Sandia National Laboratories

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A Suite of Thermodynamic and Transport Properties for Computational Simulations with Hydrogen Isotopes

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Fire Science & Technology

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Introduction

As the heaviest isotope of hydrogen, tritium (^3H or T) is radiologically active

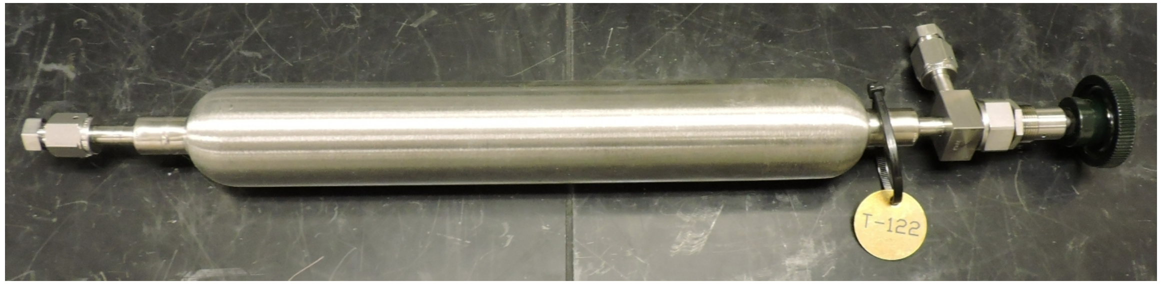
- Beta-decays to ^3He with a half-life of ~12 years
- Beta radiation does not penetrate skin, but beta radiation sources cause damage when internalized

Unlike protium (^1H) or deuterium (^2H or D), tritium is most hazardous to humans as water

- The human body metabolizes water, whereas T_2 does not appreciably penetrate skin (Mishima and Steele, 2002)

Tritium inventories at Sandia occur in small quantities stored at sub-atmospheric pressure

- Historical hydrogen (^1H) safety studies focus on different scenarios (jetting fires, explosions)
- For tritium, the key to understanding the hazard is the final extent of reaction from trace releases



Typical facility storage quantities for tritium are ~1 gram

Mishima, J. and Steele, C.M., 2002. *Oxidation of Tritium Gas under Accident and Transport Conditions. Rapport du DOE*. LA-UR-02-3803.

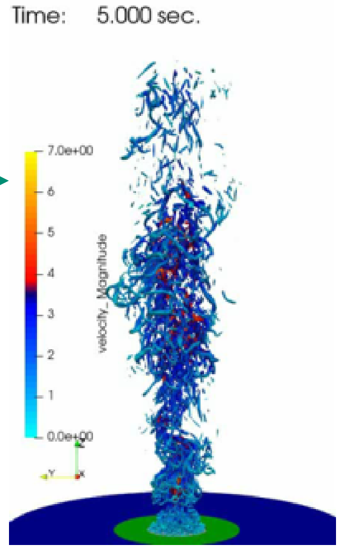
Three Aspects of Computational Hazard Analysis for Tritium with Fire

Entities with tritium inventories (including Sandia and SRNL) are federally regulated for safety

- "The bounding value given a fire defaults to 100 percent oxidation for use in safety analyses, as a realistic, less-conservative value has not been able to be identified" (DOE-STD-1129-2015)
- This project aims to provide a technical basis to consider a more lenient tritium oxidation assumption than the current approximation of 100% conversion in a facility fire

Because of the hazard and low tritium inventories, computational hazard analysis is ideal

- **Problem #1 is that there are few sources for physical properties and fire performance for tritium**
  - Focus of this presentation
- Problem #2 is that computational tools require verification and validation for credibility
  - Subject of recent and ongoing experiments and computational comparisons at Sandia →
- Problem #3 is that there are nearly infinite combinations of scenarios of potential interest
  - Principal topic of presentation by Alex Brown



Need for Tritium Physical Properties

No previous CFD studies have attempted to distinguish between the three isotopes of hydrogen interacting with a fire

- All properties available for protium and most for deuterium
- Very few tritium properties have been reported
- Properties influenced by isotope mass through interatomic potentials

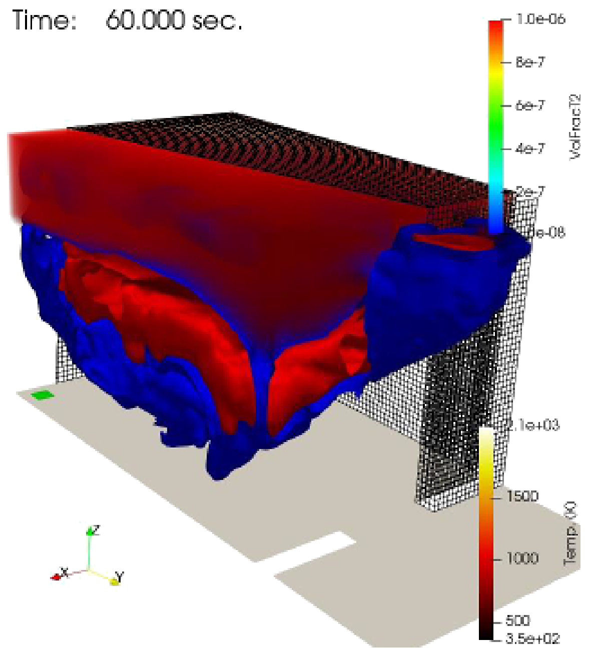
Thermodynamic properties can affect temperatures and extents of reaction through

- Heats of reaction
- Heat capacities
- Chemical equilibrium

Transport properties primarily affect diffusion rates

SIERRA/Fuego is Sandia's unstructured low-Mach number reacting flow code for simulating fires

- Utilizes Cantera-format specifications for properties of gases



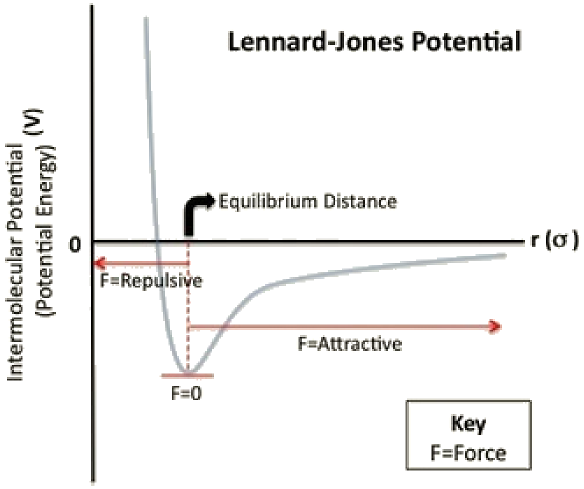


Figure C

Lennard-Jones Potential. (2020, August 15). Retrieved May 12, 2021, from https://chem.libretexts.org/@go/page/1661

Thermodynamic Properties – Source Coefficients

Cantera-style inputs in SIERRA/Fuego for thermodynamic properties use NASA polynomials

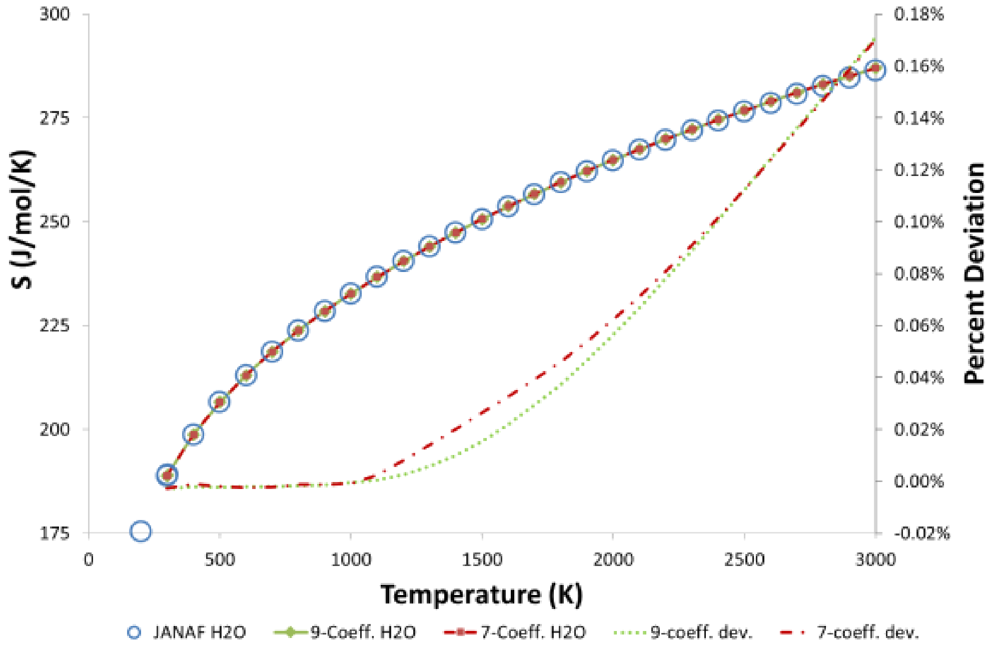
- Satisfy basic thermodynamic relationships for heat capacity, enthalpy, entropy
- Originally developed for chemical equilibrium calculations (NASA-CEA)

Different models generally yield results comparable to NIST-JANAF

- 7-coefficient model published most recently in 1993
- 9-coefficient model published subsequently in 2002 (2 new coefficients)
- 1998 NIST-JANAF Thermochemical Tables (treated as authoritative source)

Coefficients already existed for H, D, H_2, D_2, H_2O, D_2O, etc.

- Tritium species not included in NASA databases



M. W. Chase, "NIST-JANAF Thermochemical Tables," *J. Phys. Chem. Ref. Data,* vol. Monograph 9, pp. 1-1951, 1998. https://janaf.nist.gov/ (accessed 2020).

$$h^0(T) = \int c_p^0(T)\,dT$$

$$s^0(T) = \int \frac{c_p^0(T)}{T}\,dT$$

$$\frac{c_p^0(T)}{R} = b_0T^{-2} + b_1T^{-1} + b_2 + b_3T + b_4T^2 + b_5T^3 + b_6T^4$$

$$\frac{h^0(T)}{RT} = -b_0T^{-2} + b_1\frac{\ln(T)}{T} + b_2 + \frac{b_3}{2}T + \frac{b_4}{3}T^2 + \frac{b_5}{4}T^3 + \frac{b_6}{5}T^4 + \boldsymbol{\frac{b_7}{T}}$$

$$\frac{s^0(T)}{R} = -\frac{b_0}{2}T^{-2} - b_1T^{-1} + b_2\ln(T) + b_3T + \frac{b_4}{2}T^2 + \frac{b_5}{3}T^3 + \frac{b_6}{4}T^4 + \boldsymbol{b_8}$$

7-Parameter Model (1993):
B. J. McBride, S. Gordon, and M. A. Reno, "Coefficients for calculating thermodynamic and transport properties of individual species," NASA TM-4513, John H. Glenn Research Center, 1993. https://ntrs.nasa.gov/citations/19940013151

9-Parameter Model (2002):
B. J. McBride, M. J. Zehe, and S. Gordon, "NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species," NASA TP-2002-211556, John H. Glenn Research Center, 2002. https://www.grc.nasa.gov/WWW/CEAWeb/TP-2002-21556.htm

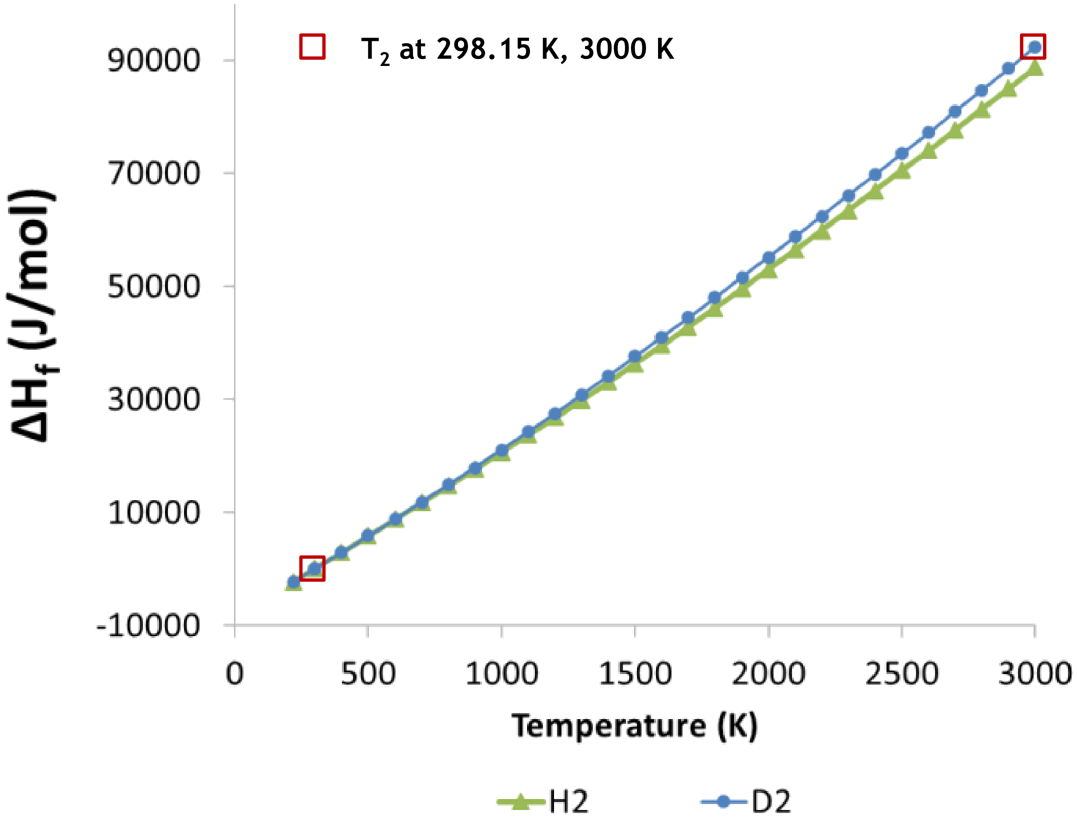
T_2 Formation Enthalpy

Formation enthalpies defined as zero at 298.15 K for all pure molecular species

- Includes all three isotopes of H_2

Chose to define T_2 formation enthalpy as identical to D_2

- Max deviation between D_2 and H_2 limited to 3% at 3000 K
  - Max deviation between T_2 and D_2 should be smaller
- Effectively specifies T_2 heat capacity as equivalent to D_2
  - Parameters defining both H_f and C_p are identical



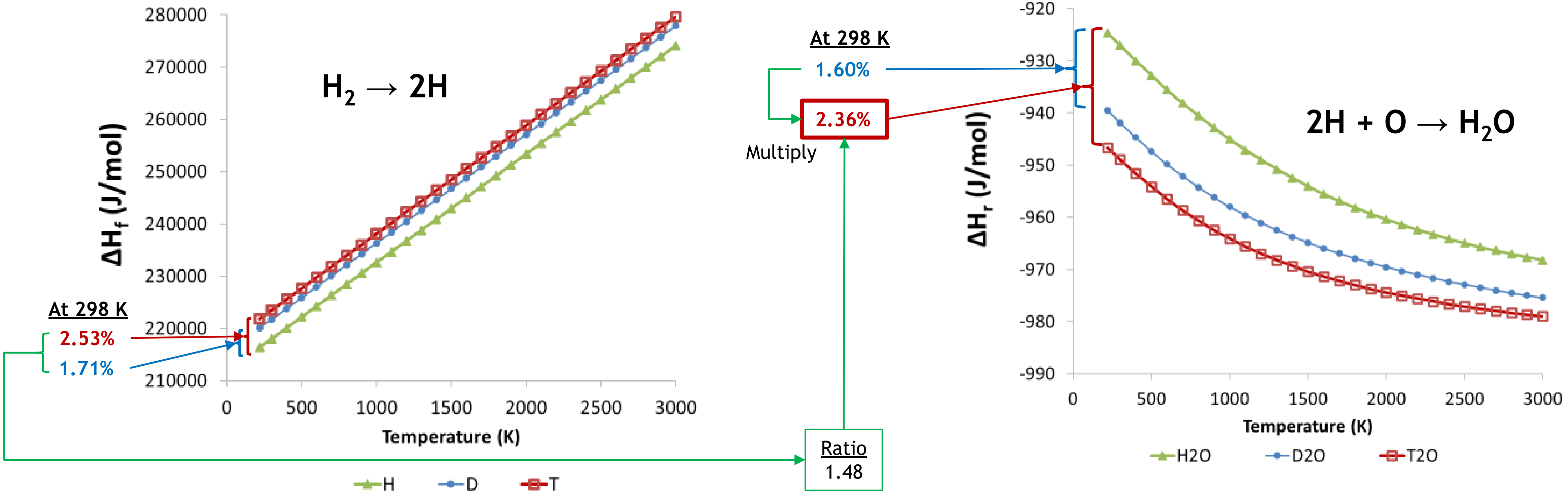
T_2O Formation Enthalpy Offset at 298 K

Dissociation enthalpies reported by Greenwood and Earnshaw (1997) allow atomic T enthalpy to be specified directly

- Leveraged ratios between H, D, and T bond formation to define water formation reaction enthalpy at 298.15 K
- Isotopic trends enforced (larger shift between H and D compared to between D and T)
- Subsequently backed out shift in T_2O formation enthalpy with respect to D_2O parameters

$$\frac{h^0(T)}{\boldsymbol{RT}} = a_0 + \frac{a_1}{2}T + \frac{a_2}{3}T^2 + \frac{a_3}{4}T^3 + \frac{a_4}{5}T^4 + \frac{\boldsymbol{a_5}}{\boldsymbol{T}}$$

← H constant offset coefficient



At 298 K

2.53%

1.71%

Ratio

1.48

Multiply

At 298 K

1.60%

2.36%

N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed. Boston: Butterworth-Heinemann, 1997.

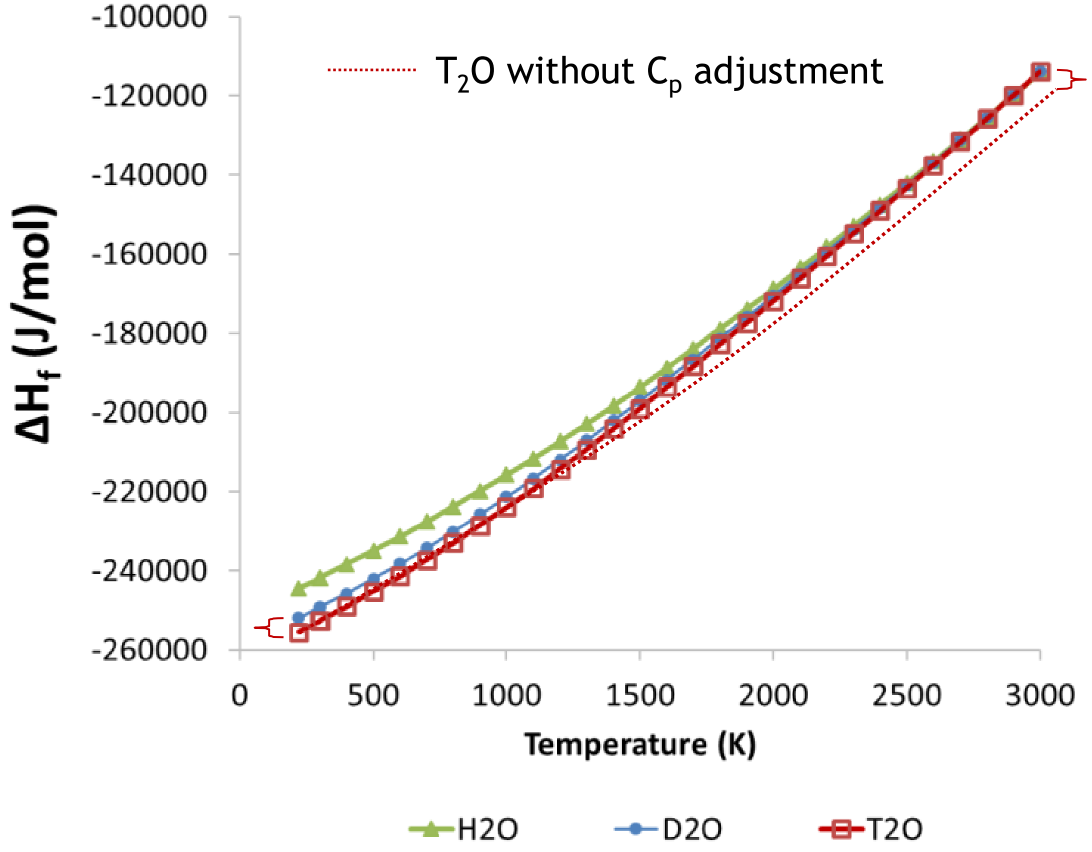
T_2O Heat Capacity

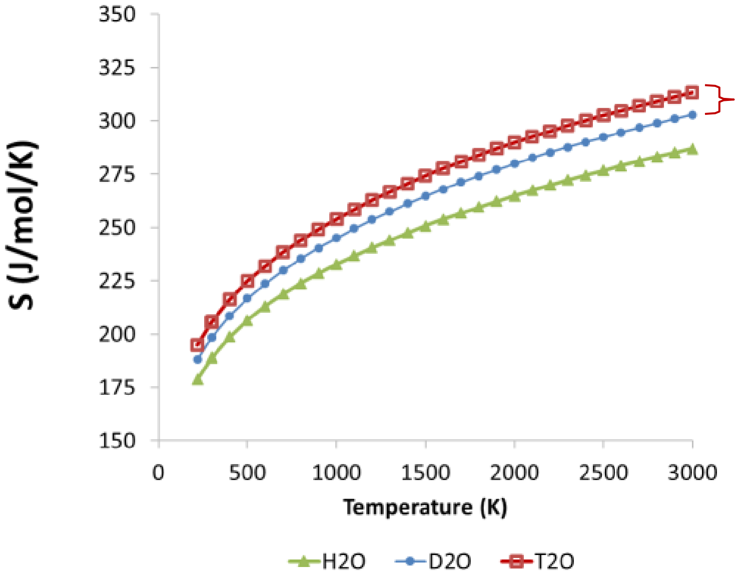
Offset between D_2 and H_2 formation enthalpies does not persist at high temperatures

- Convergence occurs near 2800 K
- Tradeoff between heat capacity modes?

C_p adjustment implemented for T_2O

- Intersection of D_2O and T_2O enthalpy assumed at 3000 K
- Prevents high-temperature divergence from isotoptic trends
- Simultaneous adjustment of 2 coefficients, others from D_2O
- C_p shift for T_2O yields S with consistent isotopic trends





S difference decreases for higher H crossover temperature

Coefficient of constant C_p or linear H or logarithmic S offset

$$\frac{h^0(T)}{RT} = a_0 + \frac{a_1}{2}T + \frac{a_2}{3}T^2 + \frac{a_3}{4}T^3 + \frac{a_4}{5}T^4 + \frac{a_5}{T}$$

$$\frac{s^0(T)}{R} = a_0\ln(T) + a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + a_6$$

Entropy for T_2

Entropy is used for chemical equilibrium calculations

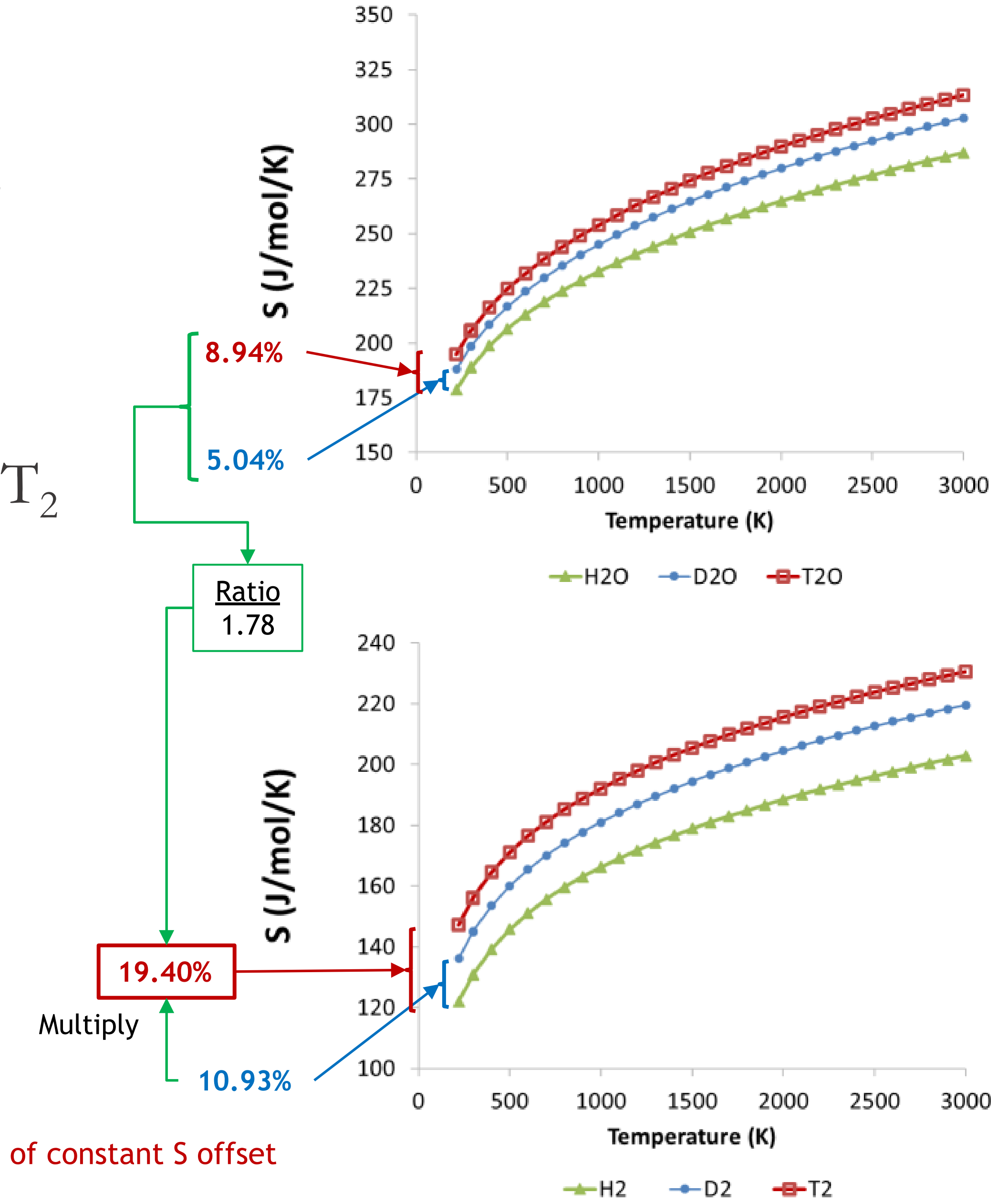
- Minimization of $\Delta G = \Delta H - T\Delta S$
- Also used to define reverse reaction rates

In the absence of data, we assume the entropy trends derived for T_2O are close to reality and applicable to T_2

- Procedure similar to enthalpy analysis
- For completeness, repeat procedure for atomic T

Use D_2 coefficients for T_2, adjust constant S offset

- Can't justify changing heat capacity, since we already decided to accept H from D_2 for T_2
- Avoids adjusting multiple parameters for 1 objective



$$\frac{s^0(T)}{R} = a_0\ln(T) + a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + \boldsymbol{a_6} \longleftarrow$$

Coefficient of constant S offset

Summary for Tritium Thermodynamics

Offsets added to coefficients for analogous D species →

Molecule	Change in a_0 or b_2 (linear C_p offset)	Change in a_5 or b_7 (H offset)	Change in a_6 or b_8 (S offset)
T_2O	0.15563196	-466.8959	0
T_2	0	0	1.33114976
T	0	213.48221	0.80489184

7-Coefficient Model (1993)

$$\frac{c_p^0(T)}{R} = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4$$

$$\frac{h^0(T)}{RT} = a_0 + \frac{a_1}{2}T + \frac{a_2}{3}T^2 + \frac{a_3}{4}T^3 + \frac{a_4}{5}T^4 + \frac{a_5}{T}$$

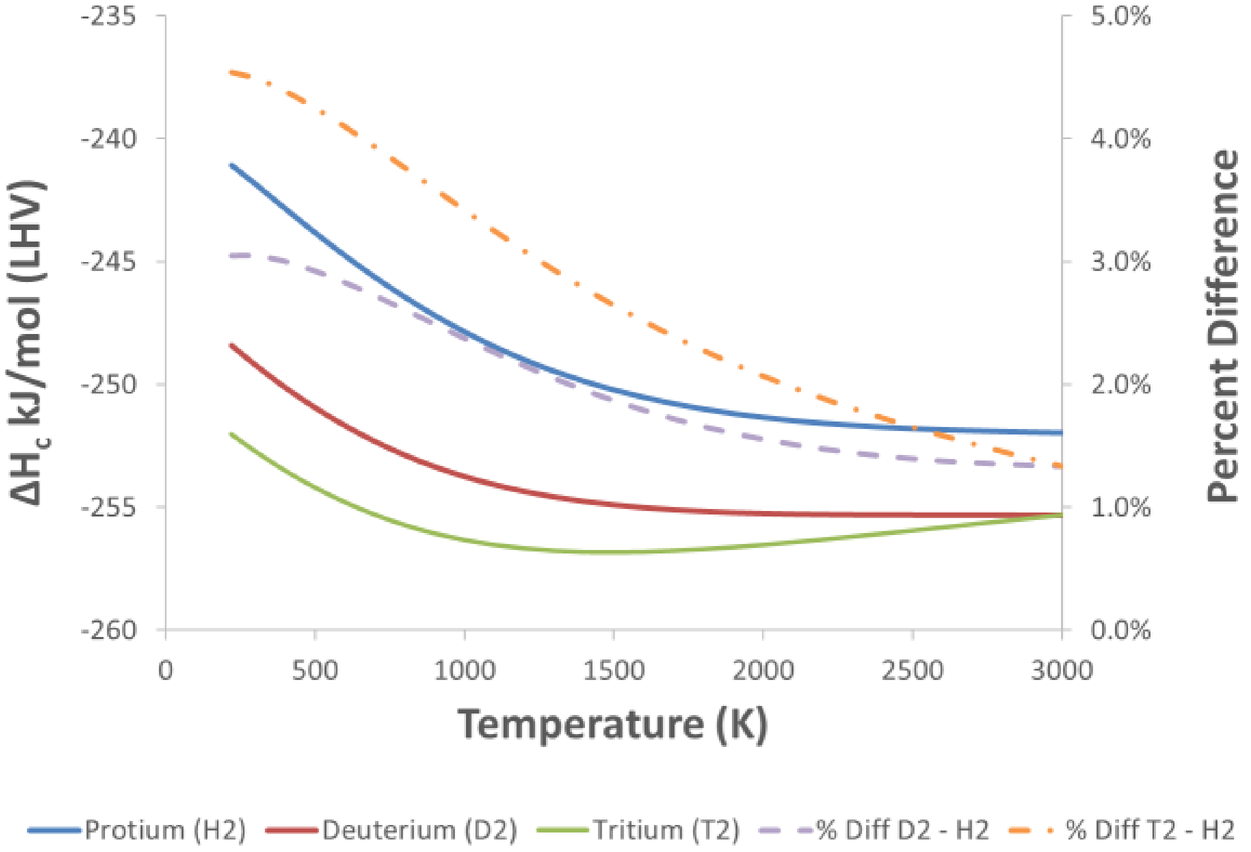
$$\frac{s^0(T)}{R} = a_0\ln(T) + a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + a_6$$

9-Coefficient Model (2002)

$$\frac{c_p^0(T)}{R} = b_0T^{-2} + b_1T^{-1} + b_2 + b_3T + b_4T^2 + b_5T^3 + b_6T^4$$

$$\frac{h^0(T)}{RT} = -b_0T^{-2} + b_1\frac{\ln(T)}{T} + b_2 + \frac{b_3}{2}T + \frac{b_4}{3}T^2 + \frac{b_5}{4}T^3 + \frac{b_6}{5}T^4 + \frac{b_7}{T}$$

$$\frac{s^0(T)}{R} = -\frac{b_0}{2}T^{-2} - b_1T^{-1} + b_2\ln(T) + b_3T + \frac{b_4}{2}T^2 + \frac{b_5}{3}T^3 + \frac{b_6}{4}T^4 + b_8$$



Transport Properties for H_2

Cantera transport property formats are patterned after TRANLIB in CHEMKIN and are based on Chapman-Enskog theory

Property coefficients can be used to compute

- Viscosity
  - Principal source of data
  - Collision integrals lookup tables require reduced temperature and reduced dipole moment
- Thermal Conductivity
  - Of lesser interest for this study, not shown
- Binary Diffusivities
  - Most likely means for differences in isotope behavior to affect the results of interest

Equations for transport properties already specify most important dependence on isotope mass

- Assael (1987) and Svehla (1995) indicate these forms are adequate for isotopologues of nonpolar H_2
  - Estimated accuracy within 4% for D_2 up to 2200 K

$$T^* = \frac{\kappa_b T}{\varepsilon_k}$$

$$\delta^* = \frac{1}{2}\frac{\mu_k^2}{\varepsilon_k \sigma_k^3}$$

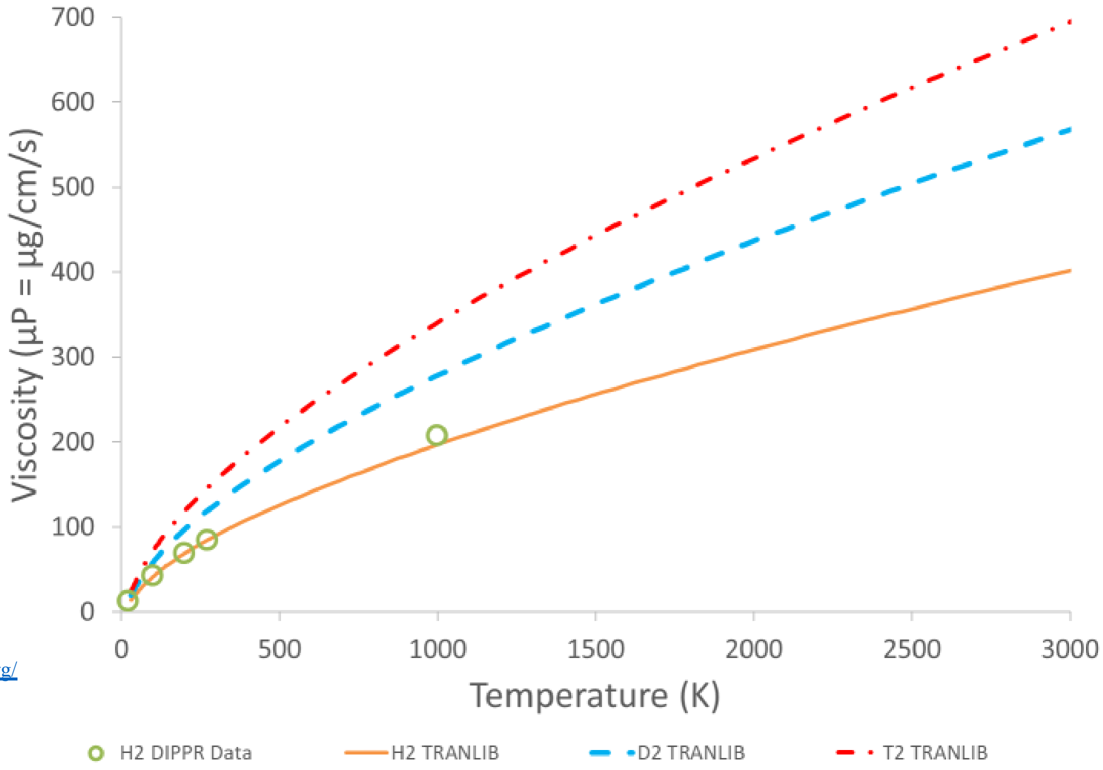
Viscosity

$$\eta_k = \frac{5}{16}\frac{\sqrt{\pi M_k \kappa_b T}}{\pi \sigma_k^2 \Omega^{(2,2)^*}}$$

Binary Diffusivity

$$D_{jk} = \frac{3}{16}\frac{\sqrt{2\pi(\kappa_b T)^3\left(\frac{1}{M_j}+\frac{1}{M_k}\right)}}{P\pi\sigma_{jk}^2\Omega^{(1,1)^*}}$$

Molecule	M_k (g/mol)	$\varepsilon_k/\varkappa_b$ (K)	σ_k (Angstroms)	μ_k (Debye)	α_k (Angstroms^3)	Z_{rot-} (at 298 K)
H_2	2.0157	38.0	2.92	0	0.79	280
D_2	4.0282	38.0	2.92	0	0.79	280
T_2	6.0321	38.0	2.92	0	0.79	280
O_2	31.998	107.4	3.458	0	1.6	3.8
N_2	28.014	97.53	3.621	0	1.76	4.0

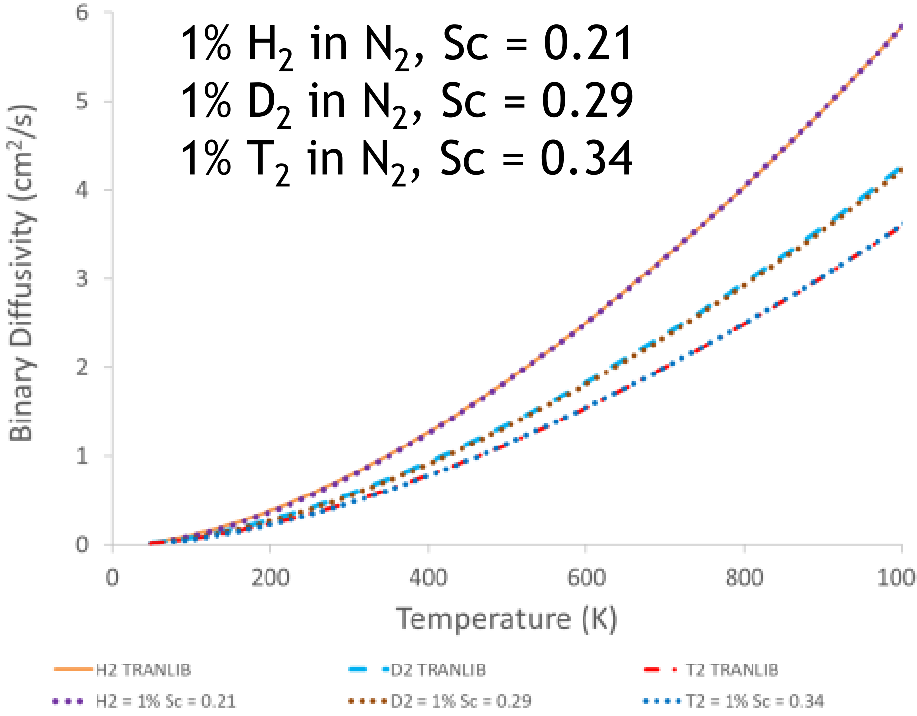


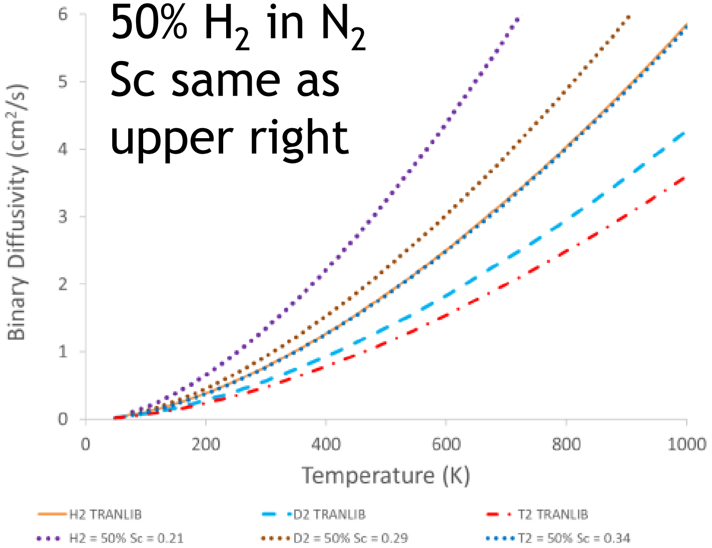
- R. J. Kee, G. Dixon-Lewis, J. Warnatz, M. E. Coltrin, and J. A. Miller, "A FORTRAN Computer Code Package for the Evaluation of Gas-Phase, Multicomponent Transport Properties," Sandia National Laboratories, Livermore, California, SAND86-8246, December 1986.
- "DIPPR Project 801: Evaluated Standard Thermophysical Property Values," Design Institute for Physical Properties, AIChE, 2010. https://dippr.aiche.org/
- M. J. Assael, S. Mixafendi, and W. A. Wakeham, "The Viscosity of Normal Deuterium in the Limit of Zero Density," *Journal of Physical and Chemical Reference Data,* vol. 16, no. 2, pp. 189-192, 1987/04/01 1987, doi: 10.1063/1.555778.
- R. A. Svehla, "Transport Coefficients for the NASA Lewis Chemical Equilibrium Program," NASA Lewis Research Center, Cleveland, Ohio, NASA Technical Memorandum 4647, 1995.

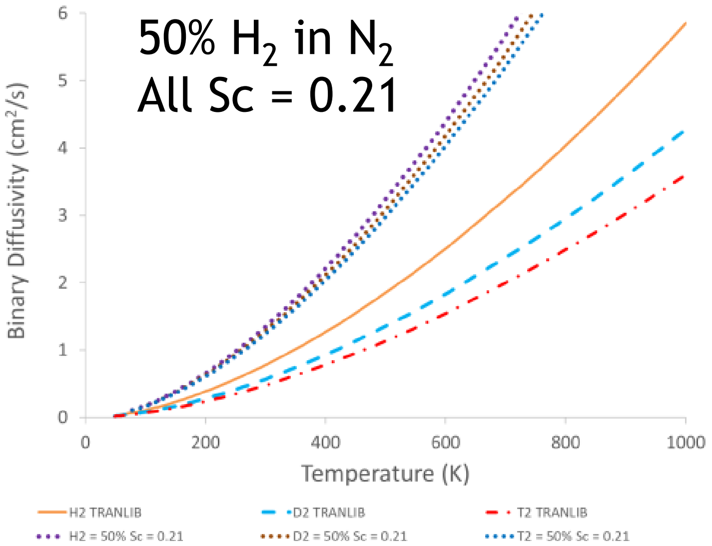
Diffusivities for Isotopologues of H_2

Schmidt number approximation for mixture diffusivity is a common default in SIERRA/Fuego and other CFD codes

- Comparisons to binary diffusivity in N_2 at right demonstrates that the Schmidt number should increase with the mass of the hydrogen isotope
- The Schmidt number should increase with large increases in the concentration of molecular hydrogen
- Variation between Schmidt-derived diffusivities for the different isotopologues is small, but increases with increasing concentration







Mixture Diffusivity from Schmidt Number

$$D_{mix} = \frac{\mu_{mix}}{\rho Sc}$$

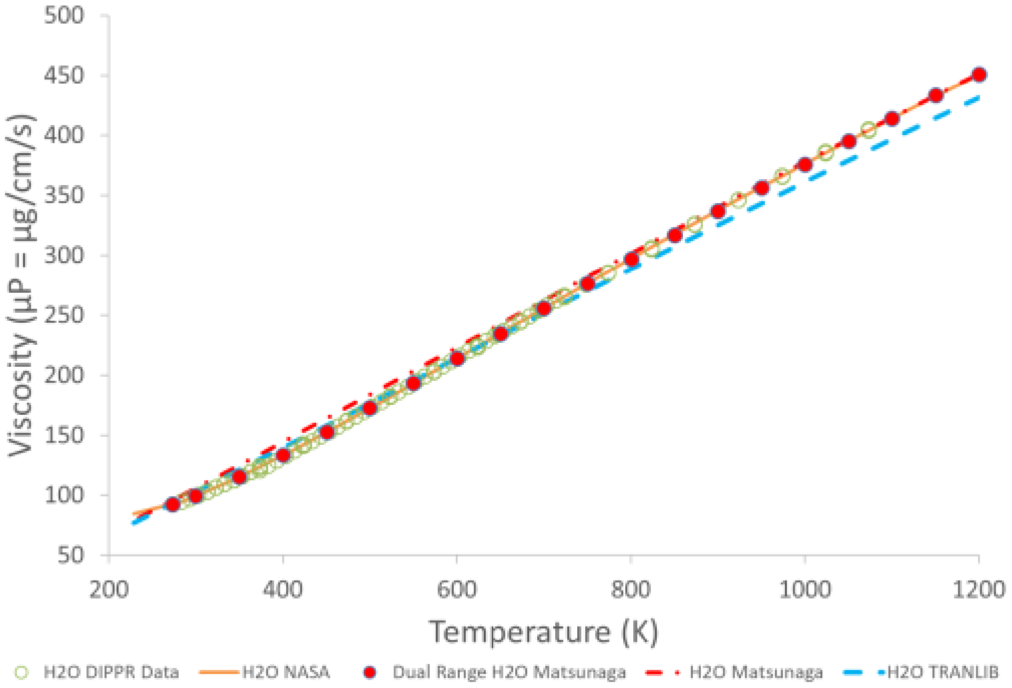
$$\Phi_{\alpha\beta} = \frac{\left(1 + \sqrt{\frac{\mu_\alpha}{\mu_\beta}\sqrt{\frac{M_\beta}{M_\alpha}}}\right)^2}{\sqrt{8\left(1 + \frac{M_\alpha}{M_\beta}\right)}}$$

$$\mu_{mix} = \sum_{\alpha=1}^{Species} \frac{y_\alpha \mu_\alpha}{\sum_{\beta=1}^{Species} y_\beta \Phi_{\alpha\beta}}$$

Transport Parameters for H_2O and Isotopologues

Various correlations with different forms yield good agreement with water vapor viscosity measurements

- TRANLIB H_2O parameters are good in the most common range
  - Maximum deviation of 7.3% from data, 2.8% on average
  - 3% average deviation above 700 K, 1% average below 700 K
- Upper-range Matsunaga (1983, >1100 K) uses Cantera/TRANLIB form
  - 1% average deviation above 700 K, 4% deviation extrapolated below 700 K
- NASA refit the dual-range Matsunaga correlation with their own form
  - Maximum deviation from data is 1.8%, 0.3% on average
  - Forms for NASA and Matsunaga below 1100 K incompatible with Cantera



Upper-range Matsunaga (1983) selected for D_2O and T_2O

- TRANLIB parameters better for H_2O below 700 K

Molecule	M_k (g/mol)	$\varepsilon_k/\varkappa_b$ (K)	σ_k (Angstroms)	μ_k (Debye)	α_k (Angstroms^3)	Z_{rot-} (298 K)
H_2O (TRANLIB, Kee 1986)*	18.0151	572.4	2.605	1.844	0	4
D_2O (Matsunaga 1983)*	20.0276	422	2.706	1.861	0	4
T_2O (Matsunaga 1983)*	22.0315	381	2.816	1.877	0	4
Alternate H_2O (Matsunaga 1983)*	18.0151	470	2.595	1.844	0	4

- R. J. Kee, G. Dixon-Lewis, J. Warnatz, M. E. Coltrin, and J. A. Miller, "A FORTRAN Computer Code Package for the Evaluation of Gas-Phase, Multicomponent Transport Properties," Sandia National Laboratories, Livermore, California, SAND86-8246, December 1986.
- N. Matsunaga and A. Nagashima, "Prediction of the transport properties of gaseous water and its isotopes at high temperatures," *The Journal of Physical Chemistry,* vol. 87, no. 25, pp. 5268-5279, 1983, https://doi.org/10.1021/j150643a042.
- "DIPPR Project 801: Evaluated Standard Thermophysical Property Values," Design Institute for Physical Properties, AIChE, 2010. https://dippr.aiche.org/
- R. A. Svehla, "Transport Coefficients for the NASA Lewis Chemical Equilibrium Program," NASA Lewis Research Center, Cleveland, Ohio, NASA Technical Memorandum 4647, 1995.

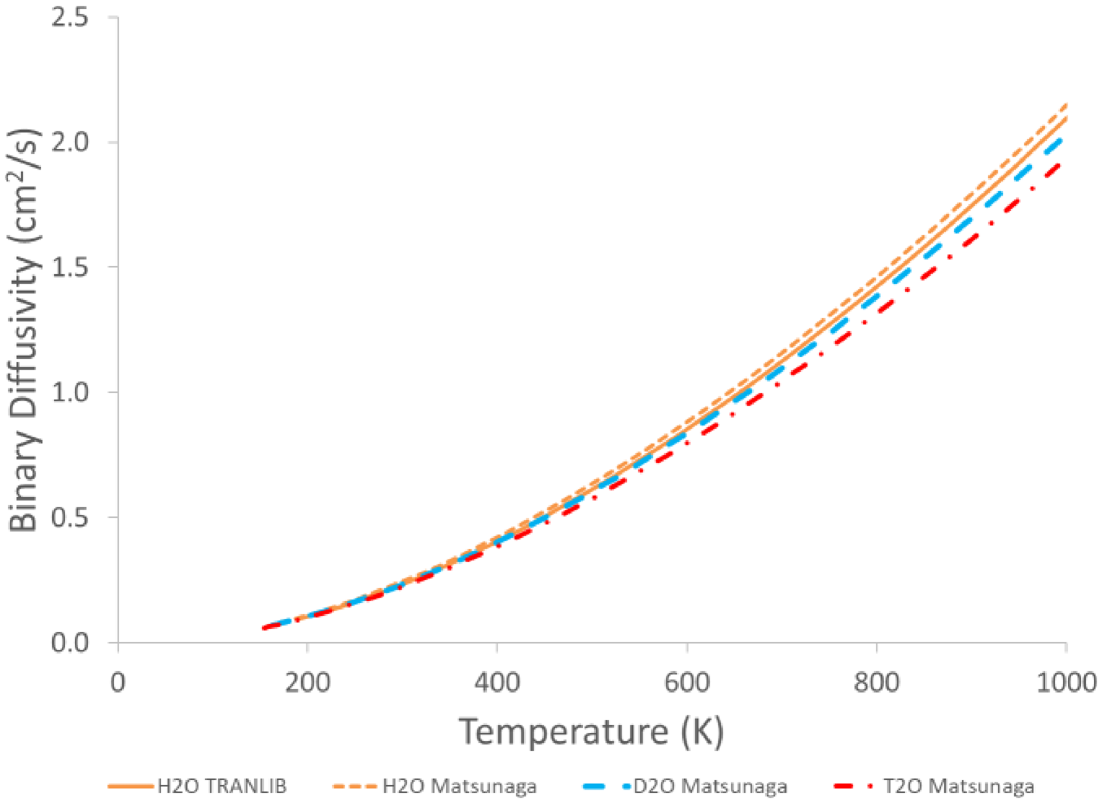
Diffusivities for Isotopologues of H_2O

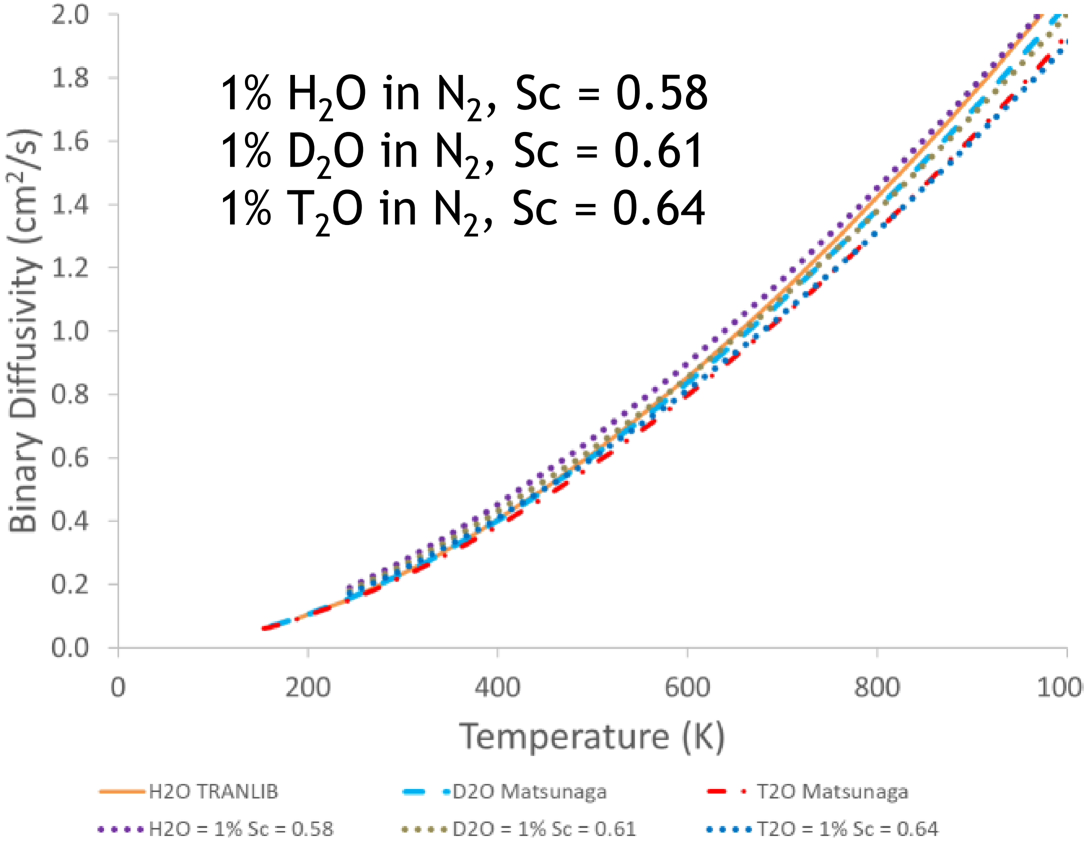
The use of unique Lennard-Jones for distinct isotopologues reduces predicted differences in diffusivities

- H_2O diffusivities comparable for TRANLIB and upper-range Matsunaga parameters

Schmidt number form has less curvature, overestimates low-temperature diffusivity

- Lacks polarity terms





Summary and Conclusions

A suite of thermodynamic and transport properties for isotopologues of hydrogen and water has been assembled

- Enables CFD-based safety assessments of tritium in fire scenarios
- Forms compatible with NASA-CEA thermodynamics and Cantera/TRANLIB transport properties

Thermodynamic properties for tritium species based on NASA coefficients for D, D_2 and D_2O

- Leveraged reported bond strengths for H_2, D_2, and T_2 to quantify isotopic trends for tritium estimates
- Adjusted minimal number of coefficients to enforce trends observed for H, C_p, and S
- Results applicable to either 7-parameter or 9-parameter model

Reviewed literature of transport properties for isotopologues of H_2 and H_2O

- Explicit molecular weight dependence in Cantera/TRANLIB forms sufficient for nonpolar H_2
  - Unmodified TRANLIB parameters recommended for H_2, D_2, and T_2
- Modified parameters from literature identified for polar isotopologues of water
- Viscosity data for H_2 and H_2O compared favorably with computed values
- Schmidt numbers for mixture diffusivities estimated from binary diffusivities of H_2 and H_2O isotopologues

Thank You

All coefficients for tritium species properties are found in the associated paper for this conference, which will be archived at www.osti.gov under document number SAND2021-4040 C

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