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THERMODYNAMIC PROPERTIES STATUS OF DEUTERIUM AND TRITIUM

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ABSTRACT

Deuterium and tritium are seeing increased use in cryogenics as a fuel for nuclear fusion energy machines. The current Equation of State (EOS) for deuterium is based on work completed before the mid 1980's and tritium does not have an EOS available in the literature. In order to assess the need for new property correlations and experimental measurements, this paper presents a review and comparison of the available thermodynamic property measurements and models for deuterium and tritium. The comparisons extend a wide range of temperatures and pressures from the onset of solidification to the highest temperature and pressure measurements available. Based on the comparisons, recommendations for new experimental measurements and thermophysical property correlations are made.

KEYWORDS: deuterium, tritium, equation of state, thermodynamic, properties.

INTRODUCTION

The rising costs and environmental effects of using natural resources for power production are increasing the desirability of nuclear energy. Nuclear fusion reactors like ITER and the National Ignition Facility (NIF) are under development to use large amounts of deuterium and tritium as fuel. With the price of tritium near \$30,000 per gram [1], the scarcity and potential negative ramifications of an accident associated with these fluids necessitates accurate thermodynamic property models.

Since the discovery of deuterium by Harold Urey in 1931, there have been several reviews of the thermodynamic properties. The first review was by Farkas [2] in 1935, followed by the extensive work by Harold Woolley et al. [3] at the National Bureau of Standards in 1948. In the late 1960s, Prydz [4] reviewed the thermodynamic properties and developed extensive property tables for deuterium. This work formed the basis for the current equation of state by McCarty and Prydz that was not finalized until 1989 [5,6].

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Souers [7] published a review of cryogenic hydrogen properties and estimated physical and chemical properties for deuterium and tritium. Schwartz and Le Roy [8] calculated the vibration-rotation levels of all six isotopes of diatomic hydrogen [9]. In the last 20 years, little to no thermodynamic property studies have been conducted on deuterium. Tritium does not have an equation of state available in the literature and experimental measurements are scarce. There have been great advances in computer technologies and equation fitting techniques since the last analysis of deuterium and tritium implying a need for an updated property review.

BEHAVIOR OF THE HEAVY HYDROGEN ISOTOPES

Hydrogen, deuterium, and tritium molecules have separable allotropes denoted as ortho and para. A detailed discussion of these forms can be found elsewhere [7,10]. Generally, ortho-para compositions have significant differences in properties related to specific heat such as enthalpy, entropy, and heat capacity. Calculated values for ortho and para heat capacities by Le Roy et al. [9] show differences of up to 40% for both deuterium and tritium. At temperatures above 40 K, differences in density are very small. The critical points and triple points for normal deuterium ($T_{\text{trp}} = 18.73$ K, $T_c = 38.34$ K) and orthodeuterium ($T_{\text{trp}} = 18.69$ K, $T_c = 38.26$ K) are slightly different [7]. At the time of this review there has not been any measured or predicted differences between the critical points and triple points of normal tritium and paratritium although the difference is likely small.

This paper has not considered the heteronuclear hydrogens: hydrogen-deuteride (HD), hydrogen-tritide (HT), and deuterium-tritide (DT). There are limited property measurements of heteronuclear hydrogens and there are no current equations of state for comparisons. Souers [7] and Le Roy et al. [9] have created extensive tables of property predictions for all six isotopes of diatomic hydrogen.

EXPERIMENTAL DATA FOR THE THERMODYNAMIC PROPERTIES OF DEUTERIUM AND TRITIUM

The current thermodynamic properties data [11-54] for deuterium and tritium are listed below in TABLES 1 and 2, respectively. The temperature and pressure range for the measurements are listed in addition to the ortho-para composition, if published. Some experiments were conducted at the saturation pressure for a given temperature and therefore the pressure is listed as 'sat'.

The radioactivity and scarcity of tritium has deterred the majority of researchers from measuring its thermodynamic properties. However, there have been numerous researchers (Hammel 1950 [55], Rogers and Brickwedde 1964 [56], Mills et al. 1978 [50], and Souers 1985 [7]) who have created property formulations and estimated property tables for tritium by extrapolating properties from hydrogen and deuterium using quantum theory. It is difficult to determine the accuracy of these formulations due to the lack of experimental data needed for a comprehensive comparison.

TABLE 1. Summary of thermodynamic property data for deuterium

Author	Year	Number of points	Temperature range (K)	Pressure range (MPa)	Composition
P-ρ-T					
Clusius & Bartholome [11]	1935	8	18.8-20.5	Sat	~

Friedman et al. [12]	1954	44	20.3-38.1	8.6-11.02	nD ₂
Hoge & Lassiter [13]	1951	50	37.2-41.2	1.42-2.23	eD ₂
Kerr [14]	1952	5	19.5-24.2	Sat	~
Liebenberg et al. * [15]	1977	1340	75-300	200-2000	nD ₂
Michels & Goudekert [16]	1941	277	273.2-423.2	0.9-305.1	~
Michels et al. [17]	1959	417	98.2-423.2	0.6-283.8	~
Rudenko & Slyusar [18]	1969	19	18.7-34.9	Sat	pD ₂
Rudenko & Slyusar [19]	1968	24	20.4-34.8	Sat	pD ₂
Cramer [20]	1965	10	298.1	10.2-141.9	~
David & Hamann [21]	1953	16	64.5-78.9	15.2-91.2	~
Beenakker et al. ^ [22]	1959	5	20.4	0.016-0.036	~
Bartholome [23]	1936	25	19.70-20.97	0.7-9.2	~
Knaap et al. [24]	1962	9	27.8-71.8	0.032-0.084	nD ₂
Saturation heat capacity					
Kerr et al. [25]	1951	8	19.9-22.7	Sat	97.8 % oD ₂
Brouwer et al. [26]	1970	18	24-27.4	Sat	nD ₂
Grenier & White [27]	1964	3	20-22	Sat	97.8% oD ₂
Clusius & Bartholome [11]	1935	8	19.4-21.7	Sat	nD ₂
Heat of vaporization					
Johnston et al. + [25]	1951	11	23.6	Sat	97.8% oD ₂
Kerr et al. [25]	1951	6	23.6	Sat	97.8% oD ₂
White et al. [28]	1959	9	24.3-37.5	Sat	97.8% oD ₂
Vapor pressure					
Brickwedde et al. [29]	1935	4	18.7-20.4	Sat	nD ₂
Friedman et al. [30]	1951	18	29-38.1	Sat	nD ₂
Grilly [31]	1951	29	18.9-27.8	Sat	nD ₂
Kerr et al. [25]	1951	7	18.6-23.7	Sat	97.8% oD ₂
Lewis & Hanson [32]	1934	5	18.7-20.3	Sat	~
Meckstroth & White [33]	1971	87	17.2-22.5	Sat	Varied
Scott et al. [34]	1934	6	15.2-20.3	Sat	nD ₂
Hoge & Arnold [35]	1951	79	18.8-38.2	Sat	eD ₂ & nD ₂
Hiza [36]	1972	14	20-34	Sat	nD ₂
Brickwedde et al. [37]	1933	1	20.4	Sat	nD ₂
Joule-Thomson					
Johnston et al. [38]	1946	45	64-80	1.7-20.1	~
Speed of sound					
Bezuglyi & Minyafaev [39]	1968	2	19-20	Sat	nD ₂
Brody et al. [40]	1980	11	298	500-5500	~
Gusewell et al. [41]	1970	7	25-31	Sat	nD ₂
Liebenberg et al. [15]	1977	1340	75-300	200-2000	nD ₂
van Itterbeek & Thys [42]	1938	3	239-297	0.08-0.09	~
van Itterbeek & Vandoninck [43]	1943	46	19-21	0.006-0.035	~
van Itterbeek & van Paemel [44]	1938	2	20.36	0.013-0.03	~
van Itterbeek & Vermaelen [45]	1942	28	68-290.6	0.04-0.1	~
Second virial coefficient					
Michels & Goudekert [16]	1941	21	273.2-423.2		
Michels et al. [17]	1959	17	98.2-423.2		
Michels et al. [46]	1960	17	98.2-423.2		
Beenakker et al. [22]	1959	1	293.6		
Knaap et al. [24]	1962	2	20.51-21.55		
Varekamp & Beenakker [47]	1959	5	18-21		
van Itterbeek & Vandoninck [43]	1943	13	23-46		
Skripka [48]	1965	27	20-159		
Schafer [49]	1937	22	23.2-273.2		

Mills et al. [50]	1978	5	100-300
Souers [7]	1979	12	98.2-298.2
Third virial coefficient			
Michels & Goudekert [16]	1941	21	273.2-423.2
Michels et al. [17]	1959	17	98.2-423.1
Michels et al. [46]	1960	17	98.2-423.2
Levelt Sengers et al. [51]	1972	21	110-530
Mills et al. [50]	1978	5	100-300
Souers [7]	1979	12	98.2-298.2

* This data was in the process of being compiled at the time this paper was submitted and has not been included in the comparisons

^ Data not included in the comparisons due to very low pressures

+ This data was provided in a private communication in reference [25]

~ Did not specify composition

TABLE 2. Summary of thermodynamic property data for tritium

Author	Year	Number of Points	Temperature range (K)	Pressure range (MPa)	Composition
P-ρ-T					
Grilly [52]	1951	11	20.6-29.1	Sat	nT ₂
Grilly [53]	1993	5	20.7-21.7	0.47-5.16	nT ₂ & eT ₂
Vapor pressure					
Grilly [54]	1950	18	20.6-29.0	0.02-0.28	nT ₂
Grilly [31]	1951	18	20.6-29.2	0.02-0.29	nT ₂
Grilly [53]	1993	4	20.7-24.4	0.023-0.084	Varied
Second virial coefficient					
Mills et al. [50]	1978	6	75-300		
Third virial coefficient					
Mills et al. [50]	1978	6	75-300		

COMPARISONS OF CALCULATED PROPERTIES TO EXPERIMENTAL DATA

Comparisons were made to the NIST Standard Reference Database Program REFPROP [57], which implements the deuterium equation of state developed by McCarty and Prydz [5]. The formulation uses a modified Benedict-Webb-Rubin (BWR) equation. This equation is solved in terms of pressure. In order to obtain thermodynamic properties this equation must be integrated which limits the exponents on the terms of the equation to even numbers. New fundamental equations are explicit in reduced Helmholtz free energy and can be solved for thermodynamic properties by taking derivatives. This allows for terms with even and odd numbered exponents providing greater flexibility, fewer terms, and a more accurate equation.

McCarty's equation of state uses the current molecular mass measurement for deuterium of 4.0282 kg/kmol [58]. The formulation uses the IPTS-68 temperature scale and has upper pressure and temperature limits of 320 MPa and 423 K, respectively. Graphical comparisons of density, vapor pressure, and speed of sound are provided in FIGURES 1-3. Percent deviations of the predictions are calculated using the equation:

$$\% \Delta X = 100 \left(\frac{X_{\text{data}} - X_{\text{calc}}}{X_{\text{data}}} \right) \quad (1)$$

where X is any property. No comparisons were made for tritium due to insufficient data and lack of an equation of state for comparison.

Comparison of the current deuterium equation to the vapor pressure data shown in FIGURE 2 shows a systematic deviation from all available experimental measurements of up to 15 % in vapor pressure. This discrepancy can be alleviated with modern fitting techniques. For example, the current equation of state for hydrogen has an estimated uncertainty in vapor pressure predictions of 0.2 % [10].

Comparison of the speed of sound data for deuterium shown in FIGURE 3 shows a systematic discrepancy exceeding 10 %. There is only one set of measurements for pressures above 0.2 MPa conducted by Gusewell et al. [41]. FIGURE 3 also shows that there are only six measurements, conducted by van Itterbeek and Vermaelen [45], between 30 and 200 K.

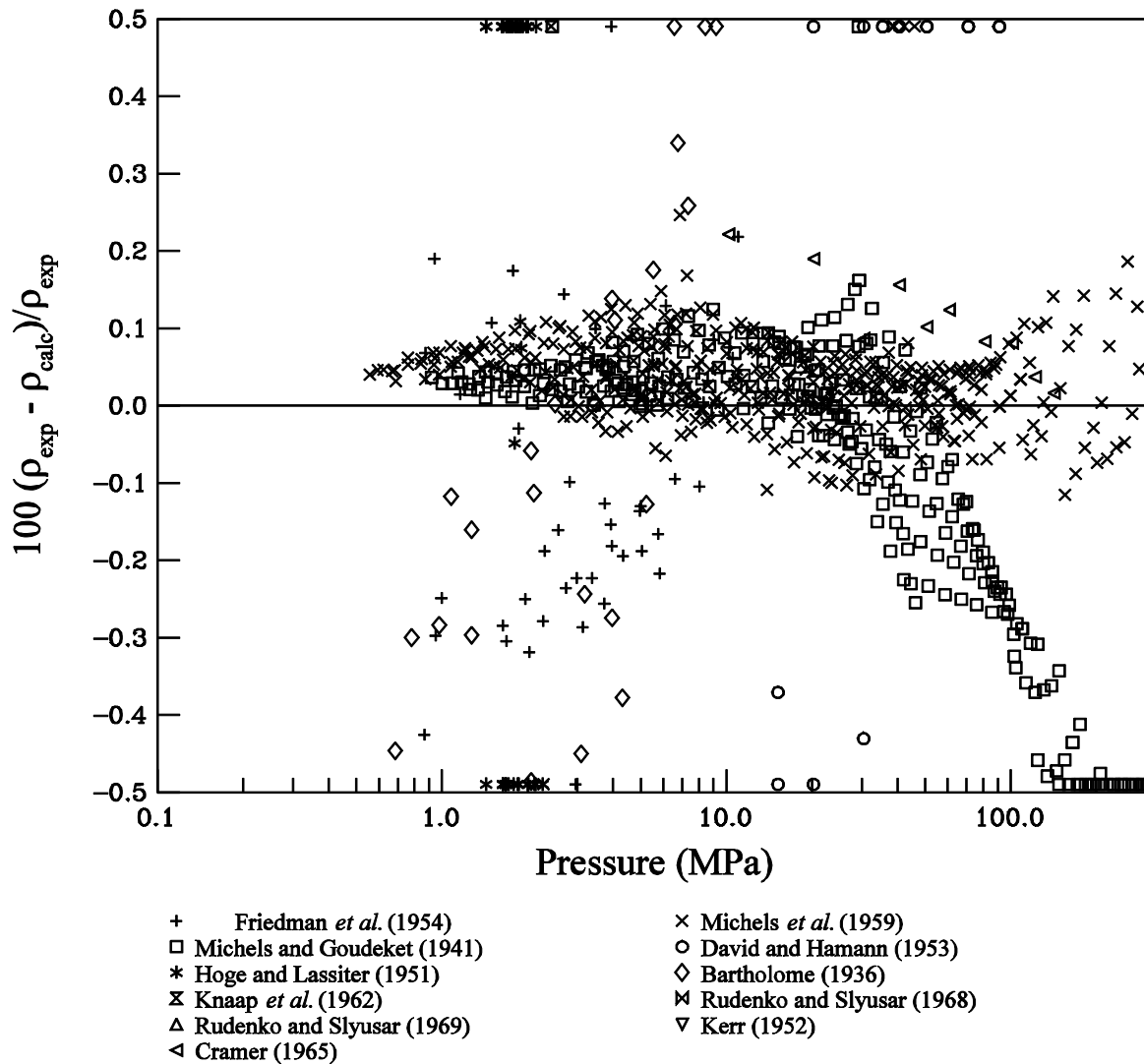


FIGURE 1. Comparisons of density calculated by use of McCarty [5] with experimental deuterium P-ρ-T data (%ΔX versus Pressure).

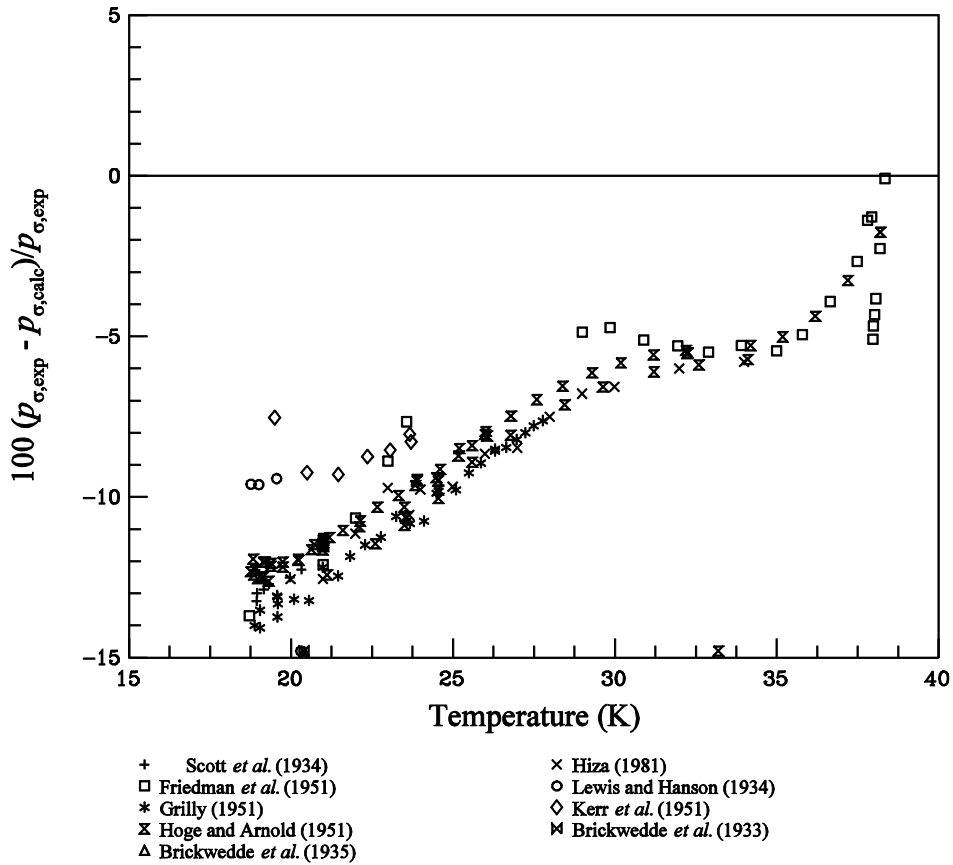


FIGURE 2. Comparisons of vapor pressure calculated by use of McCarty [5] with experimental deuterium vapor pressure data (% Δ X versus Pressure).

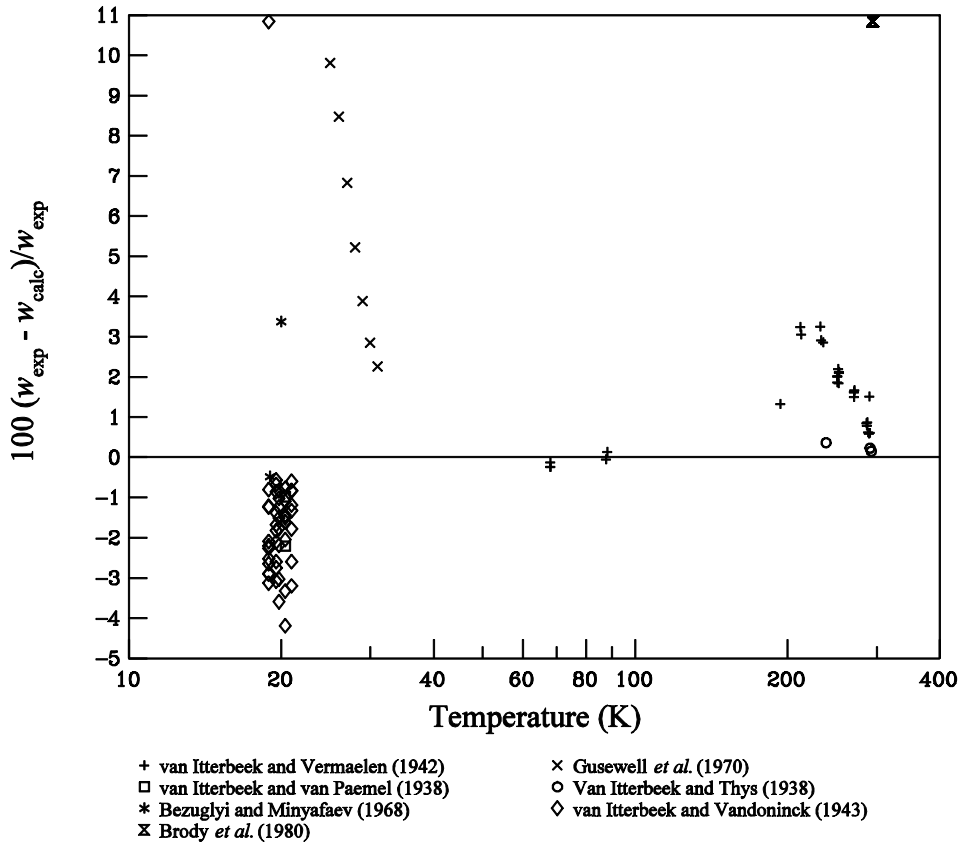


FIGURE 3. Comparisons of speed of sound calculated by use of McCarty [5] with experimental deuterium speed of sound data (% Δ X versus Pressure).

CURRENT STATUS AND RECOMMENDATIONS

The current formulation for deuterium shows deviations in the saturation region as large as 15 % in vapor pressure, and 10 % in speed of sound. Additional speed of sound and heat capacity measurements are needed for saturated and vapor states at high pressures and moderate temperatures to reduce this discrepancy. Ortho-para differences in real fluid properties of deuterium are small, however properties related to the ideal gas heat capacity need to account for changes in ortho-para composition. Formulating a new equation using updated computer modeling software will substantially reduce deviations while improving the computational speed of the formulation and extrapolation behavior.

There is a need for further measurements of thermodynamic properties of tritium in order to create a basis for an equation of state. The vapor pressure and density measurements are an excellent start towards correlation development [31,52-54]. Speed of sound measurements in the liquid phase would immensely improve the accuracy of any formulated equation of state for tritium.

Experimental measurements for deuterium and tritium need to be expanded to include temperatures and pressures commonly used by engineers and scientists to ensure accurate property predictions. The temperature range for new formulations should be expanded for commercial applications and updated to the ITS-90 temperature scale. In order to provide for accurate engineering calculations, we have begun to formulate an equation of state for deuterium with the plan to extend the work to tritium.

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