

ΔH_v = enthalpy change upon vaporization of a mole of equilibrium vapor, B.t.u./lb.-mole
 J = any unit conversion
 M_i = molecular weight of monomeric species
 p = absolute pressure, p.s.i.
 Q = a defined function, $[(z-1)\bar{V} - B]\bar{V}$
 R = gas constant
 s = entropy per unit mass, B.t.u./lb.-° F.
 Δs_v = entropy change upon vaporization of a unit mass of equilibrium vapor, B.t.u./lb.-° F.
 T = absolute temperature, ° R.
 t = temperature, ° F.
 \bar{V} = molal volume (per formula weight of monomer), cu. ft./lb.-mole
 v = specific volume, cu. ft./lb.
 z = compressibility factor, $p\bar{V}/RT$

Subscripts

i = quantity at any state
 o = quantity at 0° R.
 p = constant pressure change
 s = quantity at saturation

Superscripts

g = quantity in gas state
 l = quantity in liquid state
 $^\circ$ = standard state, 1 atm. for gas

LITERATURE CITED

- (1) Deem, H.W., Eldridge, E.A., Lucks, C.F., "The Specific Heat from 0° to 1150° C. and Heat of Fusion of Potassium," Batt-4673-T2, (August 1962).
- (2) Douglas, T.B., Ball, A.F., Ginnings, D.C., Davis, W.D. *J. Am. Chem. Soc.* 74, 2472 (1952).

- (3) Evans, W.H., Jacobson, R., Munson, T.R., Wagman, D.D., *J. Res. Natl. Bur. Std.* 55, 83 (1955).
- (4) Herzberg, G., "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," Van Nostrand New York, 1950.
- (5) Hicks, W.T., *J. Chem. Phys.* 38, 1873 (1963).
- (6) Hirschfelder, J.O. Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
- (7) Hirschfelder, J.O., McClure, F.T., Weeks, I.F., *J. Chem. Phys.* 10, 201 (1942).
- (8) Makansi, M.M., Madsen, M., Selke, W.A., Bonilla, C.F., *J. Phys. Chem.* 60, 128 (1956).
- (9) Stone, J.P., Ewing, C.T., Spann, J.R., Steinkuller, E.W., Williams, D.D., Miller, R.R., *J. CHEM. ENG. DATA* 11, 309 (1966).
- (10) *Ibid.*, p. 315.
- (11) *Ibid.*, p. 320.
- (12) Walker, B.E., Ewing, C.T., Miller, R.R., *Rev. Sci. Instr.* 33, 1029 (1962).
- (13) Walker, B.E., Grand, J.A., Miller, R.R., *J. Phys. Chem.* 60, 231 (1956).
- (14) Walling, J.F., Lemmon, A.W., Jr., "Experimental P-V-T Properties of Potassium to 1150° C." BATT-4673-T4 (April 1963).
- (15) Walling, J.F., Nuzum, H.K., and Lemmon, A.W., Jr., "Vapor Pressure and Heat of Vaporization of Potassium from 480 to 1150° C." BATT-4673-T3 (April 1963).
- (16) Weatherford, W.D., Jr., Tyler, J.C., Ku, P.M., "Properties of Inorganic Energy-Conversion and Heat-Transfer Fluids for Space Application," WADD Tech. Rept. 61-96 (November 1961).
- (17) Woolley, H.W., *J. Chem. Phys.* 21, 236 (1953).

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High-Temperature Properties of Sodium

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A virial equation of state for sodium with coefficients through the fourth virial is derived from PVT data covering a temperature range from 1750° to 2525° F. Exact thermodynamic relations involving the virial and vapor-pressure equations are used to generate saturation and superheat properties of the vapor. Values of enthalpy, entropy, specific heat, and specific volume are tabulated for some 140 selected vapor states in the temperature range from 1650° to 2550° F. and in the pressure range from 2.9 to 358.7 p.s.i.a. The thermal properties for a somewhat greater temperature range from 1400° to 2500° F. are presented as a Mollier chart.

THE existing thermodynamic properties of alkali metal vapors have for the most part been obtained by estimating imperfections from spectroscopic data. The properties so obtained are of questionable accuracy, and there is a need for an increased reliability for the evaluation of the metal vapors as working fluids in turbines and other power cycles. To meet this need, reliable thermodynamic properties of sodium, potassium, and cesium are being generated from sets of experimentally determined properties—pressure-volume-temperature, vapor pressure, and liquid density. These properties for all three metals have been reported by Stone *et al.* (10, 11, 12), and those for potassium have been reduced thermodynamically to yield a consistent body of vapor properties—enthalpy, entropy, specific heat, and specific volume (3). This article describes a similar reduction of the measured properties of sodium.

TREATMENT OF PVT DATA AND THE VIRIAL EQUATION OF STATE

The major imperfections in sodium vapor at the temperatures and pressures involved in this study stem from the existence of molecular species with two or more atoms (5). These species are present in such abundance that an equation of state of the quasichemical type (involving equilibrium constants) could have been used to represent the PVT data. However, the virial equation was preferred over the quasichemical types since the thermodynamic relationships based on it are believed to be better established.

The PVT data of Stone and coworkers (10) were fitted by the graphical method described for potassium (3) and the resulting virial equation of state is

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} \quad (1)$$

where,

$$\log |B| = -4.3519 + 6755.3/T + \log T$$

$$B < 0$$

$$\log C = -0.6137 + 10,839/T$$

$$C > 0$$

$$\log |D| = -0.0905 + 13,539/T$$

$$D < 0$$

The degree of fit of the virial equation to the observed *PVT* data is shown graphically with Figure 1 in which compressibility isotherms generated with Equation 1 are compared to experimental compressibilities at 100-degree intervals from 1775° to 2575° F. The fit of the equation can also be shown numerically. For example, all the observed compressibility data for sodium as reported by Stone *et al.* (10) may be calculated from Equation 1 with a standard per cent deviation of ± 0.35 .

The equation of state was effectively derived from experimental data over a temperature range from 2175° to 2575° F. However, equivalent data were available from 1775° to 2175° F., but the number of experimental points in this region did not permit one to obtain reliable virial coefficients by the graphical method. Consequently, before the equation of state was acceptable for calculations below 2175° F., it was necessary to determine its fit to the observed low-temperature data. Compressibility factors at low temperatures and pressures were calculated and compared to the observed values (Figure 1); the agreement was equivalent to that obtained at higher temperatures.

CALCULATION OF THERMODYNAMIC PROPERTIES AND FUNDAMENTAL DATA

The important properties of the metallic liquid and vapor are volume, enthalpy, entropy, and specific heat. These properties were computed from the virial equation of state, from exact thermodynamic relationships, or from the fundamental property equations included in this section.

Saturation Pressure of Liquid Sodium. The least-squares vapor-pressure equation derived by Stone *et al.* (11) was selected. This equation,

$$\log p_s = 8.00490 - 9980.9/T - 0.61344 \log T \quad (2)$$

is based on experimental data over the temperature range from the normal boiling point to 2540° F. and is in good agreement with the vapor pressures observed by Makansi, Muendel, Selke, (8) and Bowles and Rosenblum (1).

Specific Volume of Liquid Sodium. The correlation equation by Stone *et al.* (12) was selected. This equation,

$$1/v^l = 59.566 - 7.9504 \times 10^{-3}t - 0.2872 \times 10^{-6}t^2 + 0.06035 \times 10^{-9}t^3 \quad (3)$$

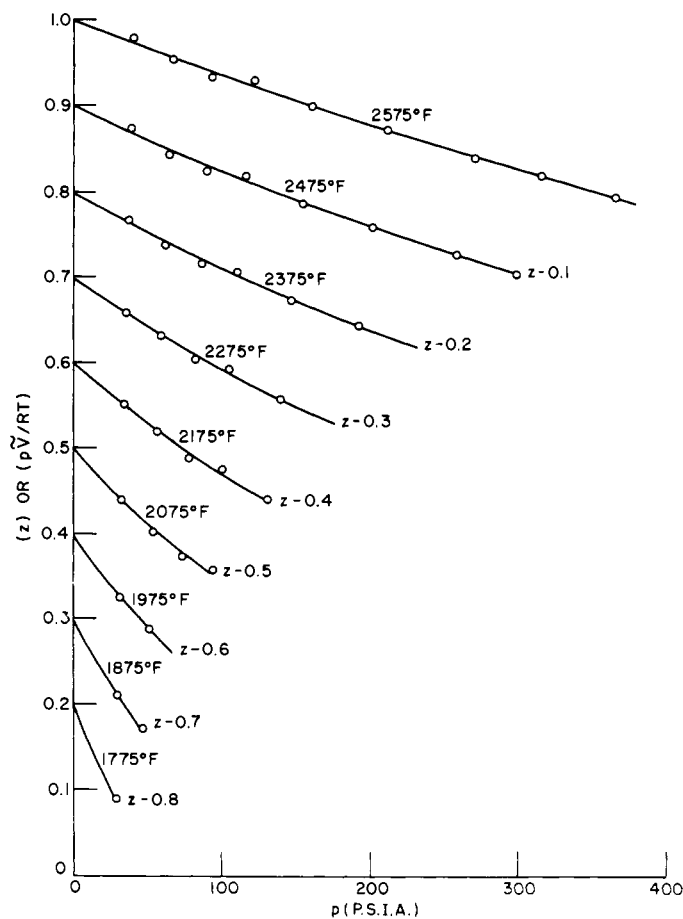


Figure 1. Compressibility of sodium vapor at several temperatures

was derived from all available data and covered a range from the melting point to 2491° F. The error limit given for the equation was $\pm 0.6\%$.

Specific Volume of Saturated and Superheated Sodium Vapor. The value of this property at any state was obtained directly from the virial equation of state.

Enthalpy, Entropy, and Specific Heat of Saturated and Superheated Sodium Vapor. These thermodynamic properties were computed along constant temperature lines with the starting point for a particular property being the value of that property for the monomeric gas at 1 atm. The working expressions for the properties are the same as those presented for potassium (3) and the computational steps are outlined in this section.

An alternate path, basing the vapor properties on those of the saturated liquid, could have been used. Properties at selected states were computed by this second path and compared to those in this article by the gas path. Even

Table I. Saturation Properties of Sodium^a

Basis: $h = 0$ and $s = 0$ for solid sodium at ° R.

t	p_s	v^l	v_s^g	h^l	Δh_s	h_s^g	s^l	Δs_s	s_s^g
1600.00	13.37	0.02157	64.8536	624.60	1692.35	2316.95	1.0173	0.8216	1.8390
1700.00	21.78	0.02197	41.2225	657.19	1665.44	2322.63	1.0327	0.7711	1.8039
1800.00	33.92	0.02238	27.3441	689.64	1639.47	2329.11	1.0474	0.7255	1.7729
1900.00	50.83	0.02281	18.8251	722.11	1614.40	2336.50	1.0614	0.6842	1.7456
2000.00	73.62	0.02326	13.3975	754.78	1589.95	2344.73	1.0750	0.6464	1.7214
2100.00	103.50	0.02372	9.7935	787.95	1565.61	2353.56	1.0881	0.6116	1.6998
2200.00	141.68	0.02420	7.3423	821.94	1540.65	2362.59	1.1011	0.5793	1.6804
2300.00	189.44	0.02469	5.6220	857.17	1514.10	2371.28	1.1140	0.5486	1.6627
2400.00	248.00	0.02521	4.3825	894.11	1484.78	2378.89	1.1271	0.5192	1.6463
2500.00	318.58	0.02575	3.4666	933.37	1451.09	2384.46	1.1405	0.4903	1.6307

^a Values are given to more significant figures than the data warrant in order to retain precision in differences.

though the over-all agreement in the values by the two paths was good and equivalent to that obtained in a similar comparison for potassium (3), the gas path for sodium was preferred over the other for the same reasons as those discussed in the potassium study (3).

Enthalpy and Entropy of Vaporization of Sodium. The latent heat of vaporization was calculated with the equation,

$$\Delta h_v = Jp_s(1563.8/T - 0.041742)(v_g^s - v_l^s) \quad (4)$$

which was derived from Equation 2 and the Clapeyron equation. The value of v_l^s at each temperature was obtained from Equation 3 and the value of v_g^s from the virial equation of state (Equation 1).

The corresponding entropy of vaporization at each saturation state was obtained by dividing the appropriate enthalpy change by the absolute temperature.

Enthalpy of Sublimation of Sodium at 0° R. All the thermodynamic properties in this report are based on the properties of solid sodium at 0° R. Therefore, the enthalpy of sublimation at 0° R. is needed to relate the enthalpy of the ideal gas to the base state. The value of the sublimation quantity is generally derived from vapor-pressure data. Evans and coworkers (2) and Hultgren *et al.* (7) analyzed existing vapor-pressure data and selected values of 25.91 and 25.89 kcal. per gram atom, respectively. These values were derived by estimating imperfections in sodium vapor, and the virial equation of state now permits a more positive determination. Accordingly, a new value was computed from the recent vapor-pressure measurements of Stone *et al.* (11). By using the method outlined by Hicks (6), the heat of sublimation was related to the saturation pressure, the virial coefficients, and the free-energy functions. The resulting relationship is

$$(\Delta H_s)_0 = -RT \left[\frac{2B}{V} + \frac{3C}{2V^2} + \frac{4D}{3V^3} + \ln p_s - \ln \frac{p_s \bar{V}_s}{RT} \right] - M_s T_s \left[\frac{f^s - h_s^s}{T} \right]_0 \quad (5)$$

Values of the sublimation quantity were computed from this relationship for all the saturation pressures reported by Stone and coworkers (11), and the results are presented graphically in Figure 2. Theoretically, a constant value of $(\Delta H_s)_0$ should be obtained for all saturation pressures, but a small temperature trend was observed. This trend can result from errors in the vapor pressure, the virial coefficients, or in any of the free-energy functions. The functions for the monomeric gas were obtained from the work of Evans *et al.* (2). Corresponding functions for the liquid were derived from the specific-heat measurements of Ginnings, Douglas, and Ball (4) and are based on the functions for solid sodium by Evans *et al.* (2). The specific heat of the liquid and the free-energy functions are known accurately to only 1700° F., and above this temperature they were obtained by an extrapolation with the specific-heat equation of Ginnings. It is believed that the true sublimation heat (25.61 mean kcal. per gram atom) is obtained from saturation data below 1700° F. and that the apparent decrease above this temperature results from error in extrapolating the specific heat of the liquid. The value of 25.61 has been used for the thermodynamic calculations in this article.

Enthalpy, Entropy, and Specific Heat of Monomeric Sodium Vapor. Relationships for these quantities in terms of temperature were derived from the tabulated properties of Evans and coworkers (2) and the enthalpy of sublimation at 0° R. was derived from the third-law treatment of vapor pressure. The equations for the monomeric gas at one atmosphere (relative to the solid at 0° R.) are

$$(h^s)_0 = 2005.15 + 0.21598 T + 12,172 e^{-43,830/T} \quad (6)$$

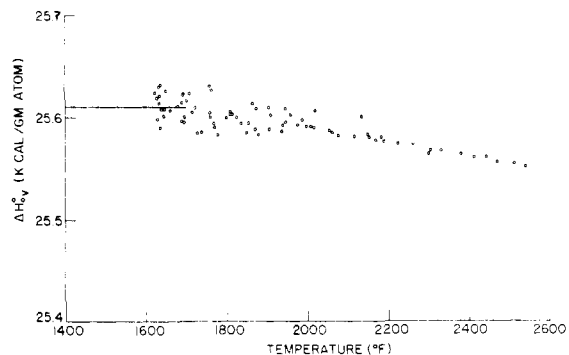


Figure 2. Enthalpy of vaporization of sodium at 0° R. as computed from vapor-pressure data

$$(s^s)_0 = 0.23859 + 0.21598 \ln T \quad (7)$$

$$(c_p^s)_0 = 0.21598 + 6.053 e^{-37,286/T} \quad (8)$$

Enthalpy and Entropy of Liquid Sodium. These properties of the saturated liquid at each temperature were obtained by subtracting the enthalpy or entropy of vaporization from the corresponding property of the saturated vapor.

THERMODYNAMIC PROPERTIES OF SODIUM AND DISCUSSION

All the saturation and superheat properties from 1650° to 2550° F. are presented in Tables I and II, and the thermal properties from 1400° to 2500° F. for both wet and dry vapors are presented graphically in a Mollier chart (Figure 3). The accuracy of the thermodynamic properties is dependent primarily upon the experimentally determined vapor-pressure equation and virial equation of state. Several factors regarding these relationships should be considered when using the tabulated properties. The virial equation of state was derived from *PVT* data covering a pressure range of 27.3 to 367.4 p.s.i.a. and a temperature range of 1758° to 2588° F. The saturated vapor-pressure equation represents data covering a pressure range of 14.7 to 350.1 p.s.i.a. and a temperature range of 1618.6° to 2539° F. Thus, the observed data effectively cover all the higher temperature and pressure states for which properties have been presented, but short extrapolations of the vapor-pressure equation and the virial equation are required to obtain properties at pressure states below 14.7 p.s.i.a.

There are a number of publications in which thermodynamic properties of sodium vapor have been calculated by estimating gas imperfections from spectroscopic data. The properties generated in this article from a *PVT* study were compared to those derived in recent publications by Makansi, Selke, and Bonilla (9) and Weatherford, Tyler, and Ku (13). If the NRL data are taken arbitrarily as a reference and the property changes from *p.* to 2.9 p.s.i.a. compared at each temperature, the enthalpy changes reported by Makansi are 5 to 20% low and the entropy changes on the average differ by $\pm 1.4\%$. Similarly, the enthalpy changes reported by Weatherford are 8% high and the entropy changes differ by $\pm 0.6\%$.

The properties reported in this paper were calculated from exact thermodynamic relationships involving a precise set of experimentally determined properties. They have been evaluated by several tests for internal consistency including the use of two computational paths, and it is believed that they are suitable for all calculations presently required for the design of systems using sodium as a heat-transfer or working fluid.

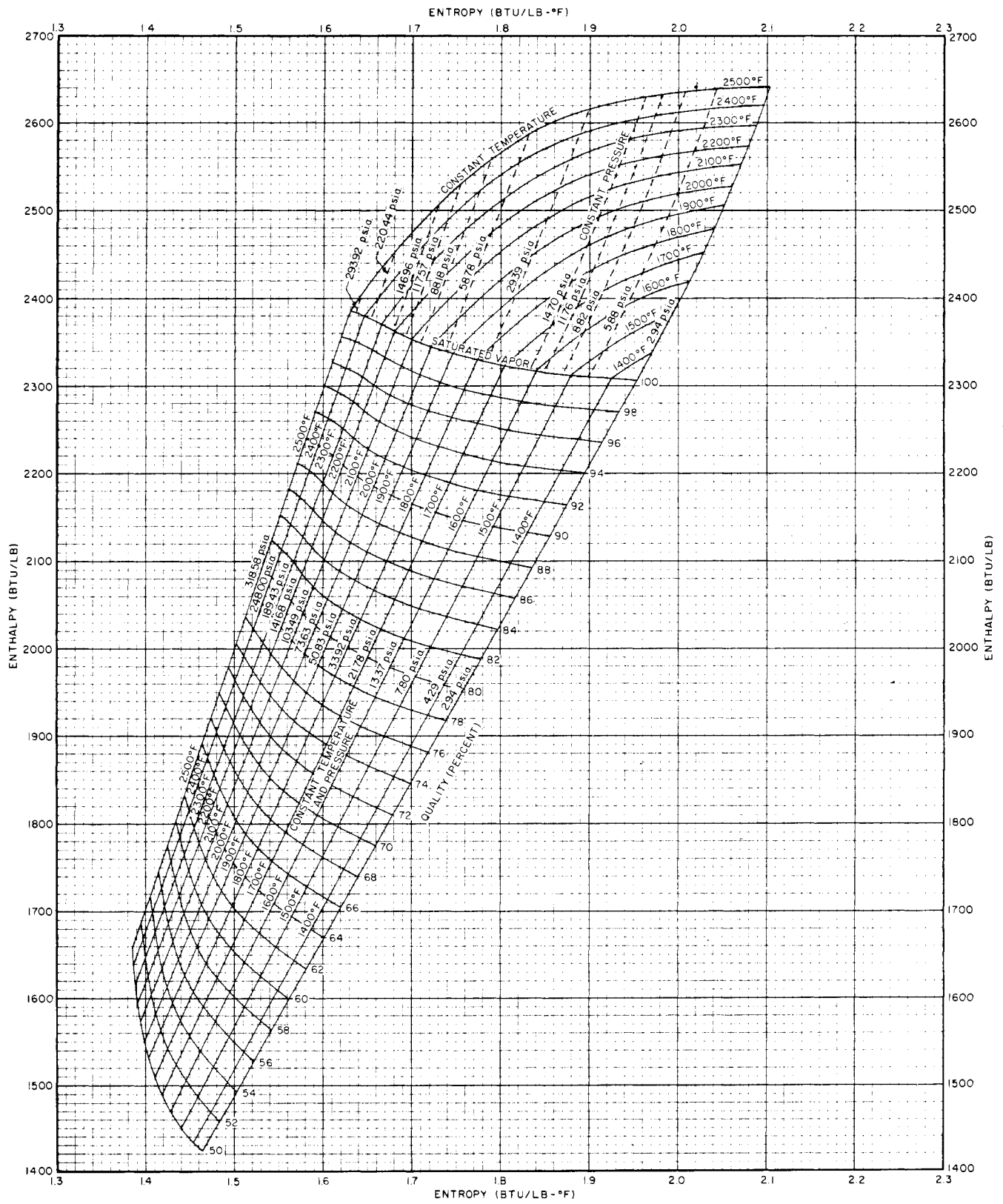


Figure 3. Mollier diagram for sodium

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NOMENCLATURE AND UNITS

B	= second virial coefficient, cu. ft. per mole
C	= third virial coefficient, (cu. ft.) ² per (mole) ²
D	= fourth virial coefficient, (cu. ft.) ³ per (mole) ³
c_p	= specific heat at constant pressure, B.t.u. per lb.-° F.
f	= free energy, B.t.u. per lb.
h	= enthalpy per unit mass, B.t.u. per lb.
Δh_v	= enthalpy change upon vaporization of a unit mass of equilibrium vapor, B.t.u. per lb.
ΔH_v	= enthalpy change upon vaporization of a mole of equilibrium vapor, B.t.u. per lb.-mole
J	= any unit conversion
M_1	= molecular weight of monomeric species
p	= absolute pressure, lb. per sq. inch
R	= gas constant
s	= entropy per unit mass, B.t.u. per lb.-° F.
Δs_v	= entropy change upon vaporization of a unit mass of equilibrium vapor, B.t.u. per lb.-° F.
T	= absolute temperature, ° R.
t	= temperature, ° F.
\bar{V}	= molal volume (per formula weight of monomer), cu. ft. per lb.-mole
v	= specific volume, cu. ft. per lb.
z	= compressibility factor, $p\bar{V}/RT$

Subscripts

0	= quantity at 0° R.
p	= constant pressure change
s	= quantity at saturation

Superscripts

g	= quantity in gas state
l	= quantity in liquid state
$^\circ$	= standard state, 1 atm. for gas

LITERATURE CITED

- (1) Bowles, K.J., Rosenblum, L., NASA TN D-2849, May 1965.
- (2) Evans, W.H., Jacobson, R., Munson, T.R., Wagman, D.D., *J. Res. Natl. Bur. Stds.* **55**, 83 (1955).
- (3) Ewing, C.T., Stone, J.P., Spann, J.R., Miller, R.R., *J. CHEM. ENG. DATA* **11**, 460 (1966).
- (4) Ginnings, D.C., Douglas, T.B., Ball, A.F., *J. Res. Natl. Bur. Stds.* **45**, 23 (1950).
- (5) Herzberg, G., "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," 2nd ed., p. 499, Van Nostrand Co., New York, 1950.
- (6) Hicks, W.T., *J. Chem. Phys.* **38**, 1873 (1963).
- (7) Hultgren, R., Orr, R.L., Anderson, P.D., Kelley, K.K., "Selected Values of Thermodynamic Properties of Metals and Alloys," Wiley, New York, 1963.
- (8) Makansi, M.M., Muendei, C.H., Selke, W.A., *J. Phys. Chem.* **59**, 40 (1955).
- (9) Makansi, M., Selke, W.A., Bonilla, C.F., *J. CHEM. ENG. DATA* **5**, 441 (1960).
- (10) Stone, J.P., Ewing, C.T., Spann, J.R., Steinkuller, E.W., Williams, D.D., Miller, R.R., *Ibid.*, **11**, 309 (1966).
- (11) Stone, J.P., Ewing, C.T., Spann, J.R., Steinkuller, E.W., Williams, D.D., Miller, R.R., *Ibid.*, **11**, 315 (1966).
- (12) Stone, J.P., Ewing, C.T., Spann, J.R., Steinkuller, E.W., Williams, D.D., Miller, R.R., *Ibid.*, **11**, 320 (1966).
- (13) Weatherford, W.D., Jr., Tyler, J.C., Ku, P.M., WADD Tech. Rept. 61-96, Nov. 1961.

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High-Temperature Properties of Cesium

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A virial equation of state for cesium with coefficients through the fifth virial is derived from compressibility data covering a temperature range from 1305° to 2550° F. and a pressure range from 16.5 to 487.9 p.s.i.a. Exact thermodynamic relationships involving the virial and vapor-pressure equations are used to generate saturation and superheat properties of the vapor. Values of the enthalpy, entropy, specific heat, and specific volume are tabulated for some 280 selected states in the temperature range from 1250° to 2550° F. and in the pressure range from 2.9 to 499.7 p.s.i.a. The thermal properties from 1050° to 2550° F. are also presented as a Mollier diagram.

DESIGN STUDIES of high-temperature power-converters employing alkali metal vapors as working fluids require an improved knowledge of their thermodynamic properties. In response to this need, experimental *PVT*, vapor-pressure, and liquid density data for three metals—sodium, potassium, and cesium—have been measured by Stone *et al.* (9, 10, 11). From the data for two of the metals, sodium and potassium, the authors have generated and published consistent sets of thermodynamic properties (5, 6). The present article extends this work to the third metal, cesium.

TREATMENT OF *PVT* DATA

Derivation of Virial Coefficients. Coefficients for the cesium equation of state in its volume expansion form (Equation 1) were derived from the experimental *PVT* data of Stone *et al.* (9), which cover a temperature range in the superheat region from 1305° to 2550° F. They were obtained graphically as described for potassium (5) by plotting experimental functions along constant temperature lines. However, two modifications of the method were required for cesium. First, the adjustment procedure (5), which was