Thermodynamic Properties of Sodium

MUNZER MAKANSI,[1] W. A. SELKE,[2] and C. F. BONILLA
Department of Chemical Engineering, Columbia University, New York, N. Y.

EVERY PRACTICAL source of energy useful to man, other than water power, needs to be transformed to work via a fluid when not used in internal combustion engines or for heat as such. In the heat engines which make use of a motive fluid as a medium for the transformation of heat energy into work, the theoretical efficiency is higher if the motive fluid is condensable over the major portion of the cycle, and if the ratio of boiling to condensing temperature is high. Except for the binary mercury-steam power cycle, the fluid used in all such condensing power cycles so far has been water.

The most common source of high temperatures for power production in any desired location at moderate cost has been chemical reactions. The highest temperature obtainable economically in this manner is about 3600° F. from the combustion of coal. In recent years, heat energy is becoming available from nuclear reactions. This heat can in principle be produced at much higher temperatures than might be obtained from chemical reactions. Nuclear power plants are currently being developed to make use of this energy. Sodium is being considered as a motive fluid for several such high-temperature power cycles. Its physical and thermodynamic characteristics together with its relative abundance and low cost make it comparable and in many respects superior to mercury as a motive fluid for high-temperature power cycles.

To design engines to use sodium as a motive fluid, values of its thermodynamic properties should be available in the form of a chart or tables. A critical examination of the literature on the thermodynamic properties of sodium leads to the following conclusions.

There are inconsistencies among the various correlating equations, in spite of a wealth of data on the vapor pressure of sodium. Moreover, the data do not extend to temperatures high enough to meet the practical operating conditions of a prospective power cycle. Actually, except for two measurements of the normal boiling point of sodium (*13, 30*) and the very recent data of Makansi, Muendel, and Selke (*24*), the experimental vapor pressure points extend only to 1113.1° K., corresponding to $P = 0.635$ atm. (*29*).

The data on the specific heat, the enthalpy, and the entropy of liquid and solid sodium along the saturation curve (*8*) extend to 1173° K. and appear to be very accurate.

Spectroscopic data indicate that sodium in the vapor phase consists of both monomer and dimer species. There exists, on the other hand, some evidence in the literature that sodium liquid does not contain any of the diatomic species. The amount of dimer in the vapor phase is determined by the reversible reaction:

$$2\text{Na} \rightleftarrows \text{Na}_2$$

There is considerable discrepancy in the literature between the numerical values of the heat of dimerization for the above reaction. Values ranging from −16,559 to −20,000 cal. per gram mole of Na_2 for the heat of dimerization at the ground state have been reported.

Recent calculations of the thermodynamic functions of the two species of sodium vapor by the methods of statistical mechanics (*14*) were based on latest values of the physical constants and spectroscopic data, and are consistent up to about 1500° K. Above this temperature the data of Evans and others (*7*) for the monatomic gas are more correct because they include energy levels above the ground state. The difference due to this correction is small, less than 0.5% at 2400° K.

In contrast to the chemical approach used by the above authors to calculate the thermodynamic functions of sodium, Sinanoglu and Pitzer (*32*) have, very recently, analyzed the system from the virial coefficient viewpoint. They have estimated that the contribution of the triplet repulsive state to the second virial coefficient is appreciable at high temperature, amounting to about 0.54% at 1720° K. and about 5.8% at 2340° K. These values are reported to be an order of magnitude estimate, because sufficient information is not available on the potential energy curve of the triplet state.

There are wide differences among the critical point values reported in the literature.

The tabulated thermodynamic properties of saturated sodium vapor (*34*) were based on a value of the heat of dimerization D_0^0, with which reconciliation among the various vapor pressure data was difficult.

The published thermodynamic diagram for sodium vapor (*15*) has the following characteristics which could be improved:

The diagram was based on 1 pound mole of the equilibrium mixture of monomer and dimer sodium vapor. Because the mole fraction of these species is not constant, the molecular weight of the equilibrium mixture is not constant; hence calculations of power cycles based on such a diagram would be difficult.

In computing the specific heat of sodium vapor from the spectroscopic data of the monomer and the dimer, the authors did not take into account the effect of the heat of dimerization. This has been shown to lead to serious error (*31*).

The diagram was based on several simplifying assumptions.

The vapor pressure curve was based on Kelley's equation (*18*), which covers experimental data extending only up to 1 atm. The curve representing this equation on a T−log P diagram was "visually extrapolated" to meet a presupposed critical point of 2273° K.

The vapor pressure equation which was used for the extrapolation was of a questionable form (*6*).

The critical point used in the construction of the diagram was based on an error (*31*).

The purpose of this research was to carry out pertinent experimental measurements, along with a more complete thermodynamic analysis of the existing data, and construct a more accurate diagram for sodium.

VAPOR PRESSURE OF SODIUM AT HIGH TEMPERATURES

Using the method of least squares, Makansi, Muendel, and Selke (*24*) fitted the following equation to their data points.

$$\log P = \frac{-5220}{T} + 4.521 \tag{1}$$

where P is in atmospheres absolute and T in ° K.

The standard error in P as calculated from this equation was 0.9% over the experimental range from 0.047 to 6.489 atm. abs. The normal boiling point as calculated from the equation is 881.3° C. (1154.5° K.).

Attempts were also made to fit a three-term equation of the type

$$\log P = \frac{A}{T} + B \log T + C \tag{2}$$

to the data points. The resulting equation was:

$$\log P\ (\text{atm. abs.}) = \frac{-5211}{T} + 0.015 \log T + 4.468 \qquad (3)$$

The standard error in this equation was also 0.9%. As the variation in the second term did not exceed 0.3% over the entire range of temperatures covered by the experimental data, fitting a three-term equation to the data points was not justified in this range and the two-term equation was satisfactory.

VAPOR-PRESSURE EQUATIONS FOR SODIUM AT LOW TEMPERATURES

To select an equation for the low-pressure range which is consistent with the equation for the high-pressure region, the boiling points at several pressures from 1 to 10,000 mm. were calculated by means of all available correlations. The computed boiling points were then compared with the values obtained from Equation 1, which are within the 95% confidence limit. This procedure showed that the Rodebush equation (*28*) agrees with Equation 1 only in the range from 500 to 1000 mm. Kelley's equation (*18*) deviates considerably from Equation 1 and tends to give higher temperatures. Ditchburn's equation (*3*) agrees with Equation 1 within the error limit in the experimental range of Equation 1. Thomson's equation (*35*), on the other hand, agrees with Equation 1 only in the range above 760 mm.

The above comparison suggests that of the two three-term equations—Kelley's and Ditchburn's—which were intended to cover a wide range of the vapor pressures, Ditchburn's equation was more dependable in predicting the vapor pressure of sodium in the experimental range covered by this work and that the agreement is excellent in the region where the two equations overlap—e.g., at the normal boiling point. Another proof of the soundness of the type of thermodynamic analysis used by Ditchburn and Gilmour to arrive at their equation is the good agreement between their vapor-pressure equation for potassium (*3*) with the data points obtained in this work on the vapor pressure of potassium in the high-pressure region (*23*). For these reasons, it was decided to use the equation of Ditchburn and Gilmour

$$\log P = \frac{-5567}{T} - 0.5 \log T + 6.354 \qquad (4)$$

in computing the thermodynamic properties of sodium vapor.

SPECIFIC HEAT OF SODIUM VAPOR

The specific heat of the equilibrium mixture of monatomic sodium, Na, and diatomic sodium in the vapor phase was calculated from the properties of the individual species as follows:

The effective specific heat of the vapor at constant pressure, $(C''p)$eff., is defined by

$$(C''_p)_{\text{eff.}} = \left[\left(\frac{\Delta H}{\Delta T}\right)_{\Delta T \to 0}\right]_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad (5)$$

where ΔH is the net difference in enthalpy of 1 gram of an equilibrium mixture of monatomic and diatomic sodium between the vapor states $(T, P, x_1, x_2)_1$ and $(T + \Delta T, P, x_1 + \Delta x_1, x_2 + \Delta x_2)_2$. In going from state 1 to state 2, a portion of species 1 is transformed into species 2, in such a way that the equilibrium conditions of the dimerization reaction

$$2\text{Na} = \text{Na}_2 (\Delta H = D^0) \qquad (6)$$

are satisfied in both states.

The transformation of Δx_1 of the monomer into Δx_2 of the dimer is associated with an enthalpy change, $(\Delta H)_c$, of a chemical nature caused by dimerization. This change is given by

$$(\Delta H)_c = (\Delta x_2)\,(D^0) \qquad (7)$$

To obtain the net enthalpy change, ΔH, between state 1 and state 2, $(\Delta H)_c$ must be added to the change of enthalpy, $(\Delta H)_s$, due to the sensible heat which, when the ideal gas laws are assumed, is given by the following equation:

$$(\Delta H)_s = (x_1 C''_{p_1} + x_2 C''_{p_2})\,T \qquad (8)$$

i.e.,

$$(\Delta H) = (\Delta H)_c + (\Delta H)_s \qquad (9)$$

Substituting ΔH from Equations 7, 8, and 9 in Equation 5:

$$(C''_p)_{\text{eff.}} = \left[(x_1 C''_{p_1} + x_2 C''_{p_2}) + \left(\frac{\Delta x_2}{\Delta T}\right)_{\Delta T \to 0} \times D^0 \right]_p \qquad (10)$$

or

$$(C''_p)_{\text{eff.}} = x_1 C''_{p_1} + x_2 C''_{p_2} + \left(\frac{\partial x_2}{\partial T}\right)_p \times D^0 \qquad (11)$$

Inatomi and Parrish did not include the important term $\left(\frac{\partial x_2}{\partial T}\right)_p \times D^0$ in their calculation of the effective specific heat of the equilibrium mixture of Na_1 and Na_2.

To calculate the effective specific heat from Equation 11, the quantities appearing on the right side of this equation must be known. The numerical values of C_{p1}, C_{p2}, the enthalpy of monomer and dimer species $(H^0 - E^0_0)_1$ and $(H^0 - E^0_0)_2$, their stoichiometric differences $(H^0 - E^0_0)_2 - 2(H^0 - E^0_0)_1 = (D^0 - D^0_0)$, and the molal free energy functions, $-(F^0 - E^0_0)_1/T$, $-(F^0 - E^0_0)_2/T$, and $\Delta F^0 - D^0_0/T$ for the reaction $2\text{Na} \rightleftharpoons \text{Na}_2$ which were calculated by Inatomi and Benton (*14*) are of satisfactory accuracy. These functions do not, however, give absolute values of either the heat of dimerization or the free energy. A knowledge of the heat of dimerization at the ground state—i.e., at absolute zero—D^0_0, is, therefore, needed before Equation 11 can be solved to compute $(C_p)_{\text{eff.}}$ The fact that x_1, x_2, $\left(\frac{\partial x_2}{\partial T}\right)_p$, and D^0 of Equation 11 are all dependent on the value of D^0_0 indicates that the selection of a correct value of D^0_0 is now the most important factor in determining the accuracy of the specific heat computation and, subsequently, the accuracy of the thermodynamic tables.

ENTHALPY OF DIMERIZATION, D^0_0

Procedure. To determine the value most consistent with the available thermodynamic properties of sodium—namely, the vapor-pressure data and the specific heats of the liquid and the vapor—the following thermodynamic analysis was carried out:

The specific heat of a saturated phase, C_s, either liquid or vapor, is defined (*4*) as the net heat effect in going from one point on the saturation line to another on the same line at infinitesimal distance from the first divided by the small increment in temperature:

$$C_s = \left(\frac{dQ}{dT}\right)_{\text{sat.}} \qquad (12)$$

From the first law of thermodynamics:

$$dQ = dE + P\,dv \qquad (13)$$

From Equations 12 and 13:

$$C_s = \frac{dE}{dT} + \frac{dv}{dT} \qquad (14)$$

applying Equation 14 to both phases and subtracting the two equations:

$$C''_s - C'_s = \frac{d(E'' - E')}{dT} + P\,\frac{d(v'' - v')}{dT} \qquad (15)$$

Now,

$$L = H'' - H' = E'' - E' + P(v'' - v') \qquad (16)$$

Differentiating 16 with respect to T:

$$\left(\frac{dL}{dT}\right)_s = \frac{d(E''-E')}{dT} + P\,\frac{d(v''-v')}{dT} + (v''-v')\left(\frac{dP}{dT}\right)_s \quad (17)$$

where $\left(\frac{dP}{dT}\right)_s$ is the slope of the saturated liquid vapor pressure–temperature curve.

From Equations 15 and 17:

$$C''_s - C'_s = \left(\frac{dL}{dT}\right)_s - (v''-v')\left(\frac{dP}{dT}\right)_s \quad (18)$$

where $\left(\frac{dL}{dT}\right)_s$ is the slope of the saturated latent heat of vaporization–temperature curve.

From the second law of thermodynamics:

$$dQ = T ds = C_p dt - T\left(\frac{\partial v}{\partial T}\right)_p dP \quad (19)$$

From Equations 12 and 19:

$$C_s = \frac{dQ}{dT} = C_p - T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{dP}{dT}\right)_s \quad (20)$$

Equation 20, in which $\left(\frac{dP}{dT}\right)_s$ is the slope of the vapor-pressure curve, represents the relation between the specific heat of a saturated phase, C_s, and the specific heat at constant pressure, C_p, of the same phase. Applying Equation 20 to the vapor phase, we get:

$$C''_s = C''_p - T\left(\frac{\partial v''}{\partial T}\right)_p\left(\frac{dP}{dT}\right)_s \quad (21)$$

Substituting C''_s from Equation 21 into Equation 18 and rearranging:

$$\left(\frac{dL}{dT}\right)_s = C''_p - C'_s + \left[v'' - v' - T\left(\frac{\partial v''}{\partial T}\right)\right]_p\left(\frac{dP}{dT}\right)_s \quad (22)$$

It may be assumed that the liquid volume, v', is negligible, and that the individual species of sodium vapor behave ideally:

$$v'' = NRT/P \quad (23)$$

$$\left(\frac{\partial v''}{\partial T}\right)_p = \left[N + T\left(\frac{\partial N}{\partial T}\right)_p\right]\left(\frac{R}{P}\right) \quad (24)$$

If 1 gram of sodium is used as a basis for calculation and 22.997 as the atomic weight for sodium,

$$N = \frac{x_1}{22.997} + \frac{x_2}{45.994} = \frac{2 - x_2}{45.994} \quad (25)$$

also,

$$dN = \frac{-dx_2}{45.994} \quad (26)$$

Substituting Equations 25 and 26 in 23 and 24:

$$v'' = \left(\frac{2-x_2}{45.994}\right)\frac{RT}{P} \quad (27)$$

$$\left(\frac{\partial v''}{\partial T}\right)_p = \left[\frac{2-x_2}{45.994} - \frac{T}{45.994}\left(\frac{\partial x_2}{\partial T}\right)_p\right]\left(\frac{R}{P}\right) \quad (28)$$

Substituting 27 and 28 in 22 and neglecting v':

$$\left(\frac{dL}{dT}\right)_s = C''_p - C'_s + \left[\frac{RT^2}{45.994}\left(\frac{1}{P}\right)\left(\frac{\partial x_2}{\partial T}\right)\right]_p\left(\frac{dP}{dT}\right)_s \quad (29)$$

Substituting 11 in 29 and rearranging:

$$x_1 C''_{p1} + x_2 C''_{p2} - C'_s + \left[\frac{RT^2}{45.994P}\left(\frac{dP}{dT}\right)_s + D^0\right]\left(\frac{\partial x_2}{\partial T}\right)_p - \left(\frac{dL}{dT}\right)_s = 0 \quad (30)$$

Equation 30 is the basic equation for the present thermodynamic analysis. Both $\left(\frac{dP}{dT}\right)_s$ and $\left(\frac{dL}{dT}\right)_s$ are obtainable directly from a simultaneous solution of the vapor-pressure equation and the Clausius-Clapeyron equation. The saturated specific heat of the liquid C'_s is known from the direct experimental measurements of Ginnings, Douglas, and Ball (*8*). Their measurements, which extend from the triple point (t = 97.8° C.) up to t = 900° C., are presented by their equation:

$$C'_s = 1.43674 - (5.8049)(10^{-4})\,t + (4.6229)(10^{-7})\,t^2 \quad (31)$$

C''_{p1} and C''_{p2} in Equation 30 are available from spectroscopic data (*14*). x_1, x_2, $\left(\frac{\partial x_2}{\partial T}\right)_p$, and D^0 are all related to D_0^0, and can be calculated by means of the thermodynamic functions of Inatomi and Benton (*14*) for any value of D_0^0. Ideally, if all the assumptions made were valid, the left side of Equation 30 should be equal to zero at all temperatures when the correct value of D_0^0 is used to compute x_1, x_2, and D^0. In view of approximations made previously, Equation 30 is not expected to hold absolutely true over the entire range of temperatures under consideration. It is expected, however, that the deviation will be greater at higher pressures (larger deviations from ideal behavior of the vapor species), and a minimum when the correct value of D_0^0 is employed.

The following trial and error procedure based on Equation 30 was followed to determine the value of D_0^0:

1. Equation 30 was replaced by the function:

$$f(T,D_0^0) = x_1 C''_{p1} + x_2 C''_{p2} - C'_s + \left[\frac{RT^2}{45.994P}\left(\frac{dP}{dT}\right)_s + D^0\right]\left(\frac{\partial x_2}{\partial T}\right)_p - \left(\frac{dL}{dT}\right)_s \quad (32)$$

2. A suitable vapor-pressure equation was selected for use in the range of temperature of interest. Actually, Equation 1 was selected for the range between 800° and 1400° K. and Equation 4 of Ditchburn was used between 400° and 1200° K. In this analysis both equations were used from 800° to 1200° K., where they overlap.

3. $\left(\frac{dP}{dT}\right)_s$ and $\left(\frac{dL}{dT}\right)_s$ were then computed from the vapor-pressure equation in combination with the Clausius-Clapeyron equation.

4. A sequence of values of D_0^0 was selected—−12,300, −14,000, −16,000, −16,836, −18,000, and −20,000 cal./gram mole Na_2. For each value of D_0^0, the values of x_1, x_2, D^0, and $\left(\frac{\partial x_2}{\partial T}\right)_p$ were computed over the entire range of temperatures.

5. The function $f(T,D_0^0)$ was then plotted *vs.* temperature with D_0^0 as a parameter. This curve represented the deviation of the left side of Equation 30 from zero.

6. The absolute values of the areas under the curves corresponding to each ΔD_0^0 and within the temperature interval of the corresponding vapor-pressure equation were then divided by the temperature interval itself. This gave the mean values of the function $|f(T,D_0^0)|$ over the range of temperatures under consideration at constant ΔD_0^0. The absolute values of $|f(T,D_0^0)|$ were used in this analysis, so that any positive and negative deviations, which might occur simultaneously in the same curve, do not cancel one another. Otherwise an apparently good fit, with minimum or zero net deviation, might be obtained in a case where the actual fit was very poor.

7. The mean values of the function $|f(T,D_0^0)|$ were then plotted as a function of parameter D_0^0.

8. The value of D_0^0 which corresponded to the minimum mean value of $|f(T,D_0^0)|$ was then considered to be the value most consistent with the experimental data.

Method of Calculation. $f_1(T,D_0^0)$ in High-Temperature Region. Equation 1 for the vapor pressure was used in the interval (T = 800° K. to T = 1400° K.). By differentiating with respect to T,

$$\left(\frac{dP}{dT}\right)_s = (2.303)(5220)\left(\frac{P}{T^2}\right) \tag{33}$$

solving simultaneously with the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{L}{T(v'' - v')} \tag{34}$$

yields

$$L = (2.303)(5220)\ RN \tag{35}$$

Differentiating with respect to T and substituting dN from Equation 25:

$$\left(\frac{dL}{dT}\right)_s = \frac{-(2.303)(5220)R}{45.994}\left(\frac{dx_2}{dT}\right)_s \tag{36}$$

Now, substituting 33 and 36 in 32:

$$f_1(T,D_0^0) \text{ (between 800° and 1400° K.)} =$$

$$x_1 C''_{p1} + x_2 C''_{p2} - C'_s + [519.3512 + D^0]\left(\frac{\partial x_2}{\partial T}\right)_p + 519.3512\left(\frac{dx_2}{dT}\right)_s \tag{37}$$

$f_2(T,D_0^0)$ in Low-Temperature Region. Starting from Equation 4 of Ditchburn and following the same procedure described above:

$$f_2(T,D_0^0) \text{ (between 400° and 1200° K.)} = x_1 C''_{p1} + x_2 C''_{p2} - C'_s$$

$$+ (553.8751 - 0.0261T + D^0)\left(\frac{\partial x_2}{\partial T}\right)_p - 0.0216\,x_2 + 0.0432$$

$$+ (553.8751 - 0.0216\,T)\left(\frac{dx_2}{dt}\right)_s \tag{38}$$

In Equations 37 and 38:

1. All quantities are based on 1-gram weight of an equilibrium mixture of monomer and dimer sodium vapor.

2. $\left(\frac{dx_2}{dT}\right)_s$ is the temperature derivative of the weight fraction of the diatomic sodium vapor for a change along the saturation line.

3. $\left(\frac{\partial x_2}{\partial T}\right)_p$ is the partial derivative of the weight fraction of the diatomic sodium vapor with temperature along a constant pressure line in the superheated region. $\left(\frac{\partial x_2}{\partial T}\right)_p$ is the value of this partial differential at pressure p and the corresponding saturation temperature. $\left(\frac{\partial x_2}{\partial T}\right)_p$ could be calculated without resorting to graphical means, while $\left(\frac{dx_2}{dT}\right)_s$ had to be evaluated graphically.

Calculation of Heat of Dimerization, D^0. Having assumed a value of D_0^0, the value of D^0 can easily be computed from the numerical values of the differences ($D^0 - D_0^0$) as obtained from the data of Inatomi and Benton (*14*). The values thus obtained were converted to the basis of 1 gram of sodium by dividing by 45.994. The assumption that the individual species of the monatomic and diatomic vapor follow the ideal gas laws implies that D^0 is independent of pressure and is a function of temperature only.

Equations for Weight Fractions x_1 and x_2. The basic equations for the equilibrium constant of the dimerization reaction of Equation 6 are:

$$\log K_p = \frac{-\Delta F^0}{RT} \tag{39}$$

and

$$x_2 = 1 - \frac{1}{(4PK_p + 1)^{1/2}} \tag{40}$$

where x_2 is the weight fraction of the dimer.

Here again, having assumed D_0^0, the numerical values of $\Delta F^0/T$ as a function of temperature can be computed from the numerical values of the function $(\Delta F^0 - D_0^0)/T$ (*14*). Substituting $\Delta F^0/T$ in Equation 39, K_p could be calculated at various temperatures. Substituting K_p in Equation 40, x_2 can thus be calculated at any temperature and pressure.

Equation for $\left(\frac{\partial x_2}{\partial T}\right)_p$. Solving Equation 40 for K_p:

$$K_p = \frac{(x_2)(2 - x_2)}{4P(1 - x_2)^2} \tag{41}$$

Taking the natural logarithm of both sides,

$$\ln K_p = \ln x_2 + \ln(2 - x_2) - 2\ln(1 - x_2) - \ln 4P \tag{42}$$

Differentiating both sides at constant pressure:

$$d\ln K_p = \frac{dx_2}{x_2} - \frac{dx_2}{2 - x_2} + 2\,\frac{dx_2}{1 - x_2} \tag{43}$$

Now, for any chemical reaction:

$$\frac{d\ln K_p}{dT} = \frac{\Delta H^0}{RT^2} = \frac{D^0}{RT^2} \tag{44}$$

substituting $d\ln K_p$ from 44 in 43 and rearranging gave

$$\left(\frac{\partial x_2}{\partial T}\right)_p = + \frac{D^0}{2RT^2}(x_2)(2 - x_2)(1 - x_2) \tag{45}$$

In Equation 45 D^0 is in calories per gram mole of Na_2, while x_2 is based on 1-gram weight of the equilibrium mixture of Na_1 and Na_2. Equation 45 was used to compute $\left(\frac{\partial x_2}{\partial T}\right)_p$.

Evaluation of $\left(\frac{dx_2}{dT}\right)_s$. $\left(\frac{dx_2}{dT}\right)_s$ is the only quantity in Equations 32, 37, and 38 which cannot be computed directly by means of suitable equations. For this reason it was evaluated graphically. For each value of D_0^0 assumed, a plot of the saturated weight fraction $(x_2)_s$ *vs.* T was prepared by means of Equations 39 and 40 and the numerical values of $(\Delta F^0 - D_0^0)/T$. These plots were then used to evaluate the slope, $\left(\frac{dx_2}{dT}\right)_s$, at various temperatures, as required by Equations 37 and 38.

Results. Two sets of calculations were made using Equations 37 and 38, respectively. Four typical curves of $f_1(T,D_0^0)$ and $f_2(T,D_0^0)$ are shown in Figures 1 and 2 as functions of temperature with D_0^0 as a parameter. For illustration purposes it suffices to present graphically the mean values of $|f_1(T,D_0^0)|$ in the range 800° to 1400° K. This is shown in Figure 3, which indicates that $|f_1(T,D_0^0)|_m$ has a sharp minimum corresponding to a value of $D_0^0 = -16{,}840$ cal./gram mole of Na_2. This analysis led to the conclusion that $D_0^0 = -16{,}840$ for the heat of dimerization at the ground state is the value most consistent with the experimental vapor pressure and spectroscopic data.

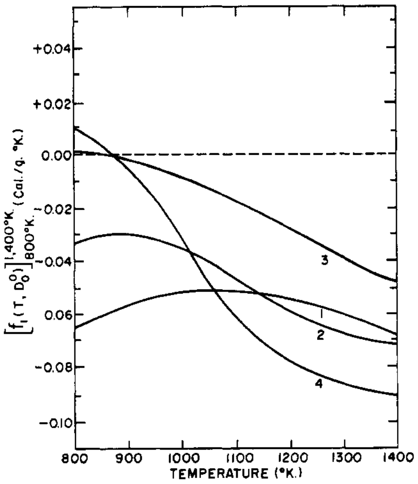

Figure 1. $F_1(T,D_0^0)$ vs. temperature

Curve	D_0^0, Cal./G. Mole Na_2
1	−14,000
2	−16,000
3	−16,840
4	−18,000

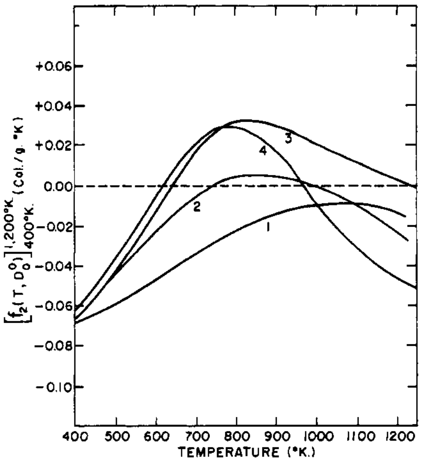

Figure 2. $f_2(T,D_0^0)$ vs. temperature

Curve	D_0^0 Cal./G. Mole Na_2
1	−14,000
2	−16,000
3	−16,840
4	−18,000

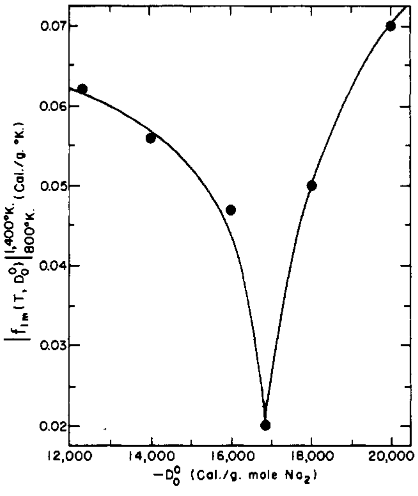

Figure 3. Mean value of $|f_1(T,D_0^0)|$ vs. D_0^0 800 to 1400° K.

Additional evidence supporting this finding is summarized below.

None of the experimental values of D_0^0 reported in the literature was less than −16,836 ± 277. The experiment of Lewis (*20*) from which the value of $D_0^0 = -16{,}836 \pm 277$ was obtained is among the most modern experiments (1931), except for Polanyi's (1932). It was the most direct and was reported with the least error.

A value of $D_0^0 = -16{,}840$ does not lead to any significant discrepancy between the vapor-pressure points in the high-temperature region as represented by Equation 1 and the vapor-pressure points in the low-temperature region as represented by Equation 4. This is evident from the almost equal mean values for $|f_1(T,D_0^0)|$ and $|f_2(T,D_0^0)|$ obtained from $D_0^0 = -16{,}840$. The effect of using other values of D_0^0 on the relative proportions of dimers and monomers is shown in Figure 4, together with the experimental values of Lewis.

The value of $D_0^0 = -18{,}200$ which was arrived at by the thermodynamic analysis of Thomson and Garelis (*34*) leads not only to inconsistent results according to our criterion but also to inconsistency between the high temperature and the low temperature vapor-pressure data, even according to the criterion of the authors themselves. The value of $D_0^0 = -16{,}840$ cal./gram mole Na_2 is used in our calculation of the thermodynamic properties in the vapor region.

ESTIMATION OF CRITICAL TEMPERATURE

The few attempts made by some authors to estimate the critical point of sodium led to widely different results. This situation called for a critical review of the correlations used for the prediction of the critical point, and particularly those aiming at predicting the critical temperature. This work consisted of using the correlations available in the literature together with new and indirect methods devised by Makansi for prediction of the critical temperature of sodium. These methods were then screened on the basis of theoretical aspects or their ability to predict the critical temperature of another metal, such as mercury, which has a high and known critical point. The most probable estimate for the critical point was then obtained from the accepted correlations.

The validity of the methods used for the prediction of the critical temperature of sodium was judged on the following basis:

The critical temperature of sodium is definitely above $T = 1408.3°$ K., because the experimental measurements of the vapor pressure of sodium extended up to this temperature without reaching a one-phase region.

Any empirical equation which is based on a direct relation between the critical temperature and the normal boiling point alone is obviously not suitable for prediction, because the normal boiling point is not a fundamental property nor does atmospheric pressure have any special significance.

In Table I are presented the values of the estimated T_c for sodium and mercury as obtained by methods other than those based on the normal boiling point alone. Each method uses a different physical property, either directly or by solving the equation relating that property with temperature at two different temperatures.

The data of Table I can be treated in two ways:

1. If one accepts the criterion that the method which predicts the critical temperature of mercury most accurately

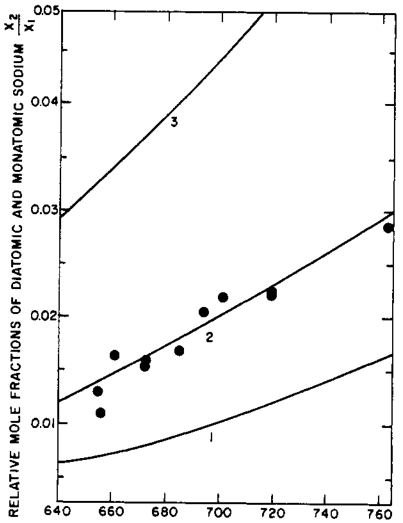

Figure 4. Relative proportions of dimer and monomer sodium

Curve	D_0^0, Cal./G. Mole Na_2
1	−16,000
2	−16,480
3	−18,000
●	Experimental points of Lewis

is the best for predicting the critical temperature of sodium, Table I shows that Watson's method is the one to use. This method yields:

$$(T_c)_{\text{Na}} = 2580^\circ\text{ K.}$$

with an error of 360° K. based on the assumption that this method involves the same relative error in both cases.

2. The estimated values of the critical temperature obtained by the various methods can be directly averaged without weighing for more or less unknown accuracy of each method and of the physical property values used therein. This yields:

$$(T_c)_{\text{Na}}\text{ (av.)} = 2566^\circ\text{ K.}$$

with a standard deviation of ±410° K. and a maximum deviation of −816° K.

There is good agreement between the results obtained by these methods of treating the data of Table I. As a working basis the critical temperature of sodium is taken to be the arithmetic average of the above two values:

$$(T_c)_{\text{Na}} = 2570^\circ \pm 410^\circ\text{ K.}$$

ESTIMATION OF CRITICAL PRESSURE AND CRITICAL VOLUME

Assuming Equation 1 for the vapor pressure of sodium can be extrapolated to the critical temperature:

$$\log P_c = \frac{-5220}{T_c} + 4.521 \qquad (46)$$

Then, by substituting 2570 for T_c, we get:

$$P_c = 300\text{ atm.}$$

Using the Guggenheim equation (*10*) for the critical constants:

$$\frac{P_c\, V_v}{R\, T_c} = 0.29 \qquad (47)$$

and substituting for P_c and T_c, we get:

$$V_c = 200\text{ cc./gram mole}$$

To convert the molecular volume into a weight basis, the data of Table II were extrapolated graphically to obtain the

Table I. Estimation of Critical Temperatures of Sodium and Mercury by Methods Based on Properties Other than Normal Boiling Point

Author	Equation	Basic Property	T_c, ° K.	
			Na	Hg[a]
Watson (*39*)	$T_c = \frac{T_e}{0.283(M/D_b)^{0.18}}$	T_e. Temp. at which vapor has molal volume of 22.4 liters	2580	1490
Guggenheim (*10*)	$L/R = 5.21\ T_c$	L. Latent heat of vaporization	2450	1420
Sugden (*33*)	$\gamma = \gamma_o(1 - T_r)^{6/5}$	γ. Surface tension	2740	3000
Gordon (*9*)	$\left(\frac{\text{d} \log P}{\text{d} \log P'}\right)_{T_r} = \frac{L}{L'} \times \frac{T_{c_f}}{T_c} = K$	Straight-line relation between $(\log P)_{Na}$ and $(\log P)_{Hg}$ at same T_r	2065	2730
Katayama (*16*)	$\gamma(M/D - \text{d})^{2/3} = K(T_c - T)$	γ. Surface tension and molal liquid volume	3170	3400
Bauer (*1*)	$\frac{V_T}{V_f} - 1 = 3.36\left[1 - \left(\frac{T_c - T}{T_c - T_f}\right)^{0.1}\right]$	V_T. Molal liquid volume at T - V_f. Molal liquid volume at triple point	1750	2730
London (*21*)	$\left[\frac{(T_c)^3}{(P_c)^2}\right]_{Na} = K(a \times b)$ and $\log P_c = \frac{-5220}{T_c} + 4.521$	a and b. Constants of van der Waals equation obtained from theory of molecular forces	3210	. . .

[a] The experimental T_c of mercury (2) is $T_c = 1733 \pm 20^\circ$ K.

Table II. Thermodynamic Properties of Sodium at Saturated Pressures

(Basis. $h = 0$ and $s = 0$ for solid sodium at 0° C.)

P, Atm. Abs.	T, ° K.	x_2 Wt. Fract. of Na_2 in Vapor	v_g(Sat.), Cc./G.	h_f(Sat.), Cal./G.	h_{fg}(Sat.), Cal./G.	h_g(Sat.), Cal./G.	s_f(Sat.), Cal./G./° K.	s_{fg}(Sat.), Cal./G./° K.	s_g(Sat.), Cal./G./° K.
10^{-8}	426.79	0.0020	1521×10^8	76.37	1088.2	1164.5	0.21100	2.5497	2.7607
10^{-6}	505.81	0.0050	1800×10^6	103.49	1083.2	1186.7	0.26549	2.1415	2.4070
10^{-5}	557.54	0.0088	1981×10^5	121.24	1078.9	1200.2	0.29615	1.9352	2.2314
10^{-4}	621.32	0.0155	2199×10^4	143.13	1072.6	1215.7	0.32978	1.7263	2.0561
10^{-3}	701.75	0.0322	2464×10^3	170.74	1060.1	1230.8	0.36705	1.5106	1.8776
10^{-2}	806.46	0.0702	2777×10^2	206.67	1035.3	1242.0	0.40909	1.2838	1.6929
0.05	896.60	0.1080	6053×10	237.61	1011.3	1248.9	0.44088	1.1279	1.5688
0.1	945.48	0.1260	3161×10	254.39	999.7	1254.1	0.45680	1.0573	1.5141
0.3	1034.89	0.1560	1135×10	285.08	980.1	1265.2	0.48396	0.9470	1.4309
0.5	1082.54	0.1725	7059	301.44	969.5	1270.9	0.49758	0.8955	1.3931
1.0	1154.61	0.1960	3716	326.20	954.2	1280.4	0.51724	0.8264	1.3437
3.0	1290.80	0.2362	1354	373.05	927.7	1300.8	0.55194	0.7187	1.2707
5.0	1369.36	0.2580	851.2	400.14	913.3	1313.4	0.57085	0.6669	1.2378
10.0	1482.53	0.2870	453.1	439.29	893.9	1333.2	0.59707	0.6029	1.2000
15.0	1560.54	0.3040	314.8	466.41	882.2	1348.6	0.61462	0.5653	1.1799
30.0	1714.85	0.3340	169.9	520.49	861.0	1381.5	0.64853	0.5021	1.1506
50.0	1856.33	0.3590	108.7	570.76	843.1	1413.9	0.67914	0.4543	1.1334

weight fraction of sodium dimer x_2 at the critical temperature $T = 2570°$ K. and hence the average molecular weight, M_c, at the critical point, yielding $x_2 = 0.44$ and $M = 33.1$. Consequently:

$$V_c = \frac{200}{33.1} = 6.07 \text{ cc./g.}$$

CALCULATION OF THERMODYNAMIC PROPERTIES OF SODIUM

Basis of Calculation and Units. The thermodynamic calculation described below is based on one unit weight of sodium. For the vapor, this is one unit weight of the equilibrium mixture of the monatomic sodium, Na_1, and the diatomic sodium, Na_2. The numerical values of the enthalpy and entropy are computed in reference to the enthalpy and entropy of the saturated solid sodium at the ice point (t = 0° C. or 32° F.). Tables II and III were prepared in the metric system, while the Mollier diagram (Figure 5) was prepared in the English system.

Fundamental Data and Assumptions. The following basic data and assumptions were used in computations of the tables of thermodynamic properties.

1. Vapor-pressure equations: Equation 4 of Ditchburn and Gilmour for the low pressure region up to 0.05 atm. abs. and Equation 1 for the high pressure region, above 0.05 atm. abs.

2. The values of Douglas and others (*5*) for the triple point of sodium—97.82° C.

3. The equations of Ginnings, Douglas, and Ball (*8*) for the thermodynamic properties of the condensed phase over the entire range—namely, the enthalpy of the saturated solid, the enthalpy of the saturated liquid, the saturated specific heat, C_s, of the solid, the saturated specific heat, C_s, of the liquid, the entropy of the saturated solid, and the entropy of the saturated liquid. These equations are summarized below:

$$H_t(\text{solid}) - H_0(\text{solid}) = 1.9926t + (3.247)(10^{-4})t^2 + (3.510)(10^{-6})t^3 \; (0 \text{ to } 97.80° \text{ C.}) \tag{48}$$

$$H_t(\text{liquid}) - H_0(\text{solid}) = 98.973 + 1.436744t - 2.90244\,(10^{-4})t^2 + (1.54097)(10^{-7})t^3 + 24{,}000\, e^{-\frac{13{,}600}{t+273}} \; (97.80° \text{ to } 900° \text{ C.}) \tag{49}$$

$$C_s(\text{solid}) = 1.19926 + (6.494)(10^{-4})t + (1.0531)(10^{-5})t^2 \; (0° \text{ to } 97.80° \text{ C.}) \tag{50}$$

$$C_s(\text{liquid}) = 1.43674 - (5.8049)(10^{-4})t + (4.6229)(10^{-7})t^2 \; (97.85° \text{ to } 900° \text{ C.}) \tag{51}$$

$$S_T(\text{solid}) - S_{273.16° \text{ K.}}(\text{solid}) = 4.16241 \log_{10} T - (5.1036)(10^{-3})T + (5.2656)(10^{-6})T^2 - 9.14016 \; (0° \text{ to } 97.8° \text{ C.}) \tag{52}$$

$$S_T(\text{liquid}) - S_{273.16° \text{ K.}}(\text{solid}) = 3.75276 \log_{10} T - (8.3303)(10^{-4})T + (2.3112)(10^{-7})T^2 - 8.67398 \; (97.8° \text{ to } 900° \text{ C.}) \tag{53}$$

4. The assumption that ideal gas laws apply to the individual species of the monomer and the dimer in the vapor phase over the entire range.

5. The assumption that liquid volume is negligible compared to the vapor volume over the entire range of calculation.

6. The data of Inatomi and Benton (*14*) on the specific heats at constant pressure of the monatomic and diatomic sodium vapor and on the enthalpy and free energy functions of these two species, as ideal gases at their standard states of 1-atm. pressure.

7. The heat of dimerization, D_0^0, at absolute zero temperature for the dimerization reaction $2\text{ Na} \rightleftarrows Na_2$ is equal to −16,840 cal./gram mole Na_2 as described previously.

Saturation Pressure and Temperature of Liquid Sodium. Temperatures corresponding to pressure below 0.01 atm. abs. were computed from Equation 4; temperatures corresponding to pressures above 0.01 atm., from Equation 1. Equation 4 was used beyond its recommended range in the very low pressures, while Equation 1 was extrapolated beyond its upper experimental limits to compute temperatures corresponding to pressures as high as 50 atm. abs.

Enthalpy and Entropy of Saturated Liquid. These properties were computed directly from the following equations:

$$h_f(\text{cal./g.}) = 1/4.1855\,[98.973 + 1.436744\,(T - 273.16) - (2.90244)(10^{-4})(T - 273.16)^2 + 24{,}000\, e^{-13{,}600/T}] \tag{54}$$

and

$$s_f(\text{cal./g.}\,° \text{K.}) = 1/4.1855\,[3.75276 \log_{10} T - (8.3303)(10^{-4})T + (2.3113)(10^{-7})T^2 - 8.67398] \tag{55}$$

which were obtained from Equations 49 and 53, respectively. These equations were also extrapolated to obtain properties beyond their temperature limits.

Weight Fraction of Diatomic Sodium Vapor. This was calculated from Equations 40 and 39 using $D_0^0 = -16{,}840$ cal./gram mole Na_2.

Latent Heat of Vaporization. This property was calculated from the following equation:

$$h_{fg} = (25474.93 - 0.9935T)\,\frac{2 - x_2}{45.994} \tag{56}$$

which was arrived at by a simultaneous solution of Equation 4 of Ditchburn and Gilmour and the simplified form of the Clausius-Clapeyron equation.

Entropy of Vaporization. At any saturation temperature the entropy of vaporization was calculated from the equation:

$$s_{fg} = \left(-0.9935 + \frac{25474.93}{T}\right)\left(\frac{2 - x_2}{45.994}\right) \tag{57}$$

which was obtained by dividing Equation 56 by T according to the definition of entropy.

Thermodynamic Properties of Saturated Sodium Vapor. At any saturation point, the enthalpy of saturated vapor, h_g, was obtained by adding the enthalpy of vaporization, h_{fg}, obtained from Equation 56 to the enthalpy of saturated liquid, h_f, obtained from Equation 54. The entropy of saturated vapor was similarly obtained by adding s_{fg} obtained from Equation 57 to s_f obtained from Equation 55. The specific volume of saturated vapor, v_f, was obtained from Equation 27.

The thermodynamic properties of saturated sodium are presented in Table II.

Specific Heat at Constant Pressure of Superheated Sodium Vapor. This was calculated by Equation 11, using −16,840 cal./gram mole Na_2 for D_0^0.

Enthalpy of Superheated Sodium Vapor. The enthalpy, h_g, in the superheated region was calculated from the specific heat data by means of the following thermodynamic equation:

$$h = h_o + \int_{T_0}^{T} (C_p)_{\text{eff.}}\, dT + \int_{P_0}^{P} \left[v - T \left(\frac{\partial v}{\partial T}\right)_p \right] dp \tag{58}$$

by considering a change along a constant-pressure line and using the enthalpy of saturated vapor as the constant of integration. The values of h_g(sat.) were obtained from Table II. The limited integral was evaluated graphically. By this procedure the enthalpy of superheated sodium vapor was evaluated at temperatures ranging from 426.79° to 2600° K. and pressures from 10^{-8} to 50 atm. abs. (Table III). The temperature intervals in these tables were

Table III. Thermodynamic Properties of Sodium Vapor in the Superheated Region

$P = 10^{-8}$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal./G./° K.	$v \times 10^{-7}$, Cc./G.
426.79[a]	1164.5	2.7607	15,213
450	1169.9	2.7735	
500	1180.9	2.7970	17,840
600	1202.5	2.8361	21,409
700	1224.1	2.8696	24,977
800	1245.7	2.8986	28,545
900	1267.3	2.9240	
1000	1288.9	2.9468	35,682
1100	1310.5	2.9674	
1200	1332.1	2.9862	42,815
1300	1353.8	3.0035	
1400	1375.4	3.0195	49,954
1500	1397.0	3.0344	
1600	1418.6	3.0484	57,091
1700	1440.2	3.0615	
1800	1461.8	3.0738	64,227
1900	1483.4	3.0855	
2000	1505.0	3.0966	71,363
2100	1526.6	3.1071	
2200	1548.2	3.1172	78,499
2300	1569.8	3.1267	
2400	1591.4	3.1359	85,636
2500	1613.0	3.1447	
2600	1634.6	3.1532	92,772

$P = 10^{-6}$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal./G./° K.	$v \times 10^{-5}$, Cc./G.
505.81[a]	1186.7	2.4070	18,003
525	1192.2	2.4176	
550	1198.1	2.4296	
600	1209.4	2.4500	21,405
700	1231.2	2.4810	24,977
800	1252.8	2.5099	28,545
900	1274.4	2.5353	
1000	1296.1	2.5581	35,682
1100	1317.7	2.5787	
1200	1339.3	2.5975	42,818
1300	1360.9	2.6148	
1400	1382.5	2.6308	49,954
1500	1404.1	2.6457	
1600	1425.7	2.6597	57,091
1700	1447.3	2.6728	
1800	1468.9	2.6851	64,227
1900	1490.5	2.6968	
2000	1512.1	2.7079	71,363
2100	1533.7	2.7184	
2200	1555.3	2.7285	78,499
2300	1576.9	2.7380	
2400	1598.5	2.7472	85,636
2500	1620.1	2.7560	
2600	1641.7	2.7645	92,772

$P = 10^{-5}$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal./G./° K.	$v \times 10^{-4}$, Cc./G.
557.54[a]	1200.2	2.2314	19,806
575	1205.6	2.2411	
600	1212.4	2.2528	21,372
650	1224.4	2.2724	
700	1236.4	2.2892	24,972
800	1258.2	2.3184	28,544
900	1279.8	2.3439	
1000	1301.4	2.3667	35,681
1100	1323.0	2.3873	
1200	1344.6	2.4061	42,818
1300	1366.2	2.4234	
1400	1387.8	2.4394	49,954
1500	1409.4	2.4543	
1600	1431.0	2.4682	57,091
1700	1452.6	2.4813	
1800	1474.2	2.4937	64,227
1900	1495.8	2.5054	
2000	1517.4	2.5164	71,363
2100	1549.0	2.5270	
2200	1560.6	2.5370	78,500
2300	1582.2	2.5466	
2400	1603.8	2.5558	85,636
2500	1625.4	2.5646	
2600	1647.0	2.5731	92,772

$P = 10^{-4}$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal./G./° K.	$v \times 10^{-3}$, Cc./G.
621.32[a]	1215.7	2.0561	21,995
635	1220.7	2.0641	
650	1225.5	2.0716	
675	1232.7	2.0824	
700	1239.2	2.0919	24,925
750	1251.3	2.1084	
800	1262.6	2.1230	28,533
900	1284.5	2.1488	
1000	1306.2	2.1716	35,680
1100	1327.8	2.1922	
1200	1349.4	2.2111	42,818
1300	1371.0	2.2283	
1400	1392.6	2.2444	49,954
1500	1414.2	2.2593	
1600	1435.8	2.2732	57,091
1700	1457.4	2.2863	
1800	1479.0	2.2987	64,227
1900	1500.6	2.3103	
2000	1522.2	2.3214	71,363
2100	1543.9	2.3320	
2200	1565.5	2.3420	78,500
2300	1587.1	2.3516	
2400	1608.7	2.3608	85,636
2500	1630.3	2.3690	
2600	1615.9	2.3774	92,772

$P = 10^{-3}$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal./G./° K.	$v \times 10^{-2}$, Cc./G.
701.75[a]	1230.8	1.8776	24,636
725	1240.7	1.8919	
750	1249.1	1.9038	
800	1263.8	1.9228	28,424
850	1276.9	1.9379	
900	1288.9	1.9513	
1000	1311.5	1.9750	35,665
1100	1333.4	1.9958	
1200	1355.2	2.0147	42,813
1300	1376.8	2.0320	
1400	1398.4	2.0480	49,953
1500	1420.0	2.0629	
1600	1441.7	2.0768	57,091
1700	1463.3	2.0899	
1800	1484.9	2.1023	64,227
1900	1506.5	2.1140	
2000	1528.1	2.1250	71,363
2100	1549.7	2.1356	
2200	1517.3	2.1456	78,500
2300	1592.9	2.1552	
2400	1614.5	2.1644	85,636
2500	1636.1	2.1732	
2600	1657.7	2.1817	92,772

$P = 10^{-2}$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal. G./° K.	$v \times 10^{-1}$, Cc./G.
806.46[a]	1242.0	1.6929	27,766
850	1264.6	1.7208	
900	1282.9	1.7421	
950	1298.0	1.7584	
1000	1311.3	1.7721	35,520
1050	1323.7	1.7840	
1100	1335.5	1.7949	
1150	1346.9	1.8044	
1200	1358.1	1.8139	42,774
1300	1380.2	1.8315	
1400	1402.1	1.8477	49,937
1500	1423.8	1.8626	
1600	1445.5	1.8765	57,082
1700	1467.1	1.8896	
1800	1488.7	1.9020	64,222
1900	1510.3	1.9136	
2000	1531.9	1.9247	71,363
2100	1553.6	1.9353	
2200	1575.2	1.9453	78,500
2300	1596.8	1.9549	
2400	1618.4	1.9641	85,636
2500	1640.0	1.9729	
2600	1661.6	1.9814	92,772

$P = 0.05$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal./G./° K.	v, Cc./G.
896.60[a]	1248.9	1.5688	60,529
900	1250.9	1.5714	
950	1280.2	1.6021	
1000	1301.9	1.6248	69,834
1050	1319.8	1.6394	
1100	1335.1	1.6533	
1150	1348.8	1.6653	
1200	1361.4	1.6761	85,448
1250	1373.5	1.6859	
1300	1385.2	1.6950	
1400	1408.0	1.7119	99,736
1500	1430.2	1.7272	
1600	1452.2	1.7414	114,090
1700	1474.0	1.7546	
1800	1495.8	1.7671	128,400
1900	1517.5	1.7788	
2000	1539.2	1.7898	142,670
2100	1560.8	1.8004	
2200	1582.4	1.8104	156,970
2300	1604.1	1,8200	
2400	1625.7	1.8292	171,250
2500	1647.3	1.8380	
2600	1668.9	1.8465	185,530

$P = 0.1$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal./G./° K.	v, Cc./G.
945.48[a]	1245.1	1.5141	31,611
950	1256.1	1.5174	
1000	1287.5	1.5480	34,243
1050	1310.6	1.5711	
1100	1329.2	1.5890	
1150	1345.2	1.6033	
1200	1359.6	1.6154	42,394
1250	1372.9	1.6262	
1300	1385.4	1.6359	
1350	1397.4	1.6450	
1400	1409.1	1.6534	49,794
1500	1431.9	1.6691	
1600	1454.2	1.6835	56,993
1700	1476.3	1.6969	
1800	1498.2	1.7093	64,175
1900	1520.0	1.7211	
2000	1541.7	1.7322	71,328
2100	1563.4	1.7427	
2200	1585.1	1.7528	78,474
2300	1606.8	1.7623	
2400	1628.4	1.7715	85,616
2500	1650.0	1.7804	
2600	1671.7	1.7888	92,756

$P = 0.3$ Atm. Abs.

T, °K.	h, Cal./G.	s, Cal./G./° K.	v, Cc./G.
1034.89[a]	1265.2	1.4309	11,349
1050	1274.9	1.4409	
1100	1307.1	1.4687	
1150	1331.1	1.4927	
1200	1351.2	1.5124	13,872
1250	1368.7	1.5231	
1300	1384.2	1.5388	
1350	1398.4	1.5494	
1400	1411.7	1.5591	16,484
1450	1424.4	1.5680	
1500	1436.6	1.5764	
1600	1460.2	1.5917	18,944
1700	1483.1	1.6056	
1800	1505.5	1.6184	21,357
1900	1527.7	1.6304	
2000	1549.6	1.6416	23,753
2100	1571.5	1.6521	
2200	1593.3	1.6622	26,141
2300	1615.1	1.6717	
2400	1636.8	1.6809	28,533
2500	1658.5	1.6897	
2600	1680.2	1.6982	30,908

Table III. Continued

$P = 0.5$ Atm. Abs.

T, ° K.	h, Cal./G.	s, Cal./ G./° K.	v, Cc./G.
1082.54[a]	1270.9	1.3931	7,059.0
1100	1282.7	1.4039	
1150	1312.1	1.4302	
1200	1336.6	1.4511	8,184.2
1250	1357.9	1.4682	
1300	1375.8	1.4824	
1350	1391.9	1.4947	
1400	1406.8	1.5055	9,826.3
1450	1420.7	1.5153	
1500	1433.9	1.5242	
1550	1446.6	1.5324	
1600	1458.8	1.5402	1,133.2
1700	1482.5	1.5546	
1800	1505.4	1.5677	1,279.4
1900	1528.0	1.5799	
2000	1550.2	1.5914	1,423.8
2100	1572.3	1.6022	
2200	1594.3	1.6125	1,567.5
2300	1616.1	1.6221	
2400	1638.0	1.6313	1,710.8
2500	1659.7	1.6401	
2600	1681.4	1.6486	1,853.9

$P = 1.0$ Atm. Abs.

T, ° K.	h, Cal./G.	s, Cal./ G./° K.	v, Cc./G.
1154.61[a]	1280.4	1.3437	3,716.1
1200	1309.0	1.3680	3,945.3
1250	1336.3	1.3902	
1300	1359.9	1.4084	
1350	1380.4	1.4237	
1400	1398.6	1.4368	4,838.6
1450	1415.1	1.4484	
1500	1430.4	1.4587	
1550	1444.8	1.4680	
1600	1458.3	1.4766	5,625.3
1650	1471.3	1.4845	
1700	1483.8	1.4920	
1750	1496.0	1.4990	
1800	1508.0	1.5057	6,371.8
1850	1519.7	1.5122	
1900	1531.3	1.5183	
2000	1554.2	1.5300	7,102.0
2100	1576.7	1.5410	
2200	1599.0	1.5513	7,825.0
2300	1621.1	1.5612	
2400	1643.2	1.5705	8,544.3
2500	1665.1	1.5795	
2600	1686.9	1.5881	9,261.7

$P = 3.0$ Atm. Abs.

T, ° K.	h, Cal./G.	s, Cal./ G./° K.	v, Cc./G.
1290.81[a]	1300.8	1.2707	1,354.0
1300	1306.5	1.2751	
1350	1336.4	1.2970	
1400	1362.5	1.3159	1,532.3
1450	1385.9	1.3323	
1500	1407.0	1.3469	
1550	1426.2	1.3593	
1600	1443.9	1.3706	1,825.9
1650	1460.3	1.3806	
1700	1475.8	1.3897	
1750	1490.5	1.3979	
1800	1504.5	1.4056	2,092.2
1850	1518.0	1.4129	
1900	1531.1	1.4196	
2000	1556.3	1.4324	2,345.4
2100	1580.5	1.4442	
2200	1604.0	1.4551	2.592.1
2300	1627.2	1.4654	
2400	1649.9	1.4751	2,836.3
2500	1672.5	1.4843	
2600	1695.2	1.4932	3,077.0

$P = 5.0$ Atm. Abs.

T, ° K.	h, Cal./G.	s, Cal./ G./° K.	v, Cc./G.
1396.36[a]	1313.4	1.2378	851.16
1400	1331.4	1.2507	883.51
1450	1358.3	1.2697	
1500	1382.7	1.2863	
1550	1405.0	1.3010	
1600	1425.4	1.3140	1,070.3
1650	1444.4	1.3257	
1700	1462.2	1.3356	
1750	1478.8	1.3445	
1800	1494.5	1.3534	1,237.9
1850	1509.4	1.3615	
1900	1523.7	1.3691	
1950	1537.5	1.3761	
2000	1550.9	1.3829	1,394.8
2100	1576.6	1.3954	
2200	1601.4	1.4069	1,545.9
2300	1625.4	1.4175	
2400	1648.9	1.4275	1,694.0
2500	1671.1	1.4369	
2600	1694.9	1.4459	1,850.8

$P = 10$ Atm. Abs.

T, ° K.	h, Cal./G.	s, Cal./ G./° K.	v, Cc./G.
1482.53[a]	1333.2	1.2000	453.08
1500	1343.0	1.2066	
1600	1394.2	1.2397	510.15
1700	1438.4	1.2693	
1800	1477.1	1.2914	600.11
1900	1511.6	1.3100	
2000	1542.9	1.3260	682.82
2100	1571.5	1.3401	
2200	1598.4	1.3528	761.98
2300	1624.4	1.3644	
2400	1649.5	1.3751	838.19
2500	1673.9	1.3850	
2600	1679.8	1.3944	912.84

$P = 15$ Atm. Abs.

T, ° K.	h, Cal./G.	s, Cal./ G./° K.	v, Cc./G.
1560.54[a]	1348.6	1.1799	314.79
1600	1369.4	1.1931	327.61
1700	1417.7	1.2225	
1800	1460.4	1.2470	389.62
1900	1498.5	1.2675	
2000	1532.9	1.2851	447.09
2100	1564.5	1.3005	
2200	1593.9	1.3128	501.28
2300	1621.6	1.3240	
2400	1647.4	1.3353	553.29
2500	1673.6	1.3459	
2600	1698.4	1.3557	603.95

$P = 30$ Atm. Abs.

T, ° K.	h, Cal./G.	s, Cal./ G./° K.	v, Cc./G.
1714.85[a]	1381.5	1.1506	169.90
1800	1422.0	1.1743	183.21
1900	1465.7	1.1979	
2000	1505.5	1.2183	213.39
2100	1542.0	1.2362	
2200	1575.9	1.2502	241.99
2300	1608.3	1.2643	
2400	1637.3	1.2759	269.36
2500	1665.7	1.2875	
2600	1692.4	1.2982	295.64

$P = 50$ Atm. Abs.

T, ° K.	h, Cal./G.	s, Cal./ G./° K.	v, Cc./G.
1856.33[a]	1413.9	1.1334	108.69
1900	1433.6	1.1438	
2000	1476.4	1.1657	122.07
2100	1516.1	1.1851	
2200	1553.1	1.2023	139.76
2300	1587.8	1.2178	
2400	1620.5	1.2317	156.68
2500	1615.5	1.2443	
2600	1681.0	1.2558	173.01

[a] Saturated

selected in such a way that linear interpolation between two successive temperatures can be made without serious error.

Entropy of Superheated Sodium Vapor. The basic equation used in the computation of the entropy of superheated sodium vapor was:

$$s = s_o + \int_{T_o}^{T} (C_p)_{\text{eff.}} \frac{dT}{T} - \int_{P_o}^{P} \left(\frac{\partial v}{\partial T}\right)_p dP \qquad (59)$$

Here again the equation was integrated graphically at constant pressure. The constant of integration, s_0, was also taken to be the entropy of saturated vapor at the pressure along which the integration was carried out. The values of s_g(sat.) at different pressures were obtained from Table II. By this method, the values of the entropy, s_g, appearing in Table III were obtained.

Specific Volume of Superheated Vapor. This was calculated by the ideal gas equation used to compute the specific volume of saturated vapor. The values of v_g appear numerically in Table III and graphically in Figure 6.

CHECKING INTERNAL CONSISTENCY OF THERMODYNAMIC PROPERTIES IN SUPERHEATED REGION

After completion of the computation of a network of the three fundamental thermodynamic properties—the enthalpy, h, the entropy, s, and the specific volume, v—the next step was to check whether the numerical values of these properties (Table III) are self-consistent. This was done by computing the specific volume by two different methods and comparing the results. The first method was direct computation of v_g from Equation 27, which had been used to obtain the values listed in Table III. The second was an indirect method by which the specific volume, v_g, was computed from enthalpy data. The equation which relates the specific volume, v, in one phase to the enthalpy, h, in the same phase (*4*) is:

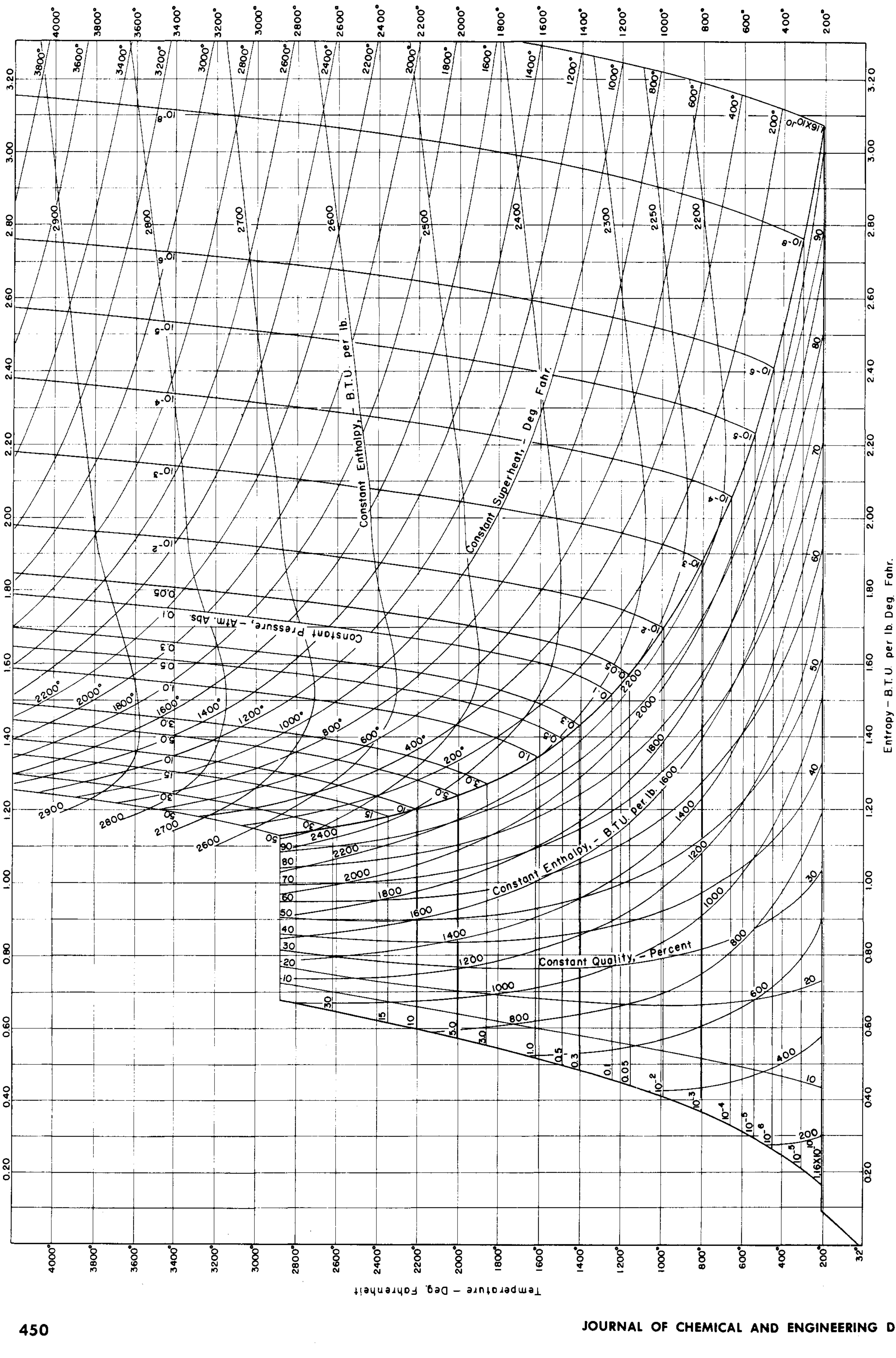

Figure 5. Temperature-entropy chart of thermodynamic properties of sodium

$$v_T = T\left[-\int_{T_0}^{T}\frac{1}{T^2}\left(\frac{\partial h}{\partial P}\right)_T dT + \frac{v_0}{T_0}\right] \qquad (60)$$

Equation 60 was used to compute the specific volume, $(v_g)_T$, of the superheated vapor at temperature T relative to the specific volume, $(v_g)_{T_0}$, of sodium vapor at another temperature, T_0. The values of $(v_g)_{T_0}$ were themselves obtained from Table III. Equation 60 was solved graphically to obtain the values of $(v_g)_T$ at two combinations of temperatures (T_1 = 1600 and T_2 = 1800° K.) and at four pressures (P_1 = 0.3 atm., P_1' = 0.5 atm., P_2 = 3.0 atm., and P_2' = 5.0 atm.). The reference volumes, $(v_0)_1$ and $(v_0)_2$, were obtained from Table III at temperatures $(T_0)_1$ = 1200° K. and $(T_0)_2$ = 1400° K., respectively.

The values of $(v_g)_T$ as calculated from the enthalpy data were then compared with the values obtained from Table III. The difference between the two values was found to be less than 0.4% in all cases. This is a gratifying check on the internal consistency of the thermodynamic network for sodium, in spite of the crude nature of solving Equation 60 graphically.

THERMODYNAMIC DIAGRAM FOR SODIUM

To make a thermodynamic network of sodium most useful to engineers, a $T - S$ diagram was constructed using degrees Fahrenheit, pounds, and B.t.u.'s. The construction of the $T - S$ diagram (Figure 5) was based on the data of Tables II and III. The lines of constant volume were not drawn on this diagram, in order to preserve the clarity of the other lines, but were drawn on a separate diagram (Figure 6).

Because of the uncertainty existing with regard to the correct values of the critical point and because the computation of the thermodynamic properties was based on some simplifying assumptions which cannot be assumed to hold true near the critical point, the saturated portion of the diagram was not extended beyond 1800° K. or 2780° F.

A comparison between the $T - S$ diagram (Figure 5) and the corresponding diagram for steam (*17*) shows that the lines of Figure 5 for sodium exhibit the same general trends as the corresponding lines for the $T - S$ diagram of steam, in all cases except the lines of constant enthalpy in the very high entropy region. In this region the sodium lines tend to become parallel among themselves at high entropies, although not parallel to the constant temperature lines. The constant enthalpy lines for steam tend, on the other hand, to become parallel to the constant temperature lines at high entropies. Theoretically, a behavior similar to the behavior of steam should be expected in the $T - S$ diagram for sodium, because in this region of high entropy the pressure is very low and at very low pressure a gas tends to behave ideally.

One property of an ideal gas is that its enthalpy is a function of temperature only. Hence, the lines of constant enthalpy should tend to become parallel to the constant temperature lines at very low pressures. At very low pressures, say below 10^{-5} atm., and at high temperatures, say above 3000° F., sodium vapor consists practically of monomer only. Hence, the effect of dimerization in causing a deviation from ideal gas laws is negligible and the anomaly in the diagram described above cannot be attributed to dimerization. One reason to which this deviation can be attributed is to assume that the calculated values of the latent heat of vaporization, L or h_{fg}, at low pressures were lower than their actual values. Increasingly higher heat of vaporization at lower pressures would have made the constant enthalpy lines (Figure 5) intersect the lower pressure lines at increasingly lower temperatures. This would bring the constant enthalpy lines more closely parallel to the constant temperature lines. Such correction would not only improve the $T - S$ diagram, but also would do away with another discrepancy encountered in the course of evaluating the heat of dimerization, D_0^0. There, it was also concluded that larger values of the heat of dimerization in the low temperature region would have further improved the agreement between Ditchburn's vapor pressure equation and the spectroscopic data.

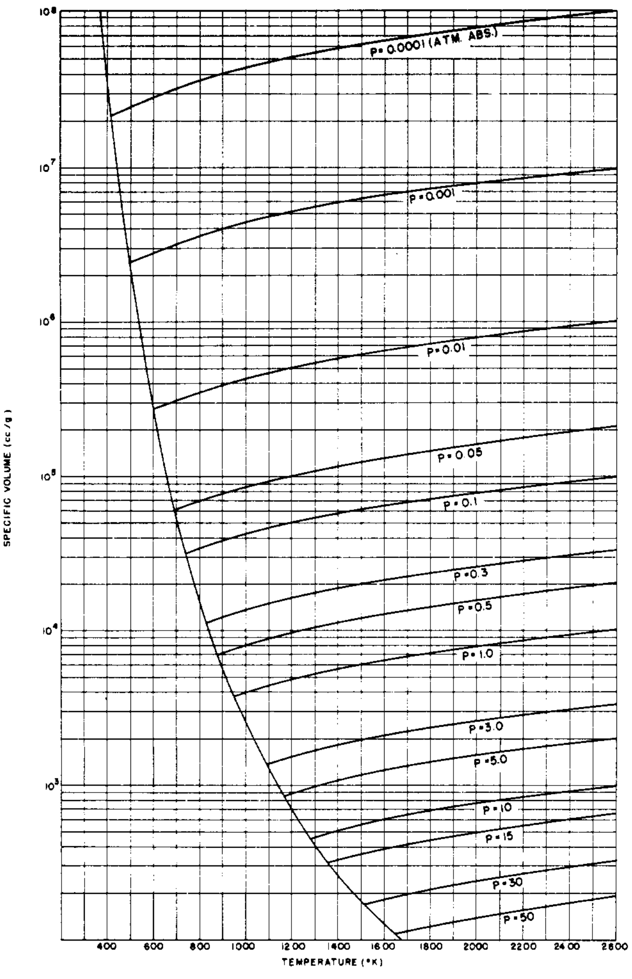

Figure 6. Specific volume of sodium vapor

The deviation from the expected behavior, as discussed above, is small. The largest change in the heat of vaporization required to correct for the above anomaly is only 25 cal. per gram at the triple point. This constitutes an addition of approximately 2.5% of the latent heat of vaporization at the triple point. Since Equation 4, from which the latent heat of vaporization was computed, is accurate only to within ±5% between 450° and 1200° K. and 10% between 400° and 1250° K., the error in the diagram is well within the error limits of the data from which it was obtained.

The above discussion does not materially minimize the usefulness of the diagram, as the deviation is small and occurs at extremely low pressures when the enthalpy data may not be used in practice at all. However, it casts a doubt on the validity of the vapor-pressure data in the literature for the low-pressure region.

ACCURACY AND LIMITATIONS OF THERMODYNAMIC DIAGRAM

The computations of the thermodynamic tables from which the $T - S$ diagram was constructed were based on certain assumptions. Hence, the accuracy of the diagram is no better than the accuracy of the assumptions and the data on which the diagram was based. Because of the uncertainty existing in the vapor-pressure data at very low pressures and because the validity of the assumptions made becomes poor at high pressures, it is concluded that the diagram is most accurate in the middle region between 0.1 and 10 atm. and the uncertainty increases gradually at points further away from this middle region.

It is also concluded that this diagram represents a considerable improvement over the diagram of Inatomi and Parrish (*15*) and, until further and more accurate experimental data become available, is suitable for all normal uses.

NOMENCLATURE

b = numerical constant of Van der Waals equation of state
c = numerical constant of molecular forces
C_p = specific heat at constant pressure
$(C_p)_{\text{eff.}}$ = effective specific heat at constant pressure of equilibrium mixture of monatomic and diatomic sodium vapor
C_s = specific heat of a saturated phase = heat effect resulting from a change along the saturation line
D = liquid density
D = heat of dimerization for the reaction: $2Na_1 \rightleftarrows Na_2$
d = vapor density (Katayama equation, Table I)
E = internal energy
e = electron; also base of natural logarithm
F = free energy
H = enthalpy per mole and sometimes per unit mass
h = enthalpy per unit mass
K = equilibrium constant
K_a; equilibrium constant in terms of activities
K_p; equilibrium constant in terms of partial pressures
L = latent heat of vaporization
M = molecular weight
N = number of molecules in unit mass
P = pressure
Q = quantity of heat
R = gas constant
S = entropy per mole and sometimes per unit mass
s = entropy of unit mass
T = thermodynamic or absolute temperature
t = temperature, ° C. or ° F.
V = molal volume
v = specific volume
X = mole fraction in general
x = weight fraction

Greek Letters and Other Symbols

γ = surface tension
Δ = finite difference; residual quantity
θ = reduced temperature defined by: $\theta = \dfrac{T - T_f}{T_c - T_f}$

Subscripts

b = boiling point
c = critical state, or chemical change
eff. = effective
f = fluid state, or triple point
fg = change due to vaporization
g = gaseous or vapor state
m = mean value
p = constant pressure change
r = reduced quantities—e.g., $T_r = T/T_c$
s = saturation conditions
t or T = constant temperature change
v = constant volume change
Na = sodium
1 = monatomic sodium, Na_1
2 = diatomic sodium, Na_2
1 and 2 = sometimes refer to different states or different points between which a certain change takes place

Superscripts

^{0} = standard state of low pressure where gases are ideal
$'$ = liquid phase, sometimes used to distinguish two related quantities
$''$ = gaseous phase

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