Pressure Dependent Kinetics: Single Well Reactions

Simple Models
- Lindemann-Hinshelwood
- RRKM Theory
- Modified Strong Collider

The Master Equation
- 1-dimensional (E)
- 2d Master Equation (E,J)
- Energy Transfer
- Troe Fitting
- Product Channels \( \text{CH}_3 + \text{OH} \)

Recombination Kinetics

Recombination is a Multistep Process - not single elementary step

\[ A + B \rightarrow AB(E) \quad k_f(E) \quad [k(T) = \int k(E) P(E)] \]

But, \( E \) is above dissociation threshold so \( AB \) just reassociates

\[ AB(E) \rightarrow A + B \quad k_d(E) \]

Need some process to take away energy and stabilize \( AB \)

Collisions with bath gas \( M \) (or photon emission)

\[ AB(E) + M \rightarrow AB(E') + M' \quad k_c \times P(E \rightarrow E') \]

Effective rate constant is some mix of \( k_f(E), k_d(E), k_c, \) and \( P(E \rightarrow E') \)

Dissociation is related to recombination through equilibrium constant
Simple Models Lindemann-Hinshelwood

Assume every collision leads to stabilization
Treat association and dissociation on canonical level

\[ A + B \rightarrow AB^* \quad k_f(T) \]
\[ AB^* \rightarrow A + B \quad k_d(T) \]
\[ AB^* + M \rightarrow AB + M' \quad k_c \]

Steady state for \([AB^*]\) =>

\[ \frac{d[AB]}{dt} = k_{eff} [A] [B] \]

\[ k_{eff} = k_f k_c [M] / ( k_d + k_c [M] ) = k_f P_{stabilization} \]

High Pressure limit ([M] → ∞)

\[ k_{eff} = k_f \]

Low Pressure limit ([M] → 0)

\[ k_{eff} = k_f k_c / k_d \]

Not accurate but good for qualitative thought
Simple Models  RRKM Theory

Treat energy dependence of association and dissociation rate constants $k_f(E)$ and $k_d(E)$

\[
\text{k}_{\text{eff}} (T,P) = \int dE \text{k}_{\text{eff}} (E) \ P(E) = \int dE \text{k}_f(E) \ P(E) \ P_{\text{stabilization}} (E,P)
\]

Use transition state theory with quantum state counting to evaluate $k_f$, $k_d$

\[
k_{\text{eff}} = \int dE \frac{N^\pm (E)}{h\rho_{\text{react}}(E)} \frac{\rho_{\text{react}}(E) \exp(-\beta E)}{Q_A Q_B} \frac{k_c [M]}{k_d (E) + k_c [M]}
\]

\[
k_{\text{eff}} = \frac{1}{hQ_A Q_B} \int dEN^\pm (E) \exp(-\beta E) \frac{k_c [M]}{k_d (E) + k_c [M]}
\]

Consider High Pressure Limit; $[M] \rightarrow \infty$

\[
k_{\text{eff}}^\infty = \frac{1}{hQ_A Q_B} \int dEN^\pm (E) \exp(-\beta E) = \frac{k_B T}{hQ_A Q_B} \int dE \rho^\pm (E) \exp(-\beta E)
\]

\[
k_{\text{eff}}^\infty = \frac{k_B T}{h} \frac{Q^\pm}{Q_A Q_B}
\]
Simple Models

Assume only a fraction $\beta_c$ of collisions lead to stabilization

$$k_{\text{eff}} = \frac{1}{hQ_A Q_B} \int dE N^\pm(E) \exp(-\beta E) \frac{\beta_c k_c [M]}{k_d(E) + \beta_c k_c [M]}$$

Consider low pressure limit; $[M] \rightarrow 0$

$$k_{\text{eff}}^0 = \frac{1}{hQ_A Q_B} \int dE N^\pm(E) \exp(-\beta E) \frac{\beta_c k_c [M]}{k_d(E)}$$

$$k_{\text{eff}}^0 = \frac{\beta_c k_c [M]}{Q_A Q_B} \int_0^\infty dE \rho_{AB}(E) \exp(-\beta E)$$

$k_{\text{eff}}^0$ does not depend on transition state! Only the threshold $E$ matters

$\beta_c$ is a fitting parameter - typical value $\sim 0.1$
Master Equation

Consider \( n(E,t) \) = time-dependent population of AB molecule at energy \( E \)

Master equation \hspace{1cm} Irreversible Formulation

\[
\frac{dn(E)}{dt} = k_c [M] \int dE' \left[ P(E,E')n(E',t) - P(E',E)n(E,t) \right] - k_d(E)n(E,t)
\]

Replace \( n(E,t) \) with normalized population \( x(E,t) = \frac{n(E,t)}{\int dE n(E,t)} \)

Steady state for \( x \) =>

\[-k(T,p)x(E) = k_c [M] \int dE' P(E,E')x(E') - k_c [M]x(E) - k_d(E)x(E)\]

Master equation \hspace{1cm} Reversible Formulation

\[
\frac{dn(E)}{dt} = k_c [M] \int dE' \left[ P(E,E')n(E',t) - P(E',E)n(E,t) \right] - k_d(E)n(E,t) + \]

\[
k_f(E) \frac{\rho_{\text{reac tan}}(E) \exp(-\beta E)}{Q_A Q_B} n_A n_B
\]
Master Equation  Symmetrized Form

\[ f^2(E) = \rho(E) \exp(-\beta E) = F(E)Q(T) \]
\[ y(E) = x(E)/f(E) \]

Discretize master equation

\[ \frac{dy}{dt} = G' y \]
\[ G'_{ij} = k_c [M] P(E_i, E_j) \frac{f(E_j)}{f(E_i)} \delta E - \left[ 1 + \frac{k_d(E)}{k_c[M]} \right] \delta_{ij} \]

Diagonalize

\[ |y(t)\rangle = \sum_{j=1}^{N} \exp(\xi_j t) |g_j\rangle \langle g_j | y(0) \rangle \]

Eigenvalues are all negative
One with smallest magnitude defines the rate coefficient
\[ k(T,p) = -\xi_1 \]
Others are related to rate of energy transfer - form continuum
Master Equation Problems at Low T

numerical difficulties with diagonalization due to large dynamic range

Various Solutions

1. Integrate in time
2. Quadruple Precision
3. Reformulate with sink for complex $\Rightarrow$ Matrix inversion
Master Equation Problems at high T

Dissociation occurs on same time scale as energy relaxation

Nonequilibrium factor $f_{ne}$

$$f_{ne} = \frac{\left(\int dE c(E)\right)^2}{\left(\int dE \frac{c^2(E)}{F(E)}\right)^2}$$

$c(E) = \text{steady state distribution}$

Deviation of $f_{ne}$ from unity indicates how much dissociation happens before relaxation

Detailed balance is still satisfied for fraction that happens after relaxation
Boltzmann Distributions

$CH_4$

Figure 8. Relative values of $f(E; T)$. The functions are normalized so that the peak is always unity.
Non-equilibrium factors

Temperature (K)

f_{ne} (dimensionless)

- i-C_4 H_3
- C_2 H_3
- C_2 H_5
- n-C_4 H_3 (vinoxy)
- acetyl
Master Equation 2-Dimensional

Total Angular Momentum J - conserved between collisions

Master equation in E and J

\[ n(E,J,t) \quad \text{or} \quad x(E,J,t) \]
\[ P(E,J,E',J') \]
\[ k(E,J) \]

Numerical solution timeconsuming

Need more information on energy transfer than we have
Approximate Reduction from 2D to 1D

E model

\[ P(E,J,E',J') = P(E,E') \varphi(E,J) \]

Rotational energy transfer like vibrational J distribution given by phase space volume

\[ \varphi(E,J) = (2J+1) \frac{\rho(E,J)}{\rho(E)} \]

\[ \rho(E) = \sum_J (2J+1) \rho(E,J) \]

\[ k(E) = \frac{\sum_J (2J+1) N^\pm(E,J)}{h\rho(E)} \]

Use \( k(E) \) and \( P(E,E') \) in 1D Master Eqn

Does not resolve J dependent thresholds

All rotational degrees of freedom are active

Incorrect low pressure limit
E, J model

like E model, but treat $k(E, J)$ properly

$$k(E) = \frac{\sum_J k(E, J) \ y(E, J)}{\sum_J y(E, J)}$$

$$y(E, J) = \frac{\phi(E, J)}{k_c[M] + k(E, J)}$$

$$x(E) = \sum_J x(E, J)$$

$$x(E, J) = \frac{k_c[M]\phi(E, J)}{Z + k(E, J)} \int dE' P(E, E') x(E')$$

Proper treatment of J dependent thresholds
Proper zero-pressure limit
Proper high-pressure limit
Consistent with detailed balance
2D Master Equation \( \varepsilon, J \) Model

\( \varepsilon, J \) model

Active energy - does not include overall rotation

\[
\varepsilon = E - E_J
\]

\[
E_J = BJ(J+1)
\]

\[
P(\varepsilon, J, \varepsilon', J') = P(\varepsilon, \varepsilon') \Phi(\varepsilon, J)
\]

\[
\Phi(\varepsilon, J) = (2J+1)\rho(\varepsilon, J)\exp(-\beta E_J)/\sum_J(2J+1)\rho(\varepsilon, J)\exp(-\beta E_J)
\]

\[
\rho(\varepsilon, J) = \text{density of states for active degrees of freedom}
\]

Thermally equilibrated J distribution

Satisfies Detailed balance
Steady State Distribution

$\text{CH}_4$

E model

E, J model
Low Pressure Limit \( \text{CH}_4 \)

Figure 1. High-temperature rate coefficients. The master-equation calculations were done with \( \langle \Delta E_d \rangle = 410 \text{ cm}^{-1} \), independent of \( T \), for the \( E,J \) and \( E \) models. A constant value of \( \langle \Delta \epsilon_d \rangle = 35 \text{ cm}^{-1} \) was assumed for the \( \epsilon,J \) ME calculations.
Low Pressure Limit

\[ H + C_2H_2 + He \rightarrow C_2H_3 + He \]

Graph showing the variation of the reaction rate constant \( k_0 \) (cm^6/molecule^2-s) with temperature (T(K)) for different models:
- 1-D ME (E model)
- 2-D ME (E,J model)
- E,J model (no tunneling)
Reduced Falloff Curves

**Reduced Falloff h+c2h2 300 K**

- low-p limit
- high-p limit
- 1-d ME
- 2-d ME
- barrierless test case
- Lindemann

**Reduced Falloff c2h3-he 1500K**

- low-p limit
- high-p limit
- 1-d ME
- 2-d ME
- barrierless test case
- Lindemann
Collision Rates

Hard Sphere

\[ k_c^{HS} = \sqrt{\frac{8kBT}{\pi \mu \pi d^2}} \]

Lennard-Jones

\[ k_c^{LJ} = k_c^{HS} \Omega_{2,2}^* \]

\[ \Omega_{2,2}^* = \frac{1.16145}{\left(T^*\right)^{0.14874}} + \frac{0.52487}{\exp(0.7732T^*)} + \frac{2.16178}{\exp(2.437887T^*)} \]

Underestimates collision rate
Correct with larger average energy transferred

Dipole Corrections

\[ T^* = \frac{k_B T}{\varepsilon} \]
Energy Transfer Forms

Exponential Down

\[ P(E, E') = \frac{1}{C_N(E')} \exp\left(-\frac{\Delta E}{\alpha}\right) \]

\[ \alpha = \alpha_0 \left(\frac{T}{298}\right)^n \]
\[ \alpha_0 \sim 50-400 \text{ cm}^{-1} \]
\[ n \sim 0.85 \]
Fit to experiment

Gaussian Down

\[ P(E, E') = \frac{1}{C_N(E')} \exp\left[-\left(\frac{\Delta E}{\alpha}\right)^2\right] \]

Double Exponential Down

\[ P(E, E') = \frac{1}{C_N(E')} \left[ (1 - f) \exp\left(-\frac{\Delta E}{\alpha_1}\right) + f \exp\left(-\frac{\Delta E}{\alpha_2}\right) \right] \]
Energy Transfer Moments

Average Energy Transferred

\[ \langle \Delta E \rangle = \int dE (E' - E) P(E, E') \]

Average Downwards Energy Transferred

\[ \langle \Delta E_d \rangle = \int_0^{E'} dE' (E' - E) P(E, E') / \int_0^{E'} dE' P(E, E') \]

\[ \langle \Delta E_d \rangle \approx \alpha \quad \text{for exponential down} \]

Average squared energy transfer

\[ \langle \Delta E^2 \rangle = \int dE (E - E')^2 P(E, E') \]
Fits to Experiment $H + C_2H_2$ Addition

$h + c_2h_2 \ 298K$

$10^{-12}$

$k(\text{cm}^3/\text{molecule-sec})$

$10^{-13}$

$10^{-14}$

$1, 10, 100, 1000$

$\text{pressure(torr)}$

$1-d \ ME$

$2-d \ ME$

- Payne & Stief (1976)
Fits to Experiment \( \text{C}_2\text{H}_3 \) Dissociation

\[
\begin{align*}
\text{Fig. 5} \ & \text{Comparison of the theoretical results for } k_{-1}(T,p) \\
& \quad \text{(C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}) \text{ with the experiments of Knyazev and Slagle.}^{21} \\
& \quad \text{The units of } n_{\text{He}} \text{ are molecule cm}^{-3}.
\end{align*}
\]
Fits to Experiment  

T dependent $\Delta E_d$

Fig. 8  Values of $\langle \Delta E_d \rangle$ as a function of temperature for several molecules and collision partners.
Energy Transfer from Trajectories

Collisional energy transfer in unimolecular reactions: Direct classical trajectories for CH$_4$=CH$_3$+H in Helium


$\alpha_0=110$ cm$^{-1}$  $n=0.81$

Barker is studying $P(E,J,E',J')$
Troe Fitting

Need to represent $k(T, P)$ for Global Models
Standard is Troe Fitting

$$k(T, p) = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]} F$$

$$\log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[ \frac{\log_{10}(p^*) + c}{N - d(\log_{10}(p^*) + c)} \right]^2}$$

$$p^* = k_0[M]/k^\infty \quad d = 0.14$$

$$c = -0.4 - 0.67\log_{10} F_{cent} \quad N = 0.75 - 1.27\log_{10} F_{cent}$$

Fit $k_0$ & $k^\infty$ to modified Arrhenius

$$k_0 = A_0 T^{n_0} \exp(-E_0 / T)$$

Fit $F_{cent}$ to:

$$F_{cent} = (1 - a)\exp(-T / T^{**}) + a\exp(-T / T^*) + \exp(-T^{**} / T)$$
Troe Fitting Problems

Limited Accuracy
Typical Errors ~ 10 to 20%

Improved Fitting Formulas


Still problems for tunneling

Multiple channels - actual P dependence is dramatically different from Troe Form

Use Log Interpolation

\[ \log k = \log k_i + (\log k_{i+1} - \log k_i) \left( \frac{\log p - \log p_i}{\log p_{i+1} - \log p_i} \right) \]

Part of Current ChemKin
$\text{CH}_3 + \text{OH}$

Potential Energy Surface
<table>
<thead>
<tr>
<th>Stationary point</th>
<th>ATcT(^a)</th>
<th>Present(^b)</th>
<th>Ref. 29(^c)</th>
<th>Ref. 51(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3) + OH</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>−90.25 ± 0.05</td>
<td>−90.4</td>
<td>−91.9</td>
<td>−87.6</td>
</tr>
<tr>
<td>CH(_3)OH(^e)</td>
<td>−89.8</td>
<td>−87.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^1)CH(_2) + H(_2)O</td>
<td>0.58 ± 0.07</td>
<td>0.03</td>
<td>−1.6</td>
<td>0.5</td>
</tr>
<tr>
<td>H(_2) + H(_2)CO</td>
<td>−69.92 ± 0.06</td>
<td>−70.0</td>
<td>−73.8</td>
<td>−68.2</td>
</tr>
<tr>
<td>H(_2) + cis-HCOH</td>
<td>−13.13 ± 0.32</td>
<td>−13.8</td>
<td>−17.1</td>
<td>−12.3</td>
</tr>
<tr>
<td>H(_2) + trans-HCOH</td>
<td>−17.77 ± 0.29</td>
<td>−18.0</td>
<td>−21.4</td>
<td>−16.4</td>
</tr>
<tr>
<td>H + CH(_2)OH</td>
<td>4.30 ± 0.09</td>
<td>4.6</td>
<td>4.3</td>
<td>7.5</td>
</tr>
<tr>
<td>H + CH(_3)O</td>
<td>13.75 ± 0.10</td>
<td>13.7</td>
<td>13.0</td>
<td>15.6</td>
</tr>
<tr>
<td>(^3)CH(_2) + H(_2)O</td>
<td>−8.42 ± 0.06</td>
<td>−8.7</td>
<td>−11.2</td>
<td></td>
</tr>
<tr>
<td>CH(_2)···H(_2)O (vdW)</td>
<td>−8.5</td>
<td>−9.2</td>
<td>−4.8</td>
<td></td>
</tr>
<tr>
<td>([^1)CH(_2) + H(_2)O ⇔ CH(_3)OH]^\dagger) (SP1)</td>
<td>−7.3</td>
<td>−7.8</td>
<td>−4.6</td>
<td></td>
</tr>
<tr>
<td>([H(_2) + H(_2)CO ⇔ CH(_3)OH]^\dagger) (SP2)</td>
<td>−0.3</td>
<td>−1.3</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>([H(_2) + cis-HCOH ⇔ CH(_3)OH]^\dagger) (SP3)</td>
<td>−2.2</td>
<td>−3.8</td>
<td>−0.6</td>
<td></td>
</tr>
<tr>
<td>([H(_2) + trans-HCOH ⇔ CH(_3)OH]^\dagger) (SP4)</td>
<td>−4.8</td>
<td>−6.4</td>
<td>−2.2</td>
<td></td>
</tr>
<tr>
<td>([CH(_3) + OH ⇔ (^3)CH(_2) + H(_2)O]^\dagger) (SP5)</td>
<td>5.6</td>
<td>6.7</td>
<td>15.8</td>
<td></td>
</tr>
</tbody>
</table>
Reactions with Products: \( \text{CH}_3 + \text{OH} \)

Experiment:

Triangles - De Avillez Pereira, Baulch, Pilling, Robertson, and Zeng, 1997

Circles - Deters, Otting, Wagner, Temps, László, Dóbé, Bérces, 1998

Theory: Master Equations

Dotted - De Avillez Pereira et al.

Solid & Dashed - Present Work

\[ \langle \Delta E_d \rangle = 133 \left( \frac{T}{298} \right)^{0.8} \text{ cm}^{-1} \]

\[ \pm 25\% \]
CH$_3$ + OH: Higher T and P ~1 atm

Shock tube studies

- 1991, Bott and Cohen (1 atm)
- 2004, Krasnoperov and Michael (100–1100 torr)
- 2006, Srinivasan, Su, and Michael (200–750 torr)
Methanol decomposition: Low pressure limit

**Experimental**
- 2004, Krasnoperov and Michael
- 2006, Srinivasan, Su, and Michael
- 1981–2000, Many others
- $k$ independent of $P$ (100–1000 torr)
- 60–90% $\text{CH}_3 + \text{OH}$

**Previous theory**
- 2001, Xia, Zhu, Lin, and Mebel (shown at 1 atm)
- Falloff below 1 atm
- ~33% $\text{CH}_3 + \text{OH}$
  ~52% $\text{CH}_2 + \text{H}_2\text{O}$
  ~15% $\text{H}_2 + \text{HCOH}$

**Present theory**
- Low-$P$ limit at 1 atm
- ~75% $\text{CH}_3 + \text{OH}$
  ~20% $\text{CH}_2 + \text{H}_2\text{O}$
  < 5% $\text{H}_2 + \text{HCOH}$
Methanol decomposition: Product branching

![Graph showing the relationship between temperature and $P_{\text{CH}_3+\text{OH}}$ at different torr pressures (760 Torr and 200 Torr). The graph includes data from Xia et al. (2001) for 760 Torr.]
Secondary kinetics of methanol decomposition

Well characterized

\[ \text{OH} + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O} \]

\[ \text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2 \]

Not well characterized

\[ \text{^3CH}_2 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{H} \]

Ambiguous experiments

\[ \text{^3CH}_2 + \text{^3CH}_2 \rightarrow \text{C}_2\text{H}_2 + 2\text{H} \]

\[ \text{CH}_3 + \text{^3CH}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H} \]

Secondary kinetics: OH Time Traces

Michael et al.

Good agreement at long times using our predicted rates for

$^{3}\text{CH}_2 + \text{OH}$
$^{3}\text{CH}_2 + ^3\text{CH}_2$
$\text{CH}_3 + ^3\text{CH}_2$
$\text{CH}_3 + \text{OH}$
Multiple-Well Multiple-Channel
Time Dependent Master Equation

1. The Kinetic Model
2. Collisionless Limit
3. CH + N₂
4. Time Dependent Populations
5. Kinetic Phenomenology
6. C₂H₅ + O₂
7. Reduction in Species at High Pressure
8. C₃H₃ + H
9. Radical Oxidation
10. C₃H₃+C₃H₃
The Kinetic Model

Energy Transfer
- Bath Gas B: $[B] >> [M] >> [R]$.
- Z; Lennard Jones
- $P(E',E)$; Exponential Down

Phenomenology
- $k R + M \leftrightarrow P$
- $k R + M \leftrightarrow W_1$
- $k R + M \leftrightarrow W_2$
- $k W_1 \leftrightarrow W_2$
- $k W_1 \leftrightarrow P$
- $k W_2 \leftrightarrow P$

RRKRM Theory
- $k_{d1}$
- $k_{a1}$
- $k_{12}$
- $k_{21}$
- $k_{p1}$
- $k_{p2}$
Multiple-Well Multiple-Channel Master Equation

\[
\frac{dn_i(E)}{dt} = k_c n_B \int dE' P_i(E,E')n_i(E') - k_c n_B n_i(E) - k_{d_i}(E)n_i(E) - \sum_{p=1}^{N_p} k_{p_i}(E)n_i(E) - \\
\sum_{j \neq i}^M k_{^{isom}}(E)n_i(E) + \sum_{j \neq i}^M k_{^{isom}}(E)n_j(E) + K_{eq_i} k_{d_i}(E)F_i(E)n_R n_m
\]

\[
\frac{dn_R}{dt} = \sum_{i=1}^M \int dE k_{d_i}(E)n_i(E) - n_R n_m \sum_{i=1}^M K_{eq_i} \int dE k_{d_i}(E)F_i(E)
\]

M Wells \quad N_p \text{ Products} \\
M+1 \text{ Chemical Species} \\
n_B \gg n_m \gg n_R \quad B=\text{Bath}, \; m=\text{Molecule}, \; R=\text{Radical} \\
Linear Master Equation
Collisionless Limit

Consider \( Z \to 0 \)

\[
\frac{d}{dt} \left| n(E,J) \right\rangle = -K(E,J) \left| n(E,J) \right\rangle + n_R n_m |b(E,J)\rangle \rho_{Rm}(E,J) \exp(-\beta E) / Q_{Rm}
\]

\[
\frac{d}{dt} \left| P(E,J) \right\rangle = D(E,J) \left| n(E,J) \right\rangle
\]

Steady State for \( n(E,J) \)

\[
\frac{d}{dt} \left| P(E,J) \right\rangle = D(E,J)K^{-1}(E,J) \left| b(E,J) \right\rangle n_R n_m \rho_{Rm}(E,J) \exp(-\beta E) / Q_{Rm}(T)
\]

\[
\left| k_0(T) \right\rangle = \frac{1}{Q_{Rm}(T)} \sum J (2J + 1) \int dED(E,J)K^{-1}(E,J) \left| b(E,J) \right\rangle \rho_{Rm}(E,J) \exp(-\beta E)
\]

Flux coefficients
CH + N₂  Prompt NO

• 1971 Fenimore  \(^2\)CH + N₂ → HCN + \(^4\)N
• 1991 Dean, Hanson & Bowman -- shock tube measurements of rate for \(^2\)CH + N₂ → Products
• 1991 Manaa & Yarkony -- located minimum crossing point for doublet to quartet transition
• 1996 Miller & Walch -- found maximum on spin forbidden path corresponds to dissociation of the quartet complex; not the doublet-quartet crossing; presume rapid ISC and fit experimental data
• 1999 Qui, Morokuma, Bowman & Klippenstein -- predicted spin-forbidden reaction to be less than observed rate by at least 10²
• 2000 Moskaleva, Xia & Lin -- predicted new spin allowed mechanism,
  \(^2\)CH + N₂ → HNCN → \(^2\)H + \(^3\)NCN
• 2007 Szpunar, Faulhaber, Kautzman, Crider & Neumark -- observed the photodissociation of DNCN to CD+N₂ and D+NCN with 1:1 branching ratio
Recent Modeling

• Williams, Fleming
  NO severely underpredicted in CH$_4$ and C$_3$H$_8$ flames

• El Bakali, Pillier, Desgroux, Lefort, Gasnot, Pauwels, da Costa,
  Fuel 85, 896, 2006
  Increasing CH + N$_2$ rate by 1-2 orders of magnitude over the
  1000 to 1500 K range yields good predictions for NO in natural
  gas flames

• Sutton, Williams, Fleming,
  Comb. Flame, 2008, in press.
  Improved modeling for CH4/O2/N2 flames with rates of El
  Bakali et al.
CAS+1+2+QC/aug-cc-pvtz

Contour Increments: Thick- 5 kcal/mol, Thin- 1 kcal/mol
The diagram shows a graph with the y-axis labeled as 
$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) and the x-axis labeled as $1000/T$ (1/K). The graph plots the rate constant ($k$) against the reciprocal of temperature ($1000/T$). The data points for different reactions are represented by various lines and markers:

- H+NCN
- TS$_1$
- TS$_3$

The lines show the decrease in rate constant as the temperature decreases.
Time-Dependent Populations

- **Discretize Energy Levels**
- **Transition Matrix; Renormalize** $\rightarrow$ real, symmetric; $G$

- \[ \frac{d}{dt} \left| w(t) \right\rangle = G \left| w(t) \right\rangle \quad y_i(E,t) = x_i(E,t) / f_i(E) \]

- \[ \left| w(t) \right\rangle = \left[ y_i(E_{0_1}), \ldots, y_i(E_{0_l}), \ldots, y_i(E_{0_1}), \ldots, y_i(E_{max}), \ldots, \left( \frac{n_m}{QR_m \delta E} \right)^{1/2}, X_R, \ldots \right]^T \]

- **Diagonalize**

- \[ \left| w(t) \right\rangle = \sum_{j=1}^{N_{I+...+N_{M+1}}} e^{\lambda_j t} \left| g_j \right\rangle \left\langle g_j \right| w(0) \]
Kinetic Phenomenology
Experimental Viewpoint

• Find regimes of single exponential decay ($\lambda$)
  – $\lambda$ implies total rate coefficient
  – Eigenvector corresponding to $\lambda$ implies branching
  – Branching implies individual rate coefficient ($k_{\text{tot}}$)

• When is decay close enough to single exponential?
  – Suppose 2nd eigenvector contributes to only 1% of the initial decay but that $\lambda_2/\lambda_1 = 100$
  – Rate coefficient will differ by a factor of two from apparent exponential decay
  – Branching similarly incorrect

• Difficult to find single exponential decay regimes in multiple well situations
Eigenvalues \( \text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \)
A Simple Solution: Separation of Timescales

• M+1 modes corresponding to chemical change have least negative eigenvalues.

• λ’s for chemical modes well separated from remaining λ’s for energy transfer

• After energy relaxation can treat populations as

\[ w_\ell(t) = \sum_{j=1}^{M+1} e^{\lambda_j t} g_{j\ell} \langle g_j | w_A(0) \rangle \]

\[ \frac{dX_i}{dt} = -\sum_{j=1}^{M+1} \lambda_j e^{\lambda_j t} \Delta X^{(A)}_{ij}; \quad \Delta X^{(A)}_{ij} = -\langle g_j | w_A(0) \rangle \delta E \sum_{\ell \in i} f_i(E_\ell) g_{j\ell} \]

• Eigenpairs \((\lambda_i, \Delta X_i)\) correspond to Normal modes of chemical relaxation
Method 1 \( t=0 \) Limit and Start in Well A

- Phenomenology
  \[ \frac{dX_A}{dt}(0) = -k_{TA} X_A(0) \]

- Master Equation
  \[ \frac{dX_A}{dt}(0) = -\sum_{j=1}^{M+1} \lambda_j \Delta X_{Aj} \]
  \[ k_{TA} = \sum_{j=1}^{M+1} \lambda_j \Delta X_{Aj} \]

- Similarly, consider \( dX_i/dt \) implies
  \[ k_{Ai} = -\sum_{j=1}^{M+1} \lambda_j \Delta X_{ij} \]

- \( k_{AR} = -\sum_{j=1}^{M+1} \lambda_j \Delta X_{Rj} \); \( \Delta X_{Rj} = -\left( \frac{Q_{Rm} \delta E}{n_m} \right)^{1/2} g_{j\ell} \left\langle g_j \left| w_A(0) \right\rangle \right. \]

- \( k_{Ap} = -\sum_{j=1}^{M+1} \lambda_j \Delta X_{pj} \); \( \left[ \Delta X_R + \Delta X_p + \sum_{i=1}^{M} \Delta X_i \right]_j = 0 \)
Method 2

Long time limit

- \( X_i(t) = \sum_{j=0}^{M+1} a_{ij} e^{\lambda_j t} \equiv \sum_{j=0}^{M+1} a_{ij} v_j \)

\[ |X\rangle = A |v\rangle \quad |v\rangle = B |X\rangle \]

- \( \frac{dX_i}{dt} = \sum_{j=0}^{M+1} \sum_{\ell=1}^{M+2} \lambda_j a_{ij} b_{j\ell} X_\ell \)

- \( \frac{dX_i}{dt} = \sum_{\ell \neq i} k_{\ell i} X_\ell - \sum_{\ell \neq i} k_{i\ell} X_i \)

- \( k_{\ell i} = \sum_{j=0}^{M+1} \lambda_j a_{ij} b_{j\ell} \quad \ell \neq i \)
$C_2H_5 + O_2$ Potential Energy Surface
$C_2H_5 + O_2$

**Eigenvalues**

![Graph](image-url)

- $\lambda_3/n_m$
- $\lambda_2/n_m$
- $\lambda_1/n_m$

$C_2H_5 + O_2 \leftrightarrow C_2H_5O_2$

$C_2H_5O_2 \rightarrow C_2H + HO_2$

$k_{exp}$

$k(\text{cm}^3/\text{molecule-s})$

$1/T(K)$
$\text{C}_2\text{H}_5 + \text{O}_2$  

T Dependent Rate Coefficients
$\text{C}_2\text{H}_5 + \text{O}_2$  P Dependent Rate Coefficients
$C_2H_5O_2 \rightarrow C_2H_4 + HO_2$  P Dependent Rate Coefficients

![Graph showing the rate coefficients for the reaction $C_2H_5O_2 \rightarrow C_2H_4 + HO_2$ as a function of pressure (P) at different temperatures (600 K, 700 K, 850 K, 1000 K, 1500 K).]
\( \text{C}_3\text{H}_7 + \text{O}_2 \) \hspace{1cm} \text{Formally Direct Pathways; QOOH}
C₃H₄ Potential Energy Surface

\[ \text{Energy (kcal/mole)} \]

\[ \text{(I)} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]
\[ \text{(II)} \quad \text{H} \quad \text{C} = \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \]
\[ \text{(III)} \quad \text{H} \quad \text{C} - \text{C} = \text{C} \quad \text{H} \quad \text{H} \]

\[ \text{\textsuperscript{1}C₃H₂+H₂} \]
\[ \text{\textsuperscript{1}H₂CCC} \quad \text{+H₂} \]
\[ \text{\textsuperscript{3}C₃H₂+H₂} \]
\[ \text{c-C₃H₂+H₂} \]
$C_3H_4$ eigenvalues

Temperature (K)

- $\lambda_1$ (I+II+III+R $\rightarrow$ P)
- $\lambda_2$ (I $\leftrightarrow$ II)
- $\lambda_3$ (I $\leftrightarrow$ III)
- $\lambda_4$ (R $\leftrightarrow$ I)
- $\lambda_5$

IERE continuum
$C_3H_4$ Rate Coefficients

$T=1300K$

$C_3H_4 a \rightarrow C_3H_4 p$

$C_3H_4 a \rightarrow c-C_3H_4$

$k (1/s)$ vs. pressure (Torr)
$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ Eigenvalues

[Graph showing eigenvalues as a function of temperature ($T(K)$) and reaction rates ($\lambda$)]
C₃H₃ + C₃H₃ Rate Coefficients
$C_3H_3 + C_3H_3$  Isomerization Rate Coefficients

1,5 hexadiyne isomerization

Miller-Melius potential

theory

Stein, et al. (1990)

Huntsman and Wristers (1967)

1,2,4,5 hexatetraene isomerization

Miller-Melius potential

50 Torr

1 atm

50 torr (HL1)

1 atm(HL1)

theory

HL1

I→II and II→III barriers

Hopf (1971)
\[ \text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \]

Product Branching in 1,5-Hexadiyne Pyrolysis
$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$  
Product Branching
$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$  Product Branching
$C_3H_3 + C_3H_3$  Rate Coefficients

![Graphs showing rate coefficients for $C_3H_3 + C_3H_3$ reactions at 10 atm pressures.](image)
$C_6H_6$ Dissociation Rates

![Graphs showing dissociation rates for fulvene and benzene at 10 atm pressure.](image)
Master Equation Codes

Eigenvalue Eigenvector Methods

VariFlex  
Klippenstein
Research Code - Not usable without personal training

MESMER  
Pilling (Leeds)
http://sourceforge.net/projects/mesmer/

Stochastic Master Equation Solvers

Experimental Perspective only

Multiwell  
Barker (Michigan)
http://esse.engin.umich.edu/multiwell/MultiWell/MultiWell%20Home/MultiWell%20Home.html

Vereecken and Peeters (Leuven)

Steady State Solvers

ChemRate  
Tsang (NIST)
http://www.mokrushin.com/ChemRate/chemrate.html