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PREPRINT UCRL-76708

Lawrence Livermore Laboratory

CONF -751026--5

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September 2, 1975

This paper was prepared for submittal to the proceedings of the International Conference on Radiation Effects and Tritium Technology for Fusion Reactors, Gatlinburg, Tennessee, October 1 to 3, 1975.

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ESTIMATED VALUES OF SOME CRYOGENIC PROPERTIES OF HYDROGEN ISOTOPES*

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ABSTRACT

The literature on cryogenic hydrogen isotopes from 4.2 to 25 K is reviewed for triple points, vapor pressures, liquid viscosities, surface tensions, and liquid and solid densities. Data are extrapolated to yield values for DT. Empirical equations are given for all isotopes for each property. At the estimated 19.71 K triple point of 1:1 D-T in D₂-DT-T₂ solution, the estimated properties are: vapor pressure, 19 420 Pa (145.7 Torr); viscosity 550×10^{-7} Pa·s; surface tension 4.23×10^{-3} N/m; liquid density, 0.0446×10^6 mol/m³ (224 Kg/m³); solid density, 0.051×10^6 mol/m³ (256 Kg/m³); and shrinkage upon freezing, -13 vol%. At 4.2 K, estimated values are: vapor pressure, 2.4×10^{-10} Pa (1.8×10^{-12} Torr) and solid density, 0.053×10^6 mol/m³ (267 Kg/m³).

INTRODUCTION

Controlled thermonuclear fusion as a source of energy has been a dream for the past generation. There is considerable activity in the magnetic confinement and laser-induced approaches to this goal. Both require heavy hydrogen DT, as fuel. To aid cryogenic engineers, we reviewed the literature of DT for triple point temperature, vapor pressure, density, viscosity, and surface tension for the liquid and solid phases along the saturation line, from 4.2 to 25 K. We extrapolated the known data to estimate values for DT and T₂ wherever gaps in knowledge appear. The data given are strictly for normal (n) H₂ and D₂ and for

* This work was performed under the auspices of the U.S. Energy Research and Development Administration.

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equilibrium HD, DT, and T₂.^{*} Changes in rotational energy, i.e., ortho-para compositions, do not greatly affect the accuracy of the listed values.

The constants listed for a given property do not always form a smooth sequence with molecular weight because of the inaccuracies of combining actual data for each isotopic species from several sources.

TRIPLE POINTS

Table 1 shows the triple point temperatures and pressures recommended by the National Bureau of Standards (NBS).¹ The molecular species DT has never been obtained in bulk quantities because the tritium beta

Table 1. Triple point temperatures and pressures of hydrogen isotopes.
(Estimates are underlined.)

Isotope	Triple point temp., K	Triple point vapor pressure	
		Pa	(Torr)
nH ₂	13.957	7205	(54.04)
HD	16.604	12400	(92.8)
nD ₂	18.71	17130	(128.5)
DT	<u>19.71</u>	<u>19420</u>	<u>(145.7)</u>
T ₂	20.62	21600	(162.0)

particle causes a rapid equilibration to the three-component mixture D₂-DT-T₂.²⁻⁴ The triple point of this solution has not been measured, and the estimated DT value of 19.71 K must be used for a 1:1 D-T mixture. The triple-point temperatures of the hydrogens do not form a smooth curve as a function of molecular weight; remeasurement of the non-H₂ values would be valuable.

^{*}Normal hydrogen contains the rotational energy characteristic of room temperature. Equilibrium hydrogen contains the rotational energy characteristic of any other specified temperature. If quickly cooled, H₂ and D₂ remain metastably trapped in the normal form; HD and DT de-excite to the equilibrium form by transitions allowed in the mixed isotopes; DT and T₂ de-excite by radiation-induced reactions.

SATURATED VAPOR PRESSURES

Of great practical importance are the vapor pressures along the saturated (equilibrium) solid to vapor and liquid to vapor phase boundaries. We use the NBS recommended vapor pressures,⁵ which include H_2 , HD, D_2 , and T_2 .⁶⁻¹² We refined these data in a recent review¹³ and replotted them using the Clausius-Clapeyron equation, altered for a perfect gas.¹⁴ For the solid, we assume a latent heat of sublimation L that is linear with temperature:

$$L = R(A + BT) \quad (1)$$

where R is the gas constant ($8.314 \text{ J/mol}\cdot\text{K}$), A and B are constants, and T is the temperature. Insertion into the Clausius-Clapeyron equation yields a form attributed to both Kirchoff and Rankine:

$$\ln P = -\frac{A}{T} + B \ln T + C, \quad (2)$$

where P is the saturated vapor pressure and C is a new constant that determines the units of pressure. Equation (2) also closely describes the liquid, although it is more empirical because the heats of vaporization do not follow the form of Eq. (1). Using Eqs. (1) and (2), we calculate the latent heats from 0 K to the solid and liquid at the triple points. All constants are given in Table 2, and derived latent heats are given in Table 3. The error of our vapor pressure estimates must surely be large compared to solution irregularities. Hence, we use the DT vapor pressure

Table 2. Vapor pressures of hydrogen isotopes, Pa (Torr).
(Estimates are underlined.)

Isotope	Empirical formula: $\ln P = -\frac{A}{T} + B \ln T + C$					
	Solid-vapor constants			Liquid-vapor constants		
	A	B	C, Pa (Torr)	A	B	C, Pa (Torr)
nH_2	98.63	1.982	10.72 (5.832)	89.00	1.680	10.83 (5.937)
HD	109.2	2.840	8.023 (3.130)	112.4	1.412	12.23 (7.335)
nD_2	137.1	2.378	10.11 (5.217)	137.1	1.067	13.95 (9.058)
DT	<u>151.5</u>	<u>2.349</u>	<u>10.56 (5.667)</u>	<u>155.8</u>	<u>0.6712</u>	<u>15.77 (10.88)</u>
T_2	156.4	2.333	10.50 (5.610)	166.0	0.6416	16.09 (11.20)

Table 3. Triple-point latent heats of hydrogen isotopes, J/mol.
(Estimates are underlined.)

Isotope	Empirical formula: $L = R(A + BT)^a$		
	Sublimation	Fusion	Vaporization
nH_2	1050	115	935
HD	1300	170	1130
nD_2	1510	204	1306
DT	<u>1645</u>	<u>240</u>	<u>1405</u>
T_2	1700	210	1490

^aFor use with solid and triple point liquid. Gas constant R 8.314 J/mol·K.

to approximate the D_2 -DT- T_2 mixture. At 4.2 K, the vapor pressure of DT is calculated to be only 2.4×10^{-10} Pa (1.8×10^{-12} Torr).

LIQUID VISCOSITY

The liquid viscosity estimates are based on H_2 , HD, and D_2 data¹⁵⁻¹⁷ which we recently reviewed.¹⁸ Viscosities were plotted for temperature vs molecular weight. The isothermal curves were linear, and extrapolations were carried out for DT and T_2 , with the liquid viscosity η expressed by the empirical equation

$$\eta = \frac{A_\eta}{T^{1.65}}, \quad (3)$$

where T is the temperature and A_η is a constant given in Table 4 for the isotopes. As liquid hydrogen is cooled to the triple point, the viscosity rises more steeply in the last one or two degrees than expressed by Eq. (3). The actual values at the triple points (Table 4) are 3 to 5% higher than those calculated from Eq. (3).

Table 4. Viscosity, surface tension, and densities of hydrogen isotopes.
(Estimates are underlined.)

Property	Empirical formula	Isotope	A_n, A_V, A_L, A_S	B_V, B_L, B_S	Value at triple point
Liquid viscosity	$\eta = \frac{A_n}{T^{1.65}}$	nH ₂	19 500 × 10 ⁻⁷	—	257 × 10 ⁻⁷ Pa·s
		HD	36 000	—	363
		nD ₂	56 000	—	466
		DT	<u>77 000</u>	—	<u>590</u>
		T ₂	<u>98 000</u>	—	<u>662</u>
Liquid vapor	$\gamma = A_V - B_V T$	nH ₂	5.27 × 10 ⁻³	0.166 × 10 ⁻³	2.95 × 10 ⁻³ N/m
		HD	6.44	.186	<u>3.36</u>
		nD ₂	7.94	.222	<u>3.77</u>
		DT	<u>9.38</u>	<u>.256</u>	<u>4.36</u>
		T ₂	<u>10.55</u>	<u>.279</u>	<u>4.78</u>
Liquid density	$\rho_L = A_L - B_L T^2$	nH ₂	0.0412 × 10 ⁶	1.45 × 10 ⁻¹	0.0383 × 10 ⁶ mol/m ³
		HD	.0442	1.30	.0406
		nD ₂	.0477	1.30	.0432
		DT	<u>.0498</u>	<u>1.35</u>	<u>.0446</u>
		T ₂	.0513	1.39	.0454
Solid density	$\rho_S = A_S - B_S T^3$	nH ₂	0.0443 × 10 ⁶	4.78 × 10 ⁻¹	0.0430 × 10 ⁶ mol/m ³
		HD	.0476	<u>3.84</u>	.0458
		nD ₂	.0507	2.90	.0488
		DT	<u>.053</u>	<u>2.5</u>	<u>.051</u>
		T ₂	<u>.055</u>	<u>2.4</u>	<u>.053</u>

Combining binary H-D solutions reduces the viscosity below that expected from a regular solution of the two constituents.¹⁶

The maximum decrease in regularity for a 1:1 mixture of liquid H₂-D₂ is -11.5%. This decrease falls with the difference in molecular weights: -7.0% for H₂-HD and -5.1% for HD-D₂. By extrapolation we estimate maximum viscosity decreases of -7.0, -3.8, and -3.1% for D₂-T₂, D₂-DT, and DT-T₂. However, the actual mixture is estimated to contain about 3:4:3 D₂-DT-T₂ respectively, for a chemically equilibrated solution of 1:1 D-T at the triple point of 19.71 K.^{4,19} Although it is difficult to estimate the regularity decrease for a ternary solution of almost equal parts, we estimate decreases of -5 to -10% for D₂-DT-T₂. Using the -5% value, we calculate a liquid viscosity of 550×10^{-7} Pa·s at the 1:1 D-T triple point of about 19.71 K.

LIQUID-VAPOR SURFACE TENSION

Surface tension measurement have been taken on liquid H₂, HD, and D₂²⁰⁻²² and have been recently reviewed.¹⁸ The isothermal surface tensions plotted vs molecular weight are again almost linear and allow ready extrapolation to the DT and T₂ estimates. We employ the empirical equation for surface tension γ ;

$$\gamma = A_Y - B_Y T, \quad (4)$$

where the A_Y and B_Y are given for the isotopes in Table 4.

The surface tension of binary H-D solutions also shows a lower actual value than that expected for a regular solution.^{21,23} For equimolar solutions, the maximum surface tension decreases from regularity are -3.8, -2.7, and -1.5% for H₂-D₂, H₂-HD, and HD-D₂. Considering the molecular weight differences, we estimate -2.3, -1.3, and -1.0% for D₂-T₂, D₂-DT, and DT-T₂. For the ternary D₂-DT-T₂ solution, this decrease could be -2 to -5% below regularity. Employing the -2% we estimate a triple-point surface tension of 4.23×10^{-3} N/m for liquid D₂-DT-T₂ at 19.71 K.

LIQUID DENSITY

National Bureau of Standards recommended values²⁴ include measurements of H_2 , HD, D_2 , and T_2 ^{12,15,25,26} which we recently reviewed.¹⁸ Estimates for DT are interpolated from isothermal molecular weight plots. The liquid density ρ_L to 25 K is estimated by the empirical formula:

$$\rho_L = A_L - B_L T^2, \quad (5)$$

where T is the temperature and the constants A_L and B_L are as listed in Table 4. Volume changes upon combining binary solutions of the hydrogens have been studied, but the results are contradictory,²⁷⁻³⁰ and we do not attempt to estimate the deviation from regularity. The estimated liquid density of 19.71 K D_2 -DT- T_2 is $0.0446 \times 10^6 \text{ mol/m}^3$ (224 Kg/m^3).

SOLID DENSITY

Some densities for H_2 , HD, and D_2 have been measured by bulk methods.^{6,31} More data are available on H_2 , HD, D_2 , and T_2 by x-ray, neutron, and electron diffraction.³²⁻³⁵ We have summarized these data recently³⁶ with the empirical expression for solid density ρ_S :

$$\rho_S = A_S - B_S T^3, \quad (6)$$

where A_S and B_S are constants given in Table 4. The T^3 form is dictated by a few 10 to 11 K D_2 points, which could be high. The H_2 data can also be represented by the T^2 form of Eq. (5). Insufficient data exist for the other isotopes. Equation (5) is applicable to both the usual hexagonal-close-packed structure and to the face-centered-cubic structure that forms below 4 K. The errors inherent in the available density data are larger than the volume change of the crystallographic transition.³⁶ There are no solid solution density data, and no estimates of deviations from regularity are possible. For solid D_2 -DT- T_2 of about 3:4:3 composition, the estimated 19.71 K density is $0.051 \times 10^6 \text{ mol/m}^3$ (256 Kg/m^3). At 4.2 K it is not possible to estimate the chemical equilibrium so we employ the molecular DT estimate of $0.053 \times 10^6 \text{ mol/m}^3$ (267 Kg/m^3).

Considerable shrinkage occurs upon freezing. For H_2 , HD, and D_2 , it is -11.0, -11.3, and -11.6 vol%.³⁶ For DT and T_2 we estimate -13 and -14%, respectively. These larger values for DT and T_2 result from a single T_2 density point measured at 4.2 K³⁷ and are therefore open to speculation. Nevertheless, considerable physical distortion is expected as liquid D_2 -DT- T_2 freezes.

SIMPLE DROPLET EXAMPLES

To illustrate the uses of the preceding data, we estimate some values for a few properties of a D_2 -DT- T_2 droplet. We first directly compare the forces of surface tension and gravity for a droplet falling in free space. We solve for the droplet radius a :

$$a = \sqrt{\frac{3}{2} \frac{\gamma F}{\rho_L g}} \quad (7)$$

where γ is the surface tension, ρ_L is the liquid density, g is the acceleration due to gravity; and F is the ratio of gravitational to surface tension forces. If F is 0.01, the radius is 170 μm ; for $F = 1$ with considerable expected distortion, the radius is 1700 μm . The stability of the drops may be surprising, even with a small surface tension, but the liquid density is also low. Thus, the expected droplet radius for liquid DT is about half that calculated for water, which has a surface tension 12 times as great.

The oscillations of the DT droplet may also be calculated. The frequency of the second-order dumbbell oscillation f_2 is³⁸

$$f_2 = \frac{1}{2\pi} \sqrt{\frac{8\gamma}{\rho_L a^3}} \quad (8)$$

and the time constant for damping the oscillation is³⁸

$$t_2 = \frac{\rho a^2}{5\eta} \quad (9)$$

For triple-point liquid DT with a 170- μm -radius droplet, the oscillation frequency is 880 Hz with a damping time of only 24 ms.

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