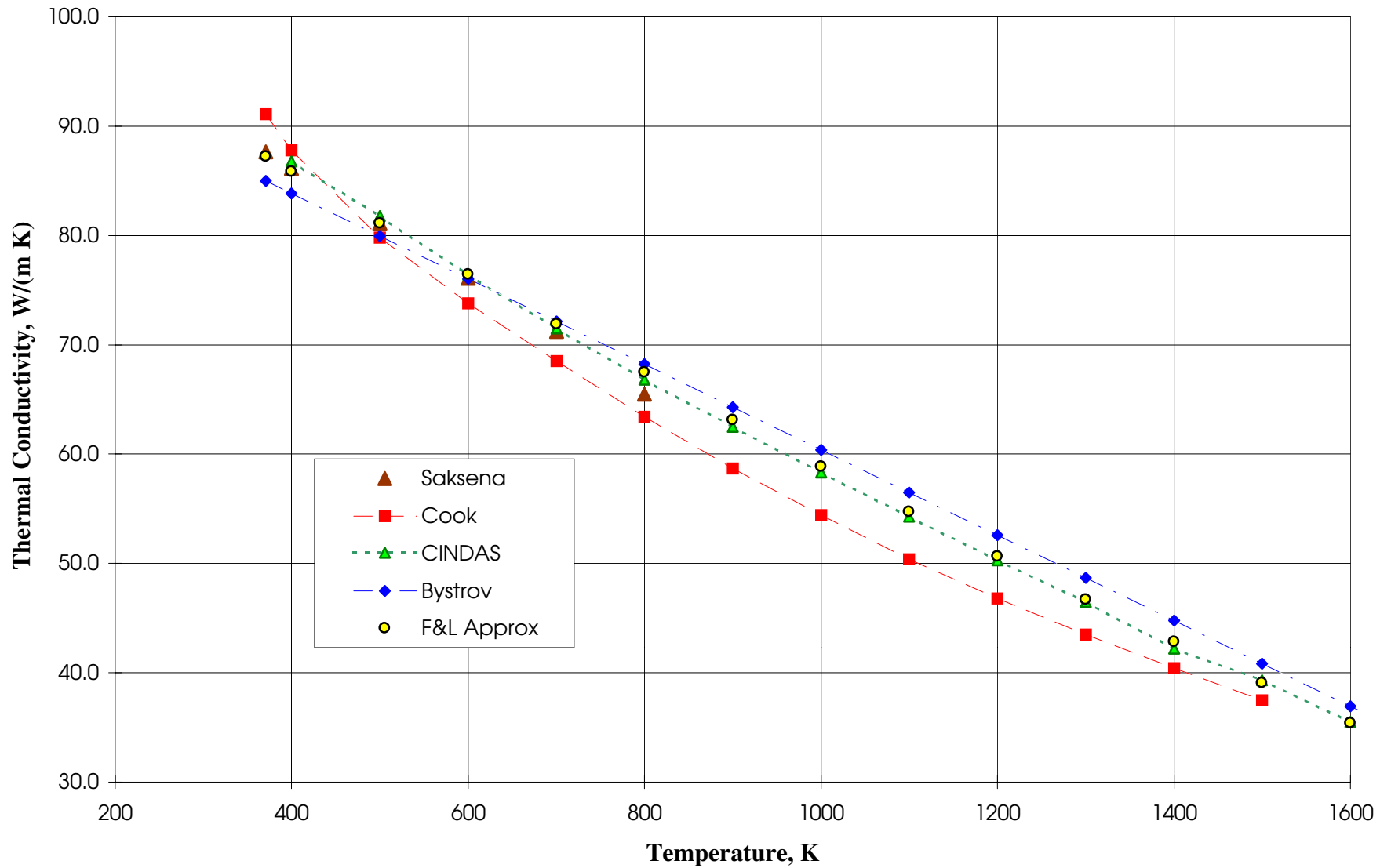


Fig. 2.1-2 Recommended Values for the Thermal Conductivity of Liquid Sodium from Five Assessments

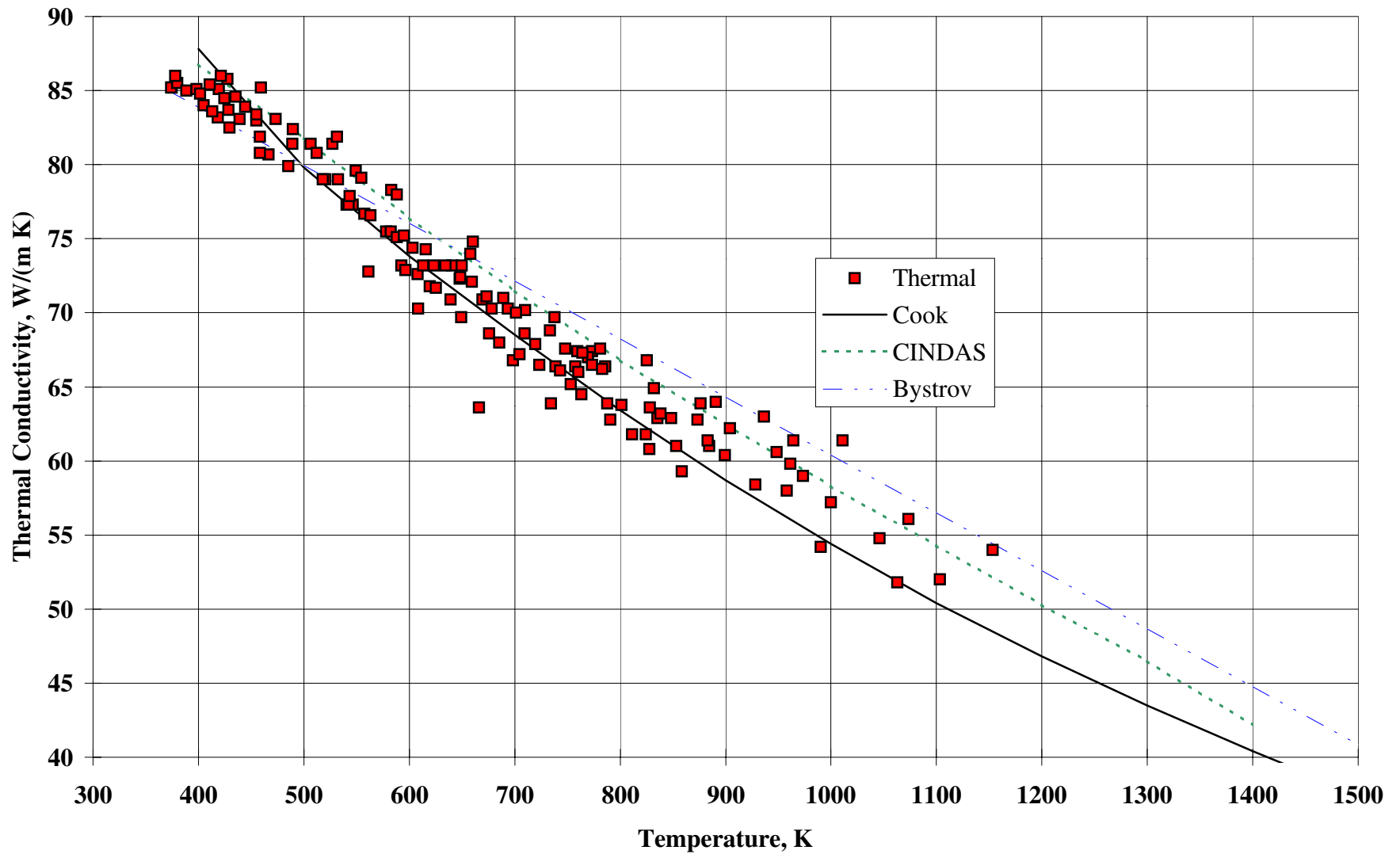


Fig. 2.1-3 Comparison of Data from Thermal Conductivity Measurements with Values from Cook and Fritsch, CINDAS, and Bystrov

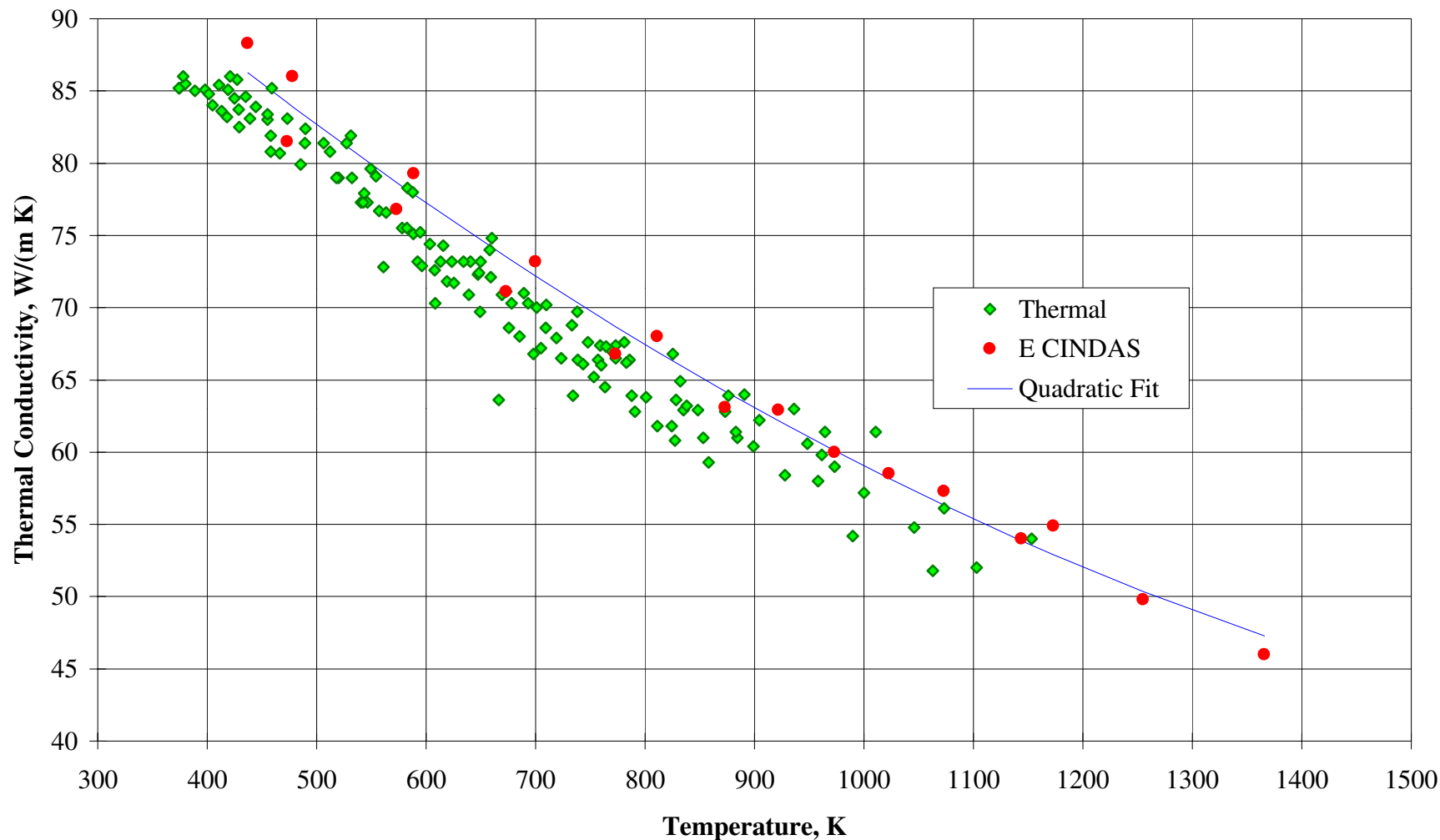


Fig. 2.1-4 Comparison of Data from Thermal Conductivity Measurements and Resistivity Data converted to Conductivity by CINDAS with Values from Quadratic Fit to Electrical Resistivities Converted to Thermal Conductivity by CINDAS

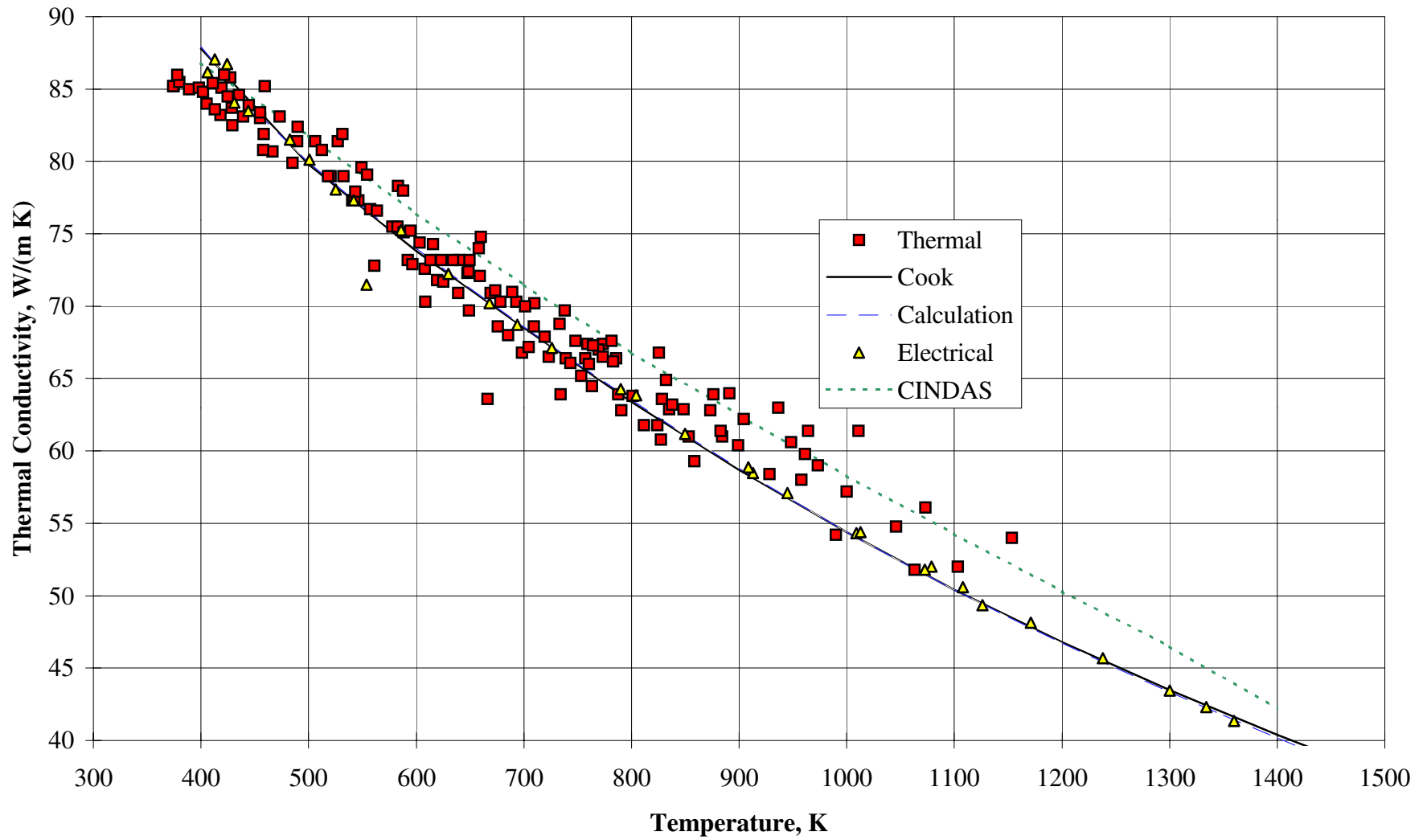


Fig 2.1-5 Comparison of Data from Thermal Conductivity Measurements and Resistivity Data Converted to Conductivity using Eq.(6) with Values from Cook and Fritsch, CINDAS, and the Calculation in this Assessment

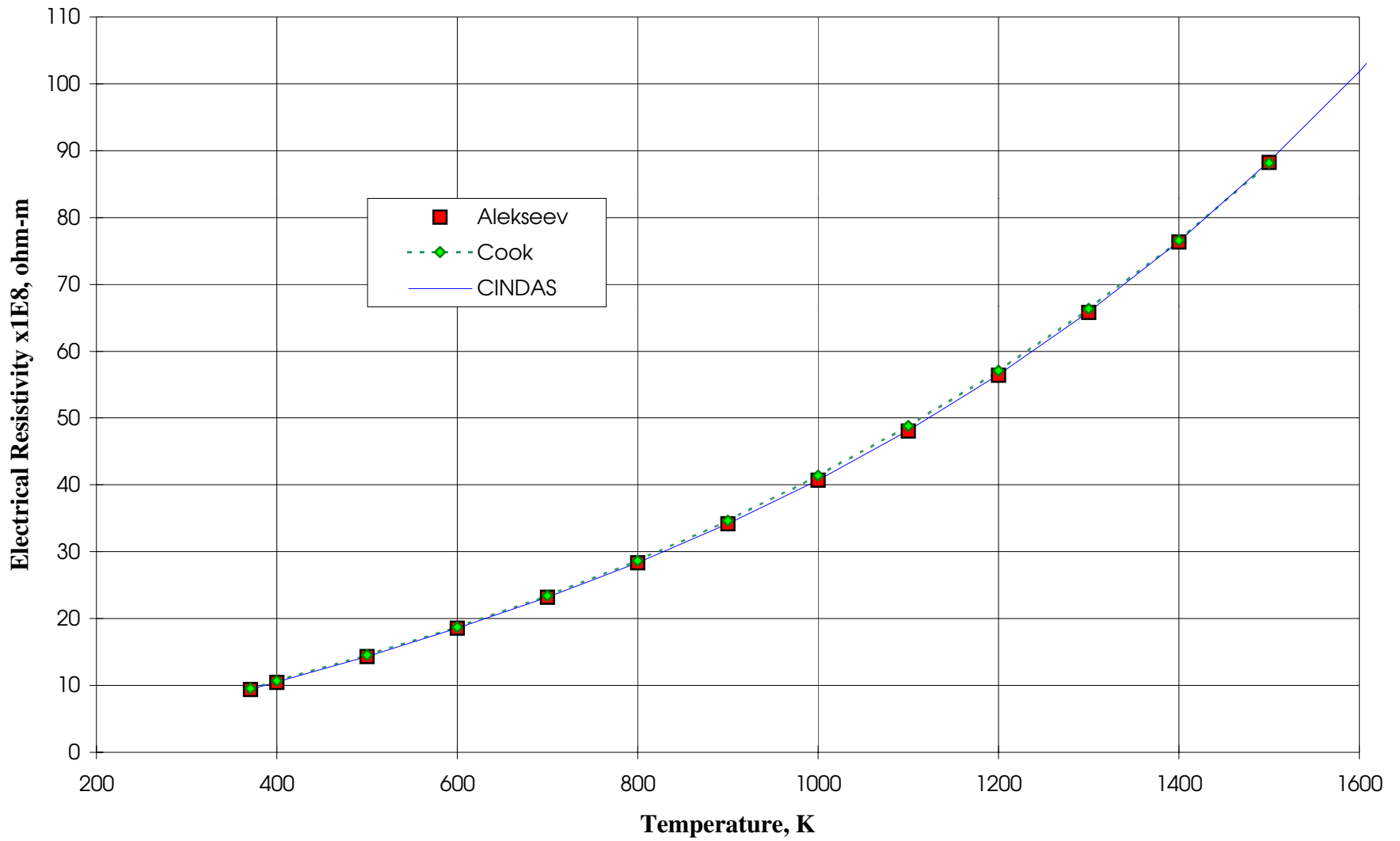


Fig. 2.1-6 Comparison of Values for the Electrical Resistivity from Cook and Fritsch, CINDAS, and Alekseev and Iakubov

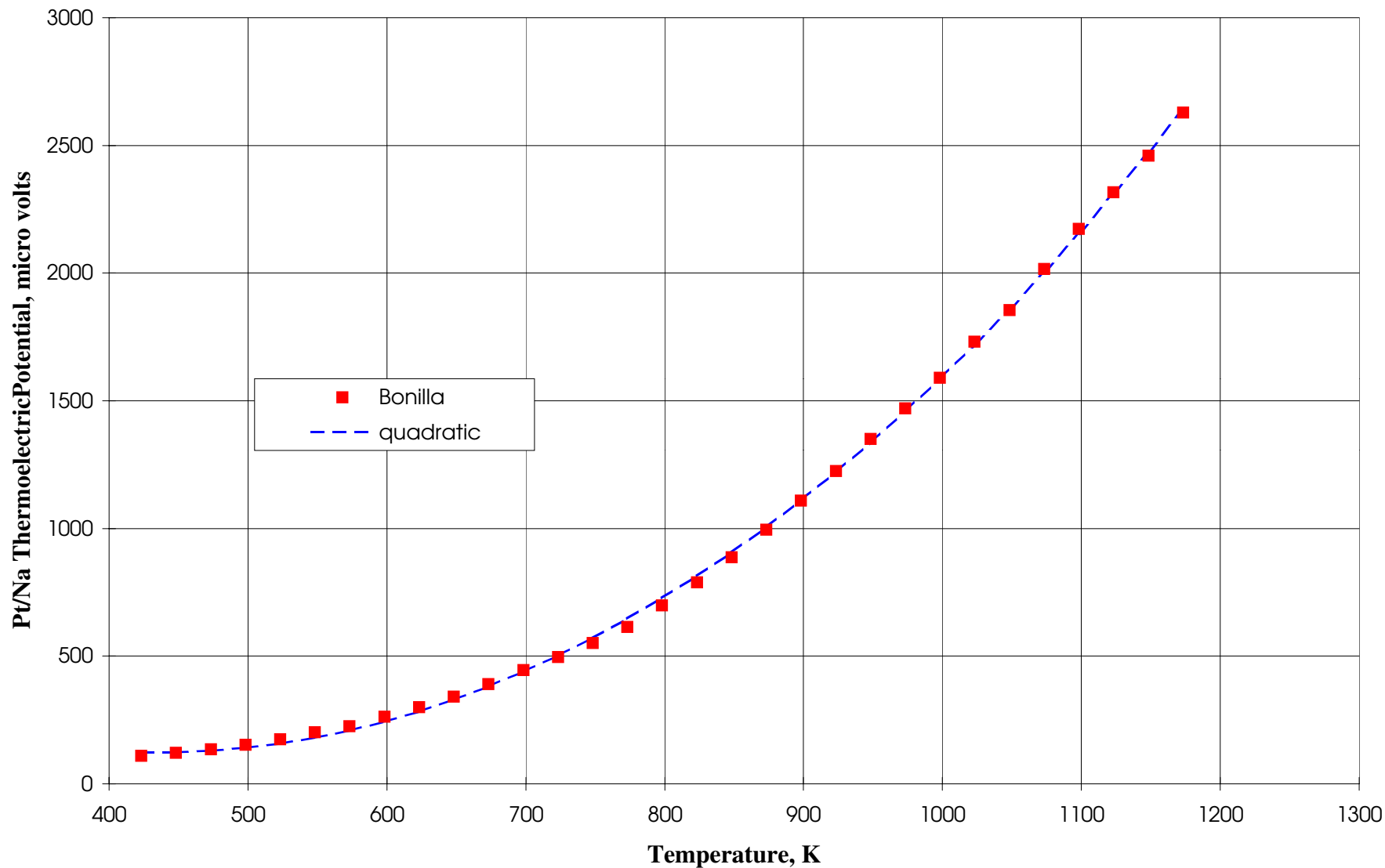
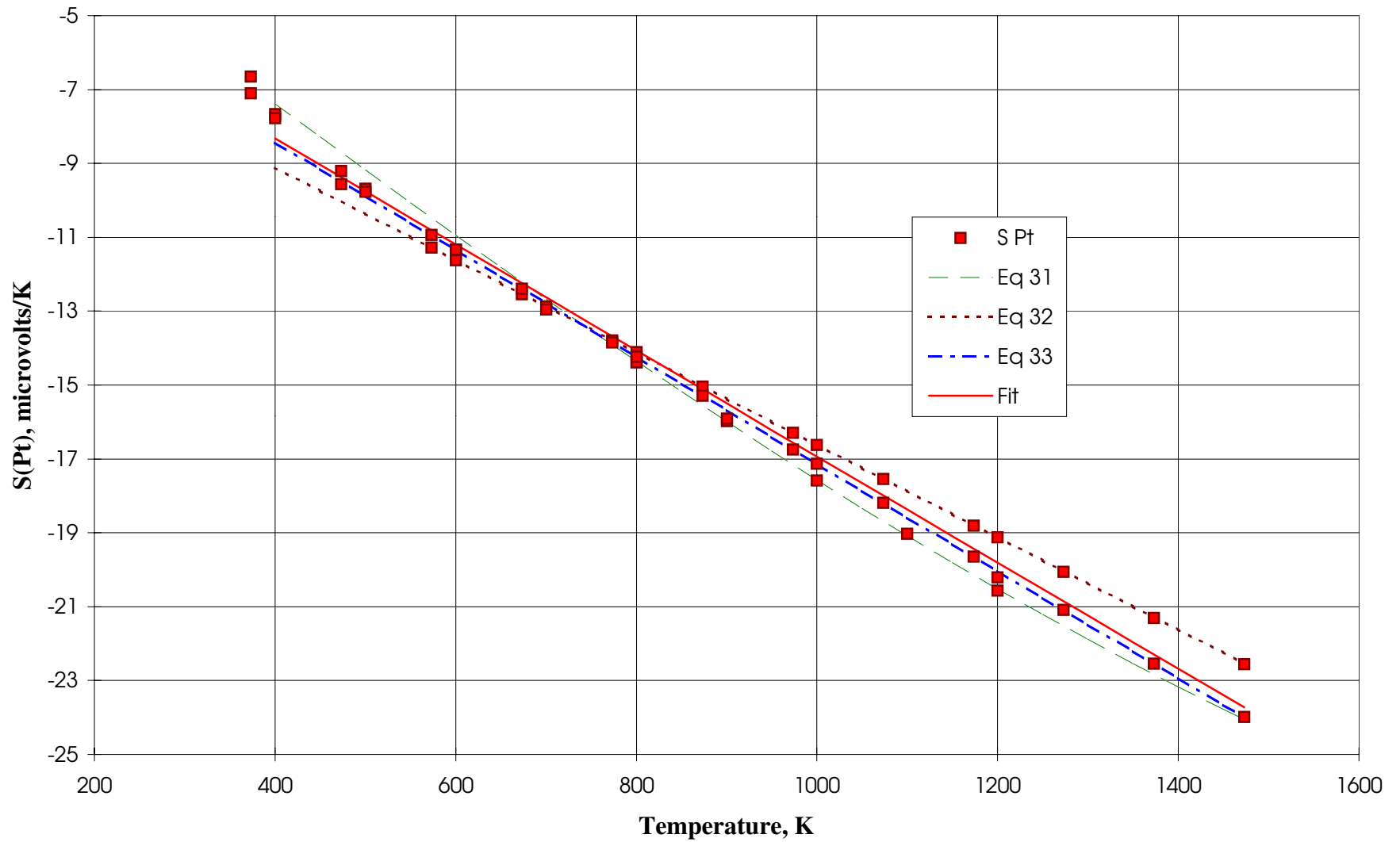


Fig 2.1-7 Quadratic Least Squares Fit to the Thermoelectric Potential of Pt Relative to Na given by Bonilla et al.



**Fig. 2.1-8 Linear Fit to the Absolute Thermoelectric Power of Pt.
Equations from Experiments are Included for Comparison**

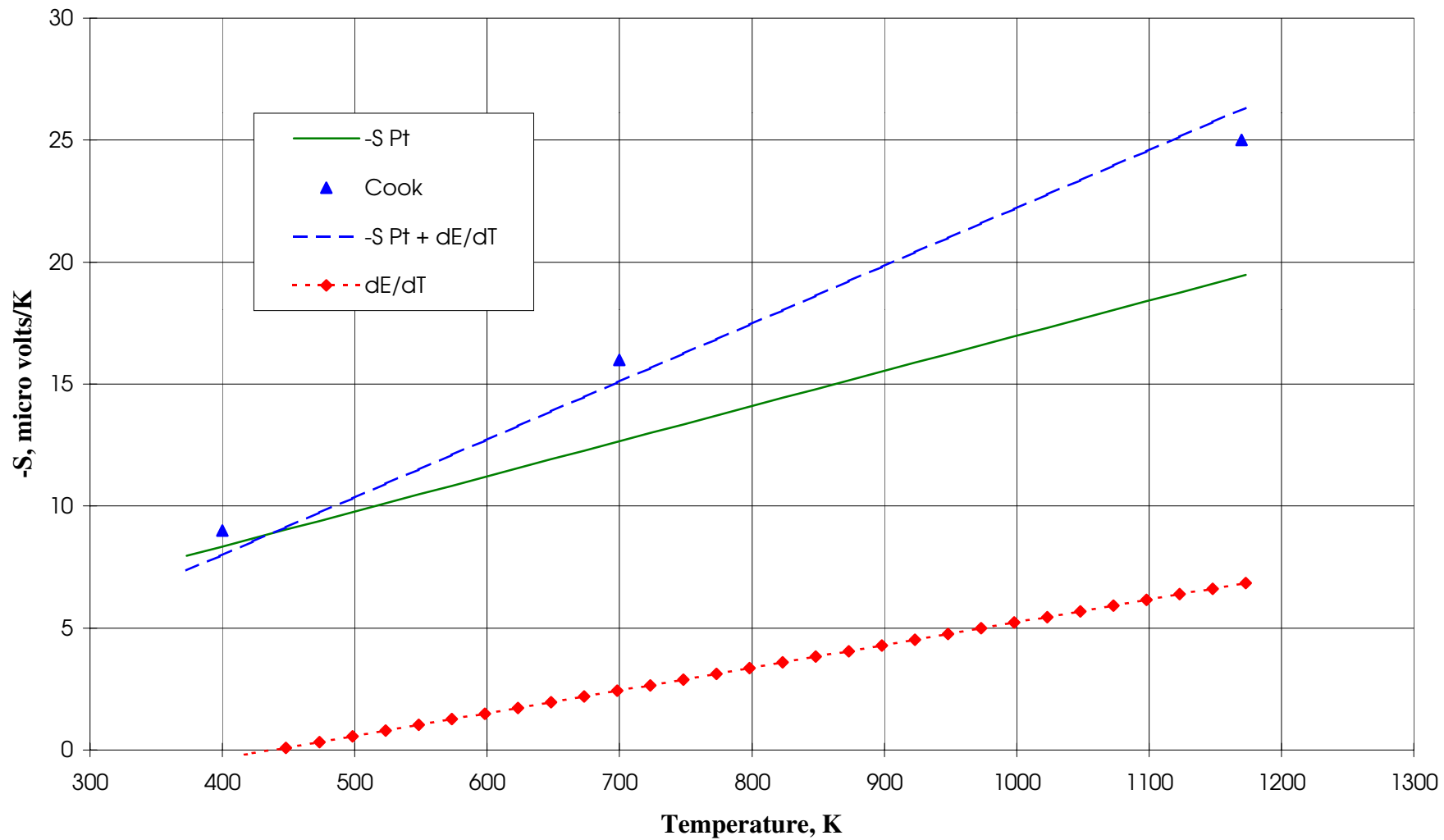


Fig. 2.1-9 The Negative of the Absolute Thermoelectric Power for Na and for Pt and Values given by Cook and Fritsch for Na. The Thermoelectric Power of Pt Relative to Na (dE/dT) is Included.

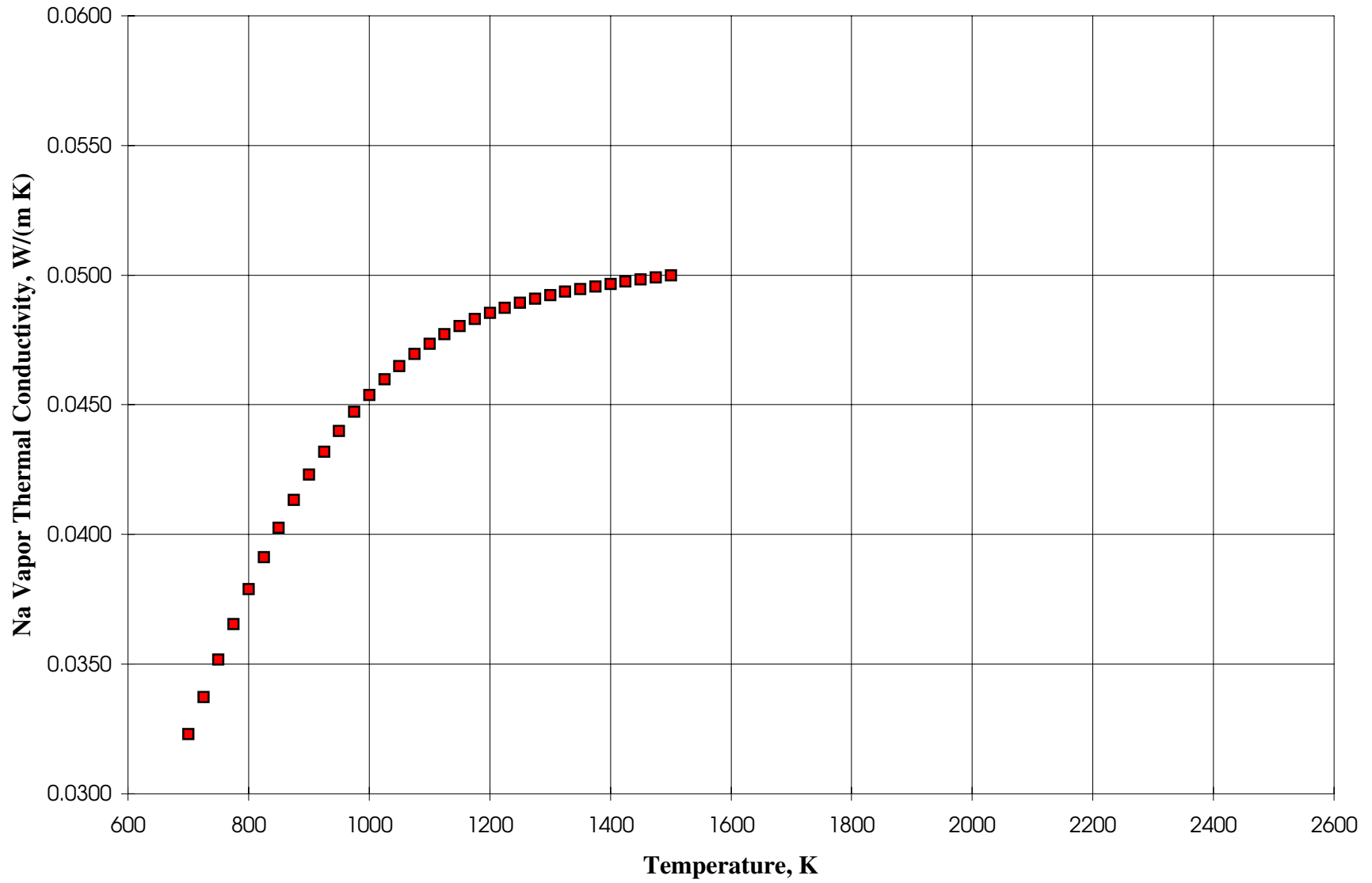


Fig. 2.1-10 Thermal Conductivity of Sodium Vapor

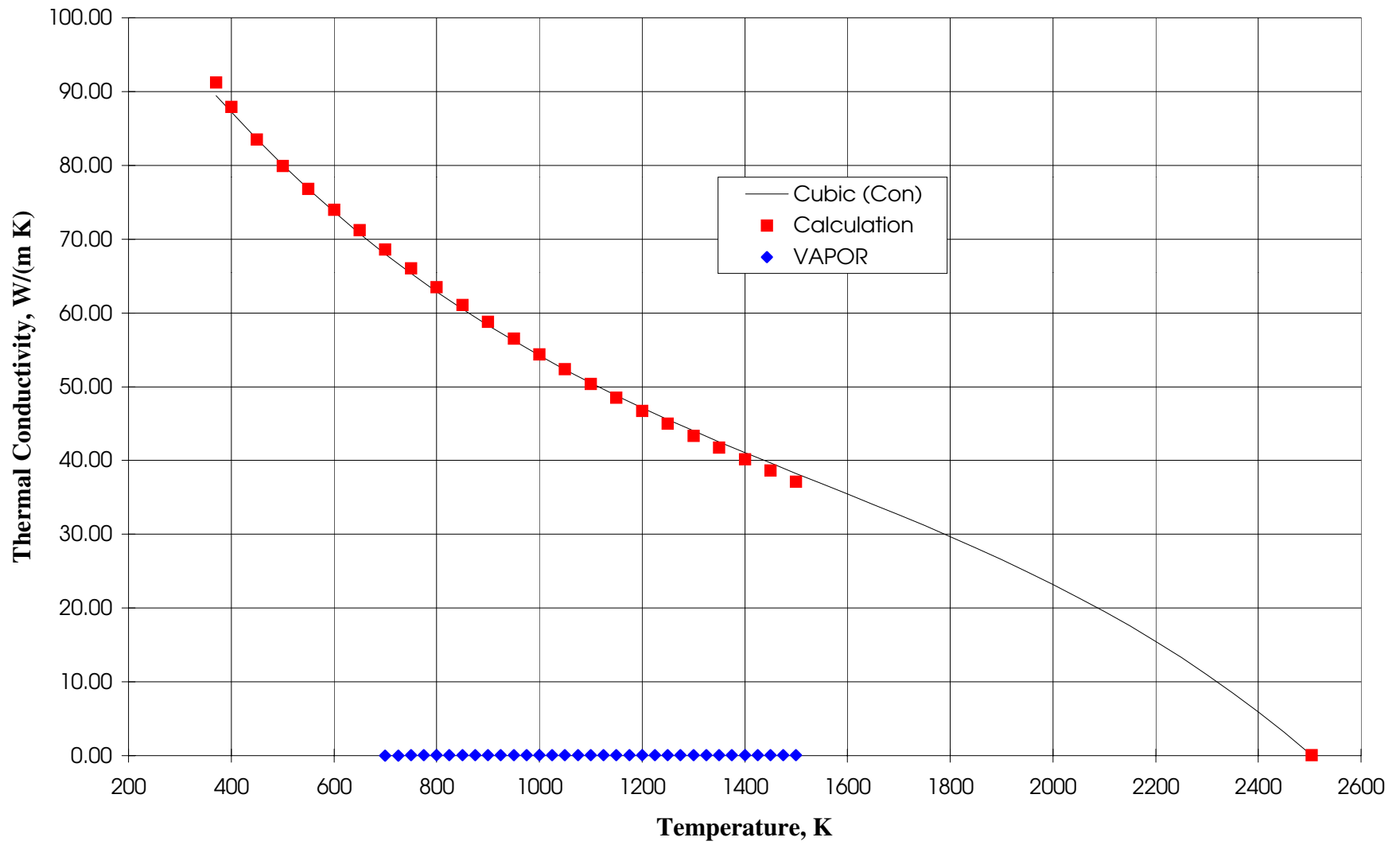


Fig. 2.1-11 Constrained Cubic Fit to Calculated Values of the Thermal Conductivity of Liquid Sodium, Calculated Values, and Vapor Thermal Conductivities

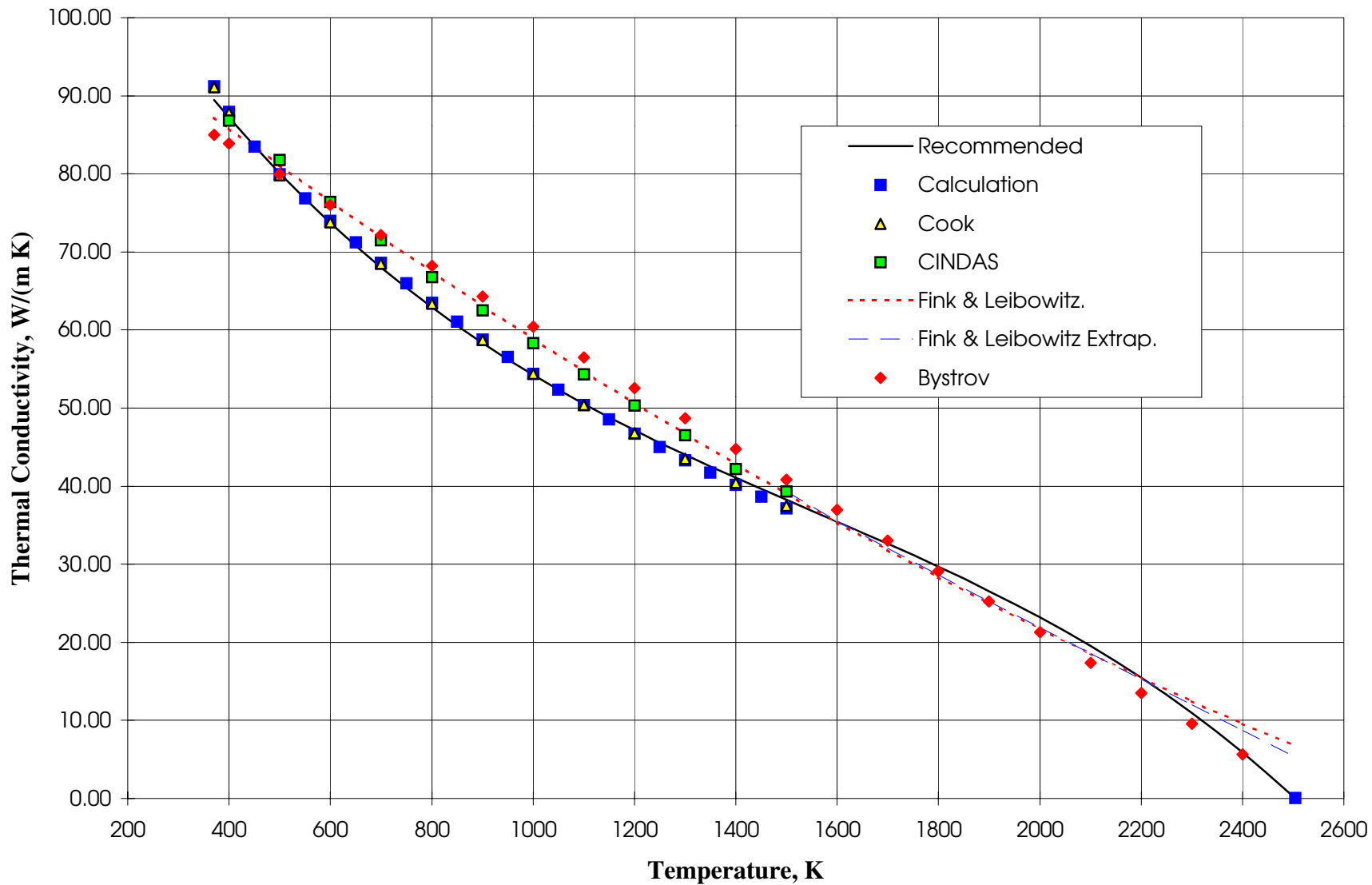


Fig. 2.1-12 Comparison of Recommended Values for the Thermal Conductivity of Sodium with Calculated Values from Other Assessments

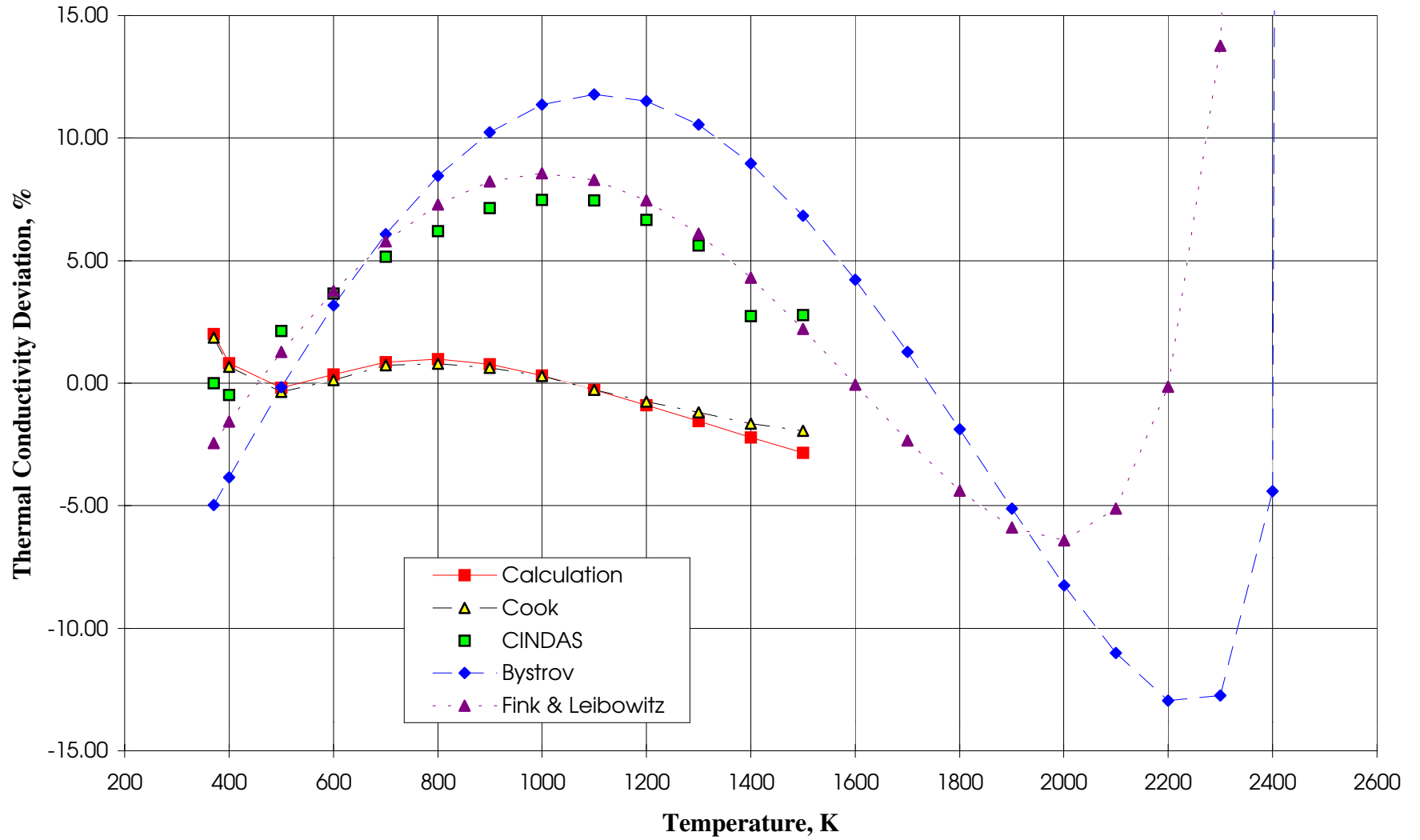


Fig. 2.1-13 Deviations of Values from Other assessments from Recommended Values of the Thermal Conductivity of Liquid Sodium

2.2 VISCOSITY

Summary

The recommended values for the dynamic viscosity of liquid sodium in Pa·s are given in Table 2.2-1. For the temperature range 371 to 2500 K, the natural logarithms of the dynamic viscosity have been calculated from the equation recommended by Shpil'rain et al.:⁽¹⁾

$$\ln \eta = - 6.4406 - 0.3958 \ln T + \frac{556.835}{T} . \quad (1)$$

The recommended value for the viscosity of sodium at the critical point, 5.8×10^{-5} Pa·s, is the value recommended by Bystrov et al.⁽²⁾ for the critical temperature of 2503 K. It was calculated using the method of Andrade⁽³⁾ by Shpil'rain et al.⁽¹⁾; in their assessment of the methods to calculate the viscosity at the critical point.

Figure 2.2-1 shows the recommended values for the viscosity of sodium with the uncertainties as dashed lines. The uncertainties are given in Table 2.2-2.

Discussion

The recommended equation for the viscosity of liquid sodium is from the assessment by Shpil'rain et al.⁽¹⁾ The measurements of the viscosity of liquid sodium⁽⁴⁻¹⁸⁾ included in the assessment are shown in Table 2.2-3. In their least squares fit to the data, Shpil'rain et al. excluded data from the experiments by Sauerwald, by Gering and Sauerwald, by Godfrey, and by Achener because the purity of the sodium used in these experiments was unknown and these data have greater scatter than data from other experiments. The form of equation used to fit the data was based on the theory given by Frenkel.⁽¹⁹⁾ In their data assessment, Shpil'rain et al. checked the consistency of their recommended equation as it approached the critical point with vapor viscosities from two sets of calculations. They compared values for the viscosity at the critical temperature, 2503 K, calculated using an Andrade equation, corresponding states, the free volume theory, and the average diameter. Values ranged from 0.5×10^{-4} Pa·s to 0.99×10^{-4} Pa·s. In their review of properties of the alkali metals, Bystrov et al.⁽²⁾ recommended 0.58×10^{-4} Pa·s for the viscosity of sodium at the critical point. This is the value obtained by Shpil'rain et al. using an Andrade equation of the form

Table 2.2-1 Recommended Values for the Dynamic Viscosity of Liquid Sodium

| Temperature (K) | Viscosity x 10 ⁴ (Pa·s) |
|-----------------|------------------------------------|
| 371 | 6.88 |
| 400 | 5.99 |
| 500 | 4.15 |
| 600 | 3.21 |
| 700 | 2.64 |
| 800 | 2.27 |
| 900 | 2.01 |
| 1000 | 1.81 |
| 1100 | 1.66 |
| 1200 | 1.53 |
| 1300 | 1.43 |
| 1400 | 1.35 |
| 1500 | 1.28 |
| 1600 | 1.22 |
| 1700 | 1.17 |
| 1800 | 1.12 |
| 1900 | 1.08 |
| 2000 | 1.04 |
| 2100 | 1.01 |
| 2200 | 0.98 |
| 2300 | 0.95 |
| 2400 | 0.92 |

$$\eta = K \frac{\sqrt{MT}}{V^{2/3}}, \quad (2)$$

where η , T , V , and M are, respectively, the critical viscosity, critical temperature, critical volume, and molecular weight.

Fink and Leibowitz⁽²⁰⁾ fit data of Ewing et al.,⁽⁸⁻⁹⁾ Chiong,⁽⁷⁾ Godfrey,⁽¹⁰⁾ Solov'ev,⁽¹¹⁾ and Fomin and Shpil'rain⁽¹⁴⁾ to an Andrade II equation,⁽³⁾ which has the form

Table 2.2-2 Estimated Uncertainty in Values for the Viscosity of Sodium Calculated from Eq. (1)

| Temperature (K) | Viscosity x 10 ⁴ Pa·s | Uncertainty, $\left(\frac{\delta\eta}{\eta}\right)$ (%) |
|--------------------------------|--|---|
| 371 ≤ T ≤ 1500 ^(a) | $\eta = \exp\left[-6.4406 - 0.3958 \ln T + \frac{556.835}{T}\right]$ | 3 - 5 |
| 1500 < T ≤ 2000 ^(b) | | 5 - 10 |
| 2000 ≤ T ≤ 2500 ^(b) | | 10 - 12 |

$$^{(a)} \frac{\delta\eta}{\eta} (\%) = 2.3 + 0.0018 T$$

$$^{(b)} \frac{\delta\eta}{\eta} (\%) = -10 + 0.01 T$$

$$\eta = A e^{\frac{C}{VT}} V^{-\frac{1}{3}} \quad (3)$$

where $A=0.11259$, $C=749.08$, and $V=1/\rho_l$ where ρ_l is the liquid density. They used a technique due to Grosse⁽²¹⁾ to extrapolate from the maximum temperature of these data (1300 K) to the critical temperature. Viscosity values calculated by Fink and Leibowitz are compared with the recommended values of Shpil'rain et al. in Fig. 2.2-2. The recommended value of the viscosity at the critical temperature, 2503.7 K, is included in the figure. Deviations of values for the viscosity calculated by Fink and Leibowitz from those given by the recommended equation are shown in Fig. 2.2-3. These deviations are defined as

$$Deviations = \frac{[\eta(F-L) - \eta(Eq. 1)] 100\%}{\eta(Eq. 1)} \quad (4)$$

Table 2.2-3 Sodium Viscosity Data Assessed by Shpil'rain et al.

| Temperature (K) | Limiting Confidence Error (%) | Purity of Sample (Mass %) | Authors | Year | Ref. |
|-----------------|-------------------------------|---------------------------|----------------------|------|--------|
| 373 | ±25 | — | Sauerwald | 1932 | 4 |
| 373 | ±25 | — | | 1932 | 5 |
| 373 - 456 | ±25 | — | Gering, Sauerwald | 1935 | 6 |
| 371 - 628 | ±1.5 | 99.8 | Chiong | 1936 | 7 |
| 377 - 466 | ±2 - 3 | 100.0 | Ewing, Grand, Miller | 1951 | 8 |
| 416 - 959 | ±3 - 10 | 100.0 | Ewing, Grand, Miller | 1954 | 9 |
| 600 - 1152 | ±15 | — | Godfry | 1952 | 10 |
| 372 - 1075 | ±3 | 99.7 | Solov'ev, Novikov | 1954 | 11, 12 |
| 1073 - 1773 | ±10 | — | Kalakutskaya | 1964 | 13 |
| 481 - 1060 | ±3 | 99.5 | Fomin, Shpil'rain | 1965 | 14, 15 |
| 391 - 1313 | ±10 - 20 | — | Achener | 1967 | 16 |
| 373 - 673 | ±3 | 99.974 | Genrikh, Kaplun | 1970 | 17, 18 |

The curvature exhibited by the deviations arises from the different functional forms used to represent the viscosity in the two assessments. Within the range of experimental data fit by both groups, the deviations are within 5%, which is less than the estimated uncertainty in some of the data, as indicated in Table 2.2-3. Above 1300 K, the maximum deviation is 7.5%.

The equation derived by the assessment by Shpil'rain et al. is recommended rather than that given by Fink and Leibowitz because it is based on an assessment of more experimental data, which extend to a higher temperature (1774 K) than the data included in the Fink and Leibowitz assessment. Some of the data that were included in the assessment by Shpil'rain et al., which were not available to Fink and Leibowitz, have low estimated uncertainties. In their review of properties of the alkali metals, Bystrov et al.⁽²⁾ recommend the equation given by Shpil'rain et al.

Uncertainty

The estimated uncertainty in the recommended values range from 3% at the melting point to 5% at 1500 K and increases to 12% at 2500 K. The uncertainties are assumed to increase linearly with temperature. Below 1500 K, the uncertainty is approximated by the linear equation

$$\frac{\delta \eta}{\eta}(\%) = 2.3 + 0.0018 T \quad (5)$$

for $371 \text{ K} \leq T \leq 1500 \text{ K}$.

Above 1500 K, the uncertainty is approximated by

$$\frac{\delta \eta}{\eta}(\%) = -10.0 + 0.01 T \quad (6)$$

for $1500 \text{ K} \leq T \leq 2500 \text{ K}$.

Uncertainties are shown as dotted lines in Fig. 2.2-1 and are given in Table 2.2-2.

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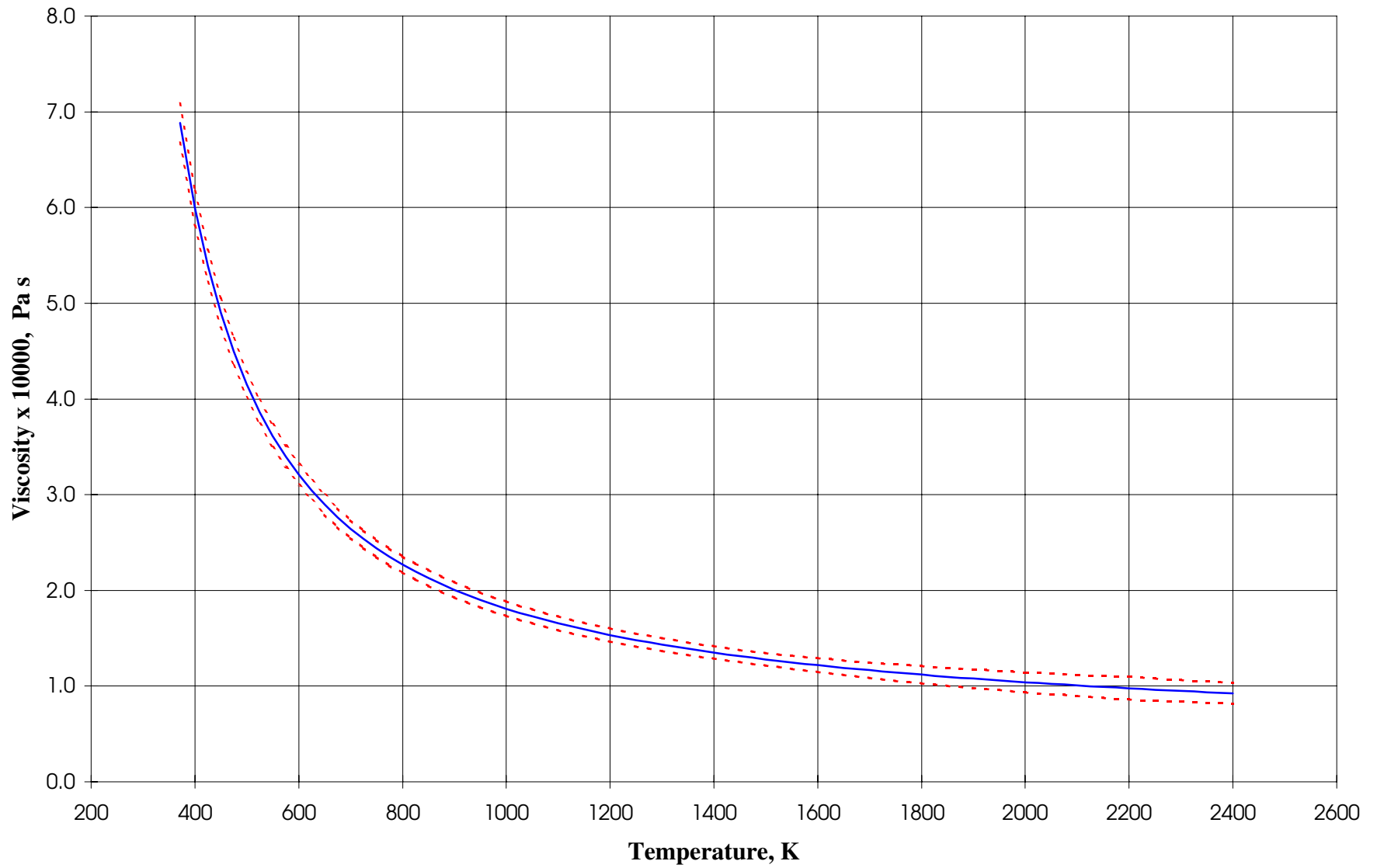


Fig. 2.2-1 Viscosity of Liquid Sodium

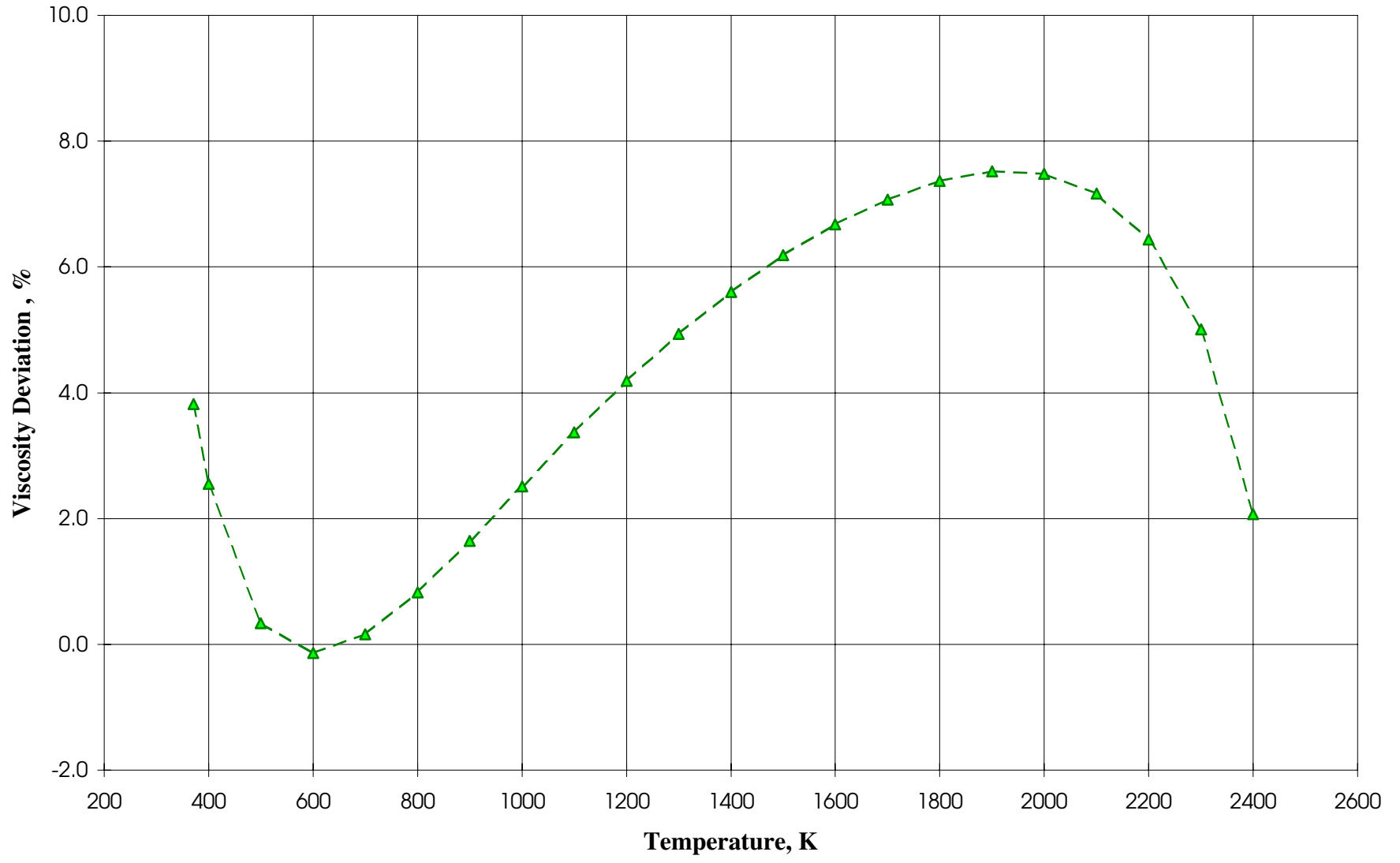


Fig. 2.2-3 Deviations of Values given by Fink and Leibowitz from Recommended Values of the Viscosity of Liquid Sodium

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