Direct Measurements of Binary Gas Phase Diffusion Coefficients for Combustion Applications

Jeffrey A. Manion (NIST)
W. Sean McGivern (NIST)
Wing Tsang (NIST)

NIST Summer Undergraduate Research Fellow Students:
Nicholas Heinz (USC)
Naoki Nitta (Rice University)

Support:
AFOSR (Julian Tishkoff)
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.


**Laminar premixed $\text{H}_2$-air flames:** computed flame speed as sensitive to diffusion as kinetics of the primary chain branching reaction


**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

- Overview of measurement methods
- Review of status – uncertainties and noble gas validation studies
- New hydrocarbon data in validated tube – C1 to C4 alkanes in Helium
- New hydrocarbon data in validated tube – C1 to C4 alkanes in Nitrogen
- Larger alkanes – New Data and Issues
  - Substrate Decomposition
  - Analytical Assumptions
- Summary
Diffusion Measurement Methods - Historical

1. Closed tube

2. Two-bulb

3. Gas Chromatography
   - Peak Broadening

Watch concentration change as $f$(time)

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

Baseline Correction with Flow Reversal

Typical FIDs and TCDs show a small drift over the several hours required for many analyses.

Timescales of hours

Reversals done every few minutes
Constant drift correction
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. 2 - 4 bar
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

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

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

Result:

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

where,

\[ \tau = t_0 - t_M - 1/2 t_{FR} \]


- \( t \) = time measured from injection of the substrate
- \( z \) = distance coordinate along diffusion tube
- \( c \) = concentration of the substrate A
- \( D_{AB} \) = binary diffusion coefficient
- \( h \) = peak height
- \( N \) = constant
- \( L \) = length of diffusion tube
- \( \tau \) = 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:

\[ \ln(h \tau^{3/2}) = \ln N - \frac{L^2}{4D_{AB}} \frac{1}{\tau} \]


Figure 2. Plot of equation for an experiment with C\textsubscript{2}H\textsubscript{6} – N\textsubscript{2} at 350 K.
Laplace Transform Analysis Not Valid at Long Times

Dilute CH₄ in He at 599.9 K
D (1.013 bar) = (2.146 ± 0.011) cm² s⁻¹
Crank-Nicholson Simulation

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

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

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

Discrete Grid

\[
z_i = z_0 + i\Delta z \\
t_n = t_0 + n\Delta t
\]

Boundary Conditions

\[
c_z |_{x=L} = c_x |_{x=0} \\
-D \left( \frac{\partial c_z}{\partial t} \right) |_{z=L} = v c_x |_{x=0}
\]

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 \( K = \frac{D\Delta t}{(\Delta z)^2} \)

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

Dilute CH₄ in He at 599.9 K

\[ D (1.013 \text{ bar}) = (2.146 \pm 0.011) \text{ cm}^2 \text{ s}^{-1} \]
Uncertainties and Effective Tube Length: Calibration with Noble Gas (He/Ar) Reference

\[ D_{\text{He-Ar}} = (0.7344 \pm 0.0042) \text{ cm}^2 \text{ s}^{-1} \text{ at } 1.013 \text{ bar and } 300 \text{ K (2}\sigma\text{ uncertainty)} \]

Argon in Helium

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

- New data in validated tube – C1 to C4 alkanes in Helium
- New data in validated tube – C1 to C4 alkanes in Nitrogen
- Larger alkanes – New Data and Issues
  - Substrate Sticking & Decomposition
  - Analytical Assumptions
Methane in Helium


Figure 8. Binary diffusion constants for dilute CH4 in He at temperatures ranging from (300–723) K. Symbols represent experimental data. The left graph shows the diffusion coefficients in cm² s⁻¹ (uncertainties not shown for clarity – see Table 3), and the right chart shows the percentage deviation from the temperature dependence obtained in the present work. Symbols and lines are identified in the inset.
Ethane in Helium


\[ D (\text{cm}^2 \text{s}^{-1}) \]

\[ T (\text{K}) \]

\[ \text{C}_2\text{H}_6/\text{He} \]

\[ n = 1.6646 \]
Propane in Helium


Butane in Helium

$C_4H_{10}/He$


Ethane in Nitrogen

$C_2H_6/N_2$

$D \text{ (cm}^2\text{s}^{-1}\text{)}$

Temp (K)

300 400 500 600 700


$n = 1.7458$
Propane in Nitrogen


Butane in Nitrogen


$C_4H_{10}/N_2$

$D$ (cm$^2$ s$^{-1}$)

Temp (K)

$n$-C$_4$H$_{10}/N_2$

$n = 1.7369$
Diffusion Coefficients of Hydrocarbons in He and N\textsubscript{2}
Temperature Dependence

\[ D(T) = a T^n \quad (T \text{ in K}) \]

<table>
<thead>
<tr>
<th>Expt</th>
<th>$10^6 \times a$ (cm$^2$ s$^{-1}$)</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_6$/He</td>
<td>37.353</td>
<td>1.6646</td>
</tr>
<tr>
<td>C$_2$H$_6$/N$_2$</td>
<td>7.4194</td>
<td>1.7458</td>
</tr>
<tr>
<td>C$_3$H$_8$/He</td>
<td>34.169</td>
<td>1.6463</td>
</tr>
<tr>
<td>C$_3$H$_8$/N$_2$</td>
<td>4.9461</td>
<td>1.7733</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$/He</td>
<td>26.276</td>
<td>1.6612</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$/N$_2$</td>
<td>5.2626</td>
<td>1.7369</td>
</tr>
</tbody>
</table>
Pentane-He

This work: $D_{n\text{-Pentane-He}}(300-600 \text{ K}) = 2.62 \times 10^{-5} T^{1.637}$

At 1000 K, our $D$ is about 50% smaller than the Hargrove/Sawyer value
Pentane in Helium – Transfer Std.

Red – 61.28 cm bent tube (effective L)
Blue – 23.00 cm straight tube (as measured)

<table>
<thead>
<tr>
<th>T / K</th>
<th>D (pentane) cm² s⁻¹</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>long</td>
<td>short</td>
</tr>
<tr>
<td>350</td>
<td>0.387</td>
<td>0.380</td>
</tr>
<tr>
<td>400</td>
<td>0.481</td>
<td>0.482</td>
</tr>
<tr>
<td>450</td>
<td>0.590</td>
<td>0.591</td>
</tr>
<tr>
<td>500</td>
<td>0.699</td>
<td>0.696</td>
</tr>
</tbody>
</table>

Sticking at 300 K

$n = 1.6370$

Sticking
Octane in Helium

$n$-C$_8$H$_{18}$/He

$n = 1.6406$
Nonane in Helium
Octane in Helium
Is decomposition the problem?
Decomposition of Nonane

![Graph showing normalized total C signal with time in minutes](image1)

<table>
<thead>
<tr>
<th>Species</th>
<th>% of Total Carbon at 327 °C (600 K)</th>
<th>% of Total Carbon at 427 °C (700 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>0.21</td>
<td>2.8</td>
</tr>
<tr>
<td>C4</td>
<td>0.35</td>
<td>0.6</td>
</tr>
<tr>
<td>C5</td>
<td>0.38</td>
<td>1.5</td>
</tr>
<tr>
<td>C6</td>
<td>0.56</td>
<td>5.7</td>
</tr>
<tr>
<td>nonane</td>
<td>98.0</td>
<td>88.2</td>
</tr>
</tbody>
</table>
“Worst-Case” (for diffusion) Decomposition

\[
\begin{align*}
\text{4} & \xrightarrow{\text{+ H}} \text{4} \\
\text{2} & \xrightarrow{\text{+ H}} \text{2} \\
\text{1} & \xrightarrow{\text{+ H}} \text{1} \\
\text{4} & \xrightarrow{\text{+ H}} \text{4}
\end{align*}
\]
Simulation Modification

Analyte

\[ k_d \]

Decomp.

\[ \frac{1}{n} \text{ Decomp} \]

Total

Analyte +

\[ L \]
Simulation Modification

\[ L \]

Analyte

\[ k_d \]

Decomp.

Total

Analyte + 1/n Decomp
Simulation Modification

Analyte

Decomp.

Total Analyte + \(1/n\) Decomp

\(k_d\)

\(L\)
Dependence on Decomposition

Fraction Decomposed in 20 min

Fractional Error

Decomposition Rate (s⁻¹)

0.01  0.1  0.2  0.27

0.1  0.01  0.001

400x10⁻⁶
Decane in Helium

![Graph showing the diffusion coefficient (D) of n-C_{10}H_{22}/He vs. temperature (Temp) in Kelvin (K)].
Extracting $D$ from data – A closer look

Issues with Analysis:

- Shrinking “linear” window as $D$ increases (higher Temps.)
- Exacerbated by low Vp substrates (detection limits)
- Looking at better methods to extract $D$ from data
- Short diffusion tube should help
Summary & Future Directions

- **Current Status**
  - $D$ within 2% accuracy for well-behaved substrates, 300 – 725 K
  - Sticking (low T) & decomposition (high T) are issues
  - Not fully understood issues for larger species (> C8) at higher T

- **Directions:**
  - Complete C1 – Cn matrix for He/N2 (mix of long and short tube data)
  - Examine geometrical effects (branching, cyclics) for selected Cn
  - Relate to theory (Wang, Violi)
  - Suggestions, requests?