

smaller than those given by Rogovaya. Some of these latter comparisons indicated that the equation of state predicted density values between those of Onnes and those of Rogovaya.

A final comparison was made between the compilation of the National Bureau of Standards Circular 564 by Hilsenrath et al. [27] and the values predicted by the equation of state. A total of 338 points was used for this comparison. The points were selected so as to well represent the entire range of data compiled by Hilsenrath et al. The temperature

range included temperatures from 100 K to 5000 K with pressures ranging from 0.01 to 100 atm. Except for one region, this comparison showed a mean density deviation of 0.08 percent. The one region where the deviations were greatest was at the high pressure-low temperature end of the tables compiled by Hilsenrath et al. (pressures near 100 atm for temperatures near 180 K). For this region, the values of Hilsenrath et al. were obtained essentially by extrapolation of existing experimental data, which may account for the larger deviations.

9. Temperature Scale Conversions

Wherever appropriate, corrections were made to convert the temperatures reported by the investigator to a consistent thermodynamic Kelvin temperature scale based on an ice point of 273.15 K. In some cases the specific temperature scale used by the experimenter was not clearly specified. In these cases, the literature was searched for other papers or information from the same laboratories, and conversions were made from these determinations. Different methods for correcting temperatures are possible, but the following were deemed most appropriate.

Conversions for the data of Michels, Levelt, and de Graaff [1] and Michels, Wijker, and Wijker [6] from the van der Waals Laboratory were made by first correcting the temperatures from the van der Waals thermometer to the International Temperature Scale and then correcting to the thermodynamic temperature scale. The net correction was less than 0.02 °C which is within the precision of the data. The corrections from the van der Waals thermometer to the International Temperature Scale were made by using the information furnished by J. M. H. Levelt-Sengers [28].

The data of Onnes and Crommelin [26], based upon an ice point of 273.09 K, were converted to the International Temperature Scale by

$$T = (t_c + 273.09) \frac{273.15}{273.09}$$

where t_c is a reported centigrade temperature.

The data of Clark et al. [14], based upon an ice point of 273.16 K, were converted to the International Temperature Scale by

$$T = (t_c + 273.16) \frac{273.15}{273.16}$$

Corrections from the International Temperature Scale to the thermodynamic temperature scale were made by using the tabular information furnished by C. R. Barber [29]. The tabular information by Barber is shown in table 9.

TABLE 9. Conversion from international to thermodynamic temperatures

Temperature, °C	$T_{th} - T_{int}$
-10	0.005
-20	.011
-30	.017
-40	.024
-50	.0295
-60	.034
-70	.0365
-80	.036
-90	.032
-100	.0245
-110	.015
-120	.0025
-130	-.010
-140	-.020
-150	-.024
-183	0

10. Derived Thermodynamic Properties

The calculation of entropy, enthalpy, and internal energy was performed by using the equation of state (40), the zero pressure (ideal gas) and specific heat (c_p°), and the vapor pressure equation (14). The relationships for calculating these derived properties have been described by Gosman [22], and Hust and Gosman [30], and are presented below.

The entropy of the gaseous phase, as well as the saturated vapor, was expressed as

$$S = S_{T_0}^\circ - R \ln \left(\frac{\rho RT}{P_0} \right) + \int_{T_0}^T \left[\frac{R}{\rho} - \frac{1}{\rho^2} \left(\frac{\partial P}{\partial T} \right)_\rho \right] d\rho + \int_{T_0}^T c_p^\circ \frac{dT}{T} \quad (49)$$

For eq (49) the reference entropy, $S_{T_0}^\circ = 3.23367$ J/g-K, for the ideal gas at $P_0 = 1$ atm, and the normal boiling point temperature at $T_0 = 87.28$ K was selected from Hilsenrath et al. [27]. The ideal gas specific heat, $c_p^\circ = \frac{5}{2} R = 0.520320$ J/g-K, was also taken from Hilsenrath et al.

The enthalpy of the gaseous phase was expressed as

$$H = H_{T_0}^\circ + \int_{T_0}^T \left[\frac{P}{\rho^2} - \frac{T}{\rho^2} \left(\frac{\partial P}{\partial T} \right)_\rho \right] d\rho + \frac{P}{\rho} - RT + \int_{T_0}^T c_p^\circ dT. \quad (50)$$

Compilations often do not tabulate $H_{T_0}^\circ$. Many times these compilations tabulate $H_{T_0}^\circ - U_0^\circ$, where U_0° is the ground-state energy. For purposes of consistency with these compilations, a value of $H_{T_0}^\circ - U_0^\circ = 45.4119$ J/g (for the ideal gas at 87.28 K) was selected from Hilsenrath [27]. Then, in order to obtain $H_{T_0}^\circ$ for eq (50), a value of $U_0^\circ = 192.5197$ J/g

was assigned to the ground-state energy. This value of U_0° was selected so that the enthalpy of the saturated liquid at 1 atm pressure agrees with the value given by Din [31].

The equation of state (40) was then substituted into eqs (49) and (50). Upon integration, the resulting expressions are

$$\begin{aligned}
 S = S_{T_0}^\circ - R \ln \left(\frac{\rho RT}{P_0} \right) + \int_{T_0}^T \frac{c_p^\circ}{T} dT \\
 + \rho \left(-n_1 + \frac{n_3}{T^2} + \frac{2n_4}{T^3} + \frac{4n_5}{T^5} \right) - \rho^2 \left(\frac{n_6}{2} \right) - \rho^3 \left(\frac{n_8}{3} \right) \\
 - \exp(-n_{16}\rho^2) \left(\frac{2n_9}{T^3} + \frac{3n_{10}}{T^4} + \frac{4n_{11}}{T^5} \right) / 2n_{16} \\
 - \exp(-n_{16}\rho^2) \left(\frac{\rho^2}{2n_{16}} + \frac{1}{2n_{16}^2} \right) \left(\frac{2n_{12}}{T^3} + \frac{3n_{13}}{T^4} + \frac{4n_{14}}{T^5} \right) \\
 + \left(\frac{2n_9}{T^3} + \frac{3n_{10}}{T^4} + \frac{4n_{11}}{T^5} \right) / 2n_{16} \\
 + \left(\frac{2n_{12}}{T^3} + \frac{3n_{13}}{T^4} + \frac{4n_{14}}{T^5} \right) / 2n_{16}^2, \quad (51)
 \end{aligned}$$

and

$$\begin{aligned}
 H = H_{T_0}^\circ + \frac{P}{\rho} - RT + \int_{T_0}^T c_p^\circ dT + \rho \left(n_2 + \frac{2n_3}{T} + \frac{3n_4}{T^2} + \frac{5n_5}{T^4} \right) \\
 + \rho^2 \left(\frac{n_7}{2} \right) - \frac{1}{2n_{16}} \left(\frac{3n_9}{T^2} + \frac{4n_{10}}{T^3} + \frac{5n_{11}}{T^4} \right) \exp(-n_{16}\rho^2) \\
 - \left(\frac{\rho^2}{2n_{16}} + \frac{1}{2n_{16}^2} \right) \left(\frac{3n_{12}}{T^2} + \frac{4n_{13}}{T^3} + \frac{5n_{14}}{T^4} \right) \exp(-n_{16}\rho^2) \\
 + \rho^5 \left(\frac{n_{15}}{5} \right) + \frac{1}{2n_{16}} \left(\frac{3n_9}{T^2} + \frac{4n_{10}}{T^3} + \frac{5n_{11}}{T^4} \right) \\
 + \frac{1}{2n_{16}^2} \left(\frac{3n_{12}}{T^2} + \frac{4n_{13}}{T^3} + \frac{5n_{14}}{T^4} \right). \quad (52)
 \end{aligned}$$

The internal energy was obtained from

$$U = H - P/\rho. \quad (53)$$

The method of calculation proceeded as follows:

a. The properties of the gaseous phase and saturated vapor were calculated with the use of eqs (51), (52), and (53).

b. The volume of vaporization ($V^g - V^l$) was calculated with the use of the equation of state (40) and the vapor pressure equation (14).

c. The slope of the vapor pressure curve dP/dT was obtained from eq. (14).

d. The entropy and enthalpy changes due to vaporization were calculated with

$$\frac{dP}{dT} = \frac{S^g - S^l}{V^g - V^l}$$

and

$$H^g - H^l = T(S^g - S^l).$$