Property Prediction for the Development of Hydrogen Isotopologue Equations of State

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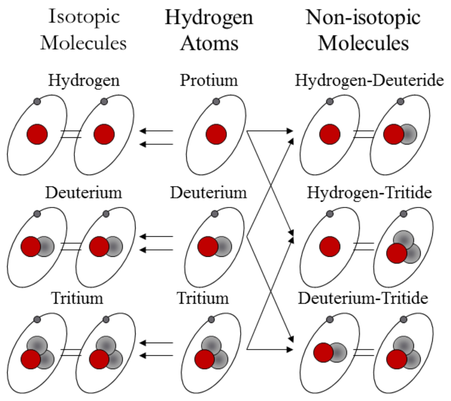

Figure 1: The molecular configurations demonstrating how hydrogen isotopes combine.

Scaling Method 1: Quantum Law of Corresponding States

Introduces a Quantum parameter Λ* defined as:

$$\Lambda^* = \frac{N_A h}{\sigma\sqrt{M\varepsilon}}$$

Λ* is unique for every element, and is the reduced de Broglie wavelength for a molecule. The quantum behavior of an element increases with Λ* . The Hydrogen's fall at the upper end of the scale along with the highest, ^{3}He. The QLCS incorporates Lennard-Jones intermolecular potentials in the reducing functions for the thermodynamic properties. Λ* plotted against reduced values yields a linear trend. The unknown value is determined by linear interpolation, a process also known as transformation. The QLCS has been successfully used in the past by a number of scientists to predict property values for H_2 and Helium-3, among others.[1, 2]

Despite our best hopes, the QLCS was unable to reliably predict known vapor pressures within the margin of error for those values. We did use the predicted densities and sound velocities in the fit since we had little or no other data available.

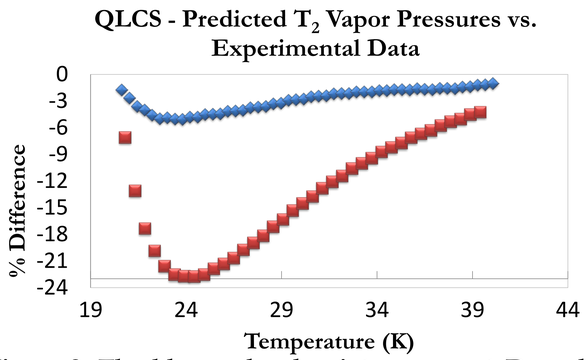

Figure 2: The blue and red points represent D_2 and H_2 vapor pressures that were respectively transformed to T_2 and compared against experimental data. Deviations were computed by $(P_{calc} - P_{exp}) / P_{exp}$

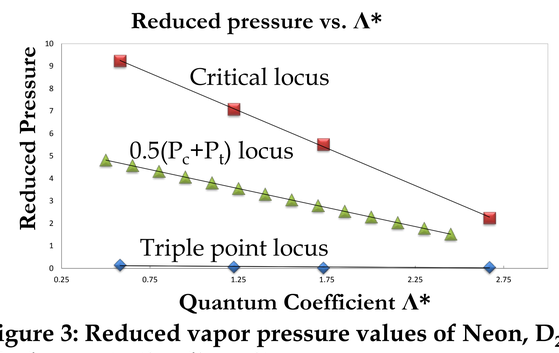

Figure 3: Reduced vapor pressure values of Neon, D_2, H_2, and He demonstrating linearity.

Introduction / Motivation

Accurate thermodynamic models for fusion energy fuels are needed as the completion date for major test facilities approaches. The recent development of models or Equations of State (EOS) for Hydrogen (H_2) and Deuterium (D_2) provided strong incentive to continue the process with other important isotopologues. My task was to collect data and assist in the subsequent fitting of the EOS for two of these – Tritium (T_2) and Hydrogen-Deuteride (HD).

A substantial lack of experimental measurements for T_2 and HD have hindered past EOS development efforts. This led us to investigate empirical methods for obtaining this essential information. My research utilized two methods for prediction, the Quantum Law of Corresponding States (QLCS), and the Geometric Mean Method (GM). Properties that we needed to predict included vapor pressures, densities, and sound velocities around the saturated liquid region and the single phase liquid region. By combining the predicted values with existing data, we endeavored to then produce a reference quality EOS.

The Equations of State

Modern EOS are explicitly defined in terms of the Helmholtz free energy. This is a thermodynamic potential, and can be likened unto more familiar potentials such as internal energy, enthalpy, or Gibbs free energy. The general form of the Helmholtz equation is shown below, where the α^0 coefficient corresponds to the ideal gas contribution. The α^r coefficient corresponds to the real fluid part of the equation, is also called the residual. τ and δ are reciprocals of the reduced temperature and density :

$$\frac{a(\rho,T)}{RT} = \alpha(\delta,\tau) = \alpha^0(\delta,\tau) + \alpha^r(\delta,\tau)$$

From the reduced Helmholtz energy, there exists a set of equations that allows one to calculate other thermodynamic properties such as enthalpies, and heat capacities by taking derivatives of this reduced Helmholtz energy. I have shown the formula for determining heat capacities below.

$$c_v(T,\rho) = -R\tau^2\left[\left(\frac{\partial^2\alpha^0}{\partial\tau^2}\right)_\delta + \left(\frac{\partial^2\alpha^r}{\partial\tau^2}\right)_\delta\right]$$

To use the equation to find a particular value, at least two thermodynamically independent pieces of information are required, and with these one can find any third value.

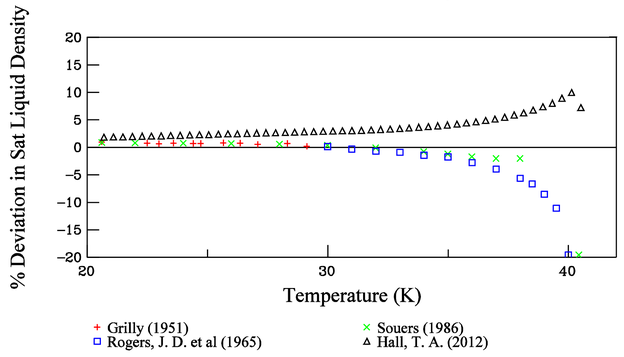

Figure 4: Comparing the EOS that is currently being fitted for tritium to existing and predicted data.

References:

[1] Leachman, J. W. J. Phys. Chem. Ref. Data, Vol. 38, No. 3, (2009)

[2] de Boer, J. Physica, Vol. 14, p. 139 (1948)

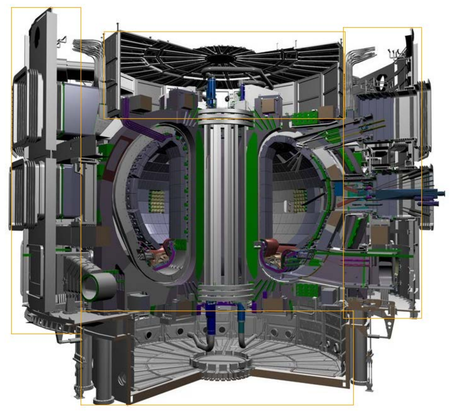

Figure 5: ITER, the fusion reactor currently under construction where D_2 and T_2 may be used as fuels.

Scaling Method 2: Geometric Mean Method

The GM is based on a simple relationship, shown below:

$$HD = \sqrt{H_2 D_2}$$

$$HT = \sqrt{H_2 T_2}$$

If we have experimental data, we can manipulated the 'X' term to minimize the deviations. For example, if we know a vapor pressure, density, or sound velocity for H_2 and D_2 at the same temperature, evaluation in the above equations will result in the respective value for HD. This method was not as applicable for T_2 due to nonexistent experimental measurements for HT. I was able to predict HD densities with a maximum deviation of O.3%.

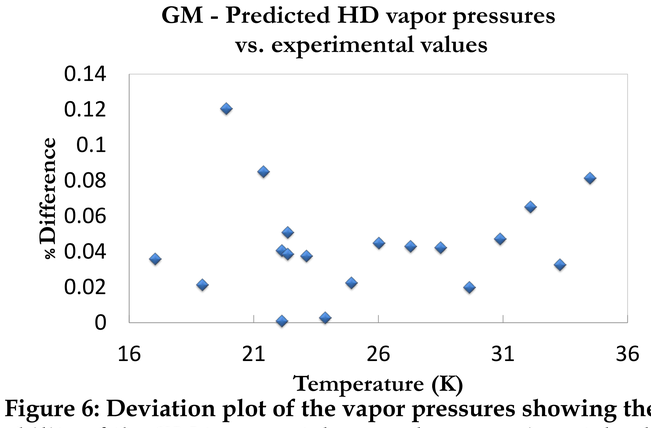

Figure 6: Deviation plot of the vapor pressures showing the ability of the GM to accurately reproduce experimental values.

Conclusions

The GM was shown to produce accurate results between the triple and critical points. However, due to an absence of experimental measurements for HT properties, we were unable use this method for tritium. The QLCS correctly predicted property values at the triple and critical point. Further investigation is necessary to determine why the intermediate values do not follow the presumed linear trend, and how to resolve the issue. The EOS will continue to be fitted until it demonstrates correct thermodynamic tendencies with minimal deviations. Ultimately, this work will be published as new fundamental equations of state for tritium and hydrogen-deuteride so we can get the ball rolling toward a new future with fusion energy.

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HYdrogen Properties for Energy Research