# Reduced Density Correlation for Hydrogen: Liquid and Gaseous States

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**The available experimental density data for hydrogen have been compiled to produce a reduced density correlation for the liquid and gaseous states. This investigation has utilized fifty-seven sources of data, extending from the early studies of Amagat (1880) to the recent contributions of Johnston, Keller, and Friedman (1954).**

**Based on the concept of a reduced density, a correlation for hydrogen has been developed ranging in temperature from the melting point (14°K.) to 3,300°K. and in pressure as high as 2,550 atm. This correlation provides continuity between the liquid and gaseous phases; whereas existing equations of state fail to describe the experimental behavior in the transitional region, particularly near the critical point.**

**Four hundred and eighty-five experimental points covering the entire region were checked to establish the reliability of this correlation, which reproduced the experimental data to within 0.49%.**

Present technological practices use generalized reduced-state correlations for the estimation of thermodynamic and transport properties of substances. The validity of this approach has proved satisfactory in the correlation of densities (*49*), viscosities (*71*), thermal conductivities (*64, 66*), and diffusion coefficients (*27*); more intensive investigations indicate that helium and hydrogen do not conform to this generalized pattern. Nelson and Obert (*59*) also recognize this inconsistency and suggest the use of a quantum parameter for these light gases.

To correlate the properties of hydrogen and helium one proposal considers adjustment of their critical constants. Newton (*60*) presents a generalized activity-coefficient chart based on an empirical correction quantity of 8 added to both the critical temperature and critical pressure of hydrogen, helium, and neon. Dodge (*26*) utilizes this concept to correlate compressibility factors; Morgen and Childs (*57*) show that this concept is valid in limited ranges of temperature and pressure. Basing their studies on hydrogen PVT data, Maslan and Littman (*52*) construct a compressibility chart. Data for the inert gases are fitted to this chart by the application of additive corrections to the critical temperature and pressure of argon, neon, and helium.

In viscosity studies Brebach and Thodos (*15*) present a reduced-state correlation for diatomic gases. To describe properly the behavior of hydrogen with this correlation it was necessary to adjust progressively the critical temperature and pressure.

Alternatively equations of state have been used to predict generalized behavior. While such equations are of a generalized form, the constants involved and their use have a specific value for each substance. Beattie and Bridgeman (*13*) point out that simple equations of state derived from theoretical considerations are inaccurate for a wide range of temperature and pressure. Furthermore empirical expansion type of equations require a large number of terms for use over a large range; hence they are inconvenient for use in thermodynamic calculations.

Owing to the anomalous behavior of hydrogen and helium, specific reduced-state correlations are recommended for the estimation of their physical properties. The present investigation concerns a comprehensive literature survey of hydrogen density data and the construction of a reduced-state correlation.

## EXPERIMENTAL BACKGROUND

To obtain sufficient experimental data for the development of the density correlation, a comprehensive literature search has been conducted. Extending from the early work of Amagat (*1 to 5*) to the recent contributions of Johnston, Keller, and Friedman (*33*), fifty-seven sources of experimental density data have been utilized in this study. The data cover the range between 14° and 773°K. and pressures as high as 12,580 atm. This range not only includes the gas phase but also extends into the liquid region. Considerable duplication was found to exist at temperature levels from 200° to 450°K. In contrast to this situation experimental data above 773°K. were nonexistent.

Despite the fact that Amagat (*2*) initiated measurements as early as 1880, his work is consistent with data reported later by other investigators. Between the period of 1901 to 1928 considerable experimental work was reported by investigators at the Physical Laboratory of the University of Leiden. This group, headed primarily by Kamerlingh Onnes, produced reliable density data extending from the saturated envelope to the gaseous state. During this period Holborn and Otto reported density data for the gaseous state only, primarily between 65° and 473°K. The experimental data of Bridgman (*17, 18*) extend up to 12,580 atm. but are limited to temperatures of 303° and 338°K.

The experimental findings of Bartlett *et al.* (*8, 9, 10*), as well as those of Deming and Shupe (*24*), permit the extension of these studies to 773°K. The recent contributions of Johnston *et al.* (*33, 34*) represent a comprehensive coverage of temperature and pressure. These investigators have produced consistent data ranging from the boiling point through the critical point and well into the gaseous region. Much of the foregoing data have been compiled by Woolley, Scott, and Brickwedde (*83*) in 1948. Their smoothed data are reported in tabular form.

## DEVELOPMENT OF REDUCED-STATE CORRELATION

A reduced-state correlation of density with temperature and pressure requires accurate values for the temperature, pressure, and density at the critical point. For hydrogen the critical values reported by Kobe and Lynn (*48*) have been accepted; these are $T_c$ = 33.3°K., $P_c$ = 12.8 atm., and $\rho_c$ = 0.0310 g./cc.

The majority of experimental data upon which this correlation has been based are not reported in terms of absolute densities. Rather, experimental densities are presented in terms of Amagat units and Amagat densities, which are values relative to those at standard conditions. The conversion of these values for hydrogen to absolute units, grams per cubic centimeter, has been accomplished by the use of $M$ = 2.016 g./g.-mole and $V_0$ = 22,428 cc./g.-mole at the standard conditions of 0°C. and 1 atm. With these constants the absolute density for hydrogen becomes

$$\rho = 8.9888 \times 10^{-5} d_A$$

$$= 8.9888 \times 10^{-5} \frac{P}{\text{A.U.}} \qquad (1)$$

Figure 1 presents a density correlation for hydrogen in which reduced density is a function of reduced temperature and reduced pressure. This correlation presents values resulting from the work of the fifty-seven investigators indicated in this figure. The data are customarily reported isothermally under varying pressures. Hence it was necessary to prepare a cross plot for several of these references. This procedure involved plotting the experimental isotherms on log-log paper with reduced density and reduced pressure as the coordinates. From these cross plots the experimental density correlation was developed by plotting the isothermal data at the pressures indicated in Figure 1.

The saturated envelope was established from the data of Kamerlingh Onnes, Crommelin, and Cath (*40*) and Mathias, Crommelin, and Kamerlingh Onnes (*53*). Additional data substantiating and extending this curve to the melting point were obtained from other references (*16*, *25*, *69*, 72, *75*, *76*, *77*, *82*). The intersections of the isobars and saturated vapor curve were located from the vapor-pressure data of Kamerlingh Onnes and Keesom (*45*), Cath and Kamerlingh Onnes (19), Keesom, Bijl, and van der Horst (*47*), and White, Friedman, and Johnston (*78*).

At pressures above $P_R$ = 15 and temperatures below $T_R$ = 6.0 the only data reported are those of David and Hamann (*22*). These data enable the interpolation over the region of $T_R$ = 2.4 to $T_R$ = 6.0 and $P_R$ = 15 to $P_R$ = 100.

As already pointed out, the experimental data are limited to temperatures of less than 773°K. The extension of this correlation to higher temperatures was accomplished through the application of a compressibility-factor chart. Values in the high-temperature region of the Nelson-Obert chart (*58*) were plotted against the reduced temperature for different reduced-pressure parameters. Since in the limit at high reduced temperatures these isobars converge to $z$ = 1.00, the relationships of this cross plot were readily extrapolated, and the extrapolated values produced linear relationships at high temperatures on the Nelson-Obert chart. By means of these linear compressibility-factor relationships

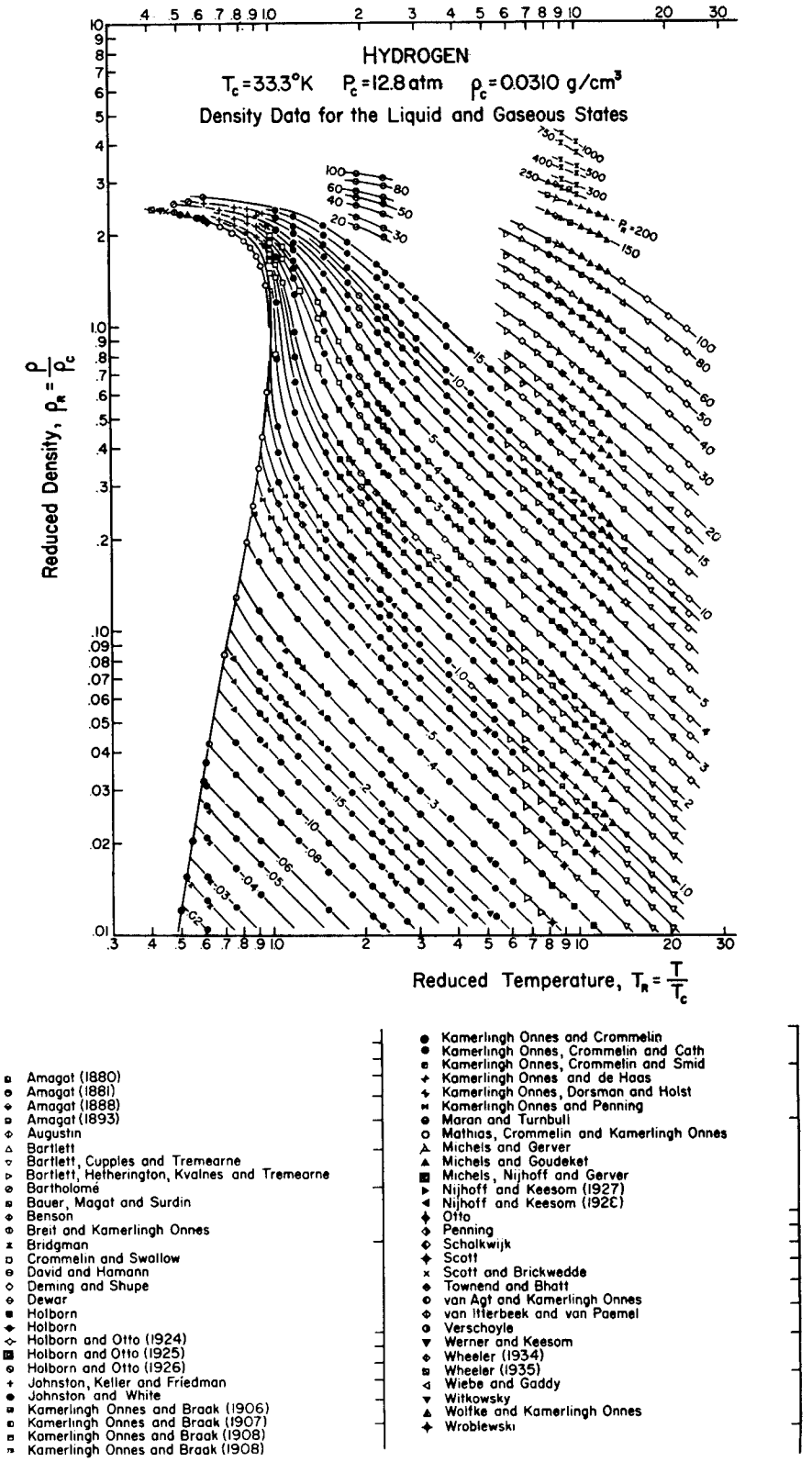


**Fig. 1. Correlation of experimental density data for hydrogen.**

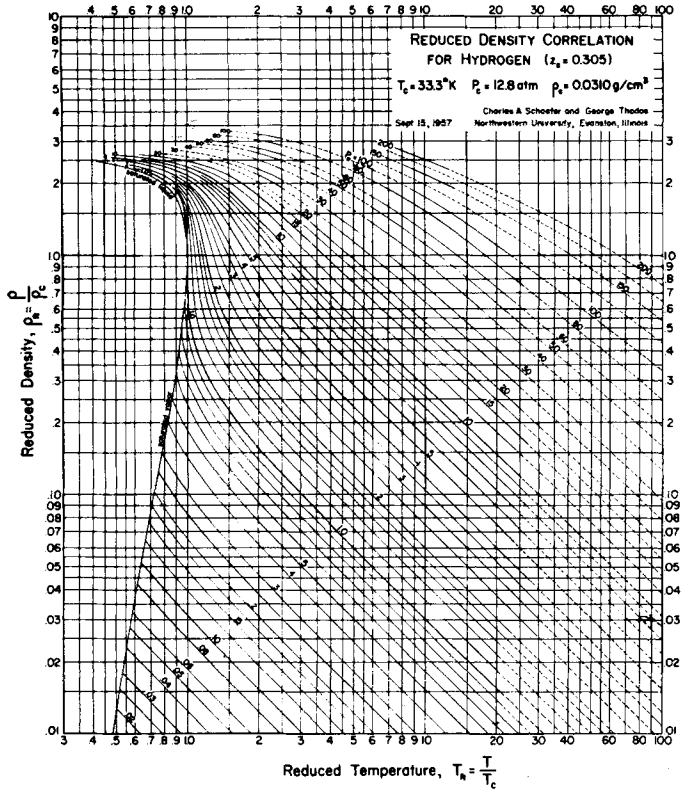


**Fig. 2. Reduced-density correlation for hydrogen (logarithmic coordinates).**

and the experimental densities at the highest reported temperatures, the isobars of Figure 1 were extended through use of the following equation:

$$\frac{\rho_R}{\rho_{R_1}} = \frac{z_1}{z}\frac{P_R}{P_{R_1}}\frac{T_{R_1}}{T_R} \qquad (2)$$

For isobaric conditions, $P_R = P_{R_1}$, Equation (2) becomes

$$\rho_R = \frac{z_1}{z}\frac{T_{R_1}}{T_R}\rho_{R_1} \qquad (3)$$

Following this approach, the authors calculated reduced densities up to temperatures of $T_R = 100$ and pressures of $P_R = 200$ as extensions of the experimentally established isobars.

Bridgman's data (*17, 18*) appear to be consistent with those of experimenters at lower pressures. Owing to the limited temperature range of his investigations, however, isobars through his data could not be reliably extended.

Figure 2* presents the final reduced density correlation based on 2,500 experimental density values. The solid lines represent regions covered by experimental points; whereas the dashed lines represent the regions involving the extensions already discussed.

The correlation presented in Figure 2 permits the rapid determination of hydrogen densities over extended conditions of temperature and pressure. However the low-temperature liquid region is not readily interpreted, because of the inherent compact nature of reduced-density correlations plotted on logarithmic coordinates. A more expedient representation of the low-temperature liquid region is realized on rectilinear coordinates as presented in Figure 3. As before, the solid lines represent regions covered by experimental points; whereas the dashed lines represent extensions of data. As already pointed out, the use of rectilinear coordinates limits the extent of the temperature range. The correlation presented in Figure 3 permits the rapid determination of hydrogen densities for the liquid- and dense-phase regions on an expanded scale; Figure 2 shows this region in a compact manner.

## DISCUSSION OF RESULTS

Since the reduced-state correlation of density with temperature and pressure (Figure 2) is based on experimental data, its reliability as a means of determining accurate density values depends upon two factors.

First is the accuracy of the experimental results as reported by the various investigators. The data (*11, 44, 51, 85*) which were obviously out of line from the general trend of the experimental points were eliminated. Otherwise no discrimination was made in preparing this correlation.

The second factor is the reliability of the correlation to reproduce values consistent with the ones determined experimentally. To determine its reliability a representative sampling of data was taken from each reference source presented in Figure 1. Four hundred and eighty-five values were read from the chart at varying temperatures and pressures so as to cover the entire range indicated by solid lines. The correlation of Figure 2 produced agreement to within 0.49% of the experimental data; it was found to be in best agreement, 0.21%, with the work of Michels *et al.* (*54, 55, 56*). The deviation from the data of Kamerlingh Onnes *et al.* (*35 to 38, 41, 42, 43, 46, 72*), Witkowsky (*81*), and Deming and Shupe (*24*) was 0.38%. The correlation reproduced the results of Amagat (*2, 3, 4, 5*), Holborn (*28*), Holborn

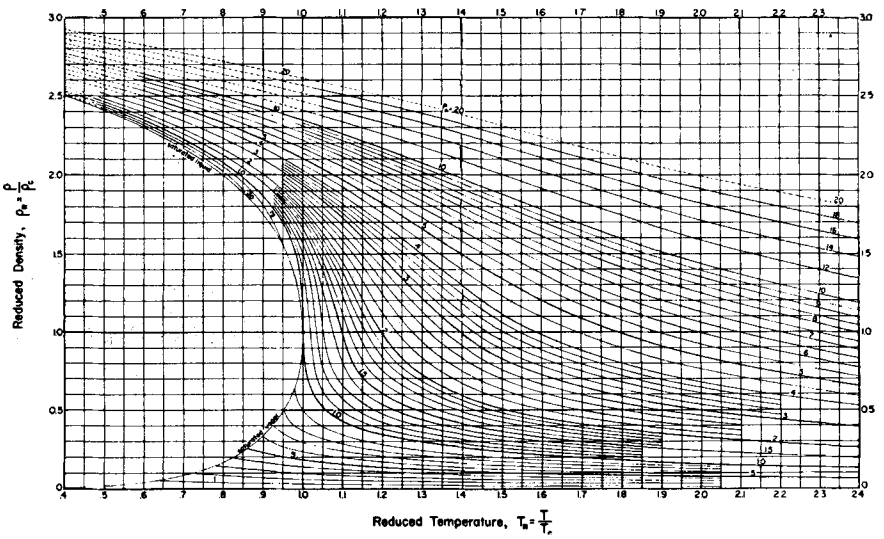


**Fig. 3. Reduced-density correlation for hydrogen in the saturated- and dense-phase regions (rectilinear coordinates).**

*An 8½ by 11-in. reproduction of Figure 2, with fine graph lines shown, is available upon request from the authors.

and Otto (*29, 31, 32*), and Johnston and White (*34*) to within 0.56%. The greatest deviations, 0.70 and 0.99%, were from the data of Bartlett *et al.* (*8, 9, 10*) and Crommelin and Swallow (*20, 21*), respectively. The deviation from the work of Crommelin and Swallow can be explained in part by the low-temperature region investigated. Near the critical point the isobars have a steep slope, and hence the chart is difficult to read.

It is concluded that owing to the comprehensive literature survey Figure 2 is a representative correlation of the available absolute-density values. Furthermore the average deviation of 0.49% indicates that the chart is reliable in producing values consistent with the experimental data.

## NOTATION

A. U. = Amagat unit
$d_A$ = Amagat density
$P$ = pressure, atm.
$P_R$ = reduced pressure
$\rho$ = absolute density
$\rho_R$ = reduced density
$T_R$ = reduced temperature
$z$ = compressibility factor
$z_1$ = compressibility factor at the reference point
$\rho_{R_1}$, $P_{R_1}$, $T_{R_1}$, = reduced states for density, pressure, and temperature at the reference point (highest reported temperature)

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