Direct Measurements of Binary Gas Phase Diffusion Coefficients for Combustion Applications

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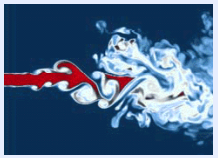


Motivation and Background

Simulations require diffusivities in a variety of situations:

Laminar diffusion flames: - preferential species diffusion affects flame structure & attributes

Takagi; Xu; Komiyama, Comb. & Flame, 1996, 106, 252.
Takagi; Xu, Comb. & Flame, 1994. 96, 50.

Turbulent flames: small scale structures are affected by diffusion.

Harstad, Bellan, Ind. & Eng. Chem.Res., 2004. 43, 645.
Okong'o, Harstad, Bellan, AIAA Journal, 2002. 40, 914.
Okong'o; Bellan, J. Fluid Mech., 2002. 464, 1.

Laminar premixed H_2-air flames: computed flame speed as sensitive to diffusion as kinetics of the primary chain branching reaction

Wang, Chem. Phys. Let., 2000. 325, 661.

Premixed alcohol, *n*-heptane, and iso-octane/air flames: sensitivity of flame speeds and extinction strain rates to diffusion can be of the same order as to the kinetics.

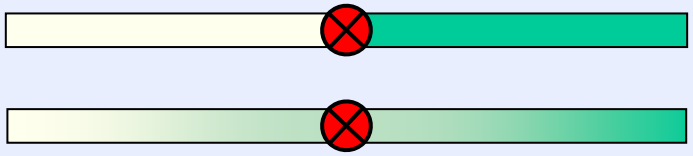
Holley, Dong; Andac; Egolfopoulos, Comb. & Flame, 2006. 144, 448.

Topics

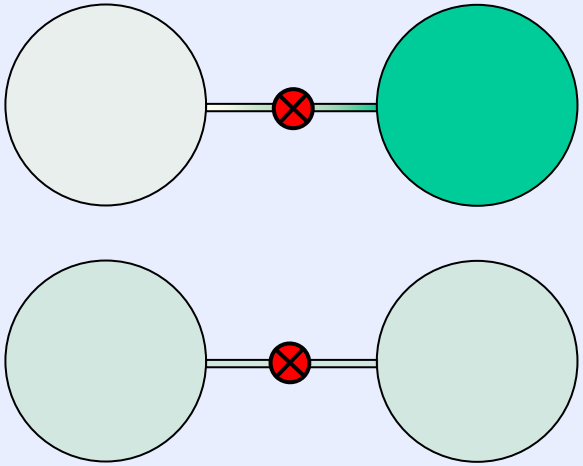
- Brief overview of measurement methods
- Description of present method
- Initial Results – selected C1 to C8 alkanes
- Closer look at uncertainties
  - Analytical assumptions; temperature; substrate sticking, substrate decomposition
  - Noble gas validation studies
- Conclusions and Coming Attractions

Diffusion Measurement Methods - Historical

1. Closed tube

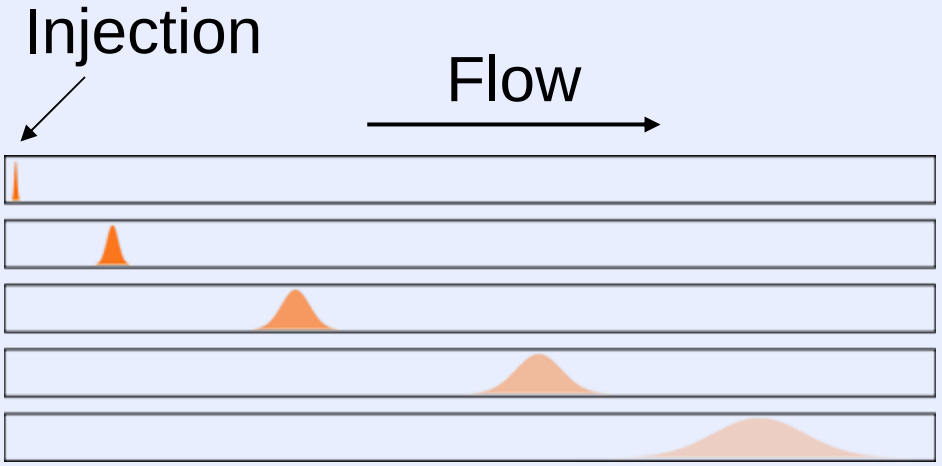


2. Two-bulb



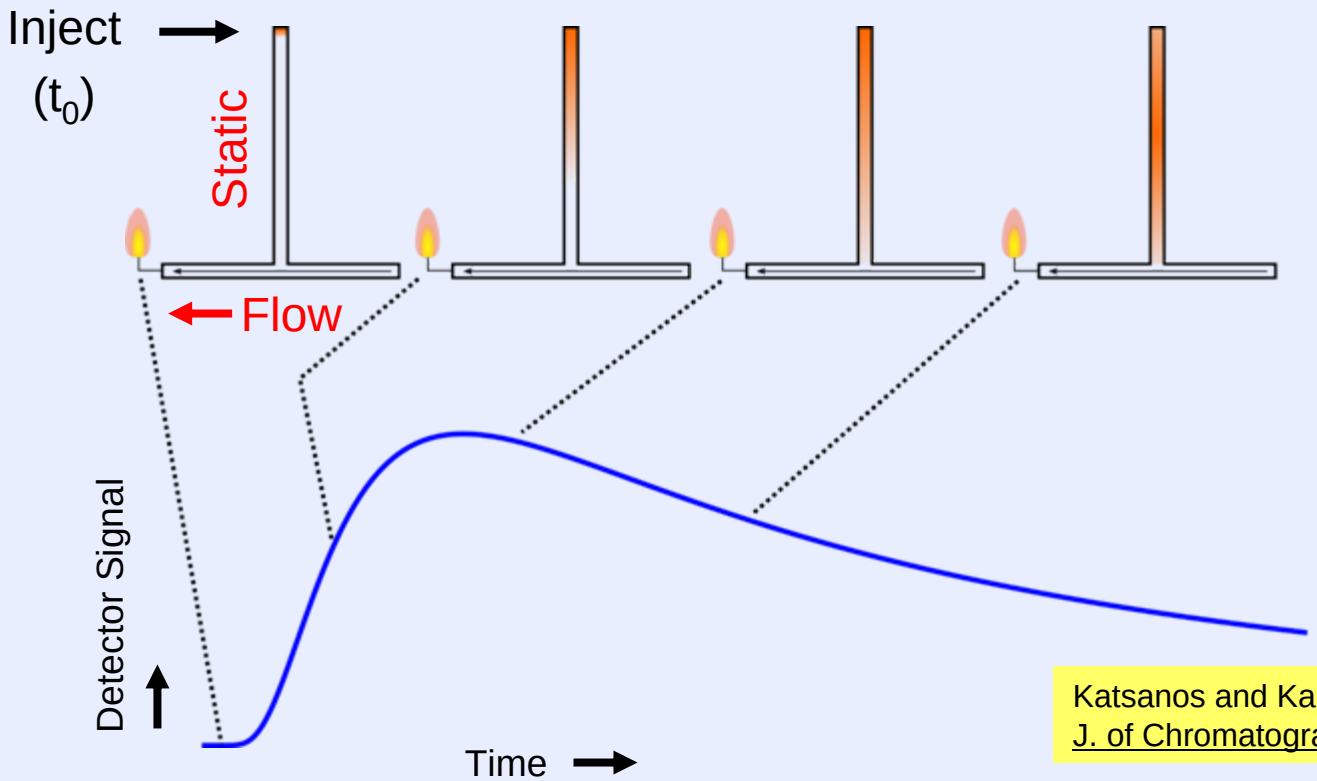
Watch concentration change as f(time)

3. Gas Chromatography
   - Peak Broadening



Watch width increase as slowly flows through (very) long tube

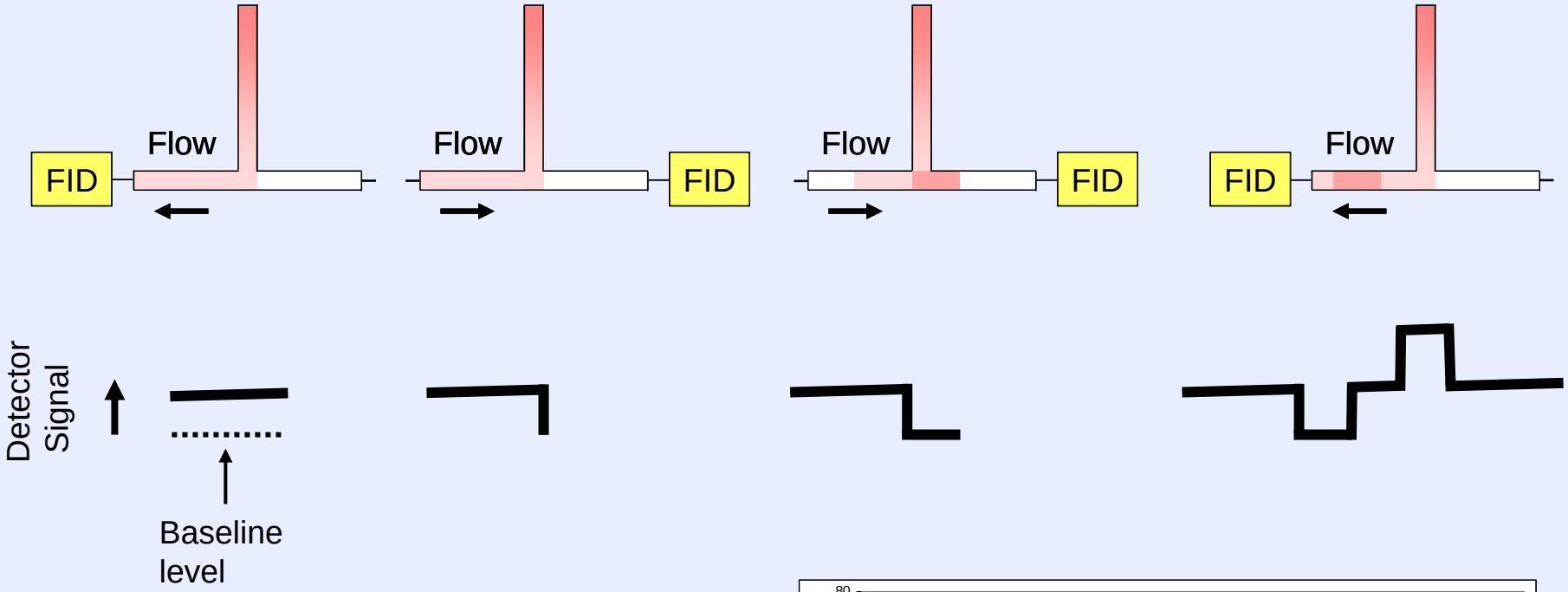
Diffusion Measurement - GC Method II

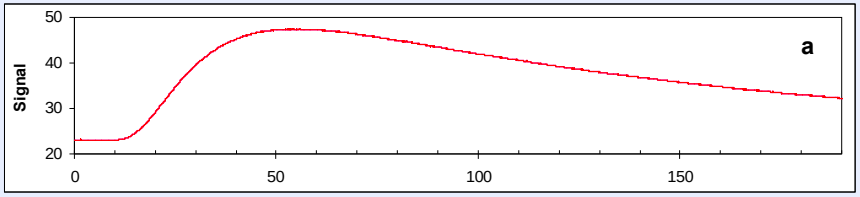


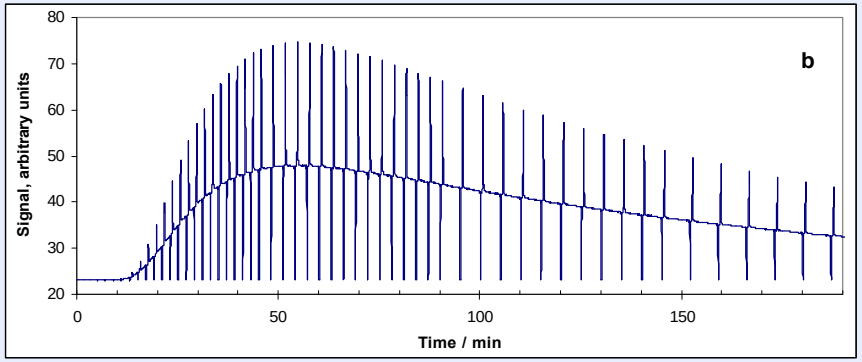
Katsanos and Karaiskakis (1982).
J. of Chromatography **237**(1): 1-14.

- Monitor concentration – time profile at exit of static diffusion column
- Separates diffusive and analytical fluxes; no valves at high T
- Baseline drift causes systematic errors ➡ Flow Reversal Methods

Double Flow Reversal Procedure



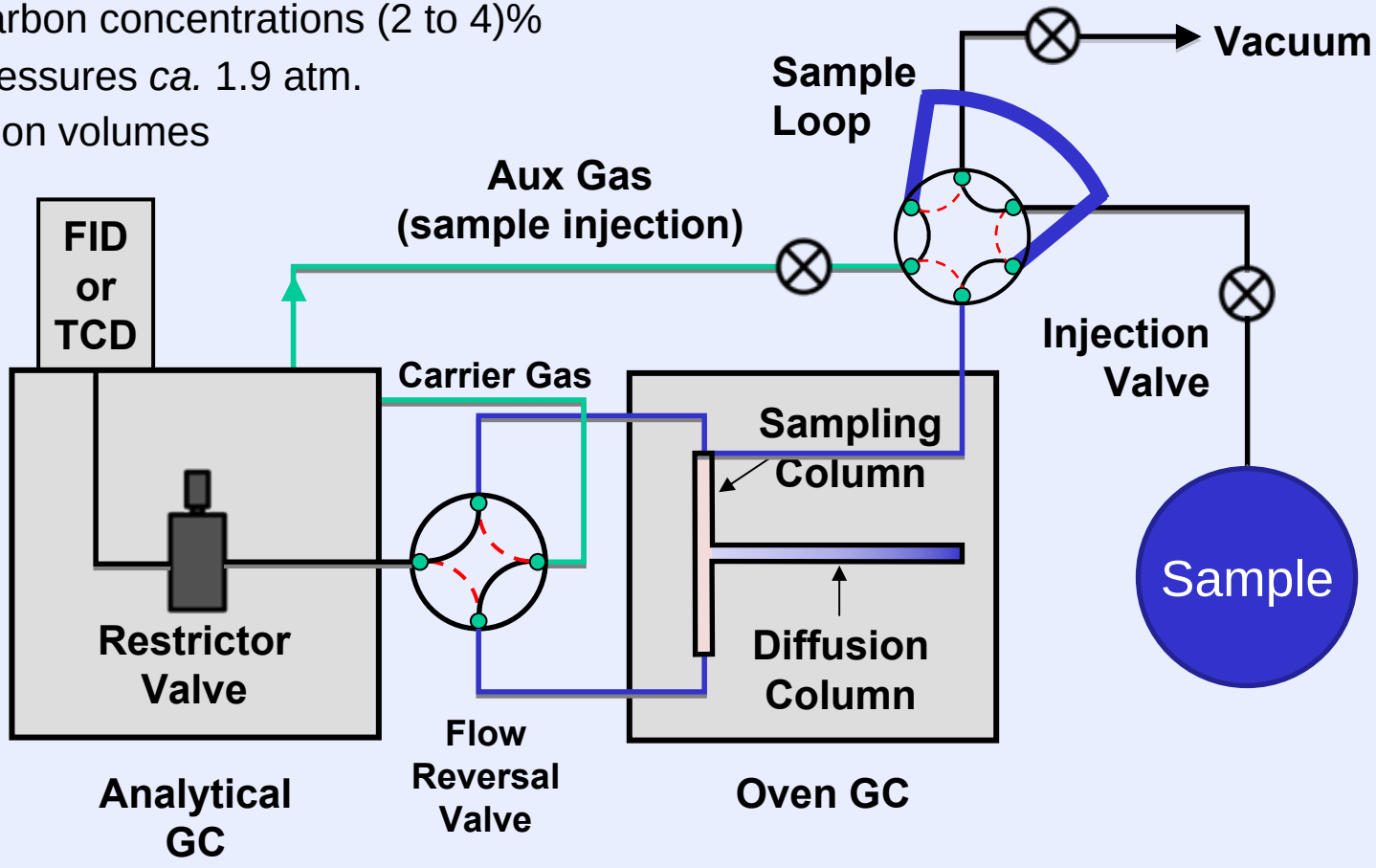




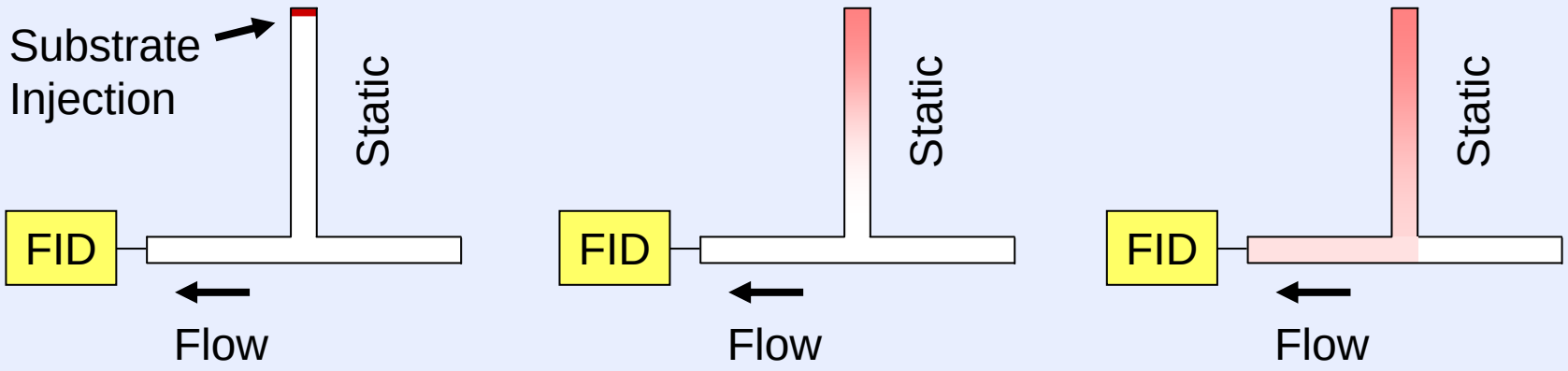
Apparatus

Some Details:

1. Valve operation, oven T controlled by GC and automated
2. Diffusion columns 61 cm or 23 cm 4.6 mm I.D. electropolished 316 SS
3. Starting hydrocarbon concentrations (2 to 4)%
4. Experimental pressures *ca.* 1.9 atm.
5. *ca.* 0.2 ml injection volumes

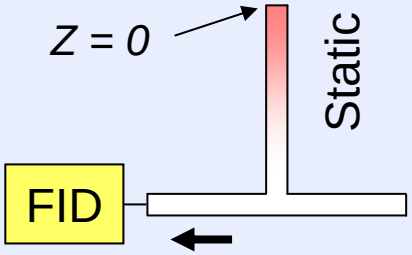


Mathematical Analysis - I



1. Relate concentration-time profile of substrate along diffusion tube to diffusion coefficient (Fick's second law)
2. Relate detector signal to concentration-time profile of substrate at exit of diffusion tube
3. Describe effects of flow reversals

Mathematical Analysis - II



Fick's Second Law

$$\frac{\partial c_z}{\partial t} = D_{AB} \frac{\partial^2 c_z}{\partial z^2}$$

t = time measured from injection of the substrate
z = distance coordinate along diffusion tube
c = concentration of the substrate A
D_{AB} = binary diffusion coefficient

Assumptions:

1. Only gas phase diffusive flow (no convection, thermal gradients, wall interactions)
2. Initial mass distribution of substrate is a delta function
3. No diffusion in sampling column
4. High flow rates, reasonable sampling times

Katsanos and Karaiskakis (1982). J. of Chromatography **237**(1): 1-14.

Result:

$$h = \frac{N \exp\left[-L^2 / 4D_{AB}(\tau)\right]}{(\tau)^{3/2}}$$

where,

$$\tau = t_0 - t_M - 1/2\, t_{FR}$$

h = peak height
N = constant
L = length of diffusion tube
τ = relates peak elution time to the time the substrate exits diffusion tube

t_0 = peak elution time measured from injection of substrate
t_M = gas hold-up time
t_{FR} = duration of flow reversal

Example Data Plot

Laplace Transform Result: $$\ln\left(h\tau^{3/2}\right) = \ln N - \frac{L^2}{4D_{AB}}\frac{1}{\tau}$$

Katsanos and Karaiskakis (1982).
J. of Chromatography **237**(1): 1-14.

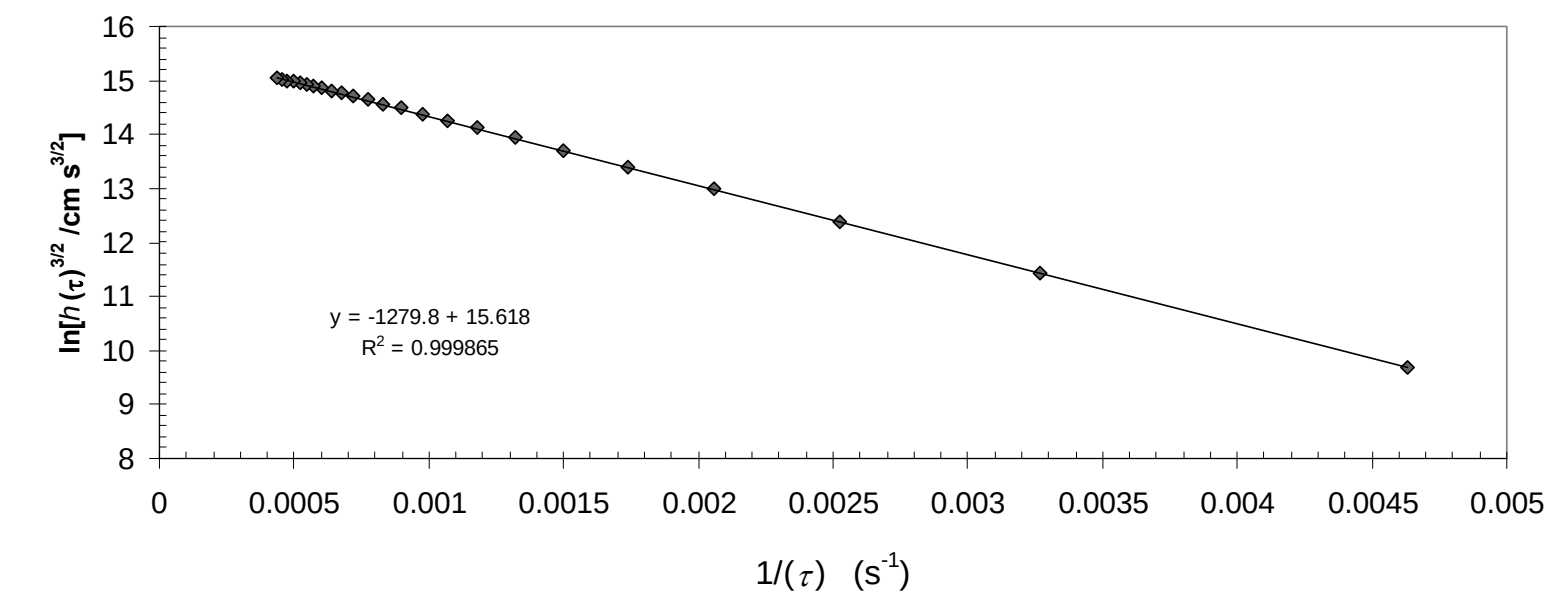
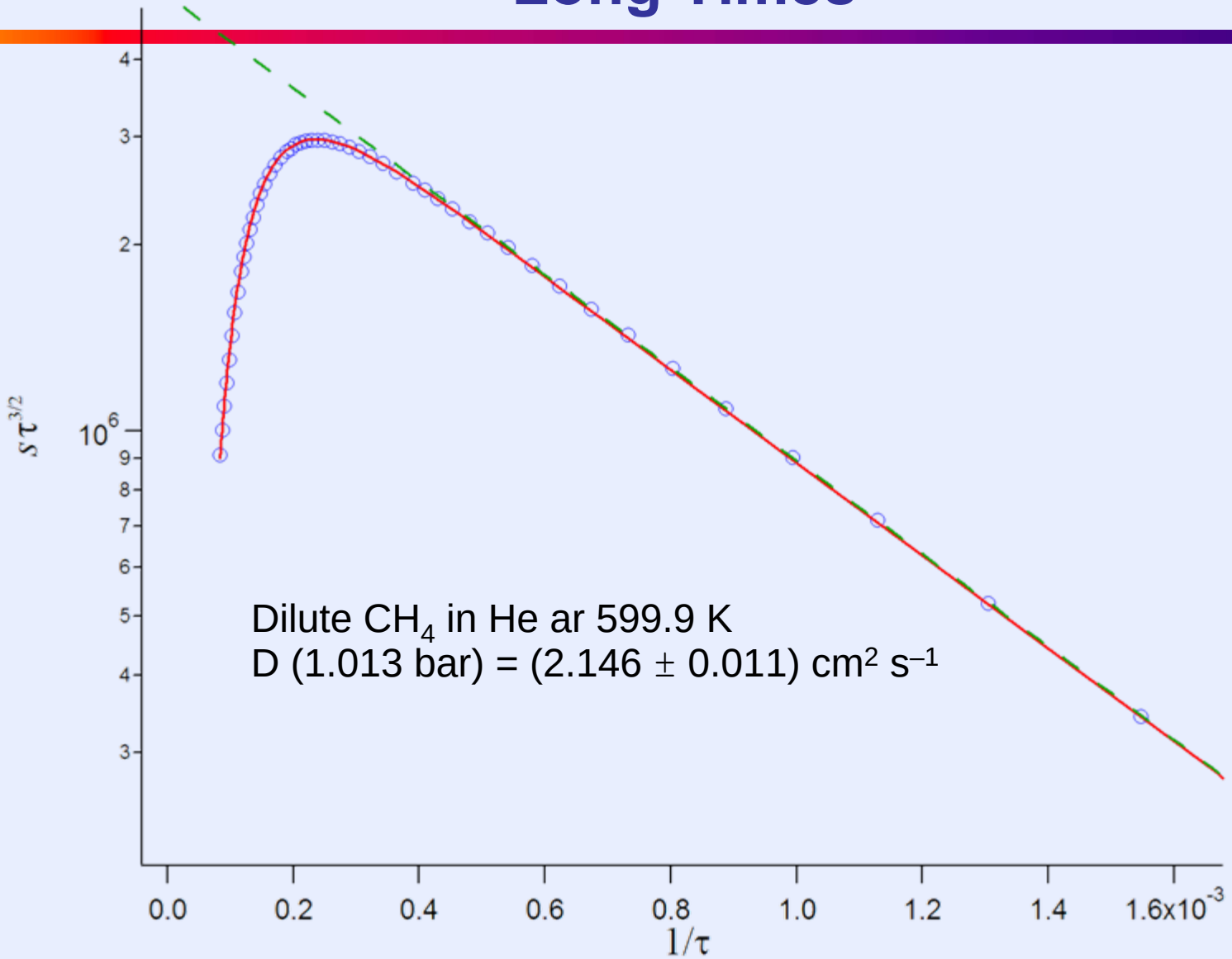


Figure 2. Plot of equation for an experiment with C_2H_6 – N_2 at 350 K.

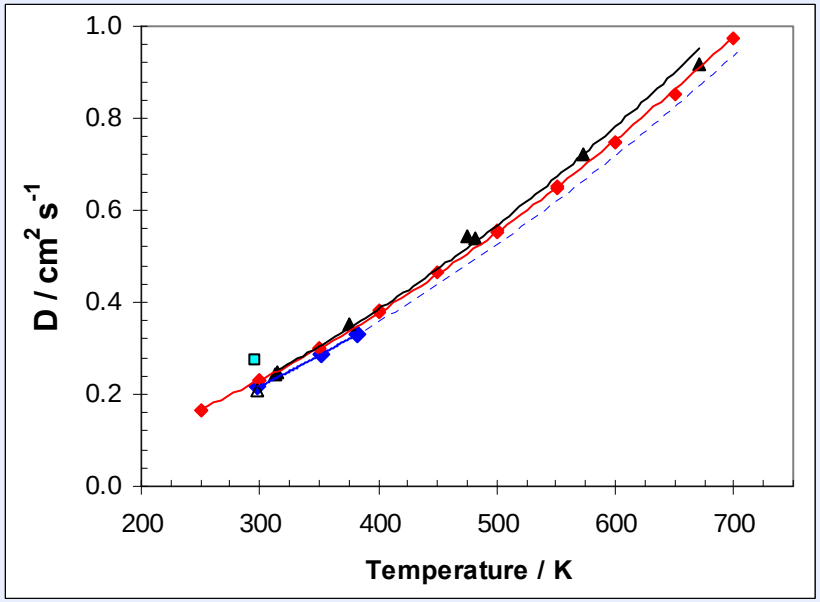
Laplace Transform Analysis is Not Valid at Long Times

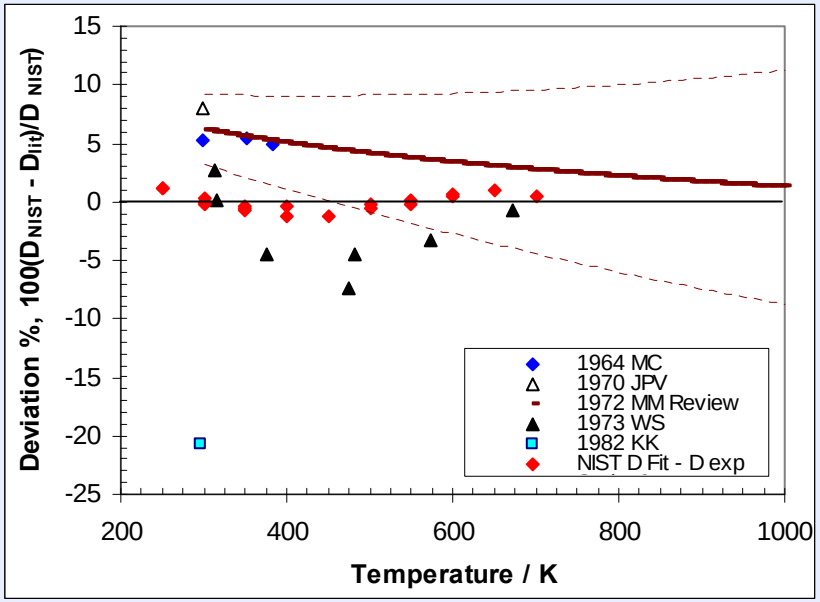


Initial Results

Selected Hydrocarbons: C1 to C8 Alkanes

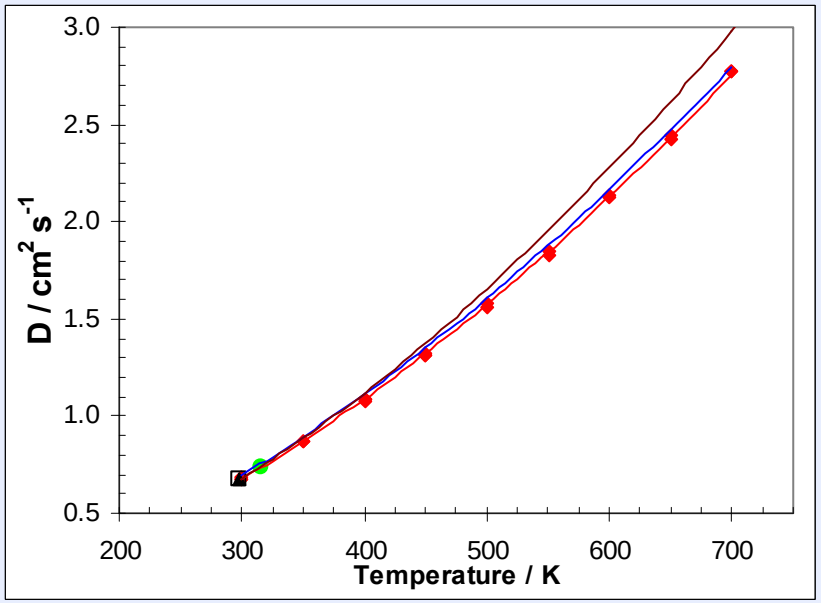
CH_4-N_2

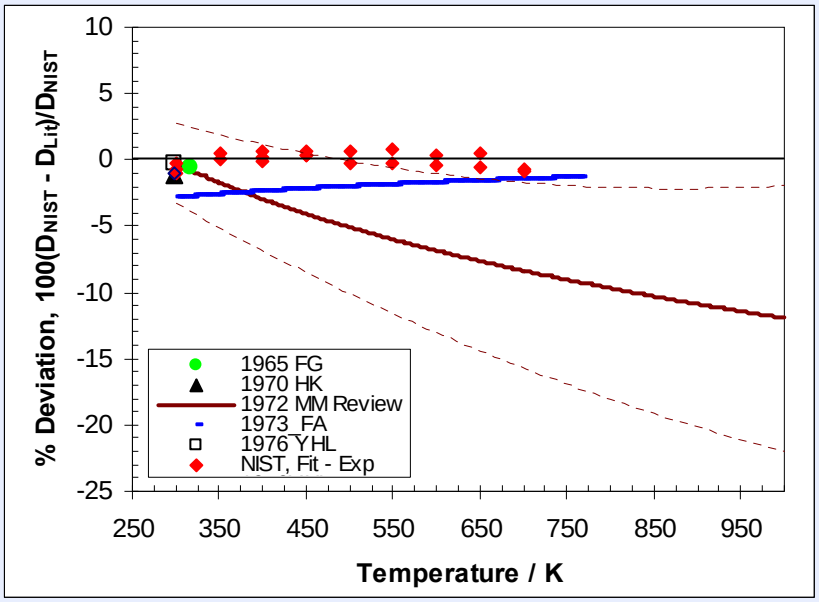




- All D_{AB} values scaled to 1 atm for comparison with literature
- This work: $D_{\mathbf{CH4\text{-}N2}} = 1.358 \times 10^{-5}\ T^{1.708}$

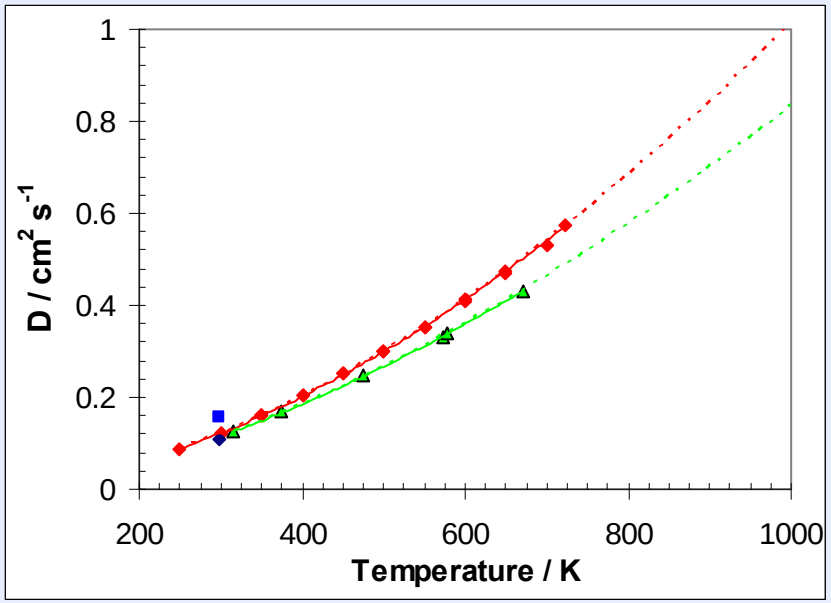
CH_4-He

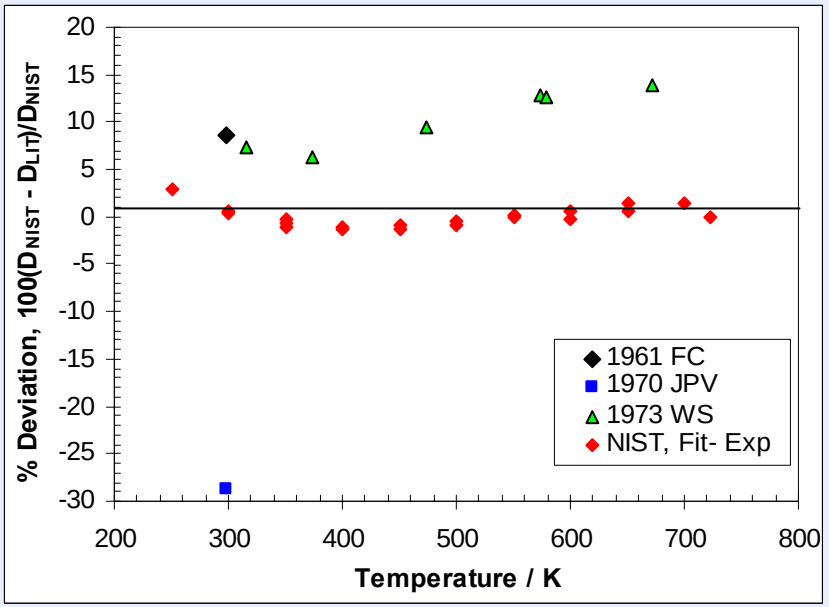




- Deviation from Marrero and Mason review due to their assumption that temperature dependence follows $T^{1.75}$
- This work: $D_{\mathbf{CH4\text{-}He}}$(300-700 K) = $5.250 \times 10^{-5}\ T^{1.659}$

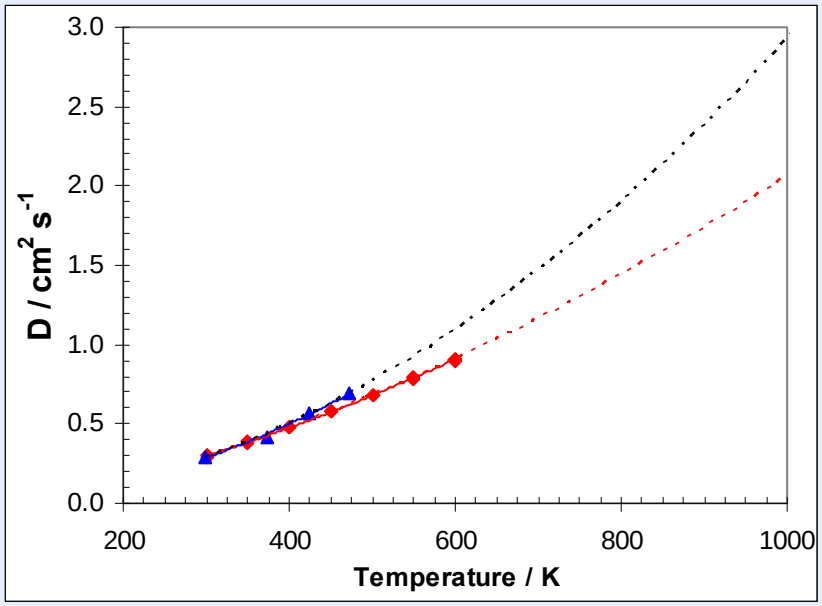
Propane-N_2

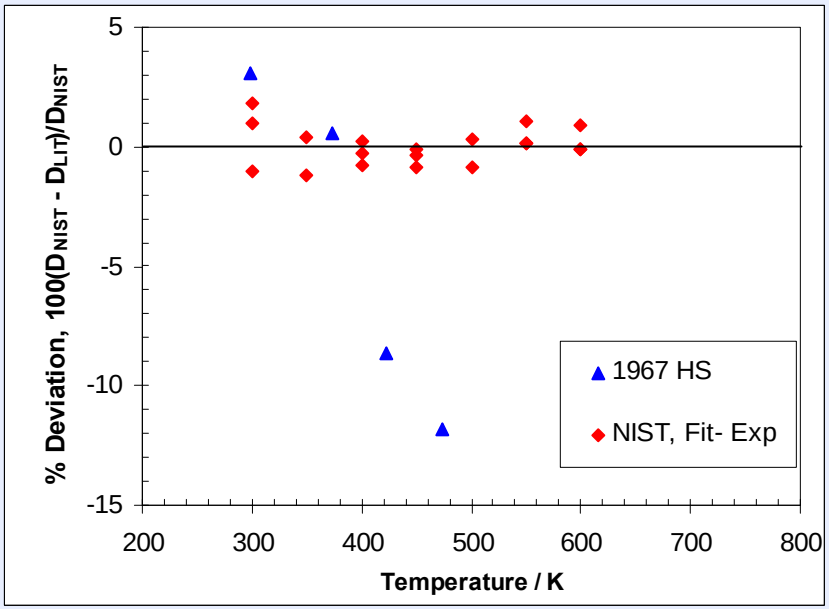




- This work: $D_{C3H8\text{-}He}$(250-725 K) = $5.359\times10^{-5}\ T^{1.759}$
- At 1000 K, our *D* is about 30% larger than Wakeham/Slater value

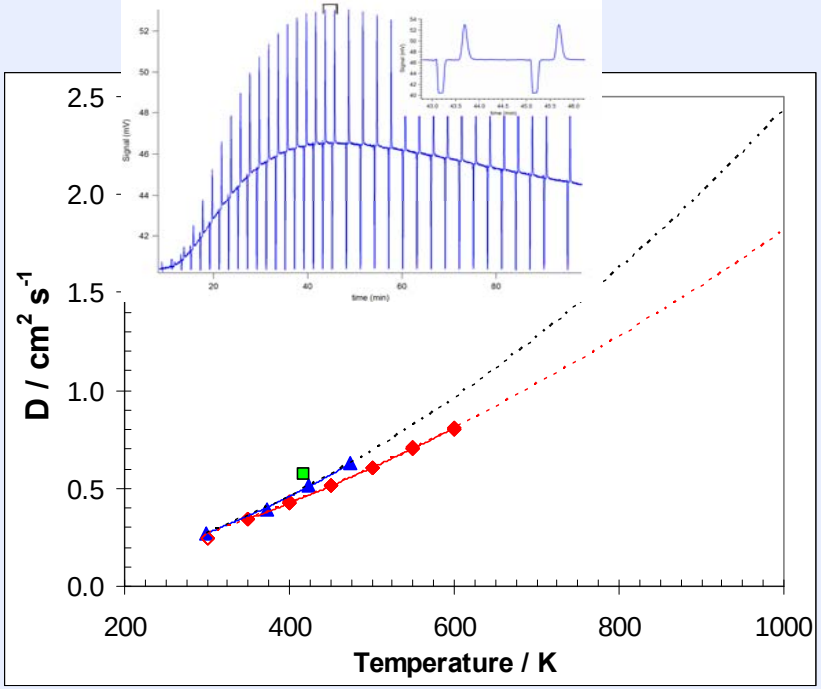
Pentane-He

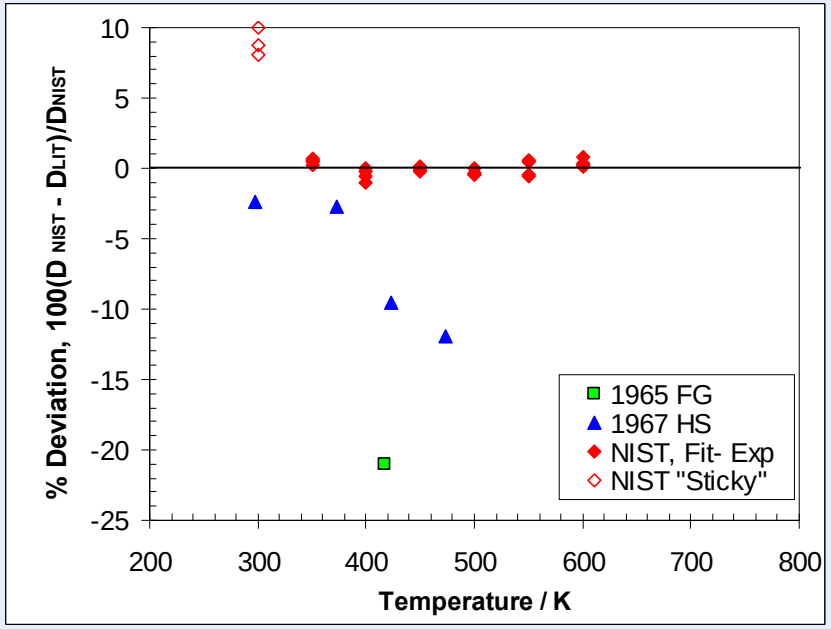




- This work: $D_{n\text{-Pentane-He}}$(300-600 K) = $3.309\times10^{-5}\ T^{1.598}$
- At 1000 K, our *D* is about 50% smaller than the Hargrove/Sawyer value

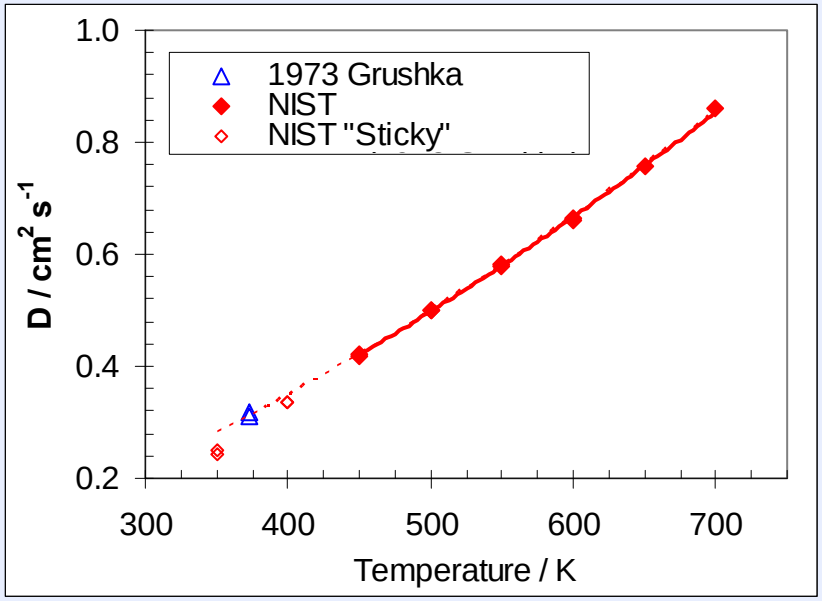
Hexane-He

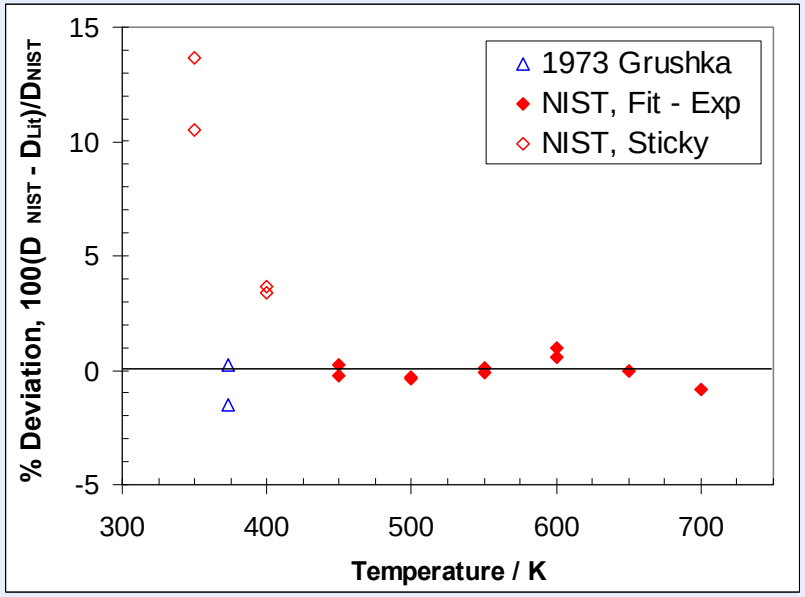




- This work: $D_{n\text{-Hexane-He}}$(350-600 K) = $3.212\times10^{-5}\ T^{1.584}$
- At 1000 K our D is about 40% smaller than the Hargrove/Sawyer value
- Peak shape in chromatogram becomes broader and non-Gaussian at 300 K - indicates sticking to walls.

n-Octane-He





- Evidence of sticking at T ≤ 400 K
- This work: $D_{\textbf{n-Octane-He}}$(450-700 K) = $3.309 \times 10^{-5}\ T^{1.598}$

Temperature Variation of D_{AB}

Binary System A–B	*T(K)*	Equation $D_{AB}/(cm^2s^{-1}) = BT^n$	*n*	Reference
CH_4–N_2	298-382	$1.183 \times 10^{-5}\ T^{1.722}$	1.722	1964Mueller
	314-671	$1.054 \times 10^{-5}\ T^{1.753}$	1.753	1973 Wakeham
	250-700	$1.358 \times 10^{-5}\ T^{1.708}$	1.708	This work
C_3H_8–N_2	317-671	$9.907 \times 10^{-6}\ T^{1.642}$	1.642	1973 Wakeham
	250-725	$5.359 \times 10^{-6}\ T^{1.759}$	1.759	This work
CH_4–He	303-764	$5.923 \times 10^{-5}\ T^{1.643}$	1.643	1973 Frost
	300-700	$5.250 \times 10^{-5}\ T^{1.659}$	1.659	This work
Ethane–He	303-764	$4.566 \times 10^{-5}\ T^{1.633}$	1.633	1973 Frost
	297-447	$5.459 \times 10^{-5}\ T^{1.599}$	1.599	1983 Katsanos
	300-700	$4.572 \times 10^{-5}\ T^{1.632}$	1.632	This work
n -pentane– He	298-473	$4.888 \times 10^{-5}\ T^{1.925}$	1.925	1967 Hargrove
	300-600	$3.309 \times 10^{-5}\ T^{1.598}$	1.598	This work
n -hexane– He	298-473	$8.440 \times 10^{-6}\ T^{1.820}$	1.820	1967 Hargrove
	350-600	$3.212 \times 10^{-5}\ T^{1.584}$	1.584	This work
n -octane– He	450-700	$2.350 \times 10^{-5}\ T^{1.603}$	1.603	This work

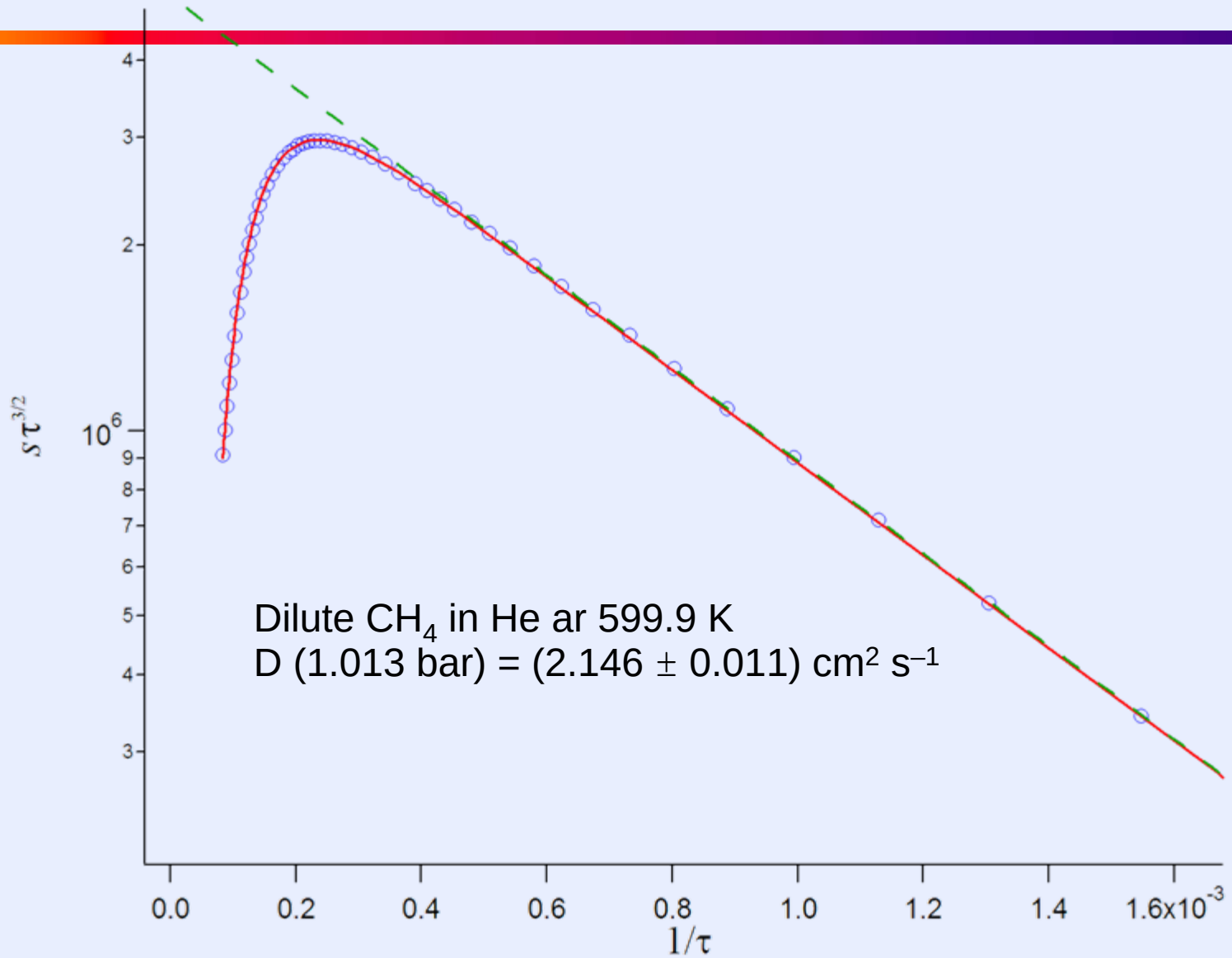
- Data suggest $n(N_2) > n(He)$

NIST

Part 2 – How good is our measurement?

- Measurements show excellent precision, ca. +/- (0.5 – 1)%
- Absolute accuracy difficult to test with hydrocarbons because of lack of reference data
- Noble gas diffusion much better studied – makes a better test
- Need to better define uncertainties:
  - Analytical procedure
  - Temperatures, pressures, tube length etc.

Laplace Transform Analysis – when is it valid?



Numerical Simulation

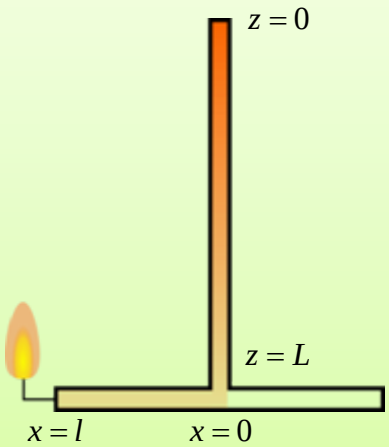
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}$$

Discrete Grid $\begin{aligned} z_i &= z_0 + i\Delta z \\ t_n &= t_0 + n\Delta t \end{aligned}$

Crank-Nicholson solution for $c(z,t)$

$$\frac{c(z_i,t_{n+1}) - c(z_i,t_n)}{\Delta t} = \frac{D}{2}\left[\frac{c(z_{i+1},t_n) - 2c(z_i,t_n) + c(z_{i-1},t_n) + c(z_{i+1},t_{n+1}) - 2c(z_i,t_{n+1}) + c(z_{i-1},t_{n+1})}{(\Delta z)^2}\right]$$

Boundary Conditions



$$c_z\big|_{x=L} = c_x\big|_{x=0}$$

$$-D\left(\frac{\partial c_z}{\partial t}\right)_{z=L} = vc_x\big|_{x=0}$$

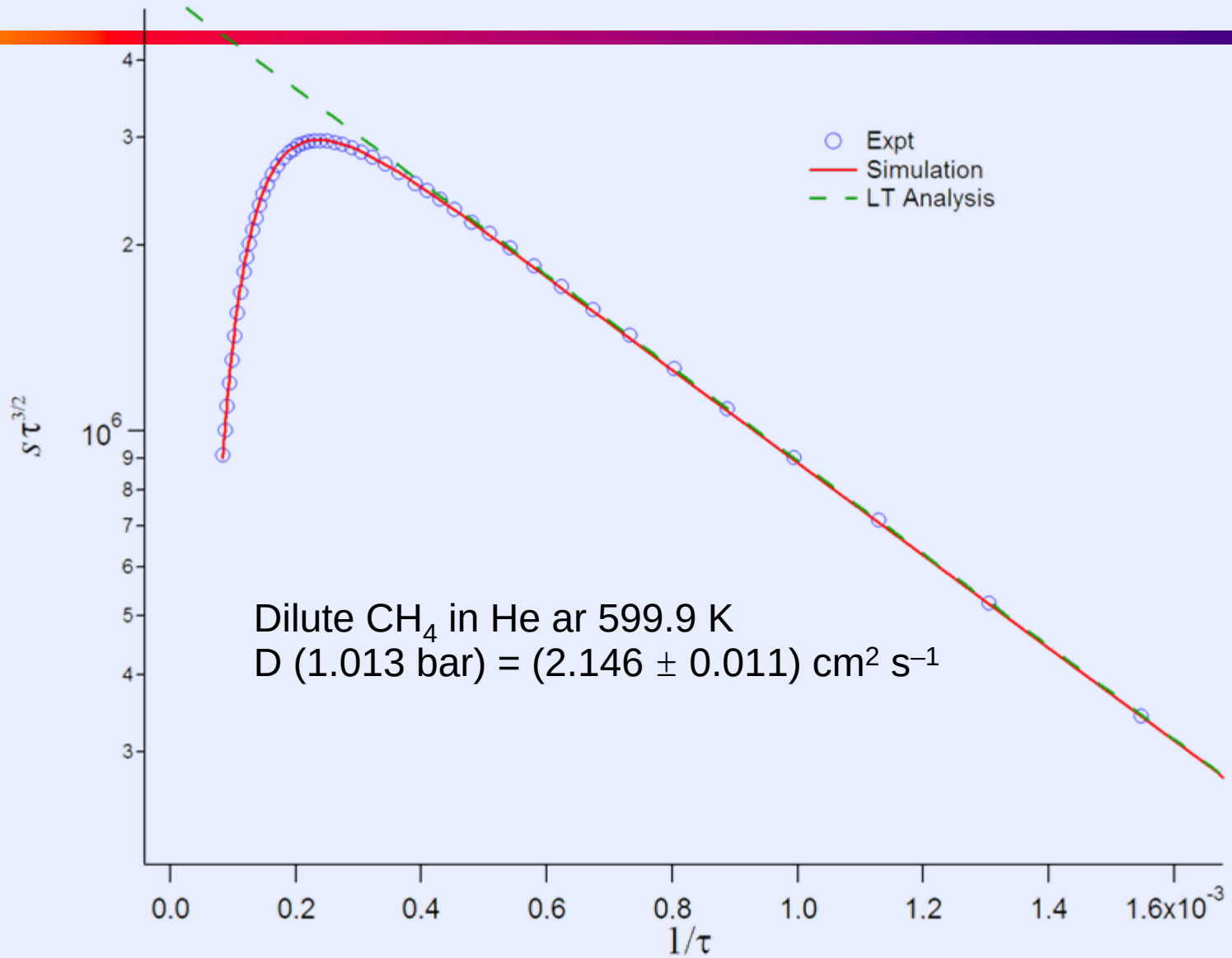
Except for reversals (not considered here), There is no sample transfer from $x<0$

$$c_i^{n+1} - \frac{K}{2}\left(c_{i-1}^{n+1} - 2c_i^{n+1} + c_{i+1}^{n+1}\right) = c_i^n + \frac{K}{2}\left(c_{i-1}^n - 2c_i^n + c_{i+1}^n\right)$$

where $K = \dfrac{D\Delta t}{(\Delta z)^2}$

is a tridiagonal matrix and may be solved efficiently using LAPACK routines.

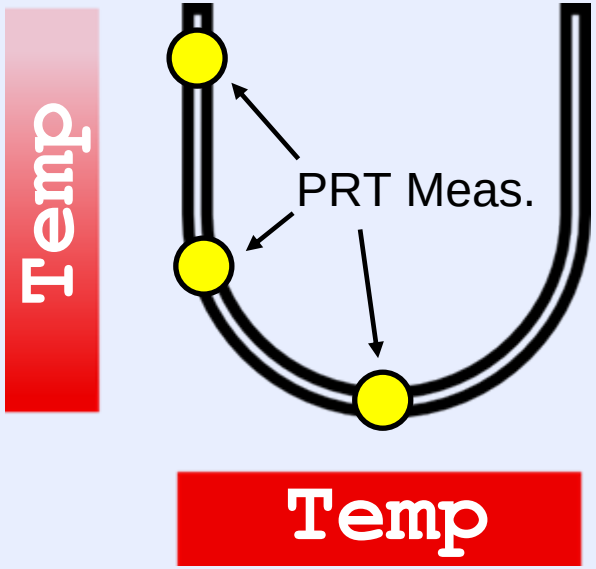
Simulation Results



Dilute CH_4 in He ar 599.9 K
D (1.013 bar) = (2.146 ± 0.011) $cm^2\ s^{-1}$

Uncertainty Analysis

Temperature – Long Tube (Bent)



Nominal T (°C)	ΔT/T
27	0.310 %
77	0.132 %
127	0.218 %
177	0.333 %
227	0.447 %
277	0.604 %
327	0.827 %
377	1.079 %
427	1.620 %
450	1.721 %

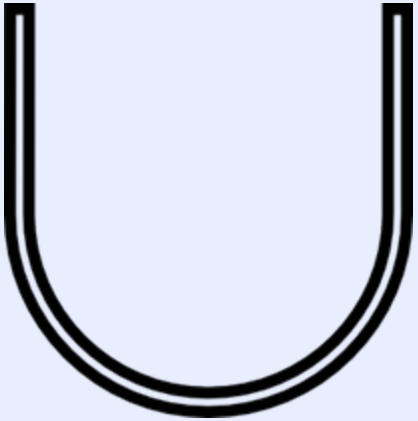
2σ uncertainty assumed to be maximum deviation in T during run.

Assumed for uncertainty: $D \propto T^{1.7}$

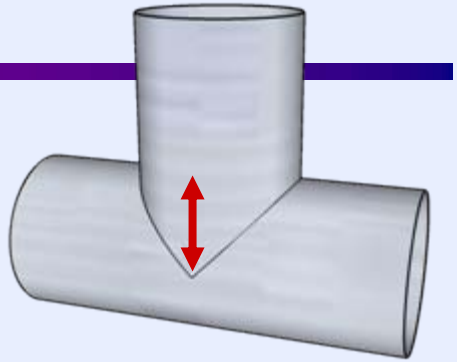
Uncertainty Analysis

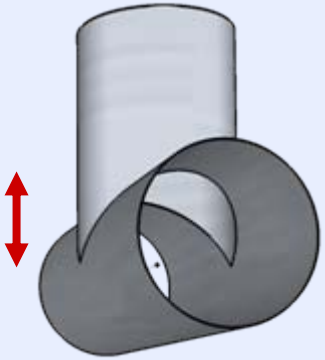
Length of Diffusion Tube

L(straight tube) =(60.79 ± 0.01) cm



L(bent tube) = 61.5 cm
at calculated midpoint
(assuming …)



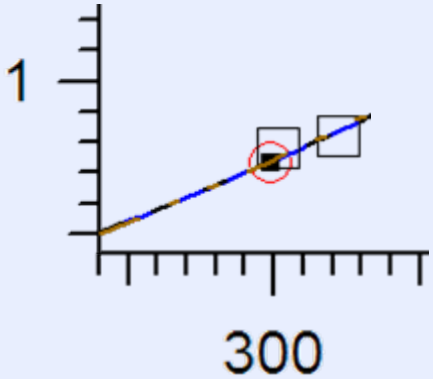


Up to 0.23 cm
in ΔL

Calibration using Reference Data:

$D_{\text{He-Ar}}$ = (0.7344 ± 0.0042) cm^2 s^{-1} at
1.013 bar and 300 K (2σ uncertainty)

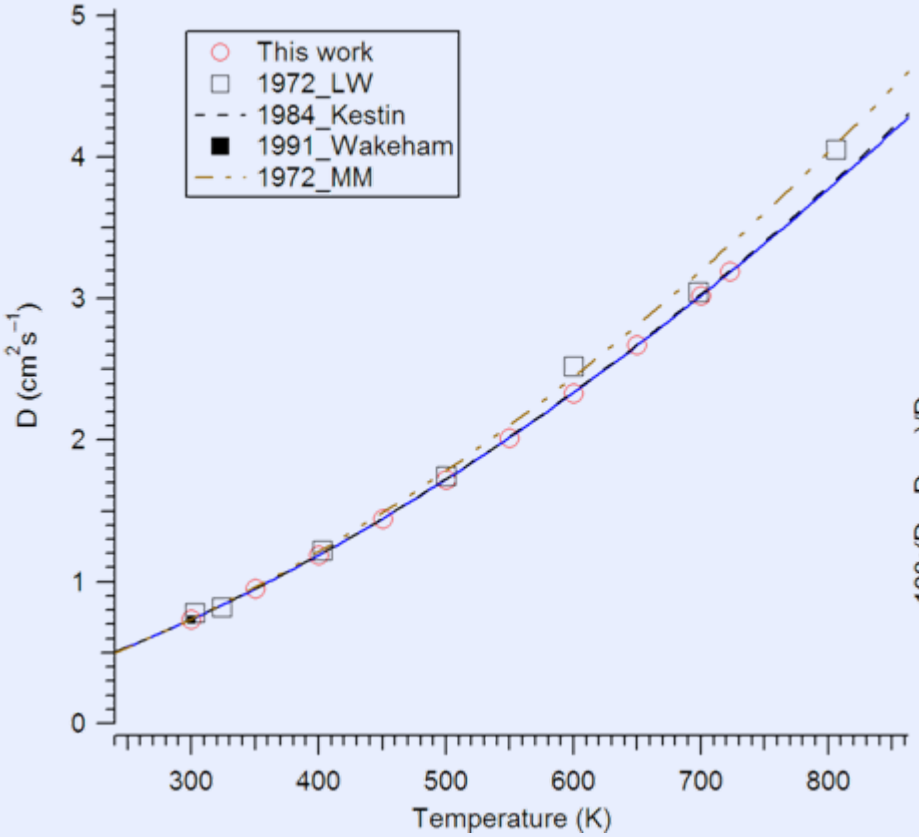
W.A. Wakeham, A. Nagashima, J.V. Sengers, *Experimental Thermodynamics, Vol. III: Measurement of the Transport Properties of Fluids*. Blackwell Scientific: Oxford, 1991; p 459.



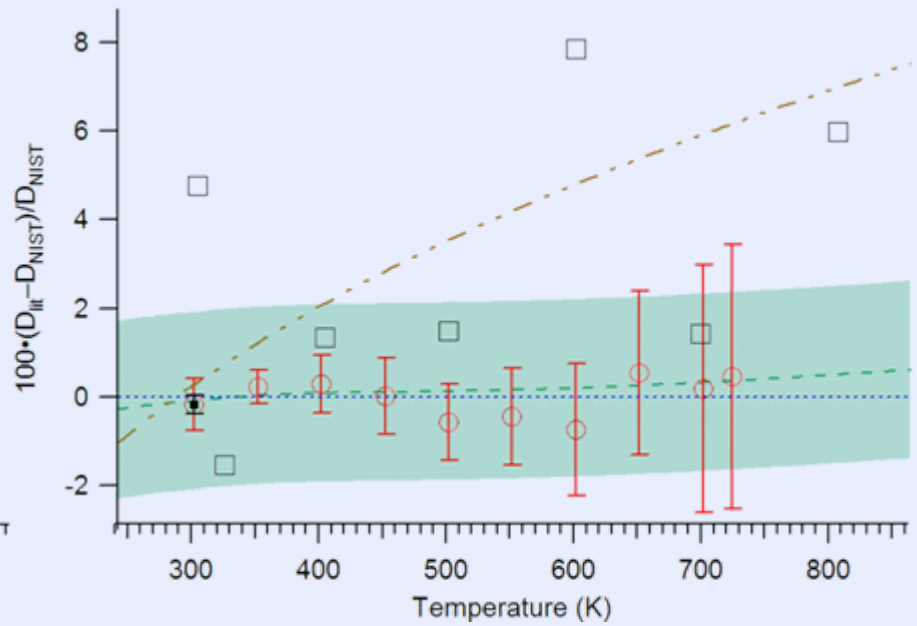
Effective length
based on Ref. Data:

L=(61.28±0.01) cm

Argon in Helium

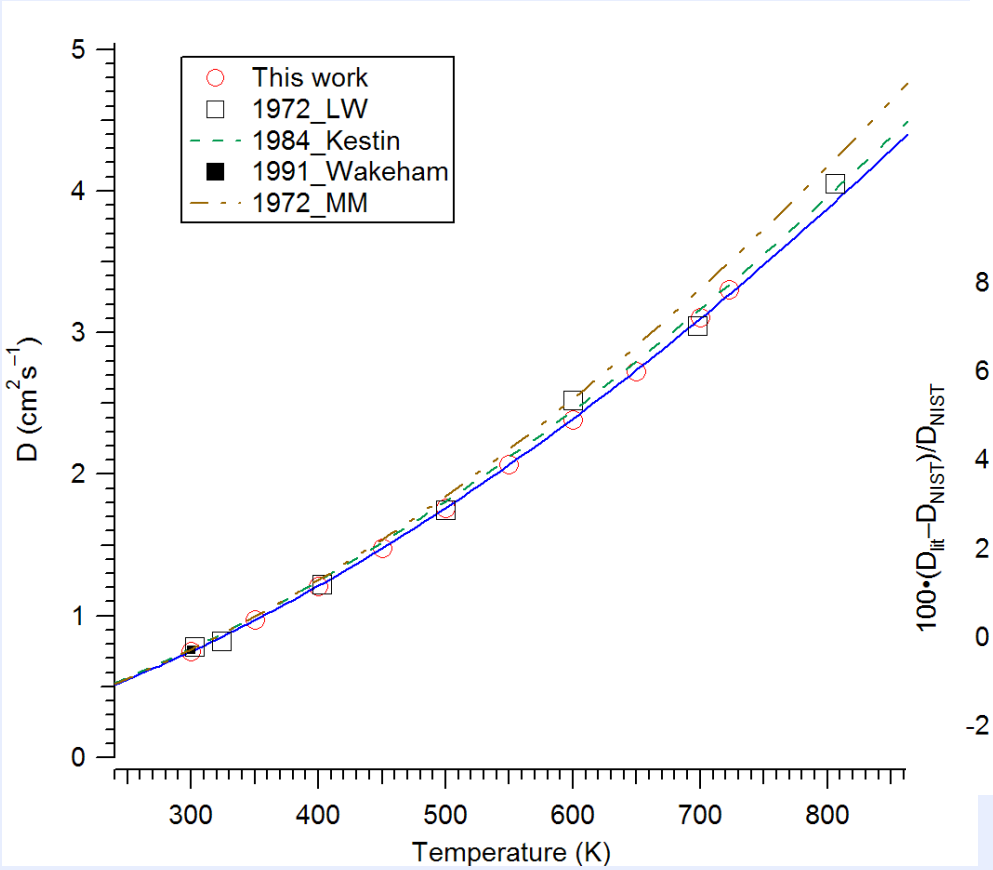


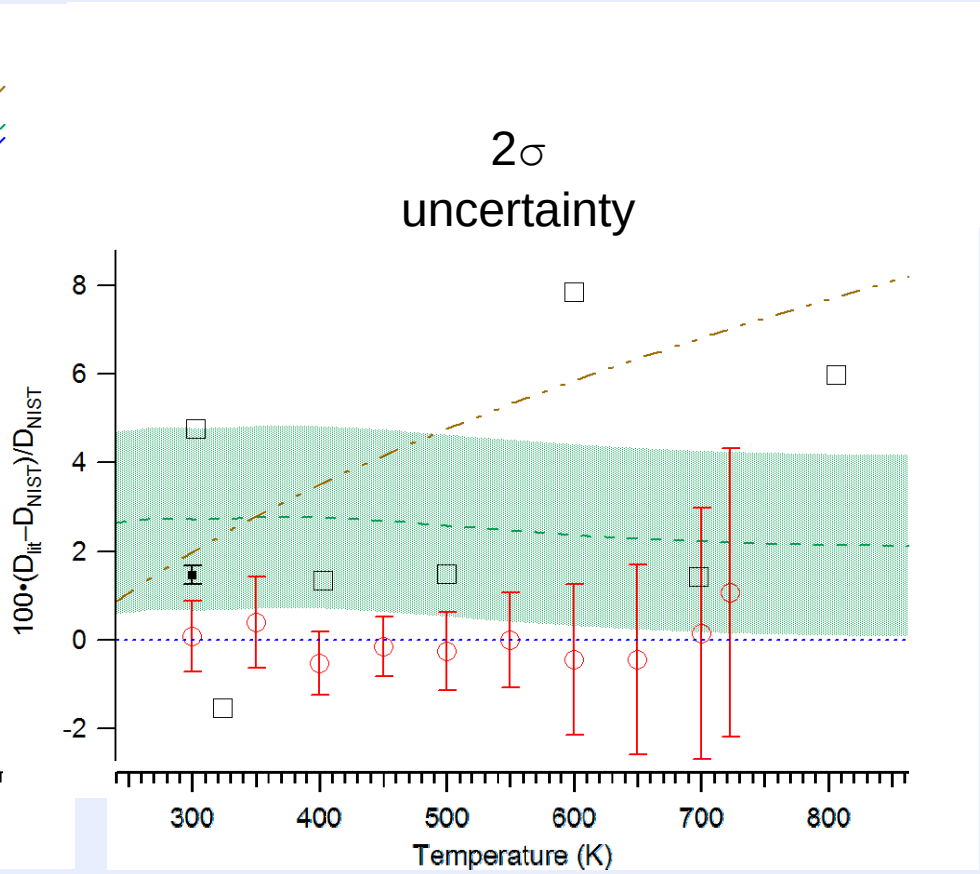
2σ
uncertainty



$$D_{12}(T) = (5.34 \pm 0.24) \times 10^{-5} (T/1\,\mathrm{K})^{1.674 \pm 0.007}\ [\mathrm{cm}^2\mathrm{s}^{-1}]$$

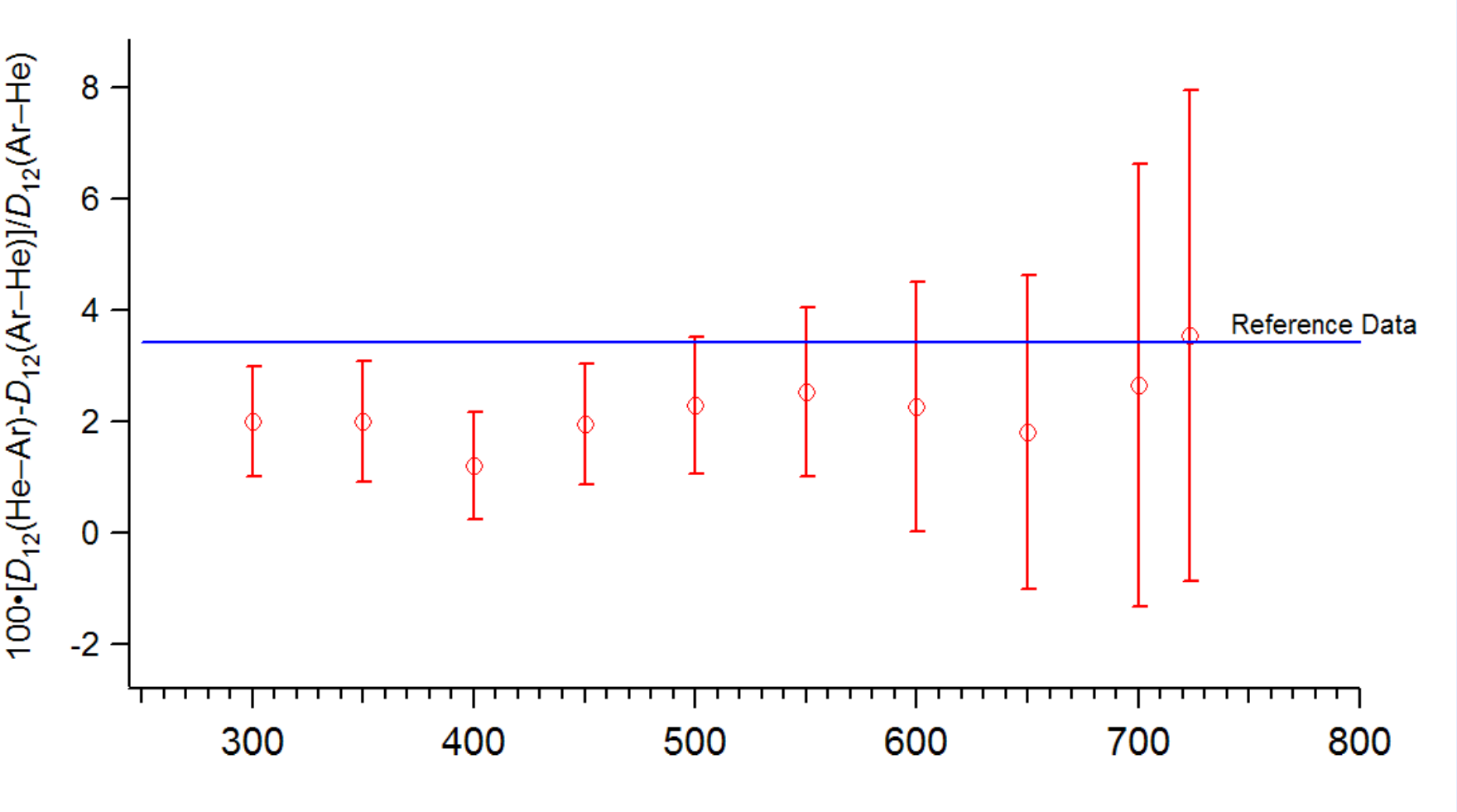
Helium in Argon



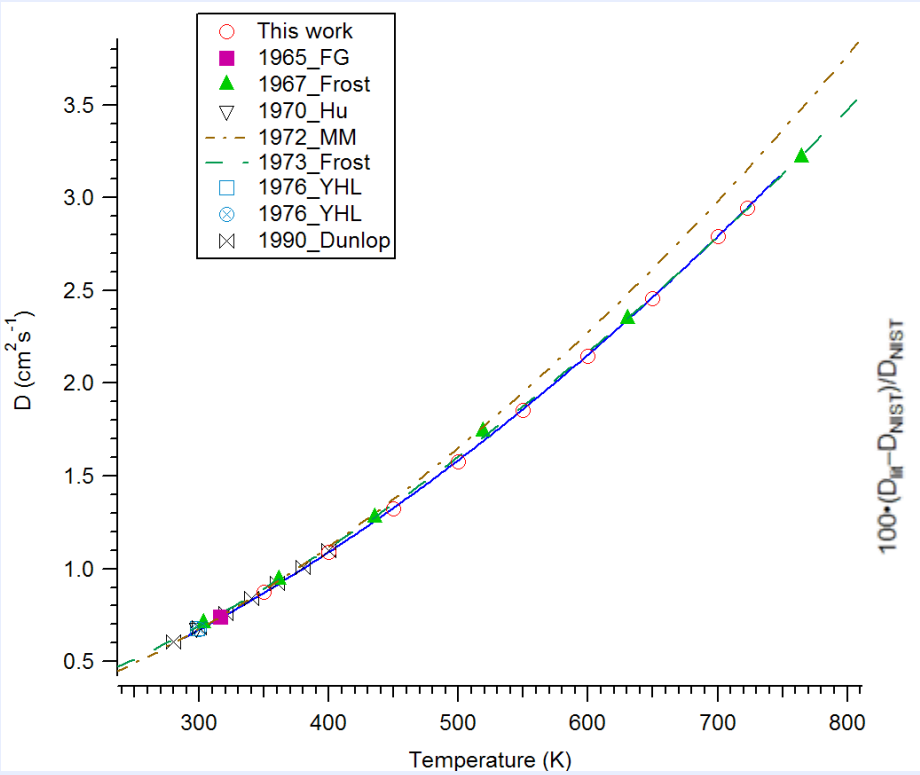


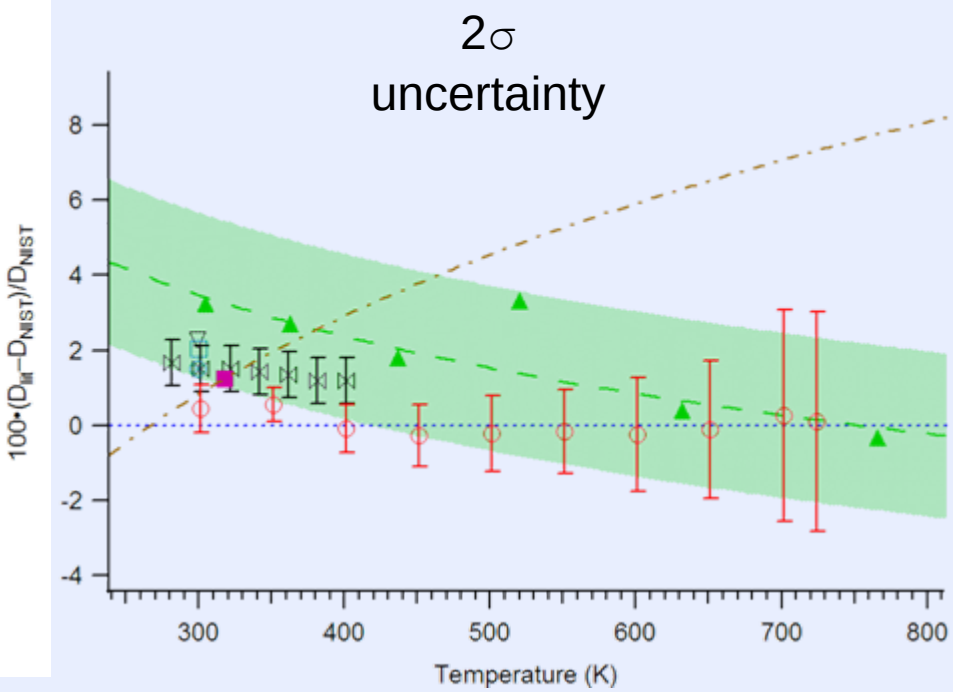
$$D_{12}(T) = (5.56 \pm 0.19) \times 10^{-5} (T/1\,\mathrm{K})^{1.664 \pm 0.006}\ [\mathrm{cm^2 s^{-1}}]$$

$D_{He\text{-}Ar}$ Concentration Dependence



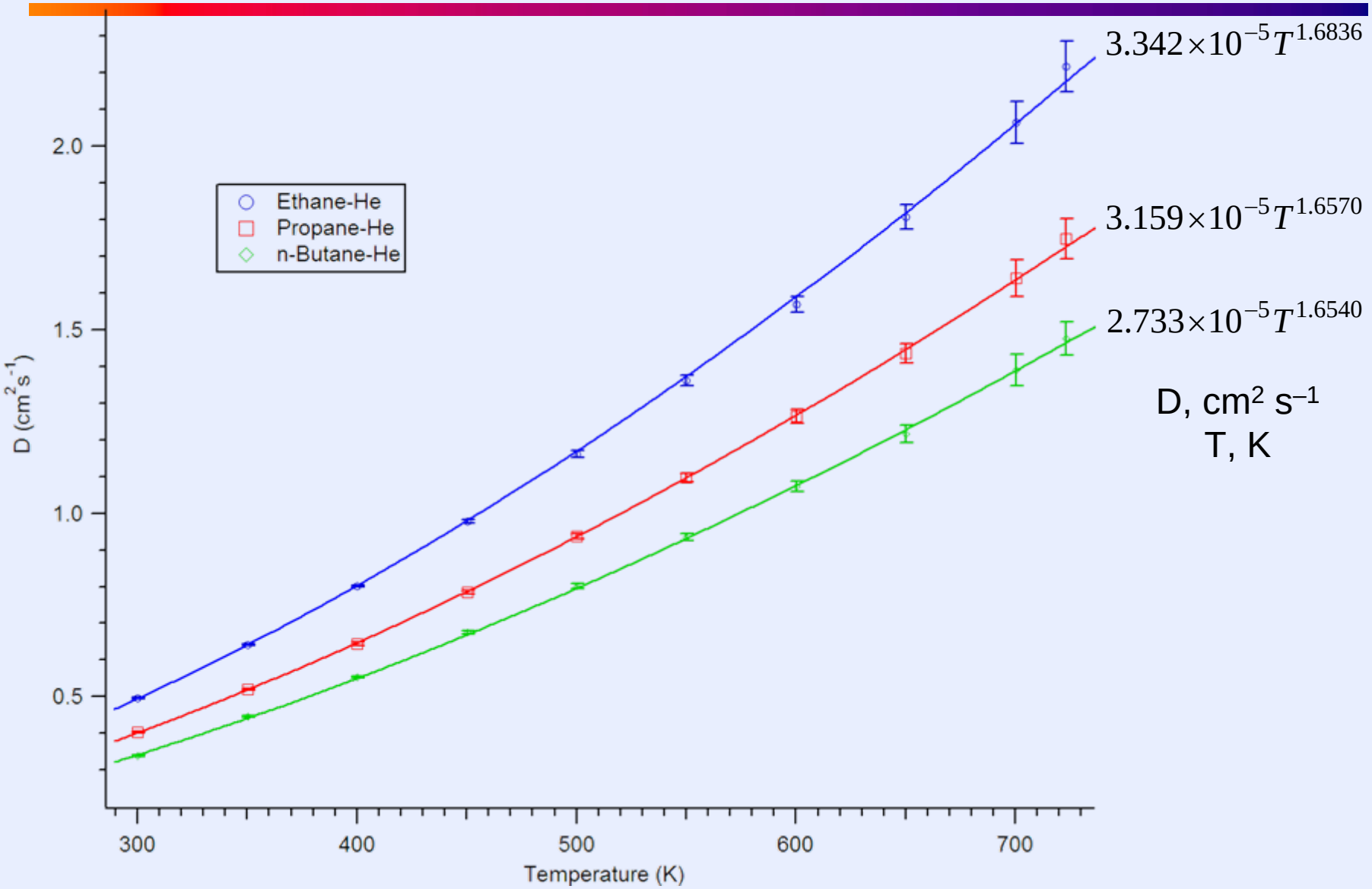
Methane in He





$$D_{12}(T) = (4.97 \pm 0.18) \times 10^{-5} (T/1\,\mathrm{K})^{1.668 \pm 0.006}\ [\mathrm{cm}^2\mathrm{s}^{-1}]$$

Longer-Chain Hydrocarbons in Improved Validated Apparatus



Remaining Experimental Issues

- **Sticking – significant with stainless tubes/low V_p hydrocarbons**
  - **Hexane sticks at T ≤ 300 K; octane at T ≤ 400 K**
  - **Restek "Silcosteel" coated tube – increased sticking slightly**
  - **Other coatings, tube materials??**
- **Substrate decomposition:**
  - **Pentane (stainless tube): <1% decomposition at 725 K in ca. 20 minutes**
  - **Longer aliphatics, alkenes, etc. untested**
- **Transfer standard for long/short tubes (large/small *D*)**

Concluding Remarks

- Demonstrated new apparatus to measure binary diffusion coefficients over a wide T range (*ca*. 250-725 K)
- Measurements show excellent precision (*ca*. +/- 0.5-1%)
- Absolute accuracy within 2% in absence of systematic errors (sticking, substrate decomposition) – should be good enough to allow extrapolation over temperature and theory/correlation development
- Data suggest T dependence of $D_{\text{A-Helium}} < D_{\text{A-Nitrogen}}$

Future Directions

- Extend studies to larger n-alkanes, C12+
- Relate results to theory (with Hai Wang & Angela Violi)
- Examine isomeric species (effect of geometry)
- Examine other bath gases
- Examine other homologous series of interest to modeling combustion of liquid fuels and their surrogates
  - Alkenes
  - Aromatics
  - Alkynes
  - Oxygenated species