Thermodynamics
Various thermodynamic relations are needed to determine heat release and the relations between forward and reverse rate coefficients

at constant $p$, $\Delta H = \Delta U + p \Delta V$

$$\Delta_r H = \sum_{\text{products}} \nu_i \Delta_f H_i - \sum_{\text{reactants}} \nu_i \Delta_f H_i$$

A statement of Hess’s Law

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \sum_i \nu_i C_{p,i} \, dt$$

at constant $T$, $\Delta G = \Delta H - T \Delta S$

$$RT \ln K = -\Delta G$$

$$K = \frac{\prod_{\text{products}} (a_i^{\nu_i})}{\prod_{\text{reactants}} (a_i^{\nu_i})}$$
Tabulated thermodynamic quantities.

1. Standard enthalpy of formation

**Standard enthalpy change of formation, \( \Delta_f H^\circ \)**

The standard enthalpy change when 1 mol of a substance is formed from its elements in their reference states, at a stated temperature (usually 298 K). The reference state is the most stable state at that temperature, and at a pressure of 1 bar.

**e.g.** \[ C(s) + 2H_2(g) \rightarrow CH_4(g) \quad \Delta_f H^\circ = -74.8 \text{ kJ mol}^{-1} \]

The standard enthalpies of formation of \( C(s) \) and \( H_2(g) \) are both zero
Standard entropy

Based on the 3rd law of Thermodynamics:
The entropy of any perfectly crystalline material at $T = 0$ is zero

**Standard molar entropy, $S^\circ_m$**
The entropy of 1 mol of a substance in its standard state based on the 3rd law

Sometimes entropies of formation are used, but this makes no difference to entropies of reaction provided consistency is maintained.
Statistical mechanics

Partition function, $Q$: \[ Q = \sum_{i} g_i \exp \left( \frac{-\epsilon_i}{kT} \right) \]

\[ U(T) - U(0) = NkT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V \]

\[ U(0) = N\epsilon_0 \]

\[ S = \frac{U(T) - U(0)}{T} + Nk(\ln Q - \ln N!) \]

\[ C_V = \left( \frac{\partial U(T)}{\partial T} \right)_V \quad ; \quad C_p = C_V + R \]
Canonical Partition Functions

Rigid Rotor Harmonic Oscillator (RRHO)

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

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

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

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

\[ Q_{\text{vib}}^{\text{class}} = \prod_{i=1}^{n} \frac{k_B T}{\hbar \nu_i} \]

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

These expressions allow entropies and heat capacities to be calculated from spectroscopic data.

Statistical Mechanics, D. A. McQuarrie, Harper & Row
Thermodynamic and spectroscopic data from NIST

- E.g. Methane, gas phase. Selected thermodynamic data, ir spectra, vibrational and electronic energy levels

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
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<tbody>
<tr>
<td>$\Delta_f H^\Theta$</td>
<td>-74.87</td>
<td>kJ mol$^{-1}$</td>
<td>Review</td>
<td>Chase 1998</td>
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<tr>
<td>$\Delta_f H^\Theta$</td>
<td>-74.6±0.3</td>
<td>kJ mol$^{-1}$</td>
<td>Review</td>
<td>Manion</td>
</tr>
<tr>
<td>$S^\Theta$</td>
<td>188.66±0.42</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
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<td>Colwell 1963</td>
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<table>
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<th>Sym. No</th>
<th>Approximate type of mode</th>
<th>Selected Freq. Value</th>
<th>Infrared Rating</th>
<th>Raman Value</th>
<th>Phase</th>
<th>Comments</th>
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<tr>
<td>a$_1$ 1</td>
<td>Sym str</td>
<td>2917 A</td>
<td>ia</td>
<td>2917.0 gas</td>
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<td></td>
</tr>
<tr>
<td>e 2</td>
<td>Deg deform</td>
<td>1534 A</td>
<td>1533 ia gas</td>
<td>1533.6</td>
<td></td>
<td>Observed through Coriolis interaction with $v_4$</td>
</tr>
<tr>
<td>f$_2$</td>
<td>Deg str</td>
<td>3019 A</td>
<td>3018.9 gas</td>
<td>3019.5</td>
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<tr>
<td>f$_2$</td>
<td>Deg deform</td>
<td>1306 C</td>
<td>1306.2 gas</td>
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</tr>
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</table>

**Species in the CCCBDB**

- Mostly atoms with atomic number less than 18 (Argon). A few have Se or Br.
- Six or fewer heavy atoms and twenty or fewer total atoms. Exception: Versions 8 and higher have a few substituted benzenes with more than six heavy atoms. Versions 12 and higher have bromine-containing molecules.

**Specific experimental properties**

1. Atomization energies
2. Vibrational frequencies
3. Bond lengths
4. Bond angles
5. Rotational constants
6. Experimental barriers to internal rotation
Computed data

- Geometries, vibrational frequencies, entropies, energies, means for comparing data

**B3LYP/6-311+G(3df,2p)**

<table>
<thead>
<tr>
<th>Mode Number</th>
<th>Symmetry</th>
<th>Frequency</th>
<th>diff</th>
<th>Symmetry</th>
<th>Frequency</th>
<th>Comment</th>
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<tbody>
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<td>1</td>
<td>$A_1'$</td>
<td>3004</td>
<td>-0</td>
<td>$A_1'$</td>
<td>3004</td>
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<tr>
<td>2</td>
<td>$A_2''$</td>
<td>523</td>
<td>-84</td>
<td>$A_2''$</td>
<td>606</td>
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<tr>
<td>3</td>
<td>$E'$</td>
<td>3175</td>
<td>14</td>
<td>$E'$</td>
<td>3161</td>
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<td>4</td>
<td>$E'$</td>
<td>1361</td>
<td>-35</td>
<td>$E'$</td>
<td>1396</td>
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</table>

The calculated vibrational frequencies were scaled by 0.967
**Methane**

**HF/6-31G**

<table>
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<th>Symmetry</th>
<th>Frequency</th>
<th>diff</th>
<th>Symmetry</th>
<th>Frequency</th>
<th>Comment</th>
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<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2872</td>
<td>-45</td>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2917</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>E</td>
<td>1530</td>
<td>-4</td>
<td>E</td>
<td>1534</td>
<td></td>
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<tr>
<td>3</td>
<td>T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2966</td>
<td>-53</td>
<td>T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3019</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1337</td>
<td>31</td>
<td>T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1306</td>
<td></td>
</tr>
</tbody>
</table>

The calculated vibrational frequencies were scaled by 0.8985
Enthalpies of formation of radicals

- Enthalpies of formation of stable compounds, such as hydrocarbons, are determined from measurements of enthalpies of combustion, using Hess's Law.
- This approach is not feasible for radicals. An IUPAC evaluation of thermodynamic data for radicals can be found in Ruscic et al. J Phys Chem Ref Data, 2005, 34, 573.
- Example: CH$_3$. Determined by:
  - Photionization spectroscopy, e.g. J Chem Phys, 1997, 107, 9852
  - Electronic structure calculations, e.g. J Chem Phys, 2001, 114, 6014
- Recommended value by IUPAC: $\Delta_f^\circ H(298.15 \text{ K}) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$
Kinetics and thermodynamics of alkyl radicals

- Measured $k(T)$ for $R + HI$, using laser flash photolysis / photoionization mass spectrometry, and combined with existing data for reverse reaction $(I + RH)$ to determine equilibrium constant. Enthalpy of reaction determined by second and third law methods.
Photoionization spectrum of CH$_3$
Litorja and Ruscic, J Chem Phys, 1997, 107, 9852

- Measure the photoionization threshold for CH$_3$ and the appearance potential of CH$_3^+$ from CH$_4$ photexcitation. Obtain the dissociation energy of CH$_3$-H:

  \[ \text{R1: } \text{CH}_3 \rightarrow \text{CH}_3^+ + e \]
  \[ \text{R2: } \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H} + e \]

  \[ \text{R2-R1: } \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \]
Direct measurement of equilibrium constant for reactions involving radicals: $H + C_2H_4 \rightleftharpoons C_2H_5$

- Laser flash photolysis, H atom resonance fluorescence.
- Reactions involved:
  - $H + C_2H_4 \rightarrow C_2H_5 \quad k_1$
  - $C_2H_5 \rightarrow H + C_2H_4 \quad k_{-1}$
  - $H \rightarrow$ diffusive loss $k_d$
- Solve rate equations - gives bi-exponential decay of $H$, $k_1$ and $k_{-1}$ and hence $K_1$ from analysis. Vary $T$, enthalpy of reactions from second or third law.
Thermodynamic databases

- **Active**, internally consistent thermodynamic databases:
A Grid Service-Based Active Thermochemical Table Framework von Laszewski et al.

Fig. 1. Enthalpy diagrams and thermochemical reaction tables.
An Part of a thermo-chemical network showing the basic ideas

Figure 1. A small subsection of the current Core (Argonne) Thermochemical Network. The full network currently contains >600 primary vertices and >3200 secondary vertices. See text for further details.
Eq. (7): $\Delta_r H(\text{H}_2\text{O} < l>) - \Delta_r H(\text{H}_2) - 0.5 \Delta_r H(\text{O}_2) = \Delta_r H (7) \pm \delta_r (7)$

Eq. (8): $\Delta_r H(\text{H}_2\text{O} < l>) - \Delta_r H(\text{H}_2) - 0.5 \Delta_r H(\text{O}_2) = \Delta_r H (8) \pm \delta_r (8)$

Eq. (9): $\Delta_r H(\text{H}_2\text{O} < l>) - \Delta_r H(\text{H}_2) - 0.5 \Delta_r H(\text{O}_2) = \Delta_r H (9) \pm \delta_r (9)$
Evidence for a Lower Enthalpy of Formation of Hydroxyl Radical

TABLE 1: Various Values for the 0 K Enthalpy of Formation of OH and Related Values for $D_0$(H−OH) and $D_0$(OH)

<table>
<thead>
<tr>
<th>source</th>
<th>$\Delta H_0$(OH)</th>
<th>$D_0$(H−OH)</th>
<th>$D_0$(OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gurvich et al.,a following Carlone and Dalby,c</td>
<td>9.35 ± 0.05 kcal/mol</td>
<td>118.08 ± 0.05 kcal/mol$^d$</td>
<td>101.27 ± 0.04 kcal/mol</td>
</tr>
<tr>
<td>Barrow,a</td>
<td>9.26 ± 0.29 kcal/mol</td>
<td>118.00 ± 0.29 kcal/mol$^d$</td>
<td>101.36 ± 0.29 kcal/mol</td>
</tr>
<tr>
<td>JANAF,f</td>
<td>9.18 ± 0.29 kcal/mol</td>
<td>117.91 ± 0.29 kcal/mol$^d$</td>
<td>101.44 ± 0.29 kcal/mol</td>
</tr>
<tr>
<td>recommended values, present experiment$^g$</td>
<td>8.83 ± 0.09 kcal/mol</td>
<td>117.57 ± 0.09 kcal/mol</td>
<td>101.79 ± 0.09 kcal/mol</td>
</tr>
<tr>
<td>present calculation</td>
<td>8.87 ± 0.16 kcal/mol</td>
<td>117.61 ± 0.16 kcal/mol$^d$</td>
<td>101.74 ± 0.16 kcal/mol</td>
</tr>
</tbody>
</table>
Accurate Enthalpy of Formation of Hydroperoxyl Radical, HO$_2$

“Howard reaction”
OH + NO$_2$ \rightarrow HO$_2$ + NO

ATcT thermo + new kinetic experiments (J. Michael, ANL): the reverse rate was indeed off by a factor of 2!
<table>
<thead>
<tr>
<th>source</th>
<th>originally reported value</th>
<th>revised value</th>
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</thead>
<tbody>
<tr>
<td>JANAF Tables$^{10,11}$</td>
<td>0.5 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>Gurvich et al.$^{19}$</td>
<td>2.3 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>Howard$^{20}$</td>
<td>2.5 ± 0.6</td>
<td>2.0 ± 0.6</td>
</tr>
<tr>
<td>Lee and Howard$^{21}$</td>
<td>3.3 ± 0.6</td>
<td>3.2 ± 0.6</td>
</tr>
<tr>
<td>Hills and Howard$^{23}$</td>
<td>3.0 ± 0.4</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td>Shum and Benson$^{24,25}$</td>
<td>&gt; 3.0</td>
<td></td>
</tr>
<tr>
<td>Heneghan and Benson$^{26}$</td>
<td>4.6 ± 0.2</td>
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</tr>
<tr>
<td>Heneghan and Benson$^{29}$</td>
<td>&gt; 3.4</td>
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<tr>
<td>Fisher and Armentrout$^{30}$</td>
<td>3.8 ± 1.2</td>
<td>3.2 ± 1.2</td>
</tr>
<tr>
<td>Litorja and Ruscic$^{31}$</td>
<td>3.3 ± 0.8</td>
<td>2.9 ± 0.6$^d$</td>
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<tr>
<td>Clifford et al.$^{32}$</td>
<td>3 ± 1</td>
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<tr>
<td>Ramond et al.$^{35}$</td>
<td>3.2 ± 0.5</td>
<td>3.2 ± 0.5</td>
</tr>
<tr>
<td>ATcT, current work$^e$</td>
<td>2.94 ± 0.06</td>
<td></td>
</tr>
</tbody>
</table>
Shock tube study of OH + NO₂

\[
C_2H_5I + NO_2 \rightarrow OH + NO
\]

1237 - 1554 K.
15 species, 23 stoichiometric mechanism, but sensitive to limited number of reactions.
Comparison with Howard data
Abstract: A simple and fast, weighted, linear least-squares refinement protocol and code is presented for inverting the information contained in a network of quantum chemically computed 0 K reaction enthalpies. This inversion yields internally consistent 0 K enthalpies of formation for the species of the network.
Figure 1. Pictorial representation of the NEAT protocol, which, after an inversion, leads to 0 K enthalpies of formation ($\Delta_f H_0$) from computed reaction enthalpies ($\Delta_r H_0$).
Incorporation of thermodynamics data into rate calculations:
Burcat: http://garfield.chem.elte.hu/Burcat/burcat.html

- Provides data in NASA polynomial form, with 7 parameters that are related to necessary thermodynamic functions of state via:

\[ \frac{C_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \]
\[ \frac{H}{RT} = a_1 + a_2 \frac{T}{2} + a_3 \frac{T^2}{3} + a_4 \frac{T^3}{4} + a_5 \frac{T^4}{5} + \frac{a_6}{T} \]
\[ \frac{S}{R} = a_1 \ln T + a_2 T + a_3 \frac{T^2}{2} + a_4 \frac{T^3}{3} + a_5 \frac{T^4}{4} + a_7 \]

Where \( H(T) = \Delta H_f(298) + [ H(T) - H(298) ] \)
- Linked to \( \Delta TcT \) and used in Chemkin.
Burcat database. Entry for CH₃

- **CH₃ METHYL-RAD** STATWT=1. SIGMA=6. IA=IB=.2923 IC=.5846 NU=3004,606.4,3161(2), 1396(2) HF298=146.7 +/-0.3 KJ HFO=150.0+/-.3 kJ REF= Ruscic et al JPCRD 2003. {HF298=146.5+/-.08 kJ REF=ATcT C} Max Lst Sq Error Cp @ 6000 K 0.44%. METHYL RADICAL IU0702C 1.H 3. 0. 0.G
  
  200.000 6000.000 B 15.03452

- 0.29781206E+01 0.57978520E-02 -0.19755800E-05
  0.30729790E-09 -0.17917416E-13

- 0.16509513E+05 0.47224799E+01 0.36571797E+01
  0.21265979E-02 0.54583883E-05

- -0.66181003E-08 0.24657074E-11 0.16422716E+05
  0.16735354E+01 0.17643935E+05

- First 7 entries are a1-7 for 1000 - 6000 K. 2nd set are a1-a7 for 200 - 1000 K. Temp ranges specified in line 1