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Standardized Equation for Hydrogen Gas Densities for Fuel Consumption Applications[1]

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ABSTRACT

We have established an equation for the density of hydrogen gas that agrees with the current standard to within 0.01 % from 220 to 400 K with pressures up to 45 MPa. The equation is a truncated virial-type equation based on pressure and temperature dependent terms. The density uncertainty for this equation is the same as the current standard and is estimated as 0.2 % (combined uncertainty with a coverage factor of 2). Comparisons are presented with experimental data and with the full 32-term equation of state.

INTRODUCTION

Motor vehicle fuel economy has been a critical measurement performed by the United States Environmental Protection Agency (EPA) for the automotive industry for close to forty years. Consumer dependence on these measurements and industry scrutiny has necessitated great care on the part of the EPA to ensure accuracy in fuel economy results.

The advent of new drive technology and fuels in motor vehicles has required establishing new methods to quantify fuel economies. To evaluate the consumption of gaseous hydrogen fuel in vehicle applications, the determination of the equilibrium temperature and pressure before and after usage within a storage tank of known, and essentially fixed, volume is one of three methods recognized in the proposed Society of Automotive Engineers (SAE) draft procedure J2572 “Recommended Practice for Measuring the Fuel Consumption and Range of Fuel Cell Powered Electric and Hybrid Electric Vehicles Using Compressed Gaseous Hydrogen”; the other two methods involve mass determination with scales and mass flow meters. The use of pressure, volume, and temperature measurements has the potential to be the most robust and economical of the three approved methods in initial test and vehicle instrumentation equipment costs, in ongoing personnel test resources, as well as for measurement precision, repeatability, accuracy, and lab to lab reproducibility.

The EPA National Vehicle Fuel and Emission Laboratory (NVFEL) is currently evaluating this method for quantifying hydrogen consumption in hydrogen-fueled fuel cell (FC) or internal combustion (IC) engines. While the SAE draft procedure recognizes pressure, volume and temperature calculations as an acceptable method, referencing the National Institute of Standards and Technology (NIST), there is no generally accepted industry-wide method of calculation. To this end, the EPA has requested that NIST establish a method to calculate motor vehicle gaseous hydrogen consumption from these parameters.

EQUATION FOR THE DENSITY OF HYDROGEN GAS

The equilibrium temperature and pressure of the gas before and after usage within a storage tank of known, and essentially fixed, volume can be used in consumption calculations. A current standard for the thermodynamic properties of hydrogen is provided by a 32-term equation of state, in which the pressure is given as a function of density and temperature. In some fuel consumption applications, this form is inconvenient to use since the equation must be solved in an iterative manner in order to provide the density in terms of pressure and temperature. In order to easily calculate gaseous hydrogen fuel consumption in vehicle applications in which temperature and pressure are measured, we have established an equation for the density of hydrogen gas in terms of pressure and temperature dependent pressure virial coefficients that

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agrees with the current standard to within 0.01 % in density from 220 to 400 K with pressures up to 45 MPa.

The method is tied to the density of hydrogen calculated from Version 5.0 of the NIST Thermodynamic and Transport Properties of Pure Fluids Database (NIST12) [1]. The density in Ref. [1] is based on an equation of state, written as a 32-term expression for pressure as a function of temperature and density, $p(T,\rho)$ [2]. This equation for the parahydrogen modification of the normal hydrogen system is considered adequate for density calculations in the region of interest. However, the necessity of inverting the $p(T,\rho)$ equation to obtain density from temperature and pressure makes it inconvenient for use in some fuel consumption applications. For this reason, we have developed a new equation for the density of hydrogen as a function of temperature and pressure, which is valid from 220 to 400 K (-64 to 260 ^{o}F) with pressures to 45 MPa (6500 psia) and which agrees with the standard of Ref. [2] to within 0.01 % in density over the entire range.

The equation of state in Ref. [2] can be considered a rather dated standard; the publication date was 1982, and the basic source of the parahydrogen equation is a 1975 National Bureau of Standards (NBS) technical report [3]. (NBS is the former name of the National Institute of Standards and Technology, NIST.) However, this standard remains in effect in several applications, and it is implemented in software standards such as Ref. [1] and the NIST Chemistry WebBook [4]. The density uncertainty for this equation was estimated as 0.2 % (combined uncertainty with a coverage factor of 2) in Ref. [2]; this uncertainty estimate was reviewed as part of the current effort, and we have retained this value. Some of the older NBS material and a bibliography of hydrogen property information can be found through the NIST hydrogen web site http://www.nist.gov/public_affairs/hydrogen.htm that is part of the larger hydrogen site for the United States Government, http://www.hydrogen.gov/.

NIST is planning to review the status of the hydrogen property formulations as part of an interagency project related to the hydrogen economy. The older property information may need to be updated because of the results of new measurements, known uncertainties in the current standard, improved methods for developing and describing thermodynamic surfaces, and the increased importance of hydrogen properties for custody transfer, design considerations, and federal vehicle fuel economy testing. The results reported here may be revised and updated in a 1-2 year period, however the immediate need for an appropriate consensus standard motivated the current work.

DEVELOPMENT OF THE EQUATION

The Younglove equation of state from Ref. [2] is a 32-term modified Benedict-Webb-Rubin (MBWR) equation written as

$$p = \rho RT + \sum_{i=1}^{19} G(i)\rho^{n_i} T^{m_i} + \sum_{i=20}^{32} G(i)\rho^{n_i} T^{m_i} \exp[\gamma\rho^2] \qquad \text{(Eq. 1)}$$

where p is the pressure, ρ is the molar density, T is the absolute temperature, R is the molar gas constant, and $G(i)$, n_i, m_i, and γ are constants that were determined from the available property data. Values of the constants can be found in Ref. [2]. This expression, together with an equation for the ideal gas heat capacity [5], enables a thermodynamically consistent calculation of many properties of hydrogen in the liquid, vapor, and supercritical phases (density, isochoric and isobaric heat capacities, sound speed, phase boundaries, enthalpy, etc.) from about 14 to 400 K with pressures to 121 MPa. This equation is implemented in software, e.g., Refs. [1] and [4], and inversion of the equation through iterative solutions is straightforward in these computer programs. Nonetheless, direct use of Eq. (1) for hydrogen consumption calculations may not be convenient.

A common equation for the density of gases is based on the virial series, which has a statistical mechanical basis in terms of the relation between the number of particles interacting and the significance of such multiparticle interactions at a particular gas density. Often, the virial equation is written in the form of an expression for the pressure as a sum of the powers of density multiplied by temperature-dependent virial coefficients. Alternatively, the temperature-dependent virial equation may be expressed in terms of the powers of pressure. For the compressibility factor, $z = p/(\rho RT)$, this becomes

$$z(p,T) = 1 + \sum_{i=2} B_i^*(T)\, p^{i-1} \qquad \text{(Eq. 2)}$$

In Eq. (2), the $B^*_i(T)$ quantities are the temperature-dependent pressure virial coefficients.

The lower virial coefficients (e.g., the second virial coefficient, B^*_2) can be calculated theoretically if the interaction potential between hydrogen molecules is known (e.g., through quantum mechanical calculations). However, the current effort has focused on establishing an equation of the form given in Eq. (2) that agrees with the standard of Ref. [1] to within 0.01 % in density over the range of interest. Therefore, no attempts were made to determine the virial coefficients theoretically.

The specific terms and coefficients were determined by calculating a set of compressibility factor values distributed in (p, T) space using the NIST12 [1] database implementation of Eq. (1) [2]. These values were then used in a structural optimization/regression algorithm [6] with the system constrained to consider the lowest virial coefficients of Eq. (2) and simple temperature dependences for B^*_i(T). This structure/parameter space was searched systematically until an equation meeting the criterion of 0.01 % agreement in density was obtained. Virial coefficients up to the sixth power were required in order to match the isothermal curvature of the

hydrogen equation of state. The resulting coefficients and exponents were truncated to the extent allowed to retain agreement with the equation of state within the tolerance specified. The equation was examined to ensure reasonable extrapolation over a broader temperature and pressure range; however, derivatives were not examined. This equation is only intended for use in density calculations over the range specified. The underlying equation of state [2] should be used for all other calculations.

The simple form adopted for the virial coefficients was

$$B^*_i(T) = \sum_{j=1}^{s} \nu_{ij} (T/100\ \mathrm{K})^{n_{ij}} \qquad \text{(Eq. 3)}$$

so that the expression for the compressibility factor, Eq. (2), becomes

$$z(p,T) = 1 + \sum_{i=2}^{6} \sum_{j=1}^{2} \nu_{ij} (p/1\ \mathrm{MPa})^{i-1} (T/100\ \mathrm{K})^{n_{ij}} \qquad \text{(Eq. 4)}$$

The constants associated with Eq. (4) are given in Table 1. The equation and its constants are given for pressure in megapascals (MPa) and temperature in kelvins (K).

Table 1: Constants Associated with the Density Equation (Eq. 4) for Normal Hydrogen from 220 to 400 K with Pressures to 45 MPa

i	j	ν_{ij}	n_{ij}
2	1	0.036719	–1.23
2	2	–0.039839	–2.22
3	1	–0.0014722	–2.68
3	2	0.0024083	–3.1
4	1	0.65994×10^{-5}	–2.7
4	2	-0.15469×10^{-4}	–4.3
5	1	-0.13383×10^{-6}	–3.3
6	1	0.15608×10^{-8}	–4.1
Molar Mass: M=2.015 88 g/mol			
Universal Gas Constant: R=8.314 472 J/(mol·K)			

The mass of diatomic hydrogen and the molar gas constant given in Table 1 are from the most recent tabulations of such information [7-9]. Although these values differ from those used in Ref. [2], the differences are too small to have any practical affect on the use of Eq. (4).

EVALUATION OF THE EQUATION

As discussed above, Eq. (4) and the related constants were established by calculating values from the equation of state [1,2] and regressing the structure and coefficients using these values. Equation (4), in turn, was evaluated through a more thorough comparison with the equation of state [1,2] and by comparing with available experimental data for the density of hydrogen over the range of the equation.

We computed densities with the new formulation (Eq. 4 with constants from Table 1) and compared them with densities obtained from the equation of state of Younglove [2] over the temperature range 220-400 K and pressures up to 45 MPa. The formulation of Eq. (4) is for the compressibility factor, and we used the current value for the gas constant (Table 1) in our calculations. One million points in this (T, p) region were randomly generated, and the results from Eq. (4) were compared with the equation of state compressibility factors from the NIST12 software [1]. The average percent deviation for these million points was –0.0016 %, with a standard deviation of 0.00189 %. The maximum positive deviation was 0.00407 %, the largest negative deviation was –0.00806 %, and thus none of the points had deviations that exceeded the required specification of 0.01 %.

Figure 1 gives a histogram of the results. Considering the divisions indicated in Fig. 1, the largest number of points (373550) had a percentage deviation between 0.001 % and 0.0025 %; the second largest group (165450 points) had deviations between 0.0025 % and 0.005 %. There were no points with deviations larger than 0.01 %, only 624 points had deviations in the range 0.0075 % and 0.01 %, and 432 points had deviations of less than 1×10^{-7} %.

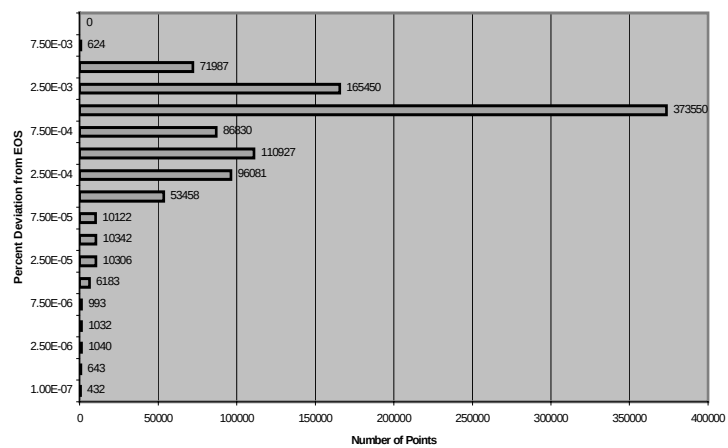

Figure 1. Histogram illustrating the frequency of percentage density deviations for a sample containing one million points.

The new formulation (Eq. 4 with constants from Table 1) can be extrapolated outside of the 220 to 400 K temperature range and the 0 to 45 MPa pressure range. In the extended region from 220 to 500 K with pressures to 80 MPa, the maximum deviation (as compared to the equation of state of Younglove [2]) is less than 0.08 %. If the upper pressure limit is lowered to 60 MPa, the maximum deviation is 0.04 %, and if the upper limit is lowered to 55 MPa, the maximum deviation is 0.016 %. In the extended region from 200 to 500 K with pressures to 80 MPa, the maximum deviation is less than 0.17 %.

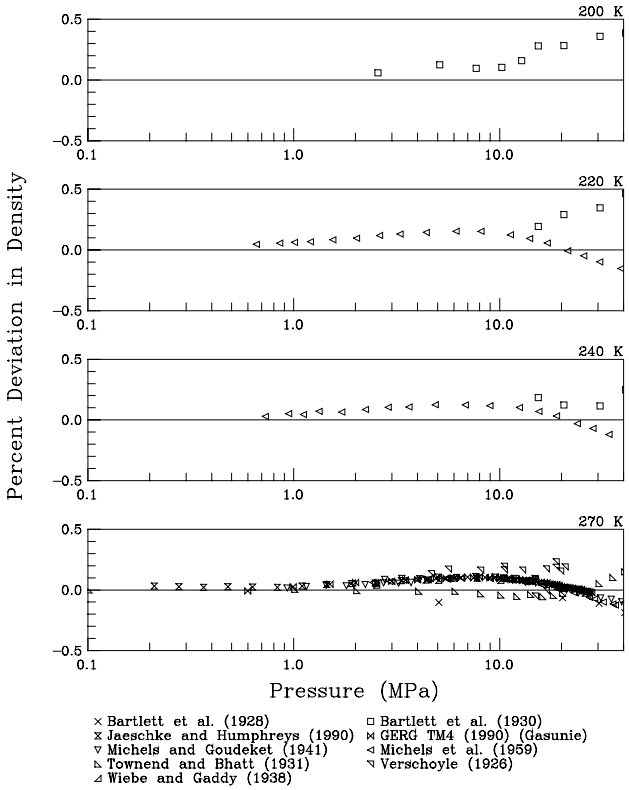

Figure 2. Density deviations as a function of pressure for temperatures from 203 to 273 K

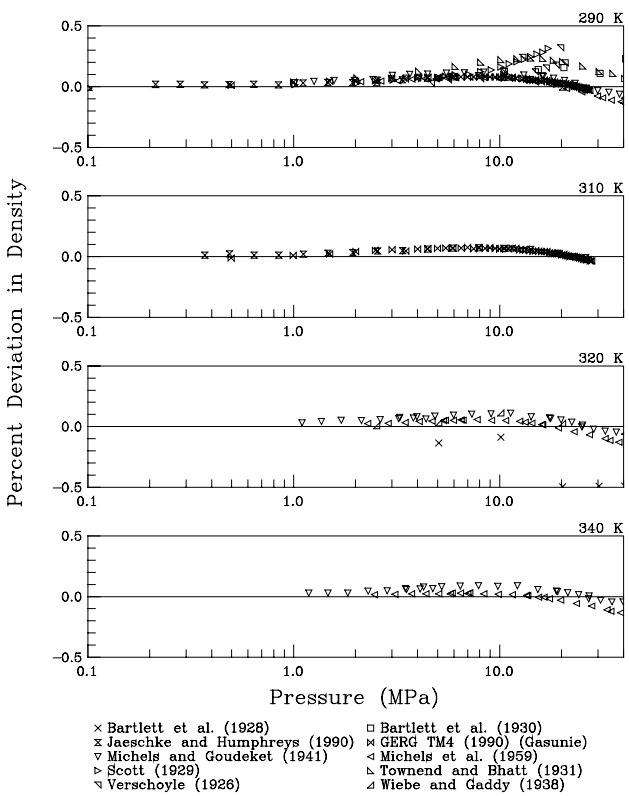

Figure 3. Density deviations as a function of pressure for temperatures from 293 to 348 K

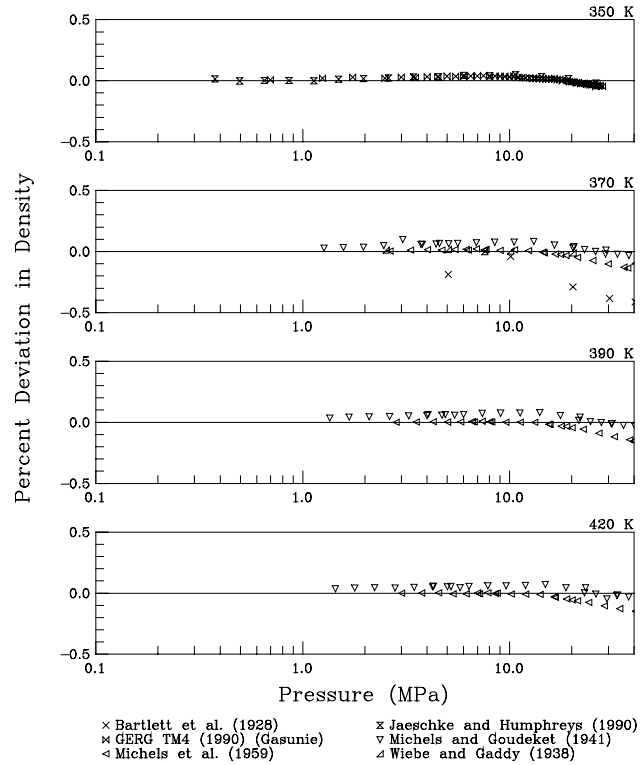

Figure 4. Density deviations as a function of pressure for temperatures from 353 to 423 K

The second type of evaluation was direct comparison with available experimental data. Figures 2-4 show the deviations between densities calculated with Eq. (4) and experimental data in the literature [10-18]. The subplots in these figures include data from various sources grouped in 10 K increments. A line comparing the representation of Eq. (4) with the equation of state of Younglove [2] is not provided, as it is extremely close to the zero line (within 0.01 % as indicated above).

Several observations can be made from the deviation plots of Figs. 2-4. Firstly, these figures generally support the uncertainty estimate for the equation of state of Younglove [2]. The estimate of 0.2 % as a combined uncertainty with coverage factor of two seems reasonable in this range considering only the scatter of the available density data and the agreement between the equation and these data. Secondly, when considering the available data shown, it appears that there is an opportunity for improvement in the standard equation of state [2]. Finally, these observations support the use of Eq. (4) for fuel consumption calculations in the restricted region based on the density calculations from an initial and final pressure and temperature.

USE OF THE EQUATION IN HYDROGEN GAS CONSUMPTION APPLICATIONS

A general method for pressure, volume, and temperature calculations to quantify hydrogen consumed was suggested to the Society of Automotive Engineers (SAE)

Working Group of the SAE Fuel Cell Standards Committee by Veenstra and Ding [19]. The Working Group needed a method to use pressure, volume, and temperature measurements to quantify the mass of hydrogen used in performing tests on the mobile vehicle fuel cell testing proposed, as this is required for the document "Recommended Practice for Measuring the Fuel Consumption and Range of Fuel Cell Powered Electric and Hybrid Electric Vehicles Using Compressed Gaseous Hydrogen", (SAE J2572) [20]. The procedure recognizes three methods of quantifying hydrogen consumed during J2572 testing: weight scales, mass flow meters, and pressure, volume, and temperature measurements. The SAE working group required independent hydrogen quantification methods that were capable of giving results that could satisfy 2 % uncertainty requirements. Consumption of gaseous hydrogen fuel can be determined from the mass extracted from a compressed fluid storage tank using only measurements of temperature and pressure. The water volume of the tank (*V*) is assumed constant over the pressures (*p*) and temperatures (*T*) involved.

The accuracy of compressible gas flow measurements can be practically considered as a "bulls eye" with 1 % uncertainty. Primary flow meters, calibrated by NIST, are given documentation certifying the calibration curve for the instrument; uncertainties of the flow calibrations are generally better than 0.16 %, and depend on the details of the calibration [21]. EPA fuel cell testing to date [22] has exhibited a general deviation of less than +/- 2 % when comparing mass calculated using the NIST hydrogen gas density equations with weight scales or mass flowmeter results. EPA considers that this satisfies the goals for hydrogen consumption accuracy desired by the SAE Working Group.

The use of pressure, volume, and temperature measurements has the potential to be the most economical of the three approved methods in initial test and vehicle instrumentation equipment costs, in ongoing personnel test costs, and as the most facile for measurement repeatability, accuracy, and result reproducibility from laboratory to laboratory. This method also makes the hydrogen consumption measurement (vehicle fuel economy in miles per kilogram of hydrogen consumed) less complex and subsequently safer than scales and mass flow meters. Weight scales require more cylinder filling and handling. Both weight scales and mass flow meter measurements require live fuel feeds to the vehicle during the dynamometer testing.

With proper calibrations of the tank water volume, and vehicle tank pressure and temperature measurement instrumentation, the method can be used to determine the mass of hydrogen consumed during a test, using static before and after measurements. EPA test results since 2002 imply that this method may be robust enough not to require long temperature normalization times to come to equilibrium, and still meet the desired accuracy, specified as +/-2 % (which can be considered an expanded combined uncertainty estimate of 2 %). Even if longer equilibration times should be required, the EPA considers this method to be both dependable and meet SAE as well as regulatory accuracy requirements [22]. Continued experimentation will allow EPA to determine if the same equations can be used to calculate dynamic instantaneous flow rates or hydrogen mass consumed on a test time basis.

The removable contents are considered hydrogen of sufficient purity to be described by the Younglove pure-fluid equation [1,2] and the properties of parahydrogen can be used for this purpose. Equilibrium is assumed to have been established when the temperatures and pressures in the "initial" and "final" states are measured.

The basic equation is

$$\Delta m = M[\rho_{\text{final}}(p_{\text{final}}, T_{\text{final}}) - \rho_{\text{initial}}(p_{\text{initial}}, T_{\text{initial}})]V$$

$$= \frac{MV}{R}\left[\frac{p_{\text{final}}}{T_{\text{final}}\, z(p_{\text{final}}, T_{\text{final}})} - \frac{p_{\text{initial}}}{T_{\text{initial}}\, z(p_{\text{initial}}, T_{\text{initial}})}\right]$$

(Eq. 5)

where Δm is the mass of hydrogen consumed and M is the molar mass. Equation (5) is quite general, although its use with Eq. (4) for the compressibility factor is restricted to the *T* and *p* ranges given earlier.

CONCLUSIONS

Fuel consumption can be determined in multiple ways. From a regulatory view, it is mandatory to have consistent methods that can be used for independent verification of each other. Equivalent measurement methods allow maximum flexibility in the regulated industry and confidence in data integrity. The determination of the mass of hydrogen gaseous fuel use from Eq. (5) is quite straightforward after accurately establishing the initial and final temperatures, pressures, and volumes. Consistent use of an expression such as Eq. (5) requires a standard method by which the compressibility factor can be calculated.

Equation (4) can form the basis of such a standard. It was developed to provide consistency with the calculations from a NIST Standard Reference Database [1], and it has been shown to provide reasonable agreement with the currently available data. The simple form of Eq. (4) agrees with the standard of Refs. [1] and [2] to within 0.01 % from 220 to 400 K (-64 to 260 ^{o}F) with pressures up to 45 MPa (6500 psia), although the estimated uncertainty of the resulting hydrogen density is 0.2 %. The equation is not adequate for the calculation of other hydrogen properties, and it may be superceded as the interest in hydrogen increases and further studies are conducted. There might be other uncertainties in the quantification of hydrogen fuel consumption that have not been explicitly considered here. These could include the suitability of the parahydrogen equation to represent the

actual fuel used, temperature and pressure dependence of the tank volume, equilibration of the temperature and pressure measurements, and other uncertainties in the measurement of temperature and pressure.

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