Combination of experiment and theory to determine rate data and understanding on reactions for application in combustion
Transition state theory

\[ A + BC \rightarrow ABC \rightarrow AB + C \]

\[ k(T) = \frac{k_B T}{h} \frac{Q^\dagger}{Q_{\text{reactants}}} \exp \left( -\frac{E^\dagger}{k_B T} \right) \]

\(Q\) - partition function, \(h\) is Planck's constant and \(k_B\) is the Boltzmann constant.

\(\dagger\) indicates the transition state

Properties of transition state (and reactants if spectroscopic and thermodynamic data are not available) determined from electronic structure calculations.

The formulation given above is the \textit{canonical} form and gives the rate coefficient as a function of \(T\).
Thermodynamic formulation of TST

\[ K(T) = \frac{Q_{\text{products}}}{Q_{\text{reactants}}} \exp \left( -\frac{\Delta E_0}{k_B T} \right) = \exp \left( -\frac{\Delta G}{RT} \right) \]

where \( K \) is the equilibrium constant and \( \Delta E_0 \) is the difference in zero point energies of the reactants and products. \( \Delta G \) is the (molar) Gibbs energy change for the reaction. Note the change from molecular to molar units and that \( R = k_B N_A \), where \( N_A \) is the Avogadro number. Applying this equation to TST:

\[ k(T) = \frac{k_B T}{h} \frac{Q^\dagger}{Q_{\text{reactants}}} \exp \left( -\frac{E^\dagger}{k_B T} \right) = \frac{k_B T}{h} \exp \left( -\frac{\Delta G^\dagger}{RT} \right) \]

\( \Delta G^\dagger \) is the Gibbs energy of activation. We will discuss later when we talk about variational transition state theory.
Approach to calculating rate coefficients using TST

- The approach is most simple for a constrained transition state – one where there is a significant maximum on the reaction coordinate.
- The potential energy surface (PES) is calculated using electronic structure methods and the TS located.
- The energy of the TS relative to the reactants is determined along with the structure of the TS (which allows the moments of inertia to be calculated) and the vibrational frequencies. \( k(T) \) can then be calculated using Transition State Theory, and assuming rigid rotor – harmonic oscillator (RRHO) behaviour.
- Problems arise with hindered internal rotors and more complex calculations are needed.
- Quantum mechanical tunnelling through the energy barrier can be important for H transfer reactions.
Canonical Partition Functions

Rigid Rotor Harmonic Oscillator (RRHO)

\[ Q = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}} Q_{\text{elec}} \]

\[ Q_{\text{trans}} = \left( \frac{2\pi M k_B T}{\hbar^2} \right)^{3/2} \]

\[ Q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I_a k_B T}{\hbar^2} \right)^{1/2} \left( \frac{8\pi^2 I_b k_B T}{\hbar^2} \right)^{1/2} \left( \frac{8\pi^2 I_c k_B T}{\hbar^2} \right)^{1/2} \]

\[ Q_{\text{vib}}^{\text{quan}} = \prod_{i=1}^{n} \frac{\exp \left( -\frac{h\nu_i}{2k_B T} \right)}{1 - \exp \left( -\frac{h\nu_i}{k_B T} \right)} \]
\[ Q_{\text{vib}}^{\text{class}} = \prod_{i=1}^{n} \frac{k_B T}{h\nu_i} \]

\[ Q_{\text{elec}} = \sum_{i=1}^{n} g_i \exp \left( -\frac{E_i}{k_B T} \right) \]

Statistical Mechanics, D. A. McQuarrie, Harper & Row
Example: $\text{OH} + \text{CH}_3\text{OCH}_3 \text{ (DME)} \rightarrow \text{CH}_2\text{OCH}_3 + \text{H}_2\text{O}$

Calculated data for reactants and TS Units cm$^{-1}$:

**OH:** Rotational constant, $B$ : 18.59; $\omega$: 3714.3

**DME:** $A,B,C$: 1.519, 0.355, 0.307 ;

$\omega$: 188.7, 254.22, 419.92, 950.09, 1115.82, 1157.57, 1190.39, 1202.53, 1270.4, 1446.82, 1473.81, 1480.5 ,1487.46, 1489.39, 1505.08, 2991.17, 3000.31, 3050.2, 3054.06, 3142.46, 3144.65

**TS:** $A,B,C$: 0.368, 0.124, 0.103

$\omega$: 82.81, 150.13, 101.54, 213.93, 351.35, 432.86, 787.08, 956.83, 963.19, 1133.62, 1154.07, 1185.78, 1248.93 ,1277.17, 1360.98, 1441.63 1464.19, 1481.61, 1492.51, 1499.16, 3017.63, 3029.74, 3089.69, 3157.99 3160.68, 3735.5

Imaginary frequency: 894.66

Zero point energy of TS , relative to reactants: -0.6 kJ mol$^{-1}$
**OH + DME**

\[ \Delta E (kJ/mol) \]

- CH\_3\_O\_CH\_2\_OH
- TS1: 8.7
- TS2: -0.6
- TS3: 1.5
- H\_2\_O + CH\_3\_O\_CH\_2: -93.0
- H\_2\_O + CH\_3\_O\_CH\_2: -107.4
- OH + DME: -22.0

**Temperature / K**

- 200
- 300
- 400
- 600
- 1000

**K (cm\(^3\) molecule\(^{-1}\) s\(^{-1}\))**

- 1.0E-3
- 2.0E-3
- 3.3E-3
- 5.0E-3

Importance of tunnelling; asymmetric Eckart barrier
(See Miller, J Am Chem Soc, 1979, 101, 6810)

\[ W_{tunn}(E) = \int_{-E_0}^{E-E_0} \rho_{TS}(E-E_T) P_{tunn}(E_T) dE_T \]

\[ P_{tunn}(E_T) = \frac{\sinh(a) \sinh(b)}{\sinh^2((a + b)/2) \cosh^2(c)} \]

\[ a = \frac{4\pi}{h\nu_i} \sqrt{E_T + E_0} \left( E_0^{-0.5} + V_i^{-0.5} \right), \quad b = \frac{4\pi}{h\nu_i} \sqrt{E_T + V_i} \left( E_0^{-0.5} + V_i^{-0.5} \right), \quad c = 2\pi \sqrt{\frac{E_0 V_i}{(h\nu_i)^2} - \frac{1}{16}} \]

NB:
- presence of van der Waals well before TS – see later discussion of Inner and outer TSs. Important in reactions of OH with oxygenates.
- several TSs - ??? effects
Microcanonical rate theory

Microcanonical rate theory examines the rate at a specific energy; it gives:

\[ k(E) = \frac{h W^\dagger(\epsilon)}{N(E)} \]

where \( W(\epsilon) \) is the sum of states at the transition state, from energy zero to \( E \) and \( N(\epsilon) \) is the density of states at energy \( E \) for the reactant(s). We will use this approach when dealing with master equation calculations.

Integrating this expression over a Boltzmann distribution of reactants gives the TST result for \( k(T) \).
Accuracy of TST calculations

• Kinetic accuracy
  – Uncertainty of barrier height is typically ~ 4 kJ mol\(^{-1}\) (1 kcal mol\(^{-1}\)).
  Graph shows a plot of \(\exp(E/RT)\) vs \(T\) with \(E = 4\) kJ mol\(^{-1}\), which represents
  The uncertainty factor in \(k\) deriving from the uncertainty in the activation energy.
  – Deficiencies in the TS model
    – Rigid rotor harmonic oscillator model
    – Tunnelling model - generally use Eckart.
• Improvements - higher level ab initio calculations, variational effects, anharmonicities, multidimensional tunnelling ...
• Often tune the barrier height obtained from lower level calculations to experimental data, allowing improved extrapolation of the latter
Effects of incorporating higher level methods into TST


• Klippenstein: OH + OH → O + H₂O
  – Green: calculation from moderate level ab initio. (Barrier = 2.8 kcal mol⁻¹)
  – Barrier constrained to experimental data (1.2 kcal mol⁻¹)
  – Black: High level ab initio (0.7 kcal mol⁻¹)
  – Red: High level constrained to experimental data (1.0 kcal mol⁻¹)
More complex system

Barker et al. J Phys Chem Letters, 3, 1549 (2012): \( \text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \)

High level ab initio calculations, semi classical transition state theory. Incorporate tunnelling. Plot shows results from first principles calculation - no tuning of the potential energy surface. Reaction is pressure dependent. Plot shows high and low pressure limits.
Radical + radical reactions
e.g. \(CH_3 + H\), \(CH_3 + CH_3\)
No barrier on surface. Transition states determined variationally
Where is the Transition State?

Calculate $Q(T,R)$ or $W(E,R)$ as function of $R$

Transition State is at position of minimum in $Q$ or $W$

$\text{CH}_3 + H$

Radical - Molecule
Saddle Point
Exp ($-\beta E$) dominates

Radical - Radical
No Saddle Point
With Decreasing $R$

Entropy Decreases
Exp ($-\beta V_{\text{min}}$) Increases
Correlation of reactant and product modes for CH$_3$+H

- Conserved Modes – Vibrations of Fragments
- Transitional Modes – Fragment Rotations, Orbital Motion, and Reaction Coordinate

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$</th>
<th></th>
<th>CH$_4$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1'$</td>
<td>3004</td>
<td></td>
<td>$A_1$</td>
<td>2917</td>
</tr>
<tr>
<td>$A_2''$</td>
<td>606</td>
<td></td>
<td>$E$</td>
<td>1534</td>
</tr>
<tr>
<td>$E'$</td>
<td>3161</td>
<td></td>
<td>$T_2$</td>
<td>3019</td>
</tr>
<tr>
<td>$E'$</td>
<td>1396</td>
<td></td>
<td>$T_2$</td>
<td>1306</td>
</tr>
</tbody>
</table>
Correlation of reactant and transition state modes of motion

- A molecule has 3N degrees of freedom where N is the number of atoms.
- An atom has 3 degrees of translational freedom
- A linear molecule has 3 translational, 2 rotational and 3N-5 vibrational degrees of freedom
- A non-linear molecule has 3 translational, 3 rotational and 3N-6 vibrational degrees of freedom.

\[ \text{CH}_3 + \text{H} \rightarrow \text{CH}_4^\ddagger \]

<table>
<thead>
<tr>
<th>Mode (translational)</th>
<th>Reactant</th>
<th>Transition State</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>R</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>V</td>
<td>6</td>
<td>0</td>
</tr>
</tbody>
</table>

- 3T → 3T
- 1R → 1R
- 2T → 2R
- 1T → Reaction coordinate
- 2R → 2V(deformation)
- 1V(umbrella) + 2V(deformation) → 3V(deformation)
- 3V(C-H stretch) → 3V(deformation)
# Methyl and Ethane frequencies

<table>
<thead>
<tr>
<th>CH₃</th>
<th>A₁'</th>
<th>3004</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₂''</td>
<td>606</td>
</tr>
<tr>
<td></td>
<td>E'</td>
<td>3161</td>
</tr>
<tr>
<td></td>
<td>E'</td>
<td>1396</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C₂H₆</th>
<th>A₁g</th>
<th>2896</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>A₁g</td>
<td>1388</td>
</tr>
<tr>
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<td>A₁g</td>
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<tr>
<td></td>
<td>A₁u</td>
<td>289</td>
</tr>
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<td></td>
<td>A₂u</td>
<td>2915</td>
</tr>
<tr>
<td></td>
<td>A₂u</td>
<td>1370</td>
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<table>
<thead>
<tr>
<th></th>
<th>E₉g</th>
<th>2969</th>
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<tbody>
<tr>
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<td>E₉g</td>
<td>1468</td>
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<td></td>
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<td></td>
<td>Eₙu</td>
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<td>1460</td>
</tr>
<tr>
<td></td>
<td>Eₙu</td>
<td>822</td>
</tr>
</tbody>
</table>
Laser flash photolysis + photionization mass spectrometry (PIMS) at low pressures and absorption spectroscopy (AS) at high pressures.

Reaction is second order in radical - so absolute, not relative, concentration needed. Use absorption cross section for AS and calibration against loss of precursor for PIMS.
Rate coefficient vs pressure
Theory - Wagner and Wardlaw, 
J. Phys. Chem. 1988, 92, 2462-2471

- Applied flexible transition state theory to calculate microcanonical rate constants, $k(E,J)$ with a RRKM model:

$$k_1(T,[M]) = \frac{1}{4} \frac{1}{Q(T)^2} \int_0^\infty \int_0^\infty \text{d}J \text{d}E \, N(E,J) \frac{k_s[M]}{k_s[M] + k(E,J)} e^{-E/kT}$$

- Two adjustable parameters linked to (i) efficiency of collisional energy transfer and (ii) the evolution of the transitional modes.

- Obtained best fit to experimental data and then fitted to the Troe parameterisation.
More recent calculations, based on ab initio surfaces
Harding et al Phys. Chem. Chem. Phys., 2007, 9, 4055

- $k_\infty$ depends sensitively on potential energy, $V$, as radicals approach.
- $V_{\text{calc}}$ depends on the level of theory used.
- Calculated $k_\infty(T)$ varies by $>\text{factor of 10}$ as level of theory is changed.
- $k_\infty(T)_{\text{calc}}$ may be more accurate than $k_\infty(T)_{\text{expt}}$, because the latter depends on extrapolation.
• High pressure limit rate coefficients for $\text{CH}_3+\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$.

• The color key is as follows: gray, CASPT2; green, CASSCF; purple, B3LYP; blue, MPW1K; orange, MP2. The black symbols represent experimental results.
\( \text{CH}_3 + \text{CH}_3 \)

\( \text{CH}_3 + \text{C}_2\text{H}_5 \)

Left:

Right:
Experimental determination of $k(CH_3 + H))$

- Laser flash photolysis producing H and CH3 with $[H] < [CH_3]$
- H by resonance fluorescence, CH$_3$ by absorption. Need absolute $[CH_3]$, since $k(H) = k[CH_3]$
Experimental results for $\text{CH}_3 + \text{H}$

$\text{CH}_3$ absorption analysed via

$$D(t) = 1 - \exp\left\{-\left(\Delta_0^{-1} - 2k_2t/\sigma L\right)^{-1}\right\}$$

Where $D(t) = \Delta I/I_0$

$\text{H}$ fluorescence analysed via

$$[\text{H}]' = [\text{H}_0]' \left\{1 + \frac{2k_2}{\sigma} \frac{\Delta_0}{L} \right\}^{-1} \left(\frac{k_1}{\sigma}(\sigma/2k_2)\right)^L \exp(-k_3t)$$

- Where $k_2$ refers to $\text{CH}_3 + \text{CH}_3$ and $k_3$ to other 1$^{\text{st}}$ order loss processes for
- Plot show rate coefficients vs $p$ at 300, 400, 500, 600 K.
\( \text{CH}_3 + \text{H}. \) Parameterisation and determination of \( k^\infty \)

- Parameterisation using Troe method (see earlier)
- Also determined \( k^\infty \) using master equation method coupled with inverse Laplace transform (see later)

<table>
<thead>
<tr>
<th>( T/\text{K} )</th>
<th>( 10^{10}k_1^\infty(\text{H})/ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</th>
<th>( 10^{29}k_1^O(\text{H})/ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</th>
<th>( F^\text{cent} )</th>
<th>( \beta_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>7.6 ± 1.6</td>
<td>2.7 ± 0.4</td>
<td>0.659</td>
<td>0.45</td>
</tr>
<tr>
<td>400</td>
<td>4.7 ± 1.2</td>
<td>3.1 ± 0.6</td>
<td>0.627</td>
<td>0.39</td>
</tr>
<tr>
<td>500</td>
<td>3.1 ± 0.6</td>
<td>3.0 ± 0.5</td>
<td>0.599</td>
<td>0.34</td>
</tr>
<tr>
<td>600</td>
<td>1.8 ± 0.6</td>
<td>2.5 ± 0.8</td>
<td>0.566</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Positive T dependence for $k_\infty$, contrast –ve dependence for CH$_3$+CH$_3$. 
Shock tube study of the thermal decomposition of $C_2D_5I/CH_3I/Kr$ mixtures which generated D atoms and CH$_3$ radicals. [H] and [D] were monitored by ARAS. A rate constant of $2.20 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was measured for the reaction $\text{CH}_3 + \text{D} \rightarrow \text{CH}_2\text{D} + \text{H}$. This rate constant was converted to the high pressure limit for $\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$ using the theoretical ratio of 1.6 determined theoretically by Klippenstein, Georgieskii, and Harding. (Proc. Comb. Inst. 2002, 29, 1229.)
H + Alkyl Radical

Potential Energy Surface

Blue = attractive contours
Red = repulsive contours

Gorin model (D M Golden)
Excluded angles of approach
Two Transition States

Schematic Potential Energy Surface for Radical Molecule Addition

inner transition state  outer transition state

van der Waals well
• Inner TS
  – Entropic Barrier
  – Covalent Bond Formation
  – Rigid Rotor Harmonic Oscillator
• Outer TS
  – Long Range TST
• Effective TS

\[ \frac{1}{W_{\text{eff}}} = \frac{1}{W_{\text{inner}}} + \frac{1}{W_{\text{outer}}} \]
OH + C₂H₄
C$_2$H$_4$ + OH

High P Limit

Fits to available data
slight adjustment of inner TS energy
Master equation model for pressure dependent reactions
Modelling dissociation and association reactions -
master equation analysis

Collisional energy transfer between grains

Dissociation and association

Energy grains - Bundles of energy levels

A+B

- Set up rate equation for concentration in each grain.
- Express as matrix equation:
  \[ \frac{dc}{dt} = Mc \]
- Time dependent grain concentrations depend on initial concentrations and on eigenvalues and eigenvectors of \( M \)
- Eigenvalue of smallest magnitude is the negative of the dissociation rate coefficient.
Master equation for dissociation

\[ \frac{\partial}{\partial t} \rho(E, t) = \omega \sum_{E'} P(E|E') \rho(E', t) - \omega \rho(E, t) - k(E) \rho(E, t). \]

\[ P(E|E') = A(E) \exp(-\alpha(E' - E)) \quad E' \geq E, \]

\[ P(E|E') = A(E') \exp(-\alpha(E - E')) \left( \frac{f(E')}{f(E)} \right) \quad E < E'. \]

\[ \frac{\partial}{\partial t} \rho(E, t) = \hat{M} \rho(E, t), \]

Solution:

\[ \rho(E, t) = \sum_i c_i \varphi_i(E) \exp(\lambda_i t) \]

\[ \frac{d[A]}{dt} = -k_u [A], \quad [A](t) = [A]_0 \sum_E \rho(E, t) \]

\[ k_u = -\lambda_1. \]
H.O. Pritchard
The quantum theory of unimolecular reactions (CUP 1982)

- \( \log(-\lambda_i) \) for dissociation vs pressure at fixed \( T \)
- Numerically smallest eigenvalue gives the rate coefficient - fig shows limits \( k_\infty \) at high \( p \) and \( k_0[M] \) at low \( p \).
- Relaxation eigenvalues are well separated and the system is well behaved - a rate coefficient can be assigned.
Association reaction

\[ B + C \rightleftharpoons A. \]

\[
\frac{\partial}{\partial t} \rho(E, t) = \hat{M} \rho(E, t) + g(E, t).
\]

\[
g(E, t) = R(t) \phi(E) = k_{a,\infty}[B](t)[C](t)\phi(E),
\]

\[
\phi(E) = \frac{k(E)f(E)}{\int k(E)f(E)dE}.
\]

\[
k_a = \frac{-\lambda_2}{[C] + 1/K_{eq}}
\]

\[
k_u = \frac{-\lambda_2}{1 + K_{eq}[C]}.
\]
Structure of $\mathbf{M}$ for an isomerisation reaction

$$
\frac{\partial}{\partial t} \rho^A(E, t) = \omega \sum_{E'} P(E|E') \rho^A(E', t) - \omega \rho^A(E, t) \\
- k^A(E) \rho^A(E, t) + k^B(E) \rho^B(E, t),
$$

$$
\begin{pmatrix}
M^A_{11} & \omega P^A_{12} & \ldots & \omega P^A_{1n} & 0 & \ldots & 0 & 0 \\
\omega P^A_{21} & M^A_{22} & \ldots & \omega P^A_{2n} & \vdots & \ddots & \vdots & \vdots \\
\vdots & \vdots & \ddots & \vdots & 0 & \ldots & k^B_{l-1} & 0 \\
\omega P^A_{n1} & \omega P^A_{n2} & \ldots & M^A_{nn} & 0 & \ldots & 0 & k^B_{l} \\
0 & \ldots & 0 & 0 & M^B_{11} & \omega P^B_{12} & \ldots & \omega P^B_{1l} \\
\vdots & \vdots & \vdots & \vdots & \omega P^B_{21} & M^B_{22} & \ldots & \omega P^B_{2l} \\
0 & \ldots & k^A_{n-1} & 0 & \vdots & \vdots & \ddots & \vdots \\
0 & \ldots & 0 & k^A_{n} & \omega P^B_{l1} & \omega P^B_{l2} & \ldots & M^B_{ll}
\end{pmatrix}
$$
More complex reactions.

- Similar approach to dissociation problem
- Numerically smallest eigenvalues related to phenomenological rate constants (chemically significant eigenvalues)
Inverse Laplace transform and association rate coefficients

\[ \mathcal{L}^{-1}\{F(s)\} = f(t) = \frac{1}{2\pi i} \lim_{T \to \infty} \int_{\gamma-iT}^{\gamma+iT} e^{st} F(s) \, ds, \]

\[ k_{\infty}(T) = \frac{\int_0^\infty k(E_R) N(E_R) \exp(-\beta E_R) \, dE_R}{\int_0^\infty N(E_R) \exp(-\beta E_R) \, dE} \]

\[ = \int_0^\infty k(E_R) N(E_R) \exp(-\beta E_R) \, dE / Q_R \]

- Inverting this relationship allows \( k(E) \) to be determined from the high pressure limiting rate constant. Most effectively performed using the association rate constant.

Microcanonical dissociation rate constants from inverse Laplace transform of canonical association rate constant

$\beta = 1/RT \ Q(\beta)$ is the rovibronic partition function, $K(\beta)$ is the equilibrium constant and $N(E)$ is the rovibronic density of states of the association complex. $N_p$ is the convoluted densities of states of the reactant species $A + B \rightarrow C$

$$k_\infty(\beta) = A'_{\infty} \left( \frac{1}{\beta} \right)^{n_\infty} \exp(-\beta E_\infty)$$

$$k(E) = \frac{\mathcal{L}^{-1}[Q(\beta)K(\beta)k_\infty(\beta)]}{N(E)}$$

$$k(E) = \frac{A'_{\infty}C'}{N(E)\Gamma(n_\infty + 1.5)} \int_{0}^{E-E_\infty} N_p(x)$$

$$\times [E - E_\infty - \Delta H_0^0 - x]^{n_\infty + 0.5}$$

$$C' = \left( \frac{2\pi(M_AM_B)}{M_A + M_B} \right)^{3/2}$$
$\text{OH + } C_2H_4 \text{ at low T}$

$\text{OH + } C_2H_4 \rightarrow \text{HOC}_2\text{H}_4$
Comparison of master equation fits with theory of Greenwald et al.

**Fig. 9** Bold lines are ME calculations fit to the He data from Table 1, at 200 (■), 260 (grey ▲), 295 (●) and 400 K (grey ◆). The dotted lines are the theoretical results using the Greenwald et al.\textsuperscript{18} expression for the temperature dependence of $k_\infty$. 
High temperature, $\text{OH} + \text{C}_2\text{H}_4$


- OH radicals were produced by shock-heating t-butyl hydroperoxide, $\text{Me}_3\text{COOH}$, and monitored by laser absorption near 306.7 nm
- 890–1366 K, 2.3 atm
OH + C$_2$H$_4$ (Vasu et al.)
Uncertainty contributions in the determination of OH + C₂H₄

- Contributions from uncertainty in rate coefficients:
  \[ \text{CH}_3\text{COCH}_3 + \text{OH} \text{ (fractional uncertainty 0.3) } 0.1\% \]
  \[ \text{CH}_3 + \text{OH} \rightarrow ^3\text{CH}_2 + \text{H}_2\text{O} \text{ (factor 2) } 3.9\% \]
  \[ \text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{OH} \text{ (factor of 2) } 1.5\% \]
  \[ \text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}= \text{ (Factor of 2) } 1.5\% \]

Also contributions from temperature, fitting process, OH absorption coefficient, mixture concentration, wavemeter reading

Overall uncertainty: 22.8\%
Product yields - contribution from theory


- Slight tuning of surface (~0.4 kcal mol$^{-1}$) by reference to experimental data.

- Note formation of vinyl alcohol >800 K, Confirmed by Taatjes et al.

Master equation
Chemically significant eigenvalues
More complex reactions.

• Similar approach to dissociation problem
• Numerically smallest eigenvalues related to phenomenological rate constants (chemically significant eigenvalues)

Reminder For a Dissociation reaction: eigenvalue of smallest magnitude is the negative of the dissociation rate constant.
Chemically significant eigenvalues for isomerisation

\[
A \rightleftharpoons B.
\]

Two species, two CSEs

System is conservative, so \( \lambda_1 = 0 \)

Reaction system relaxes to equilibrium state. Relaxation rate constant = \( |\lambda_2| = k_f + k_r \)

Relaxation time = \( \tau \)

\[
\tau = (k_f + k_r)^{-1}
\]

\[
\frac{d[A]}{dt} = -k_f[A] + k_r[B]
\]

\[
\frac{d[B]}{dt} = k_f[A] - k_r[B],
\]

\[
c = \begin{pmatrix} [A] \\ [B] \end{pmatrix}
\]

\[
\frac{dc}{dt} = \mathbf{M}_c c,
\]

\[
\mathbf{M}_c = \begin{pmatrix} -k_f & k_r \\ k_f & -k_r \end{pmatrix}
\]

\[
-\lambda_2 = k_f + k_r.
\]

\[
k_f / k_r = K_{eq}, \quad k_f = \frac{-\lambda_2}{1 + 1/K_{eq}}
\]

\[
k_r = \frac{-\lambda_2}{1 + K_{eq}}.
\]
Effect of sulfur oxides on fuel oxidation

Peter Glarborg Hidden interactions—Trace species governing combustion and emissions. 31st Symposium

- $SO_2 + H \ (\pm M) \ \rightleftharpoons \ HOSO \ (\pm M) \ (R1)$
- $HOSO + H \ \rightleftharpoons \ SO + H_2O \ (R2)$
- $SO + O_2 \ \rightleftharpoons \ SO_2 + O \ (R3)$

- How do we provide rate data for reactions of this sort?

- Are there hidden complexities in a simple association reaction like (R1)?
H + SO₂
experiment + theory

- Potential energy surface for H + SO₂, from electronic structure calcs
- Approach: Experimental investigation using vuv LIF for H
- Master equation analysis, constrained to experimental data

Experimental decay trace for H + SO₂
Gives eigenvalue and hence k at selected p and T.

Eigenvalues from ME analysis.
Red - TS1
Blue TS2
Green TS3

Determination of individual phenomenological rate constants from eigenvalues / eigenvectors

Total number of eigenvalues is equal to the total number of grains. The 3 eigenvalues of smallest magnitude relate to the phenomenological rate coefficients of the macroscopic chemical system (chemically significant eigenvalues)

\[ H + SO_2 \leftrightarrow HSO_2 \quad (1) \]
\[ H + SO_2 \leftrightarrow HOSO \quad (2) \]
\[ H + SO_2 \rightarrow OH + SO \quad (3) \]
\[ HSO_2 \leftrightarrow HOSO \quad (4) \]
\[ HSO_2 \rightarrow OH + SO \quad (5) \]
\[ HOSO \rightarrow OH + SO \quad (6) \]

\[
\frac{dc}{dt} = \begin{pmatrix}
-k_1 - k_4 - k_5 & k_4 & k_1 \\
 k_4 & -k_4 - k_2 - k_6 & k_2 \\
 k_1 & k_2 & -k_1 - k_2 - k_3
\end{pmatrix}
\begin{pmatrix}
[HOSO] \\
[HOSO] \\
[H]
\end{pmatrix}
\]
Experimental characterisation of the TS2 and TS3 regions of the surface

- **TS2** is significant in the 400 - 800 K region.
- Too slow to study experimentally using LFP.
- ?Characterise using flow reactor methods?

- **TS3** is even more difficult to investigate. Use the reverse reaction, OH + SO, via detailed balance.

![Graph showing the relationship between temperature (T/K) and rate constant (log10 (kR1/10^{-11} cm^3 molecule^{-1} s^{-1}))](attachment:graph.png)
Issues

- Overlap of chemically significant eigenvalues with energy relaxation eigenvalues: can lead to problems in defining rate constants (e.g. Tsang et al, Robertson et al in alkyl radical decomposition.

- Use of OH + SO to calculate forward $k_5$ using detailed balance. Does detailed balance always apply - are the forward and reverse rate constants always related through the equilibrium constant? (Miller and Klippenstein, Miller et al.)

- Important issue in combustion - e.g. CHEMKIN generally introduces forward and reverse reactions, linked via thermodynamics.
1,2-Pentyl isomerisation and dissociation

\[ 1\text{-C}_5\text{H}_{11} \rightleftharpoons 2\text{-C}_5\text{H}_{11} \]
\[ 1\text{-C}_5\text{H}_{11} \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_7 \]
\[ 2\text{-C}_5\text{H}_{11} \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \]

\[ 1\text{-C}_5\text{H}_{11} \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \]  
\[ 2\text{-C}_5\text{H}_{11} \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_7 \]

\[ \lambda_{1,2} = \frac{-(k_C + k_D) \pm \sqrt{(k_C + k_D)^2 - 4(k_C k_D - k_{-7} k_{-7})}}{2} \]

where \( k_C = k_7 + k_8 + k_{10} \) and \( k_D = k_{-7} + k_9 + k_{11} \).
1,2 pentyl isomerisation and dissociation
Rate coefficients extracted with Bartis Widom analysis,

\[ \text{1-C}_5\text{H}_{11} \rightleftharpoons \text{2-C}_5\text{H}_{11} \]  \hspace{1cm} (R7)

\[ \text{1-C}_5\text{H}_{11} \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_7 \]  \hspace{1cm} (R8)

\[ \text{2-C}_5\text{H}_{11} \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \]  \hspace{1cm} (R9)

\[ \text{1-C}_5\text{H}_{11} \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \]  \hspace{1cm} (R10)

\[ \text{2-C}_5\text{H}_{11} \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_7 \]  \hspace{1cm} (R11)

\[ \log(k_s^{-1}) \]  \hspace{1cm} 400 K

\[ \log(k_s^{-1}) \]  \hspace{1cm} 600 K
Behaviour at high temperatures: overlap of CS and relaxation eigenvalues
Binomial expansion of quadratic solution for $\lambda_1$

$$-\lambda_1 \approx \frac{k_8 + k_{10}}{1 + K_7} + \frac{k_9 + k_{11}}{1 + K_7^{-1}} \quad \text{where} \quad K_7 = k_7/k_{7.}$$

- Full triangles: ratio of $\lambda_1$ from the full quadratic solution to $\lambda_1$ from the ME.
- Open squares: ratio of $\lambda_1$ from the full quadratic solution to $\lambda_1$ from above approximation.

\[
\begin{align*}
1-\text{C}_5\text{H}_{11} & \rightleftharpoons 2-\text{C}_5\text{H}_{11} \quad \text{(R7)} \\
1-\text{C}_5\text{H}_{11} & \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_7 \quad \text{(R8)} \\
2-\text{C}_5\text{H}_{11} & \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \quad \text{(R9)} \\
1-\text{C}_5\text{H}_{11} & \rightarrow \text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \quad \text{(R10)} \\
2-\text{C}_5\text{H}_{11} & \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_7 \quad \text{(R11)}
\end{align*}
\]
Binomial expansion of quadratic solution for $\lambda_2$

$$-\lambda_2 \approx k_7 + k_{-7} + k_8 + k_9 + k_{10} + k_{11} \approx k_7 + k_{-7}$$

- full diamonds: ratio of $\lambda_2$ from full quadratic solution to $\lambda_2$ from the ME.
- Open triangles: ratio of $\lambda_2$ from Eq. full quadratic solution to $\lambda_2$ from equation above (full expression.)
- Open squares: ratio of $-\lambda_2$ from full quadratic expression to $(k_7 + k_{-7})$. 

![Graph with data points labeled as full diamonds, open triangles, and open squares. The graph shows the ratio of $\lambda_2$ estimates against temperature (T/K).]
Comparison of the time dependence of the mole fraction of the 1- and 2-pentyl isomers using the summed grain populations from the ME and using the phenomenological rate coefficients from the ME in a biexponential representation: (a) 600 K; (b) 1000 K.
Conclusions

• All wells can contribute to all sink channels irrespective of whether they are directly connected to the transition state that leads to a given set of products.

• ‘Well-skipping’ is significant and is characterized by non-standard fall-off curves which exhibit a decline in rate coefficient with increasing pressure, indicative of the competition between collisional relaxation and reaction.

• Product yields are very sensitive to the difference in dissociation energies for 1- and 2-pentyl. The calculations give a difference of only 4 kJ mol\(^{-1}\), and ancillary experiments are essential to define the system more accurately. Because of the complexity of the system, the experiments must be interpreted with a master equation analysis.
Autoignition chemistry

- RH
- OH
- R
- O₂
- RO₂
- QOOH
- OH + R'OOH
- OH
- R'O
- OH
- RH
- OH
- R
- O₂
- RO₂
- QOOH
- OH + R'OOH
- OH
- R'O
- OH
- RH
- OH
- R
- O₂
- RO₂
- QOOH
- OH + R'OOH
- OH
- R'O
- OH

Termination

- Smaller radical (R₁) + Alkene (A₁)
- HO₂ + Alkene (A₂)

Propagation

- Products + OH

Branching
Determination of product yields in $C_2H_5 + O_2$

- Taatjes et al. (J. Phys. Chem. A 104 (2000) 11549 - 11560) observed the formation of OH and HO$_2$, determining the fractional yields. Used 100% yield of HO$_2$ from $CH_2OH + O_2$ to calibrate the system.
- HO$_2$ yield↑ as T↑ and p↓
- Two timescales at higher T
- OH yield is small.
- Theoretical interpretation and relevance to autoignition chemistry will be discussed later.

\[
C_2H_5 + O_2 \rightarrow C_2H_5O_2^* \\
C_2H_5O_2^* + M \rightarrow C2H_5O_2 + M \\
C_2H_5O_2^* \rightarrow C_2H_4 + HO_2 \\
C_2H_5O_2 + M \rightarrow C_2H_4 + HO_2
\]
$C_2H_5, C_3H_7 + O_2$

- Three regimes, low, transition, high T.
- In transition region, thermal rate constant jumps from one eigenvalue to the other - the two eigenvalues are mixed in this region.
- At high T, ethyl peroxy is stabilised and HO$_2$ is formed from its dissociation. $k$ is, in practical terms, independent of $p$.
- At low T, reaction involves the pressure dependent formation of RO$_2$ and direct formation of HO$_2$. 
Cyclohexyl + O2
Time dependence of OH formation
Importance of formally direct route to OH

Fig. 5  Calculated OH concentration at 7.9 bar and 586 K using different models. The solid black line is the Knepp et al.\textsuperscript{13} model; the dashed black line is the Knepp et al. model, but without formally direct pathways. The dashed blue line is the Silke et al.\textsuperscript{41} mechanism, and the solid blue line is Silke et al. model, adding all rate coefficients from the ME calculation.
Evidence for chain branching at lower T
Dimethyl ether: $\text{CH}_3\text{OCH}_2 + \text{O}_2$

Eskola et al.
\[ \text{CH}_3\text{OCH}_2 + \text{O}_2: \text{major mechanism} \]
Species profiles, 550 K, 1 bar

Graph showing species profiles with different concentrations.
Master equation: rate constant analysis

\[ \begin{align*}
  &\text{R} \\
  &\text{I}_1 \\
  &\text{I}_2 \\
  &\text{OH} \\
\end{align*} \]

\[ \begin{align*}
  k_1 &\quad k_2 \\
  k_3 &\quad k_4 \\
  k_5 &\quad k_6 \\
  k_7 &\quad k_8 \\
  k_9 &\quad \\
\end{align*} \]

\[ I_1 = \text{RO}_2 \]
\[ I_2 = \text{QOOH} \]
Phenomenological rate coefficients from a Bartis Widom analysis
Routes to branching: $\text{CH}_3\text{OCH}_2 + \text{O}_2 (+ \text{O}_2)$

- Anderson and Carter: Molecular Physics 2008, 106, 367-396
MESMER: An Open-Source Master Equation Solver for Multi-Energy Well Reactions

David R. Glowacki,*,‡ Chi-Hsiu Liang,† Christopher Morley,‡ Michael J. Pilling,† and Struan H. Robertson*,§


Abstract

.......Master Equation Solver for Multi-Energy Well Reactions (MESMER), a user-friendly, object-oriented, open-source code designed to facilitate kinetic simulations over multi-well molecular energy topologies where energy transfer with an external bath impacts phenomenological kinetics. MESMER offers users a range of user options specified via keywords ......

[Diagram: Molecular energy topologies and reactions involving energy transfer]
Master Equation Solver for Multi-Energy well Reactions (MESMER)

- Open source, object oriented code (C++)
- facilitates kinetic simulations of multi-well systems where energy transfer with a bath gas impacts phenomenological kinetics
- Provides interface with results of electronic structure calculations to allow set up of multi-well system
- Outputs choices include chemically significant (and other) eigenvalues, species concentrations vs time, phenomenological rate constants.
- Allows fitting to experimental data using $\chi^2$ minimisation
Excited electronic states in combustion
Chemistry of methylene (CH$_2$)

- CH$_2$ exists as a triplet ($^3$CH$_2$) and a singlet ($^1$CH$_2$), separated in energy by ~ 9 kcal mol$^{-1}$.
- The upper state (singlet) is much more reactive. It is involved, e.g., in the production of C$_3$H$_3$, a soot precursor and in the chemistry of Titan.
- The singlet is deactivated to the triplet on collision with unreactive (and reactive) gases.
- Our understanding of the mechanism of deactivation in reactive systems is limited, especially at combustion temperatures.
- Laser flash photolysis CH$_2$CO at (308 nm).
- Detection $^1$CH$_2$ by LIF, e.g. line from $^3$1$_{12}$ state in $^1$A$_1$ (0,0,0) at 589.21 nm.
- Pressure 1 - 10 Torr.
  Rapid initial rotational relaxation of $^1$CH$_2$(0,0,0).
- Collision induced intersystem crossing (CIISC) and reactions investigated for rotationally relaxed $^1$CH$_2$ (0,0,0)
$^1\text{CH}_2 + M - \text{CIISC}$

1. Kinetics from decay of CH₂ - the overall rate constant decreases as T ↑.

2. If same mechanism for deactivation as for Ar, then reactive channel becomes unimportant at higher T???

3. Monitor H using VUV LIF; growth shows same kinetics as CH₂ decay.

4. Calibrate H signal to determine what fraction of the CH₂ loss occurs by reaction and what fraction by deactivation.
$\text{CH}_2 + C_2\text{H}_2$
Rate coefficient for deactivation to the triplet now decreases with $T$. Doesn’t fit in with the behaviour found for inert gases. What is the mechanism?
What is the yield of $H + C_3H_3$ for the reactive channels?

- Used Mesmer to calculate the yields of $H+C_3H_3$ vs $C_3H_4$ (just reactive channels).
- Results above appropriate to calculations for Titan (Faraday Discuss., 2010, 147, 173-188)