Topic 4
Thermodynamics
Thermodynamics

• We need thermodynamic data to:
  – Determine the heat release in a combustion process (need enthalpies and heat capacities)
  – Calculate the equilibrium constant for a reaction – this allows us to relate the rate coefficients for forward and reverse reactions (need enthalpies, entropies (and hence Gibbs energies), and heat capacities.

• This lecture considers:
  – Classical thermodynamics and statistical mechanics – relationships for thermodynamic quantities
  – Sources of thermodynamic data
  – Measurement of enthalpies of formation for radicals
  – Active Thermochemical Tables
  – Representation of thermodynamic data for combustion models
Various thermodynamic relations are needed to determine heat release and the relations between forward and reverse rate coefficients.

\[
\Delta_r H = \sum_{\text{products}} v_i \Delta_f H_i - \sum_{\text{reactants}} v_i \Delta_f H_i \\
\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \sum_i v_i C_{p,i} \, dt
\]

A statement of Hess’s Law:
The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which the reaction may be divided.

\[
RT \ln K = -\Delta G \\
K = \frac{\prod_{\text{products}} (a_i^{v_i})}{\prod_{\text{reactants}} (a_i^{v_i})}
\]
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.

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

The standard enthalpies of formation of $C(s)$ and $H_2(g)$ are both zero

The reference state for carbon is graphite.
Standard entropy

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

**Standard molar entropy, $S_{\Theta m}$**
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.
Molecular partition functions: rigid rotor harmonic oscillator (RRHO) – a reminder

\[ q_{\text{total}} = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elect}} \]

\[ q_{\text{trans}} = \left[ \frac{2\pi m kT}{\hbar^2} \right]^{3/2} V \]

\[ Q = \frac{q}{V} \]

\[ q_{\text{rot}} = \frac{kT}{\sigma \hbar B c} \]

\[ q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left\{ \frac{kT}{\hbar c} \right\}^{1/2} \left\{ \frac{1}{ABc} \right\}^{1/2} \]

\[ q_{\text{vib}} = (1 - e^{-\frac{\hbar c \omega}{kT}})^{-1} \]

\[ q_{\text{vib}} = \prod_{i=1}^{\alpha} \left( 1 - e^{-\frac{\hbar c \omega_i}{kT}} \right)^{-1} \]

\[ q_{\text{elect}} = \sum_{\text{levels},i} g_i e^{-\beta \varepsilon_i} \]

These expressions allow thermodynamic data to be calculated from spectroscopic data and from electronic structure calculations.
Thermodynamic quantities from partition functions

\[ U = U(0) - N \left( \frac{\partial \ln q}{\partial \beta} \right)_V = U(0) + NK^2 \left( \frac{\partial \ln q}{\partial T} \right)_V \]

\[ \beta = \frac{1}{kT} \quad U(0) = N_A \varepsilon_0 \]

\[ S = \frac{U - U(0)}{T} + R \ln q - R \ln N_A + R \]

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V ; \quad C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad C_p \]

\[ = C_V + R \text{ (ideal gas)} \]
Thermodynamic and spectroscopic data from NIST

- http://webbook.nist.gov/chemistry/
- 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>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_f H^\theta$</td>
<td>-74.87</td>
<td>kJ mol(^{-1})</td>
<td>Review</td>
<td>Chase 1998</td>
</tr>
<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>
<td>N/A</td>
<td>Colwell 1963</td>
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</table>

<table>
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<tr>
<th>Sym. Species</th>
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<th>Approximate type of mode</th>
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<th>Infrared Rating</th>
<th>Infrared Value</th>
<th>Raman Phase Value</th>
<th>Comments</th>
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<tr>
<td>a(_1)</td>
<td>1</td>
<td>Sym str</td>
<td>2917 A</td>
<td>ia</td>
<td>2917.0 gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>2</td>
<td>Deg deform</td>
<td>1534 A</td>
<td>1533 ia</td>
<td>1533.6</td>
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</tr>
</tbody>
</table>
The CCCBDB contains links to experimental and computational thermochemical data for a large selected set of gas-phase atoms and molecules. Tools for comparing experimental and computational ideal-gas thermochemical properties.

**Species in the CCCBDB**
- Mostly compounds with 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

$$\text{CH}_3$$

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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<td>1</td>
<td>$A_1'$</td>
<td>3004</td>
<td>-0</td>
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<tr>
<td>2</td>
<td>$A_2''$</td>
<td>523</td>
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<td>$A_2''$</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>
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<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>
</tr>
</thead>
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<td>-45</td>
<td>$A_1$</td>
<td>2917</td>
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<td>2</td>
<td>$E$</td>
<td>1530</td>
<td>-4</td>
<td>$E$</td>
<td>1534</td>
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<tr>
<td>3</td>
<td>$T_2$</td>
<td>2966</td>
<td>-53</td>
<td>$T_2$</td>
<td>3019</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$T_2$</td>
<td>1337</td>
<td>31</td>
<td>$T_2$</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:
  - Photoionization 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.
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:
  
  $H + C_2H_4 \rightarrow C_2H_5 \quad k_1$
  
  $C_2H_5 \rightarrow H + C_2H_4 \quad k_{-1}$
  
  $H \rightarrow \text{diffusive loss} \quad k_d$

- Solve rate equations - gives bi-exponential decay of H, $k_1$ and $k_{-1}$ and hence $K_1$ from analysis. Vary T, enthalpy of reaction from second or third law.
Photoionization spectrum of CH₃
Litorja and Ruscic, J Chem Phys, 1997, 107, 9852

- Measure the photoionization threshold for CH₃ and the appearance potential of CH₃⁺ from CH₄ photexcitation. Obtain the dissociation energy of CH₃-H:

  $\text{CH}_3 \rightarrow \text{CH}_3^+ + e$ \hspace{1cm} \text{R1}

  $\text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H} + e$ \hspace{1cm} \text{R2}

  \text{R2-R1:} \hspace{0.5cm} \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$
The bond enthalpy change at 298 K is the enthalpy change for the reaction $R-H \rightarrow R + H$:

$$DH_{298}(R - H) = \Delta_f H_{298}(R) + \Delta_f H_{298}(H) - \Delta_f H_{298}(RH)$$

The bond energy (change) or dissociation energy at zero K is:

$$D_0(R - H) = E_0(R) + E_0(H) - E_0(RH)$$

Bond energies can be converted to bond enthalpy changes using the relation $U = H + pV = H + RT$, so that, for $R-H \rightarrow R + H$, $\Delta U = \Delta H + RT$. At zero K, the dissociation energy is equal to the bond enthalpy change.

Berkowitz et al provide an extensive dataset for R-H bond energies using radical kinetics, gas-phase acidity cycles, and photoionization mass spectrometry.
Thermodynamic databases

- **Active**, internally consistent thermodynamic databases:


Welcome to the ATcT website!

Active Thermochemical Tables (ATcT) are a new paradigm of how to develop accurate, reliable, and internally consistent thermochemical values (such as enthalpies of formation, Gibbs energies of formation, bond dissociation energies, reaction enthalpies, etc.) for stable, reactive, and transient chemical species by utilizing the fullest all available experimental measurements as well as state-of-the-art theoretical data. As opposed to traditional sequential thermochemistry (A begets B, which begets C, etc.), ATcT is based on constructing, analyzing, and solving the underlying Thermochemical Network (TN). The ATcT approach redefines thermochemistry to a new orbit by rectifying fundamental deficiencies ingrained in the traditional approach to thermochemistry. It also acts as a unique bridge that efficiently interfaces experiments and theory and integrates the best aspects of both. Finally, ATcT introduces to thermochemistry a number of entirely new capabilities that were never available before.

The latest released version (TN 1.122) continues to include a find functionality, as well as a provenance analysis of the enthalpy of formation of each of the ~1200 species (except the elements in their standard states), accessible by clicking on the species name.

The species-specific page now includes a number of new features, such as a 3D depiction of the target species, a list of other highly correlated enthalpies of formation, as well as a list of most influential determinations including the target species.

Another new feature is the ability to calculate 0 K and 298.15 K reaction enthalpies, bond dissociation enthalpies, gas-phase acidities, proton affinities, etc. on the fly, accessible by clicking the ‘Reaction Search’ at the bottom of the yellow Find Bar.

You can check out the thermochemical values by selecting "Thermochemical Data" from the navigation bar above.

Page generated: 05/14/2017

Latest version: https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php
1199 species included in version 1.122 (as of 09/05/2016)
A Grid Service-Based Active Thermochemical Table Framework von Laszewski et al.

**Reaction Table**

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>C(s) + O$_2$(g) $\leftrightarrow$ CO$_2$(g)</td>
<td>-393.5</td>
</tr>
<tr>
<td>1</td>
<td>C(s) + O$_2$(g) $\leftrightarrow$ CO(g) + 0.5 O$_2$(g)</td>
<td>-283.0</td>
</tr>
<tr>
<td>2</td>
<td>CO(g) + 0.5 O$_2$(g) $\leftrightarrow$ CO$_2$(g)</td>
<td>-110.5</td>
</tr>
</tbody>
</table>

**Fig. 1.** Enthalpy diagrams and thermochemical reaction tables.
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): \( \Delta_f H(\text{H}_2\text{O} \triangleleft) - \Delta_f H(\text{H}_2) - 0.5 \Delta_f H(\text{O}_2) = \Delta_r H (7) \pm \Delta_r (7) \)

Eq. (8): \( \Delta_f H(\text{H}_2\text{O} \triangleleft) - \Delta_f H(\text{H}_2) - 0.5 \Delta_f H(\text{O}_2) = \Delta_r H (8) \pm \Delta_r (8) \)

Eq. (9): \( \Delta_f H(\text{H}_2\text{O} \triangleleft) - \Delta_f H(\text{H}_2) - 0.5 \Delta_f H(\text{O}_2) = \Delta_r H (9) \pm \Delta_r (9) \)
Evidence for a Lower Enthalpy of Formation of Hydroxyl Radical

Note that these are values at 0 K
Current ATcT value is 8.904 ± 0.006 kcal mol⁻¹

<table>
<thead>
<tr>
<th>source</th>
<th>ΔH₂⁰(OH)</th>
<th>D₀(H−OH)</th>
<th>D₀(OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gurvich et al., b following Carlone and Dalby c</td>
<td>9.35 ± 0.05 kcal/mol</td>
<td>118.08 ± 0.05 kcal/mol d (41301 ± 17 cm⁻¹)</td>
<td>101.27 ± 0.04 kcal/mol (35420 ± 15 cm⁻¹)</td>
</tr>
<tr>
<td>Barrow e</td>
<td>9.26 ± 0.29 kcal/mol</td>
<td>118.00 ± 0.29 kcal/mol d (41270 ± 100 cm⁻¹)</td>
<td>101.36 ± 0.29 kcal/mol (35450 ± 100 cm⁻¹)</td>
</tr>
<tr>
<td>JANAF f</td>
<td>9.18 ± 0.29 kcal/mol</td>
<td>117.91 ± 0.29 kcal/mol d (41240 ± 100 cm⁻¹)</td>
<td>101.44 ± 0.29 kcal/mol (35480 ± 100 cm⁻¹)</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 d (41120 ± 30 cm⁻¹)</td>
<td>101.79 ± 0.09 kcal/mol (35600 ± 30 cm⁻¹)</td>
</tr>
<tr>
<td>present calculation</td>
<td>8.87 ± 0.16 kcal/mol</td>
<td>117.61 ± 0.16 kcal/mol d (41135 ± 55 cm⁻¹)</td>
<td>101.74 ± 0.16 kcal/mol (35585 ± 55 cm⁻¹)</td>
</tr>
</tbody>
</table>
Example: \( \text{CH}_3 \)

<table>
<thead>
<tr>
<th>Formula</th>
<th>( \Delta_f H^\circ(0 \text{ K}) )</th>
<th>( \Delta_f H^\circ(298\text{ K}) )</th>
<th>Uncertainty</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3(\text{g}) )</td>
<td>149.788</td>
<td>146.374</td>
<td>( \pm 0.08 )</td>
<td>( \text{kJ mol}^{-1} )</td>
</tr>
</tbody>
</table>

95% uncertainty limits

- **Top contributors to the provenance of \( \Delta_f H^\circ \) of \( \text{CH}_3 \ (\text{g}) \):**
  The top 20 contributors account only for 72.5% of the provenance of \( \Delta_f H^\circ \) of \( \text{CH}_3 \ (\text{g}) \). A total of 99 contributors would be needed to account for 90% of the provenance.

- **Link to latest version of ATcT:**
  [https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php](https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php)
Provenance of ATcT determination of the enthalpy of formation of ethyl

- $\Delta_f^\circ H(C_2H_5) = 119.86 \pm 0.28 \text{ kJ/mol at 298.15 K}$
- See website for provenance

https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php
Example of current accuracy in ATcT

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

- the enthalpy of the reaction is equivalent to the difference in bond dissociation energies of \( \text{H}_2 \) and \( \text{CH}_2 \), and noting that \( D_0(\text{CH}_2) = \text{TAE}_0(\text{CH}_2) - \text{TAE}_0(\text{CH}) \), the recently published ATcT total atomization energies (TAE\(_0\)) for \( \text{CH}_2 \) and \( \text{CH} \) and the ATcT enthalpy of formation for \( \text{H} \) produce a quite accurate 0 K enthalpy of the reaction of \( 3.36 \pm 0.08 \text{ kcal/mol} \) (\( 14.04 \pm 0.35 \text{ kJ/mol} \)). The latest ATcT value is nearly identical, \( 3.397 \pm 0.04 \text{ kcal/mol} \) (\( 14.21 \pm 0.16 \text{ kJ/mol} \)), though it has further gained in accuracy due to additional refinements of the ATcT TN\(^*\).

- Propagating the uncertainty in the equilibrium constant:

\[
\ln K = -\frac{\Delta_r H^\Theta}{RT} + \frac{\Delta_r S^\Theta}{R}
\]

\[
\sigma_{\ln K}^2 = \frac{\sigma_{\Delta_r H^\Theta}^2}{(RT)^2} + \frac{\sigma_{\Delta_r S^\Theta}^2}{R^2}
\]

- Determine \( \sigma_{\ln K}^2 \) at 1000 K for combustion applications and at 10 K for applications in interstellar chemistry, based solely on the enthalpy change

- * Note the heavy reliance on theory
Ab Initio Computations and Active Thermochemical Tables Hand in Hand: Heats of Formation of Core Combustion Species Klippenstein, Harding, Ruscic, J. Phys. Chem. A 2017, 121, 6580−6602

• High level ab initio electronic structure based predictions of $\Delta_f^\circ \mathcal{H}(0 \text{ K})$ for 348 C, N, O, and H containing species - essentially all core combustion species with 34 or fewer electrons.

• The accuracy of the theoretical predictions is explored through (i) examination of the magnitudes of the various corrections, (ii) comparisons with other high level calculations, and (iii) through comparison with the ATcT values.

• Inclusion of these theoretical results into the ATcT thermochemical network is expected to significantly improve the thermochemical knowledge base for less-well studied species.
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.
RESPECTH
Reaction Kinetics, Spectroscopy, Thermodynamics database

- [http://respecth.chem.elte.hu/respecth/](http://respecth.chem.elte.hu/respecth/)

- Thermodynamics section:

  - thermochemical data calculated by the method NEAT;

  - high-accuracy thermochemical data for $\text{H}_2^{(16)}\text{O}$;

  - A mirror of Burcat's thermochemistry database (see next slide), with species searching and function plotting additions.
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:

\[
\begin{align*}
C_p/R &= a_1 + a_2 \, T + a_3 \, T^2 + a_4 \, T^3 + a_5 \, T^4 \\
H/RT &= a_1 + a_2 \, T /2 + a_3 \, T^2 /3 + a_4 \, T^3 /4 + \frac{a_5 \, T^4}{5} + \frac{a_6}{T} \\
S/R &= a_1 \ln T + a_2 \, T + a_3 \, T^2 /2 + a_4 \, T^3 /3 + \frac{a_5 \, T^4}{4} + a_7
\end{align*}
\]

Where \( H(T) = \Delta H_f(298) + [ H(T) - H(298) ] \)

- Linked to \( ATcT \) 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 HF0=150.0 +/-0.3 kJ REF= Ruscic et al JPCRD 2003. {HF298=146.5 +/-0.08 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. 2**nd **set are a1-a7 for 200 - 1000 K. Temp ranges specified in line 1**
A big data framework to validate thermodynamic data for chemical species

Buerger et al. Combustion and Flame 176 (2017) 584-591

- validate data for the standard enthalpy of formation for 920 gas-phase species containing carbon, oxygen and hydrogen retrieved from the NIST Chemistry WebBook.
- Use error cancelling balanced reactions (specifically isodesmic reactions) to calculate a distribution of possible values for the standard enthalpy of formation of each species.
- method automates the identification and exclusion of inconsistent data
- exploits knowledge of the structural similarities between species and the consistency of the data to identify which species introduce the most error and recommend what future experiments and calculations should be considered
An adaptive distance-based group contribution method for thermodynamic property prediction
He et al., Phys.Chem.Chem.Phys., 2016, 18, 23822

- standard enthalpy of formation (Hf, 298K) for alkanes, alkenes, and their radicals at the M06-2X/def2-TZVP//B3LYP/6-31G(d) level
- Multiple linear regression (MLR) and artificial neural network (ANN) fitting used to obtain the contributions from individual groups and group interactions for further predictions
- characterizes the group interaction within a molecule with an exponential decay function of the group-to-group distance, defined as the number of bonds between the groups
- More accurate than conventional group additivity using same training sets
Exercise 3

The NASA polynomial coefficients, a1-a5, between 1000 K and 3000 K for N₂ are:
2.95257637E+00 1.39690040E-03 -4.92631603E-07
7.86010195E-11 -4.60755204E-15

\[ \frac{C_p}{R} = a_1 + a_2 \, T + a_3 \, T^2 + a_4 \, T^3 + a_5 \, T^4 \]

Calculate the heat capacity over the temperature range 1000 - 3000 K. Calculate the vibrational contribution to the heat capacity given that the translational and rotational contributions are \(3R/2\) and \(R\) respectively. (Remember \(C_p = C_v + R\))

Compare these results from those calculated from statistical mechanics. The vibrational heat capacity is given by:

\[ C_v = R \Omega^2 \frac{e^\Omega}{(e^\Omega - 1)^2} \quad \text{where} \quad \Omega = \frac{hc\omega}{kT} \]

\(hc/k = 0.659\) cm K; \(\omega (N_2) = 2359\) cm\(^{-1}\)

Comment on the differences
Reminder

- Look back at slides on Statistical Mechanics:

- Translational partition function
  \[ q_{\text{trans}} = \left( \frac{2\pi m k T}{\hbar^2} \right)^{3/2} V \]

- Rotational partition function
  \[ q_{\text{rot}} = \frac{kT}{\sigma h B c} \]

- Energy
  \[ U = U(0) - N \left( \frac{\partial \ln q}{\partial \beta} \right)_V = U(0) - N k T^2 \left( \frac{\partial \ln q}{\partial T} \right)_V \]

- Heat Capacity
  \[ C_V = \left( \frac{\partial U}{\partial T} \right)_V ; \quad C_p = \left( \frac{\partial H}{\partial T} \right)_p \]
Exercise 3

Vibrational heat capacity for N2

NB The statistical mechanics calculation is based on a harmonic oscillator model for N2. Incorporating anharmonicity will increase the calculated heat capacity.