Mapping the Density of Argon, Hydrogen, and Deuterium Over a Wide Range of Pressures and Temperatures in a Diamond Anvil

Thomas Folan

August 2023

Table of Contents

1. Introduction
    1.1. Important Phase Points
        1.1.1. Argon
        1.1.2. Hydrogen
        1.1.3. Deuterium
    1.2. Desired Ranges
    1.3. Achieved Ranges
        1.3.1. Phase Determination
        1.3.2. Density Determination
    1.4. Programming Details
    1.5. Conclusion
2. Appendix
3. Citations

1. Introduction

Fermilab is considering giving NK Labs use of a new muon beamline in the MTA hall for the purposes of studying muon-catalyzed fusion. For this experiment, NK Labs has designed and built a diamond anvil which is to be used to both expand the known behavior of muon catalyzed fusion over a wider range of pressures and temperatures than ever before and to improve upon the accuracy of previous measurements. The anvil system determines internal pressure (through spectroscopy of ruby dust in the compression chamber) and temperature (through thermocouples embedded into the core part of the diamond anvil). It is expected that the observed characteristics of this muon-catalyzed fusion will have some sort of correlation with the density of the mixture under compression, and so it was decided that a set of python scripts be made to automatically determine the density from the pressure and temperature measured by the anvil's sensors. As a Caveat to this goal, a secondary set of scripts would need to be made to determine the phase state of the mixture due to phase state affecting density calculations. The specific substances chosen to be calculated for were argon, for anvil testing; hydrogen, since it will act as a control in the study; and deuterium, an integral part of the mixture to be used in the actual fusion.

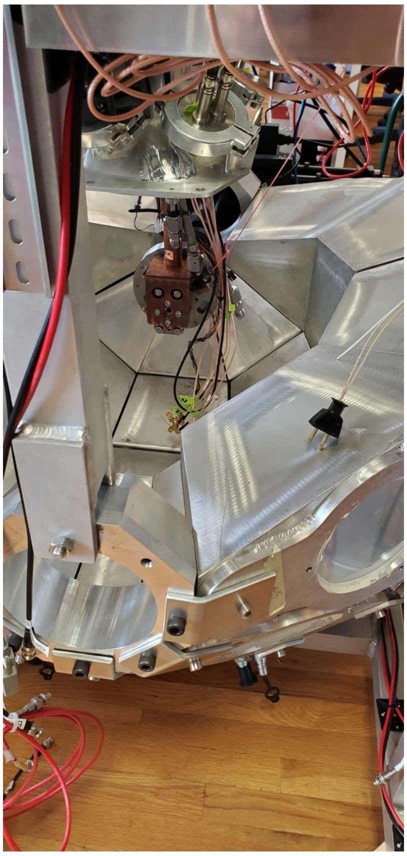

Figure 1: Diamond anvil cell without thermal Shielding

1.1. Important Phase Points

Due to the critical point and triple point parameters being useful for utilizing the equations found in the appendix, I have deemed it fit to make a compiled list of the pressures and temperatures of the critical and triple points of argon, hydrogen, and deuterium.

1.1.1. Argon

Temperature at the triple point: 83.8058 K [1]
Pressure at the triple point: 0.068891 MPa [1]
Temperature at the critical point: 150.687 K [1]
Pressure at the critical point: 4.863 MPa [1]

1.1.2. Hydrogen

Note: these are for the "equilibrium hydrogen", meaning hydrogen that has been left at a single pressure and temperature for an extended length of time.
temperature at the triple point: temperature at the triple point = 13.803 K [2]
pressure at the triple point: pressure at the triple point = 0.007042 MPa [2]
temperature at the critical point: 32.938 K [2]
pressure at the critical point: 1.2928 MPa [2]

1.1.3. Deuterium

temperature at the triple point: 18.69 K [3]
pressure at the triple point: 0.017130 MPa [3]
temperature at the critical point: 38.262 K [3]
pressure at the critical point:1.665 MPa [5]

1.2. Desired Ranges

The ideal range to be covered was stated by NK Labs as being 0.1-5 GPa and 5-1500 K for argon, hydrogen, and deuterium.

Due to the above range being relatively large for the short time allocated for this project, two priority regions were chosen. The first was 0.1-1 GPa and 20-500 K for Hydrogen The second was 0.1-1 GPa and 90-500 K for argon

1.3. Achieved Ranges

1.3.1. Phase Determination

1. Argon

   Overall, an accurate phase determination was made from 65-350 K with reasonable extrapolation behavior up until at least 700 K, which exceeds the maximum desired pressure of 5.0 GPa with the melting pressure of argon being around 5.3 GPa, at 700K effectively allowing for reasonable determination of phase state over the entire ideal range. The resulting phase plot can be seen in Fig. 1.

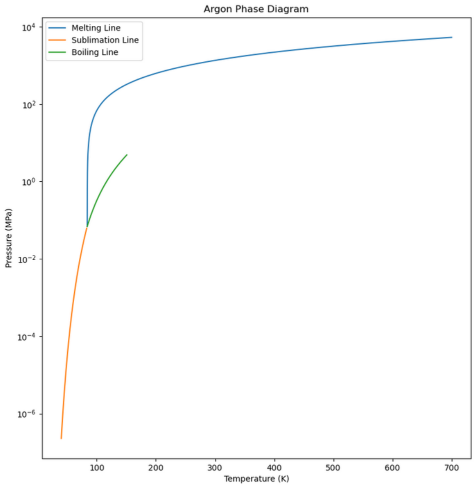

Figure 2: Calculated argon phase plot.

1. Melting Line

   For determination of the phase state of argon above the temperature at the triple point and pressure, it is absolutely essential that the melting line is determined.
   For the determination of the melting line,

Eq.(1) was selected from Tegeler et al.[1] for calculating the melting pressure from the ambient temperature. It promises an accurate determination of the melting line from the triple point at 83.8058 K up to 350 K with a maximum error range of less than ±2%. The source for higher pressure measurements was noted by the author of the paper as having systematic error, and so was discarded from the paper's equation fitting process. The tested region covers most of the priority range with the equation appearing to remain reasonable at the higher pressures and temperatures of the whole ideal range.

It should be noted that at points above the temperature at the critical point and pressure, the melting line determines a transition between a supercritical fluid state and a solid state.

2. Evaporation Line

For determination of phase in-between the temperature at the triple point, temperature at the critical point, and below the melting pressure, knowledge of vapor pressure is essential.

For this purpose, Eq.(2) was selected from Tegeler et al.[1], promising a maximum error range of less than ±0.2% across its entire applicable range. Above the temperature at the critical point, but below the pressure at thecritical point, argon remains a vapor at all temperatures within the ideally desired range.

3. Sublimation Line

To determine the state of argon at temperatures and pressures below those found at argon’s triple point, it is essential to know the sublimation line.

For the determination of the sublimation line, Eq.(3) was selected from Tegeler et al.[1] for calculating the sublimation pressure from the ambient temperature, promising a maximum error range of less than ±1.5% from the triple point at 83.8058 K down to around 65 K. If the ambient pressure is higher than the sublimation pressure at a certain temperature, then the argon will be solid. Otherwise, the argon will sublimate into a vapor. It should be noted that the entirety of argon's sublimation line is well below the lowest planned pressure, but given its availability and ease of implementation, it made it worthwhile to add this capability to the program.

2. Hydrogen

Overall, an accurate phase determination was made that practically covers the entire ideal range. The pressures for phase transitions at the higher and lower temperatures not covered by the following equations are at pressures outside of the range of pressures that tests were planned to be conducted at. The raw temperature range with which phase state determinations can be made with known accuracy is 10 K to 550 K. The resulting phase plot can be seen in Fig. 2.

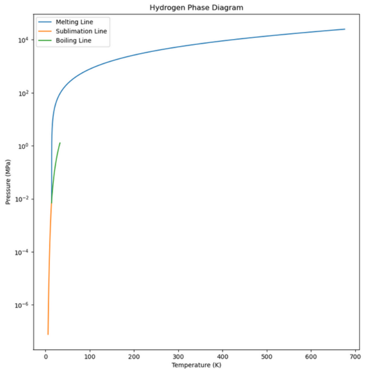

Figure 2: Calculated hydrogen phase plot.

1. Melting Line

For determination of the phase state of hydrogen above the temperature at the triple point and pressure at the triple point it is absolutely essential that the melting line is determined.

For the determination of the melting line, Eq.(4) was was selected from Datchi el al.[6] for calculating the melting temperature of hydrogen. It promises a maximum error range with less than ±3% error from the pressure at the triple point to out in excess of 10 GPa, covering the entire ideal range with ease and accuracy. It should be noted that at points above the temperature at the critical point and above the pressure at the triple point, the melting line determines a transition between a supercritical fluid state and a solid state.

2. Evaporation Line

For determination of phase in-between the temperature at the triple point, temperature at the critical point, and below the melting pressure, knowledge of vapor pressure is essential.
For this purpose, two equations were selected from P. C. Souers[4], Eq.(5) and Eq.(6) with Eq.(5) handling temperatures from the triple point to 20K and Eq.(6) handling the range from 20 K to the critical point. The source of these equations promises a maximum error range of about ±0.1 K over the entire range with both of these equations employed. These equations are for "equilibrium hydrogen", meaning hydrogen left at a certain pressure and temperature for a length of time. This was due to equilibrium hydrogen's vapor pressure, the determination of evaporation, being the most thoroughly and accurately mapped out. Above the temperature at the critical point, but below the pressure at the critical point, hydrogen remains a vapor at all temperatures within the ideally desired range.

3. Sublimation Line

To determine the state of hydrogen at temperatures and pressures below those found at hydrogen’s triple point it is essential to know the sublimation line. For this purpose, the equation for calculating the sublimation pressure of para-hydrogen, Eq.(7) was taken from R. D. McCarty et al.[2]. The source promises a maximum error range of about ±1% down to 10 K. The equation for para-hydrogen was selected over the equation for "normal hydrogen" due to its maximum error range being 5 times lesser at the higher temperatures nearer to the triple point.
It should be noted that the entirety of hydrogen's sublimation line is below the lowest planned pressure, but given the eventual plan to go to temperatures below the triple point, it made it worthwhile to add this capability to the program.

3. Deuterium

Overall, an accurate determination of phase state was made that covers from 10K to about 630K. The resulting phase plot can be seen in Fig. 3.

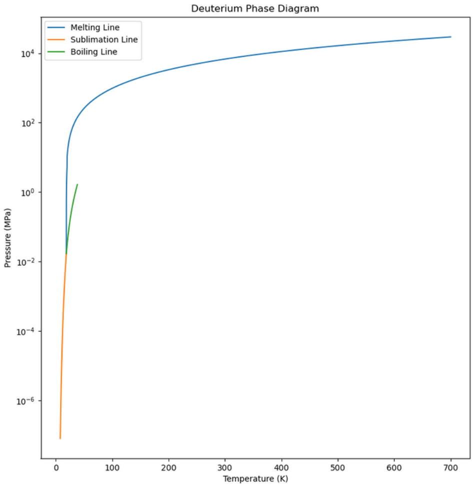

Figure 3: Calculated phase plot of deuterium.

1. Melting Line

2. For determination of the phase state of deuterium above the temperature at the triple point and pressure at the triple point it is absolutely essential that the melting line is determined.
In the case of Deuterium, two equations

had to be utilized to adequately cover the ideal range, those being Eq.(8) from Roder et al [7] and Eq.(9) from Driessen et al. [8] with Eq.(8) covering from 0->1 kbar (100 MPa) and Eq.(9) covering from 1 kbar to 18 kbar(0.1 GPa to 1.8 GPa). Eq.(9) claims a maximum error range of ±1% over its range while Eq.(8) gives no estimate of accuracy or range. When graphed, the melting curves meet with no obvious changes at 1 kbar. As well, Eq.(8) is much closer to predicting deuterium's critical point than Eq.(9). As such, it can be assumed that Eq.(8) has acceptable accuracy near 1 kbar and better accuracy than Eq.(9) at lower pressures.

3. Evaporation Line

   For determination of phase in-between the temperature at the triple point, temperature at the critical point, and below the melting pressure, knowledge of vapor pressure is essential.
   For this purpose, Eq.(10)[9] was utilized. When compared to experimental data on vapor pressure, the vast majority of the experimental data falls within ±3% across the entire range from Deuterium's triple point to its critical point. Above the temperature at the critical point, but below the pressure at the critical point, deuterium remains a vapor at all temperatures within the ideally desired range.

4. Sublimation Line

   To determine the state of deuterium at temperature and pressures below those found at deuterium’s triple point, knowing deuterium’s sublimation line is essential.
   For this purpose, Eq.(11) was taken from P. C. Souers[4]. Eq.(11) covers from 14K deuterium's triple point with around ±0.01K accuracy.
   It should be noted that the entirety of deuterium's sublimation line is well below the lowest planned pressure, but given the eventual plan to go to temperatures below the triple point, it was deeemed worthwhile to add this capability to the program.

1.3.2. Density Determination

1. Argon

   Overall, argon's density was mapped for its fluid region from its triple point at 83.8 K to 700 K, covering the priority range. Sadly, no adequately accurate equation for the density of solid argon was discovered over the length of this research project.

1. Fluid

   The fluid domain, encompassing vapor, liquid, and supercritical fluid phases; makes up the lower pressure and higher temperature parts of the region to be mapped.
   For the determination of Argon's density in the fluid region, Eq.(12) was chosen from Tegeler et al. [1]. Eq.(12) uses the density and temperature of the argon to determine the pressure is it under, By utilizing an optimization algorithm, the density was numerically solved for by having the computer take iterative guesses at density until the equation, taking the experimental temperature in Kelvin and a guessed density in kg/m^3, output the experimentally observed pressure in MPa. In this way, the pressure and temperature observed in the diamond anvil cell could be utilized to find the density of the argon under compression. This equation is supposed to cover from argon's triple point to 700 K, but it is stated that it should theoretically give reasonable results out to 17000 K. The paper shows the equation predicting the density of argon against various papers with exceptional accuracy. In most cases, it achieves accuracy better than ±1%.

2. Solid

No sufficiently accurate equation for the density of solid argon was found that worked within the ideal range of pressures.

2. Hydrogen

   Overall, the fluid region of hydrogen was mapped from 0->2 GPa with maximum temperatures up to 1000 K. The solid region mapped out from 0->2.5 GPa from 0K to the melting line. The accuracy within the fluid region decreases with pressure, but can be considered to range from 0.1% at lower pressures up to a maximum of ±5% as the pressure approaches 2000 MPa. It should be noted that the fluid region density calculations can handle multiple types of isomers. Within the Solid region, the maximum error range is claimed to be around ±1.5%.
   These equations completely cover the priority region in all phase states along with around half of the ideal region.

1. Fluid
   The fluid domain, encompassing vapor, liquid, and supercritical fluid phases; makes up the lower pressure and higher temperature parts of the region to be mapped. For this purpose, a preexisting script, made by Ara Knaian of NK Labs, was utilized. The script implements Eq. (14) of Leachman et al.[10], solving for the pressure of Hydrogen. This equation is capable of handling unique isomers. The density is numerically solved for by utilizing an optimization algorithm that has the computer take iterative guesses at density until the Eq.(14). taking the experimental temperature in Kelvin and a guessed density in cm^3/mole, output the experimental pressure observed in the diamond anvil in MPa.
   The paper claims to be accurate out to 2 GPa and 1000 K.The paper shows maximum error range of ±2% error past 500 K with it remaining consistent out to 1000 K. In most cases, the equation is better than ±1% error.

2. Solid

   The solid domain makes up the higher pressure and lower temperature parts of the region to be mapped.
   For mapping this region, equation (13) of Driessen et al.[8] was utilized. The most notable part of this equation's implementation were the multiple blatant typos and omissions in the equation and its coefficients, only found and corrected by cross-checking the paper with other papers by the same author that utilized the same basic equation. However, after correcting these errors and implementing the equation in full, it showed high levels of correlation with other sources such as Anderson et al.[11], confirming Eq.(5)'s basic validity. The source paper claims that the equation should have a maximum error in the range of ±1.5% with error increasing at higher pressures. The paper claims that the equation should work out to 2.5 GPa.
   This is the same equation as utilized for solid deuterium. This is possible due to the equation being a fit equation based upon arbitrary variables. The paper provides separate sets of variables for hydrogen and deuterium.
   It should be noted that the specific isomer of hydrogen modeled by this equation is para-hydrogen.

3. Deuterium

   Overall, the fluid region of deuterium was mapped from 0->2 GPa with maximum temperatures up to 1000 K. The solid region was mapped out from 0->2.5 GPa and from 0K to the melting line.
   The accuracy within the fluid region decreases with pressure, but can be considered to range from 0.1% at lower pressures up to a maximum of ±5% as the pressure approaches 2000 MPa. It should be noted that the

fluid region density calculations can handle multiple types of isomers. Within the Solid region, the maximum error range is claimed to be around ±1.5%.

1. Fluid

   The fluid domain, encompassing vapor, liquid, and supercritical fluid phases; makes up the lower pressure and higher temperature parts of the region to be mapped. For this purpose, a preexisting script, made by Ara Knaian of NK Labs, was utilized. The script implements Eq. (15) of Richardson et al.[9], solving for the pressure of Hydrogen. Equation (15) is also notable for being capable of handling unique isomers.
   The density was numerically solved for by utilizing an optimization algorithm that has the computer take iterative guesses at density until the equation, taking the experimental temperature in Kelvin and a guessed density in cm^3/mole, output the experimental pressure observed in the diamond anvil in MPa.
   The paper claims to be accurate out to 2 GPa and 1000 K, but the error rapidly rises at these higher pressures and temperatures, approaching ±4%. At lower pressures and temperatures, such as under 1 GPa, the maximum error range may be considered ±2.5%.

2. Solid

   The solid domain makes up the higher pressure and lower temperature parts of the region to be mapped.
   For mapping this region, equation (13) of Driessen et al.[8] was utilized. The most notable part of this equation's implementation were the multiple blatant typos and omissions in the equation and its coefficients, only found and corrected by cross-checking the paper with other papers by the same author that utilized the same basic equation. However, after correcting these errors and implementing the equation in full, it showed high levels of correlation with other sources such as [11], confirming Eq.(5)'s basic validity. The source paper gives no explicit guess at the accuracy of Eq.(5) with deuterium's coefficients, however, it does state that there is an "excellent agreement" between experimental data and the fit equation at pressures above 246 bar (24.6 MPa). The paper claims that the equation should work out to 2.5 GPa.
   This is the same equation as utilized for solid hydrogen. This is possible due to the equation being a fit equation based upon arbitrary variables. The paper provides separate sets of variables for hydrogen and deuterium.
   It should be noted that the specific isomer of deuterium modeled by this equation is ortho-deuterium.

1.4. Programming Details

The various scripts produced on the basis of this research were implemented in Python for ease of interoperability with preexisting NK Labs programs. The various scripts produced were incorporated into a modular project centered around a dispatching function that automatically determines the correct functions and data to return based upon the input of a temperature in kelvin, pressure in MPa, substance, and isomer. This organization should allow for the capabilities of this program to be readily expanded by the addition of further equations that may be better at handling the more extreme conditions not completely covered by the fruits of this research project.

1.5. Conclusion

After two weeks of research and programming, equations were discovered to map out the phase state and density of argon, hydrogen, and deuterium sufficiently well across a wide enough range of pressures and temperatures to cover the priority regions laid out by NK Labs with the glaring exception of an accurate determination of the density of solid argon within the solid region. For Hydrogen and Deuterium, a significant portion of the Ideally desired range was also ultimately covered. The discovered equations were also correctly implemented in code, allowing for the accurate and automatic determination of conditions within NK Lab's diamond anvil based upon known and observed conditions.

Future research should focus upon the expansion of the mapped range of phase states and density with particular attention paid to the mapping of the density of solid argon in order to fully map out argon's priority region.

2. Appendix

Equation (1) $\frac{p_m}{p_t}=1+a_1[(\frac{T}{T_t})^{1.05}-1]+a_2[(\frac{T}{T_t})^{1.275}-1]$

with
p_{m} = Melting pressure of argon
T_{t} = temperature at the triple point of argon = 83.8058 K
T = Temperature in Kelvin
a_1 = -7476.2665
a_2 = 9959.0613

Equation (2) $\ln(\frac{p_s}{p_c})=\frac{T_c}{T}(a_1\vartheta+a_2\vartheta^{1.5}+a_3\vartheta^2+a_4\vartheta^{4.5})$

with
p_{s} = vapor pressure of argon
p_c = pressure at the critical point of argon = 4.863 Mpa
T = Temperature in Kelvin
T_{c} = temperature at the critical point of argon = 150.687 K
$\vartheta=(1-T/T_c)$
a_1 = -5.940 978 5
a_2 = -1.355 388 8
a_3 = -0.464 976 07
a_4 = -1.539 904 3

Equation (3) $\ln(\frac{p_{\text{sub}}}{p_t})=\frac{T_t}{T}[a_1(1-\frac{T}{T_t})+a_2(1-\frac{T}{T_t})^{2.7}]$

p_{sub}= Argon's pressure of sublimation.
T_{t} = temperature at the triple point of argon = 83.8058 K.
T = Temperature in Kelvin.
p_{t} = pressure at the triple point of argon = 68.891 kPa.
A_1 = -11.391604.
a_2 = -0.39513431.

Equation (4) $T_m=T_0(1+P/0.0286)^{0.589}\exp(-4.6*10^{-3}P)$
T_m = Hydrogen's melting temperature in Kelvin.
T_0 = Hydrogen's melting point at zero pressure = 14.025K.

P = Pressure in GPa from 0 to 15 GPa.

Equation (5) $\ln(P_{\text{sub}}(\mathrm{eH_2}))=15.46688-\frac{101.3378}{T}+5.432005*10^{-2}T-1.105632*10^{-4}T^2$

P = Equilibrium hydrogen's vapor pressure in Pa.

T = Temperature in Kelvin from 13.81 to 20K.

Equation (6) $\ln(P_{\text{sub}}(\mathrm{eH_2}))=7.67696-\frac{71.102}{T}+2.44498\ln(T)$

P = Equilibrium hydrogen's vapor pressure in Pa.

T = Temperature in Kelvin from 20K to 32K.

Equation (7) $\log(P)=\frac{A}{T}+B\log(T)+C$

P = Hydrogen’s sublimation pressure in mmHg.
T = Temperature in Kelvin from 13.81 to 10K.
A = -90.77568949.
B = 2.489830940.
C = 4.009857354.

Equation (8) $\frac{(P-P_t)}{(T-T_t)}=A\exp(\frac{-\alpha}{T})+BT+C$

P = Melting pressure of deuterium in atm (1 atm = 0.101325 MPa).
T = Temperature in kelvin.
P_t = Deuterium’s critical pressure in atm = 0.169 atm.
T_t = Deuterium’s triple temperature in kelvin = 18.69 K.
α = 5.693.
B = 2/3.
C = 3.85.

Equation(9) $P_m-0.5431+3.666*10^{-3}T^{1.677}$
P_m = Deuterium’s melting pressure in kbar (1 kbar = 100 Mpa).
T = Temperature in Kelvin.

Equation (10) $\ln(\frac{p_s}{p_c})=\frac{T_c}{T}[N_1\theta+N_2\theta^{1.5}+N_3\theta^{2.83}+N_4\theta^{4.06}+N_5\theta^{5.4}]$

p_s = vapor pressure of deuterium MPa.
p_c = pressure at the critical point of deuterium = 1.665 Mpa.
T = Temperature in Kelvin.
T_c = temperature at the critical point of deuterium = 38.262 K.
$\theta=1-T/T_c$
N_1 = -5.5706
N_2 = 1.7631
N_3 = -0.5458
N_4 = 1.2154
N_5 = -1.1556

Equation (11) $\ln(p_s(nD_2))=19.1918-\frac{177.476}{T}+6.63*10^{-3}(T-16.5)^2$

p_s = Sublimation pressure of deuterium in Pa.
T = Temperature in Kelvin.
Equation (12) $\frac{(p(T,\rho))}{(\rho RT)}=1+\delta\alpha_\delta^r$
ρ = Argon’s density in kg/m^3
p = Ambient pressure in Mpa
T = Temperature in Kelvin.
R = Ideal gas constant = 8.314
$\delta = \rho/\rho_c$
    ρ = Argon fluid density in kg/m^3
    ρ_c = Argon critical point density = 535.6 kg/m^3
α_δ^r = Refer to Eq.(12.1)

Equation(12.1)

$$\alpha_\delta^r=\sum_{i=1}^{12} n_i d_i \delta^{(d_i-1)}\tau^{(t_i)}+\sum_{i=13}^{37} n_i e^{(-\delta^{(c_i)})}[\delta^{(d_i-1)}\tau^{(t_i)}(d_i-c_i\delta^{(c_i)})]+\sum_{i=38}^{41} n_i \delta^{(d_i)}\tau^{(t_i)} e^{(-\eta_i(\delta-\epsilon_i)^2-\beta_i(\tau-\gamma_i)^2)}[\frac{d_i}{\delta}-2\eta_i(\delta-\epsilon_i)]$$

α_δ^r = Derivative of Helmholtz free energy.

$\delta = \rho / \rho_c$

ρ = Argon fluid density in kg/m^3

ρ_c = Argon critical point density = 535.6 kg/m^3

$\tau = T_c / T$

T = Temperature in Kelvin

T_c = temperature at the critical point of argon = 150.687 K

n_i = refer to table 1.

d_i = refer to table 1.

t_i = refer to table 1.

c_i = refer to table 1.

η_i = refer to table 1.

β_i = refer to table 1.

γ_i = refer to table 1.

ϵ_i = refer to table 1.

Equation (13) $P(V,T)=P_0(V)+P^*(V,T)$

NOTE: This equation is free of the erratum found in its source paper.

V = Volume in cm^3/mole.

T = Temperature in Kelvin.

P_0 = Refer to Eq.(13.1)

P^* = Refer to Eq.(13.2)

Equation(13.1) $P_0(V)=Y^5\sum_{i=1}^{n} B_i(Y^2-1)^i$

$Y=(V_0 V)^{(1/3)}$

V_0 = Refer to table 2.

B_i = Refer to table 2.

(13.2) $P^*(V,T)=\frac{(\gamma(V))}{V}\frac{(9N_0 k_B)}{(\theta_D^3(V))}T^4\int_0^{x_D}(\frac{x^3}{(e^x-1)})dx$

$\gamma(V)$ = refer to 13.2.1

$\theta_D(V)$ = refer to 13.2.2

$x_D=\theta_D/T$

$N_0 k_b$ = ideal gas constant = 8.314

Equation (13.2.1) $\gamma(V)=\frac{-(d\ln\theta_D(V))}{(d\ln(V))}$

Equation (13.2.2) $\theta_D(V)=\prod_{k=0}^{n}\exp(C_k x^k)$

$x = \ln(V) - \ln(V_0)$

C_k = refer to table 3

n = number of applicable C_k variables in table 3

Equation (14) $P=\rho^2 * \alpha_\rho^d$

P = Pressure in Mpa

ρ = Fluid hydrogen density in mole/m^3

α_ρ^d = Refer to Eq.(14.1)

Equation (14.1) $\alpha_\rho^d=R*T*\alpha_\delta^d/\rho_c$

R = Ideal gas constant = 8.314

T = Temperature in Kelvin
ρ_c = Hydrogen’s critical point density = Refer to table 5.
α_δ^d = Refer to Eq.(14.2)

Equation (14.2) $\alpha_\delta^d = \alpha_\delta^0 + \alpha_\delta^r$
α_δ^0 = Refer to Eq.(14.3)
α_δ^r = Refer to Eq.(14.4)

Equation (14.3) $\alpha_\delta^0 = 1/\delta$
$$\delta = \frac{\rho}{\rho_c}$$
$$\rho = density = \frac{mol}{m^3}$$
ρ_c = Refer to table 5.
ρ = Density in mole/m^3
ρ_c = Hydrogen’s critical point density = Refer to table 4.

Equation (14.4) $\alpha_\delta^r = \sum_1^7 h_\delta^d + \sum_8^9 h_\delta^d * \vartheta + h * \vartheta_\delta^d + \sum_{10}^{14} h_\delta^d + \theta + h + \theta_\delta^d$
h_δ^d = Refer to Eq.(14.4.1)
ϑ = Refer to Eq.(14.4.2)
h = Refer to Eq.(14.4.3)
ϑ_δ^d = refer to Eq.(14.4.4)
θ = refer to Eq.(14.4.5)
θ_δ^d = refer to Eq.(14.4.6)

Equation (14.4.1) $h_\delta^d = N_i d_i \delta^{(d_i - 1)} * \tau^{(t_i)}$
$$\delta = \frac{\rho}{\rho_c}$$
$$\rho = density = \frac{mol}{m^3}$$
ρ_c = Refer to table 5.
N_i = Refer to table 6.
d_i = Refer to table 6.
t_i = Refer to table 6.
τ = Critical Temperature in Kelvin/ Temperature in Kelvin
Equation (14.4.2) $\vartheta = \sum_1^9 \exp\left(-\delta^{(p_i)}\right)$
$$\delta = \frac{\rho}{\rho_c}$$
$$\rho = density = \frac{mol}{m^3}$$
ρ_c = Refer to table 5.
p_i = refer to table 6

Equation (14.4.3) $h = N_i * \delta^{(d_i)} * \tau^{(t_i)}$
$$\delta = \frac{\rho}{\rho_c}$$
$$\rho = density = \frac{mol}{m^3}$$
ρ_c = Refer to table 5.

N_i = Refer to table 6.
d_i = Refer to table 6.
t_i = Refer to table 6.
τ = Critical Temperature in Kelvin/ Temperature in Kelvin

Equation (14.4.4) $\vartheta_{\delta}^{d}=p_i*(-\exp(-\delta^{(p_i)})*\delta^{(p_i-1)})$
$\delta=\frac{\rho}{\rho_c}$
$\rho=density=\frac{mol}{m^3}$
ρ_c = Refer to table 5.

Equation (14.4.5) $\theta=\exp(\phi_i*(\delta-D_i)^2)+\beta_i*(\tau-\gamma_i)^2$
$\delta=\frac{\rho}{\rho_c}$
$\rho=density=\frac{mol}{m^3}$
ρ_c = Refer to table 5.

τ = Critical Temperature in Kelvin/ Temperature in Kelvin
γ_i = Refer to table 7.
β_i = Refer to table 7.
D_i = Refer to table 7.
ϕ_i = Refer to table 7.

Equation(14.4.6) $\theta_{\delta}^{d}=2*\phi_i*(\delta-D_i)*\exp(\beta_i*(\tau-\gamma_i)^2+\phi_i*(\delta-D_i)^2)$
$\delta=\frac{\rho}{\rho_c}$
$\rho=density=\frac{mol}{m^3}$
ρ_c = Refer to table 5.

τ = Critical Temperature in Kelvin/ Temperature in Kelvin
γ_i = Refer to table 7.
β_i = Refer to table 7.
D_i = Refer to table 7.
ϕ_i = Refer to table 7.

Equation (15) $P=\rho^2*\alpha_{\rho}^{d}$
P = Pressure in Mpa
ρ = Fluid hydrogen density in mole/m^3
α_{ρ}^{d} = Refer to Eq.(15.1)

Equation (15.1) $\alpha_{\rho}^{d}=R*T*\alpha_{\delta}^{d}/\rho_c$
R = Ideal gas constant = 8.314
T = Temperature in Kelvin
ρ_c = Hydrogen's critical point density = Refer to table 8.
α_{δ}^{d} = Refer to Eq.(15.2)

Equation (15.2) $\alpha_{\delta}^{d}=\alpha_{\delta}^{0}+\alpha_{\delta}^{r}$
α_{δ}^{0} = Refer to Eq.(15.3)

α^r_δ = Refer to Eq.(15.4)

Equation (15.3) $\alpha^0_\delta = 1/\delta$
$\delta = \frac{\rho}{\rho_c}$
$\rho = density = \frac{mol}{m^3}$
ρ_c = Refer to table 8.

Equation (15.4) $\alpha^r_\delta = \sum_1^8 h^d_\delta + \sum_9^{14} h^d_\delta * \vartheta + h * \vartheta^d_\delta + \sum_{15}^{21} h^d_\delta + \theta + h + \theta^d_\delta$
h^d_δ = Refer to Eq.(15.4.1)
ϑ = Refer to Eq.(15.4.2)
h = Refer to Eq.(15.4.3)
ϑ^d_δ = refer to Eq.(15.4.4)
6 = refer to Eq.(15.4.5)
θ^d_δ = refer to Eq.(15.4.6)

Equation (15.4.1) $h^d_\delta = N_i d_i \delta^{(d_i - 1)} * \tau^{(t_i)}$
$\delta = \frac{\rho}{\rho_c}$
$\rho = density = \frac{mol}{m^3}$
ρ_c = Refer to table 8.
N_i = Refer to table 9.
d_i = Refer to table 9.
t_i = Refer to table 9.
τ = Critical Temperature in Kelvin/ Temperature in Kelvin
Equation (15.4.2) $\vartheta = \sum_1^9 \exp\left(-\delta^{(p_i)}\right)$
$\delta = \frac{\rho}{\rho_c}$
$\rho = density = \frac{mol}{m^3}$
ρ_c = Refer to table 8.
p_i = refer to table 9.

Equation (15.4.3) $h = N_i * \delta^{(d_i)} * \tau^{(t_i)}$
$\delta = \frac{\rho}{\rho_c}$
$\rho = density = \frac{mol}{m^3}$
ρ_c = Refer to table 8.
N_i = Refer to table 9.
d_i = Refer to table 9.
t_i = Refer to table 9.
τ = Critical Temperature in Kelvin/ Temperature in Kelvin

Equation (15.4.4) $\vartheta^d_\delta = p_i * \left(-\exp\left(-\delta^{(p_i)}\right) * \delta^{(p_i - 1)}\right)$
$\delta = \frac{\rho}{\rho_c}$

$\rho = density = \frac{mol}{m^3}$

ρ_c = Refer to table 8.

Equation (15.4.5) $\theta = \exp(\phi_i * (\delta - D_i)^2) + \beta_i * (\tau - \gamma_i)^2$

$\delta = \frac{\rho}{\rho_c}$

τ = Critical Temperature in Kelvin/ Temperature in Kelvin

γ_i = Refer to table 9.

β_i = Refer to table 9.

D_i = Refer to table 9.

ϕ_i = Refer to table 9.

Equation(15.4.6) $\theta_\delta^d = 2 * \phi_i * (\delta - D_i) * \exp(\beta_i * (\tau - \gamma_i)^2 + \phi_i * (\delta - D_i)^2)$

$\delta = \frac{\rho}{\rho_c}$

$\rho = density = \frac{mol}{m^3}$

ρ_c = Refer to table 8.

τ = Critical Temperature in Kelvin/ Temperature in Kelvin

γ_i = Refer to table 9.

β_i = Refer to table 9.

D_i = Refer to table 9.

ϕ_i = Refer to table 9.

Table 1:[1]

i	n_i	d_i	t_i	c_i	η_i	β_i	γ_i	ϵ_i
1	0.09	1	0					
2	0.71	1	0.25					
3	-1.68	1	1					
4	-0.15	1	2.75					
5	-0.12	1	4					
6	-0.12	2	0					
7	0.4	2	0.25					
8	-0.27	2	0.75					
9	0.24	2	2.75					
10	0.01	3	0					
11	-0.04	3	2					
12	0.02	4	0.75					
13	-0.32	1	3	1				
14	0.33	1	3.5	1				
15	0.03	3	1	1				
16	-0.307 770 860 02437e-1	4	2	1				
17	0.09	4	4	1				
18	-0.09	5	3	1				
19	0	7	0	1				
20	0	10	0.5	1				
21	0	10	1	1				
22	-0.01	2	1	2				
23	-0.02	2	7	2				
24	-0.06	4	5	2				
25	0.06	4	6	2				
26	0	8	6	2				
27	-0.01	3	10	3				
28	0.4	5	13	3				
29	-0.39	5	14	3				
30	-0.19	6	11	3				
31	0.16	6	14	3				
32	0.05	7	8	3				
33	-0.28953417958014e-1,	7	14	3				
34	-0.01	8	6	3				
35	0	9	7	3				
36	0	5	24	4				
37	0	6	22	4				
38	0.01	2	3		20	250	1.11	1
39	-0.69	1	1		20	375	1.14	1
40	1.53	2	0		20	300	1.17	1
41	0	3	0		20	225	1.11	1

Table 2: [8]

	p-H_2	o-D_2
$V_0 cm^3/mole$	23.21	19.95
B_1, bar	2790.1	4766.5
B_2, bar	4959.5	10101
B_3, bar	1868	
B_4, bar	-32.16	

Table 3:[8] (NOTE: High density means that the volume is less than 16cm^3/mole)

	H_2		D_2	
	LOW DENSITY	HIGH DENSITY	LOW DENSITY	HIGH DENSITY
C_0	4.6	4.6	4.52	4.55
C_1	-2.21	-2.21	-2.31	-1.84
C_2	-0.59	-0.61	-2.79	-0.18
C_3		-0.2	-5.12	
$V_0 cm^3 / mole$	23.21		19.95	

Table 5:[10]

	Temperature (K)	Pressure (Mpa)	Density (mol/m^3)
	Parahydrogen		
Critical point	32.94	1.29	15518
Triple point	13.8	0.007 041	38185
	Normal hydrogen		
Critical point	33.15	1.3	15508
Triple point	13.96	0.01	38200
	Orthohydrogen		
Critical point	33.22	1.310 65	15445
Triple point	14.01	0.007 461	38200

Table 6:[10]

	Parahydrogen				Normal hydrogen				Orthohydrogen			
i	N_i	t_i	d_i	p_i	N_i	t_i	d_i	p_i	N_i	t_i	d_i	p_i
1	-7.33	0.69	1	0	-6.94	0.68	1	0	-6.83	0.73	1	0
2	0.01	1	4	0	0.01	1	4	0	0.01	1	4	0
3	2.6	1	1	0	2.11	0.99	1	0	2.12	1.14	1	0
4	4.66	0.49	1	0	4.52	0.49	1	0	4.38	0.51	1	0
5	0.68	0.77	2	0	0.73	0.8	2	0	0.21	0.56	2	0
6	-1.47	1.13	2	0	-1.34	1.14	2	0	-1.01	1.62	2	0
7	0.14	1.39	3	0	0.13	1.41	3	0	0.14	1.83	3	0
8	-1.05	1.62	1	1	-0.78	1.75	1	1	-0.88	2.4	1	1
9	-1.01	1.16	3	1	0.35	1.31	3	1	0.8	2.11	3	1
10	-0.06	3.96	2	--	-0.02	4.19	2	--	-0.71	4.1	2	--
11	0.04	5.28	1	--	0.02	5.65	1	--	0.06	7.66	1	--
12	0.07	0.99	3	--	0.03	0.79	3	--	0.07	1.26	3	
13	-0.04	6.79	1	--	-0.02	7.25	1	--	-0.09	7.59	1	--
14	0.12	3.19	1	--	0.06	2.99	1	--	0.65	3.95	1	--

Table 7: [10]

i	ϕ_i	β_i	γ_i	D_i
			Parahydrogen	
10	-1.74	-0.19	0.8	1.55
11	-0.55	-0.2	1.52	0.18
12	-0.06	-0.03	0.66	1.28
13	-2.13	-0.24	0.68	0.63
14	-1.78	-0.33	1.49	1.71
			Normal hydrogen	
10	-1.69	-0.17	0.72	1.51
11	-0.49	-0.22	1.34	0.16
12	-0.1	-0.13	1.45	1.74

13	-2.51	-0.28	0.72	0.67
14	-1.61	-0.4	1.54	1.66
		Orthohydrogen		
10	-1.17	-0.46	1.54	0.64
11	-0.89	-0.4	0.66	0.39
12	-0.04	-0.09	0.76	0.94
13	-2.07	-0.44	0.66	0.4
14	-1.31	-0.57	1.43	0.96

Table 8: [9]

	Temperature (K)	Pressure (MPa)	Density(mol/m^3)
Critical point	38.34	0.665	17327
Triple point	18.724	0.017257	43283

Table 9: [9]

i	N_i	t_i	d_i	p_i	ϕ_i	β_i	γ_i	D_i
1	0.01	1	4					
2	10.54	0.46	1					
3	-10.14	0.56	1					
4	0.36	0.63	2					
5	0.18	1.2	3					
6	-1.13	0.31	1					
7	-0.05	1.31	3					
8	-0.68	1.12	2					
9	1.35	1.25	2	1				
10	-0.87	1.25	2	1				
11	1.72	1.4	1	2				
12	-1.92	1.63	1	2				
13	0.12	1	3	2				
14	-0.08	2.5	2	2				
15	1.69	0.64	1		-0.87	-0.61	0.63	1.46
16	-4.24	0.66	1		-0.64	-0.58	0.71	1.79
17	1.86	0.71	2		-0.67	-0.57	0.64	1.65
18	-0.59	2.25	3		-0.65	-1.06	0.82	0.64
19	1.52	1.52	3		-0.75	-1.01	0.99	0.97
20	2.36	0.67	1		-0.78	-1.03	1.22	1.89
21	-2.3	0.71	3		-0.69	-1.03	1.2	1.08

3. Citations

[1] C. Tegeler, R. Span, and W. Wagner, "A new equation of state for argon covering the fluid region for temperatures from the melting line to 700 K at pressures up to 1000 mpa," J. Phys. Chem. Ref. Data 28(3), 779–850 (1999). https://doi.org/10.1063/1.556037

[2] R. M. McCarty and H. Rhoder, Selected Properties of Hydrogen (Engineering Design Data), edited by J. Hord (National Bureau of Standards, Boulder, CO, 1981). https://nvlpubs.nist.gov/nistpubs/Legacy/MONO/nbsmonograph168.pdf

[3] H. J. Hoge and J. W. Lassiter, "Critical temperatures, pressures, and volumes of hydrogen, deuterium, and hydrogen deuteride," J. Res. National Bur. Stand. 47, https://doi.org/10.6028/JRES.047.010 (1951). https://nvlpubs.nist.gov/nistpubs/jres/47/jresv47n2p75_A1b.pdf

[4] S. P.c, "Cryogenic hydrogen data pertinent to magnetic fusion energy," UCRL–52628 (NTIS, Livermore, 1979). https://doi.org/10.2172/6205719

[5] I. A. Richardson, J. W. Leachman, and E. W. Lemmon, "Fundamental equation of state for deuterium," J. Phys. Chem. Ref. Data 43(1), 013103 (2014). https://doi.org/10.1063/1.4864752

[6] F. Datchi, P. Loubeyre, and R. LeToullec, "Extended and accurate determination of the melting curves of argon, helium, ice(H2O),and hydrogen(H2)," Phys. Rev. B 61(10), 6535–6546 (2000). https://doi.org/10.1103/physrevb.61.6535

[7] H. M. Roder, G. E. Childs, R. D. McCarty, and P. E. Angerhofer, Survey of the Properties of the Hydrogen Isotopes Below Their Critical Temperatures (US Department of Commerce, 1973). https://books.google.com/books?hl=en&lr=&id=ckn_UnEiuQkC&oi=fnd&pg=PA11&dq=melting+pressure+of+deuterium+rhoder&ots=d0ffkW0g85&sig=WxgVj7CboLuX7lddjOGOA7EovA4#v=onepage&q=melting%20pressure%20of%20deuterium%20rhoder&f=false

[8] A. Driessen and I. F. Silvera, "An improved experimental equation of state of solid hydrogen and deuterium," J. Low Temp. Phys. 54(3-4), 361–395 (1984). https://doi.org/10.1007/bf00683282

[9] I. A. Richardson, J. W. Leachman, and E. W. Lemmon, "Fundamental equation of state for deuterium," J. Phys. Chem. Ref. Data 43(1), 013103 (2014). https://doi.org/10.1063/1.4864752

[10] J. W. Leachman, R. T. Jacobsen, S. G. Penoncello, and E. W. Lemmon, "Fundamental equations of state for parahydrogen, normal hydrogen, and orthohydrogen," J. Phys. Chem. Ref. Data 38(3), 721–748 (2009). https://doi.org/10.1063/1.3160306

[11] M. S. Anderson and C. A. Swenson, "Experimental compressions for normal hydrogen and normal deuterium to 25 kbar at 4.2 K," Phys. Rev. B 10(12), 5184–5191 (1974). https://doi.org/10.1103/physrevb.10.5184