Chemical Kinetic Modelling for Combustion

Prof. Henry Curran

Copyright ©2019 by Prof Henry Curran. This material is not to be sold, reproduced or distributed without prior written permission of the owner, Prof Henry Curran.
Overview/Aims

➢ 5 days / 15 lectures

➢ Day 1

➢ (1-3) Basic thermodynamic principles

➢ Day 2

➢ (4) Basic kinetic principles

➢ (5,6) Experimental JSR, FR, RCM & ST contribution to kinetics

➢ Day 3

➢ (7-9) Small species mechanism development
Overview/Aims

- 5 days / 15 lectures
  - Day 4
    - (10-12) Large hydrocarbon mechanism development
  - Day 5
    - (13-15) Oxygenated hydrocarbon mechanism development
Basic kinetic and thermodynamic principles
Kinetics and equilibrium

The diagram illustrates the relationship between concentration and time for a reaction. The concentration of A decreases with time, while the concentration of B increases. The diagram shows the transition from kinetics to equilibrium, with a dotted line indicating the point of equilibrium.

[A]₀

[B](t)

[A](t)

0 0

Time

Copyright © 2006 Pearson Education, Inc., publishing as Benjamin Cummings
Thermodynamics

Properties of interest:

- Entropy
- Enthalpy
- Heat capacity (C_p or C_v)
  - Can be used for extrapolation of above
- Gibbs free energy (follows from S and H)

Why?

- Chemical equilibria (ln K = -ΔG/RT)
- Chemical insight/will a reaction happen?
  - endo vs. exothermic, spontaneous or not
- Heat release, adiabatic flame temp. etc.

Slide courtesy of Dr. Pierre-Alexandre Glaude
Effect of thermochemistry on $\tau$

Effect of thermochemistry on $\tau$

$n$-Pentane oxidation

$\phi = 1.0$ in air

Enthalpy of Formation

Molar standard enthalpy of formation $\Delta_fH^\circ$:

- Is the heat involved when one mole of a substance is produced from its elements in their standard state (1 bar for gases, usually 25°C).

- Standard enthalpy of formation of ammonia

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightarrow NH_3$$

- Conventionally, standard enthalpy of elements is fixed to 0 kJ/mol at standard state.
  - $H_2$ for hydrogen gas, $O_2$ for oxygen etc.
Thermodynamic data

Tabulated data
- Standard enthalpy of formation, $\Delta_f H^0$
- Standard entropy of formation, $\Delta_f S^0$
- Specific heat capacity, $C_p(T)$

Sources of data
- Experiments
- Ab initio calculations
- Empirical schemes based on observed rules in experimental or ab initio data

$\Delta_f Y = \Delta_f Y^0(P) - \Delta_f Y^0(R)$

Elements in stable form at standard stae
Thermodynamic data: Experimental sources

Enthalpy of formation, $\Delta_r H$
- Determine the enthalpy change of any reaction $\Delta_r H$
- Calculate enthalpy of formation from $\Delta_r H$
  and those of known reaction partners

$$\Delta_f H^0(R) = \Delta_r H + \Delta_f Y^0(P)$$

Entropy of formation, $\Delta_r S$
- Rarely measured directly
  (from temperature dependence of $K_r$)
- Calculated from experimental molecular parameters
  using statistical thermodynamics

Specific heat capacities, $C_p$
- Can be measured directly for stable species
- Calculated from experimental molecular parameters
  using statistical thermodynamic

*n*(vibration)
$\Theta$ (inertia)

generally simplified formulas of statistical thermodynamics
Enthalpy of Formation

Variation with temperature:

- At constant pressure:
  \[ \Delta H_{(T_2-T_1)} = Q_p = C_p \Delta T \]
  
  - \( C_p \) is the heat capacity at constant pressure of the compound.
  
  - By integration, the enthalpy of formation of a compound at a temperature \( T \) is calculated by:
    \[
    \Delta_f H^\circ_T = \Delta_f H^\circ_{298K} + \int_{298}^T \Delta_r C_p^\circ dT = \Delta_f H^\circ_{298K} + \int_{298}^T \left(C_p^\circ_{molecule} - C_p^\circ_{elements}\right) dT
    \]

- Permits derivation an analytic expression as a function of \( T \)
Entropy

- Linked to the number of states of the particles in the system
- In a reversible transformation $\Delta_r S = Q/T$
- The entropy represents the extensivity of the thermal energy of a system at the temperature $T$.
- Entropy of elements at 0 K = 0 kJ/mol
- **Free Energy** (Gibbs, $G$) indicates spontaneity of reaction
  - Dependent on Enthalpy and Entropy
  - Contribution of Entropy becomes important as $T$ increases
    $$G = H - TS$$
Thermodynamics

How do we determine $C_p$, $S$, $H$?

- Experiment—Combustion Calorimetry
  - Foundation of thermodynamics BUT....
  - Time consuming
  - Difficult/expensive
  - Fine for stable species, what about radicals?

Y.I. Alexandrov  Thermochim. Acta 382, 55
Non-experimental methods

Ab initio quantum chemistry
- Solving the Schrödinger equation for a molecule provides its energy and its thermodynamic properties
- In principle.
- In fact, the methods of ab initio quantum chemistry are approximate

Estimation of thermodynamic parameters based on empirical rules
- Group additivity method

Ab initio methods
- are based on a few approximations
- and a real effort to fix the problems of the approximations

Group additivity
- within certain limits of accuracy the thermodynamic properties of properly selected groups add up to that of a molecule data can be borrowed from information on one or more similar molecules the question is the “limit of accuracy”.

Slide courtesy of Prof György Lendvay, Eötvös University, Budapest, Hungary
Group Additivity

What is it?

- Empirical method for estimation of thermodynamics
- Pioneered by Prof. Sidney W. Benson

Thermodynamic functions dependent on:
- Nature of each atom in a molecule and
- Nature of each of their bonding partners (short range effects)
- Long range effects can be important

- Molecule split into groups
- Each group makes a contribution to thermo. functions of molecule
Group Additivity

Consider Ethane:

- Simple molecule with 2 identical groups (C/C/H₃)
  \[
  \text{H}_3\text{C}—\text{CH}_3
  \]

- Thermodynamics well known

- \( \Delta H_f^0 = -84. \pm 0.4 \text{ kJ/mol (NIST)} \)
  - Contribution of each group = -42.0 kJ/mol

- \( C_p \ 298.15 \text{ K} = 52.49 \text{ J/mol (NIST)} \)
  - Contribution of each group = 26.25 J/mol

- \( S^0 \ 298.15 \text{ K} = 229.28 \text{ J/mol} \)
  - Contribution of each group.....not as simple
  - Corrections for molecular symmetry are applied
Group Additivity

**Entropy calculations:**

- **Sum of the group contributions:** intrinsic entropy $S_i$
- **Correction for symmetry:**
  \[ \delta S^\circ = -R \ln \sigma \]
- $\sigma = \text{number of symmetries in the molecule} = \sigma_{\text{ext}} \times \sigma_{\text{int}}$
  - $\sigma_{\text{ext}} \text{ number of external symmetries (rotation of molecule)}$
  - $\sigma_{\text{int}} \text{ number of internal symmetries (rotations around single bonds)}$
- **Ethane** $\sigma_{\text{ext}} = 2$, $\sigma_{\text{int}} = 9$, total correction $= -R \ln(18)$
- **Similar corrections for optical isomers** $= +R \ln(\# \text{ of OI})$
Group Additivity

What about free radicals?

- Estimated through definition of ‘Bond Increments’ or ‘Bond Dissociation’ values for H, S and C_p

- RH -> R·+H· Δ_f H = Bond Dissociation Energy (BDE)

\[
\Delta H_f^0 (R\cdot) = \text{BDE} + \Delta H_f^0 (RH) - \Delta H_f^0 (H\cdot)
\]

- Varies based on type of C-H bond broken
- Heat of formation of ‘parent’ species
- Well known Δ_f H = 52.1 kcal/mol
Group Additivity

BDE Groups

- Strength of C–H bond depends on stability of radical

\[
\text{H}_3\text{C} - \text{CH}_2^* \quad \text{Type} = \text{primary, 101.1 kcal/mol}
\]

\[
\text{H}_3\text{C} \quad \text{H}^* \quad \text{C}^* \quad \text{CH}_3 \quad \text{Type} = \text{secondary, 98.45 kcal/mol}
\]

\[
\text{C}^* \quad \text{CH}_3 \quad \text{C}^* \quad \text{CH}_3 \quad \text{Type} = \text{tertiary, 96.50 kcal/mol}
\]
Group Additivity

BDE Groups

- Strength of C–H bond depends on stability of radical
- Electron delocalization leads to more stable radicals
  - Reduces BDE

Type = primary allylic, 88.2 kcal/mol

Compare with primary alkane (101.1 kcal/mol)
Group Additivity

BDE Groups

- Locally bonded electronegative atoms reduce BDE

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{O} \quad \text{CH}_3 \\
\end{align*}
\]

96.2 kcal/mol

Compare with primary alkane (101.1 kcal/mol)
Group Additivity

Can be applied to:

- Alkanes, alkenes, alkynes
- Alcohols, ethers
- Ketones, aldehydes
- Cycloalkanes, aromatics
- Pretty much everything...BUT...
- Parameterization against experiment and/or quantum chemical calculations necessary for best results and widest range of applicability
Groups and super-atoms

Atom differentiation according to the type of liaison

C: \( \text{sp}^3 \) carbon atom, 4 single bonds

\( C_d \): \( \text{sp}^2 \) carbon atom, 1 double bond, 2 single, \( \equiv \) divalent atom

\( C_t \): \( \text{sp} \) carbon atom, 1 triple bond, 1 single, \( \equiv \) monovalent atom

\( C_a \): allene-like carbon atom, \( \text{C} = \text{C} = \text{C} \), ending atoms are \( C_d \)

\( C_B \): carbon-atom in aromatic rings, \( \equiv \) trivalent atom

\( C_{BF} \): “fused carbon” carbon-atom belonging to several aromatic rings, \( \equiv \) trivalent atom

Super-atoms:

\( \text{C}=\text{O} \), carbonyl group \( \equiv \) (CO) divalent

\( \text{NO}, \text{NO}_2, \text{SO}_2, \text{PO} \ldots \)
Benson’s groups

Table A.1. Group Values for $\Delta H^\circ_f$, $S^\circ_{int}$, and $C^\circ_{pT}$, Hydrocarbons

<table>
<thead>
<tr>
<th>Group</th>
<th>$\Delta H^\circ_f$</th>
<th>$S^\circ_{int}$</th>
<th>$C^\circ_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298</td>
<td>298</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>800</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>C–(H)₂(C)</td>
<td>−10.20</td>
<td>30.41</td>
<td>6.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.77</td>
</tr>
<tr>
<td>C–(H)₂(C)₂</td>
<td>−4.93</td>
<td>9.42</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.34</td>
</tr>
<tr>
<td>C–(H)(C)₃</td>
<td>−1.90</td>
<td>−12.07</td>
<td>4.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.05</td>
</tr>
<tr>
<td>C–(C)₄</td>
<td>0.50</td>
<td>−35.10</td>
<td>4.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.76</td>
</tr>
<tr>
<td>C₆H₆–(H)₂</td>
<td>6.26</td>
<td>27.61</td>
<td>5.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.27</td>
</tr>
<tr>
<td>C₆H₆–(H)(C)</td>
<td>8.59</td>
<td>7.97</td>
<td>4.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.45</td>
</tr>
<tr>
<td>C₆H₆–(C)₂</td>
<td>10.34</td>
<td>−12.70</td>
<td>4.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.08</td>
</tr>
<tr>
<td>C₆H₆–(C₆H₆)</td>
<td>6.78</td>
<td>6.38</td>
<td>4.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.99</td>
</tr>
<tr>
<td>C₆H₆–(C₆H₆)₂</td>
<td>6.78</td>
<td>6.38</td>
<td>4.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.99</td>
</tr>
<tr>
<td>C₆H₆–(C₆H₆)₃</td>
<td>8.64</td>
<td>(−14.6)</td>
<td>(4.40)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(5.37)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(5.93)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(6.18)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(6.50)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(6.62)</td>
</tr>
<tr>
<td>C₆H₆–(C₆H₆)₄</td>
<td>6.78</td>
<td>6.38</td>
<td>4.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.99</td>
</tr>
</tbody>
</table>
Group Additivity

2,2,4-trimethylpentane (iso-octane):

\[\text{C-(H)\textsubscript{3}(C)} \quad 5 \text{ groups}\]
\[\text{C-(H)\textsubscript{2}(C)\textsubscript{2}} \quad 1 \text{ group}\]
\[\text{C-(H)(C)\textsubscript{3}} \quad 1 \text{ group}\]
\[\text{C-(C)\textsubscript{4}} \quad 1 \text{ group}\]

\[\sigma_{\text{ext}} = 1, \sigma_{\text{int}} = 729\]
Correction to symmetry
\[-R \ln(729) = -13.1 \text{ cal/mol/K}\]
Gauche (C–C) interactions

(a)

(b)
1,5 (H–H) Interaction

\[ \text{1.5 kcal/mol} \]
## Group additivity in action

### 2,2,4-trimethylpentane (iso-octane):

<table>
<thead>
<tr>
<th>group</th>
<th>number</th>
<th>$\Delta H^\circ$ (298K) kcal/mol</th>
<th>$S^\circ$ (298K) cal/mol/K</th>
<th>$C_p^\circ$ (300 K) cal/mol/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/C/H$_3$</td>
<td>5</td>
<td>–10.03</td>
<td>30.42</td>
<td>6.26</td>
</tr>
<tr>
<td>C/C2/H$_2$</td>
<td>1</td>
<td>–4.960</td>
<td>9.42</td>
<td>5.44</td>
</tr>
<tr>
<td>C/C3/H</td>
<td>1</td>
<td>–2.130</td>
<td>–12.02</td>
<td>4.39</td>
</tr>
<tr>
<td>C/C4</td>
<td>1</td>
<td>0.100</td>
<td>–34.99</td>
<td>4.01</td>
</tr>
<tr>
<td>gauche</td>
<td>3</td>
<td>0.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H/REPEL/15</td>
<td>1</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>symmetry</td>
<td></td>
<td></td>
<td>–R ln729</td>
<td></td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>–53.54</td>
<td>101.41</td>
<td>45.14</td>
</tr>
</tbody>
</table>
Benson’s Additivity Method


Decomposition into groups and corrections done by the user

NIST database program Stein et al. (1991) Webbook

(http://webbook.nist.gov/chemistry/grp-add/)


CRANIUM : groups of Joback, estimation of other properties

($T_{eb}$, $T_{fus}$, $T_c$, $P_c$...)

(http://www.molknow.com/Online/Estimation.htm)

Quantum Chemistry softwares

Semi-empirical approach: MOPAC...

Ab initio : Gaussian, Spartan, Jaguar, Molpro, ...
Thermochemistry in Chemkin

Chemkin uses standard state thermodynamic properties given as polynomial fits to the specific heats at constant $p$

$$\frac{C^o_p k}{R} = \sum_{n=1}^{N} a_{nk} T^{(n-1)}$$

$$H_k^o = \int_0^T C_p^o dT$$

$$\frac{H_k^o}{RT} = \sum_{n=1}^{N} \frac{a_{nk} T^{(n-1)}}{n} + \frac{a_{N+1,k}}{T}$$

where $a_{N+1,k} R$ is the standard heat of formation at 0 K, but is normally evaluated from the heat of formation at 298 K.
Thermochemistry in Chemkin

\[ S_k^0 = \int_0^T \frac{C_{pk}^0}{T} dT \]

\[ \frac{S_k^0}{R} = a_{1k} \ln T + \sum_{n=2}^{N} \frac{a_{nk} T^{(n-1)}}{(n-1)} + a_{N+2,k} \]

where \( a_{N+2,k} R \) is evaluated from knowledge of the standard-state entropy at 298 K.

These are stated for arbitrary-order polynomials, but Chemkin is designed to use NASA polynomials. In this case seven coefficients are needed for each of two temperature ranges. These fits follow the form:
Thermochemistry in Chemkin

\[ \frac{C_p^0 k}{R} = \sum_{n=1}^{N} a_{nk} T^{(n-1)} \]

\[ \frac{C_p^0 k}{R} = a_{1k} + a_{2k} T + a_{3k} T^2 + a_{4k} T^3 + a_{5k} T^4 \]

\[ \frac{H_k^0}{R} = \int_{0}^{T} \frac{C_p^0 k}{R} dT = a_{1k} T + \frac{a_{2k}}{2} T^2 + \frac{a_{3k}}{3} T^3 + \frac{a_{4k}}{4} T^4 + \frac{a_{5k}}{5} T^5 + a_{6k} \]

\[ \frac{H_k^0}{RT} = a_{1k} + \frac{a_{2k}}{2} T + \frac{a_{3k}}{3} T^2 + \frac{a_{4k}}{4} T^3 + \frac{a_{5k}}{5} T^4 + \frac{a_{6k}}{T} \]

Other thermodynamics properties are easily given in terms of \(C_p^0, H^0, \text{and } S^0\)
Thermochemistry in Chemkin

\[
\frac{C_p^0 k}{R} = \sum_{n=1}^{N} a_{nk} T^{(n-1)}
\]

\[
\frac{C_p^0 k}{R} = a_{1k} + a_{2k} T + a_{3k} T^2 + a_{4k} T^3 + a_{5k} T^4
\]

\[
\frac{S_k^o}{R} = \int_0^T \frac{C_p^0}{RT} dT = a_{1k} \ln T + a_{2k} T + \frac{a_{3k}}{2} T^2 + \frac{a_{4k}}{3} T^3 + \frac{a_{5k}}{4} T^4 + a_{7k}
\]

Other thermodynamics properties are easily given in terms of \(C_p^0\), \(H^o\), and \(S^o\)
### NASA polynomials

**THERMO**

<table>
<thead>
<tr>
<th>300., 1000., 5000.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6H5O</td>
</tr>
<tr>
<td>3/20/89 THERMC</td>
</tr>
<tr>
<td>6H 50 1 0G 300.000</td>
</tr>
<tr>
<td>5000.000 1404.000</td>
</tr>
<tr>
<td>1.57324764E+01 1.54394760E-02-5.31383756E-06 8.28591116E-10-4.82238305E-14</td>
</tr>
<tr>
<td>1.76799222E+03-6.20052317E+01-3.73072513E+00 6.71840729E-02-5.88121307E-05</td>
</tr>
<tr>
<td>2.61335718E-08-4.61968583E-12 4.31827564E+03 4.02213334E+01</td>
</tr>
<tr>
<td>CH3OC3</td>
</tr>
<tr>
<td>3/20/89 THERMC</td>
</tr>
<tr>
<td>2H 60 1 0G 300.000</td>
</tr>
<tr>
<td>5000.000 1364.000</td>
</tr>
<tr>
<td>8.43631162E+00 1.30235626E-02-4.45885307E-06 6.93233262E-10-4.02757540E-14</td>
</tr>
<tr>
<td>-2.62777965E+04-2.24530764E+01 1.53263200E+00 2.37669572E-02-8.14177550E-06</td>
</tr>
<tr>
<td>-5.29451929E-10 5.96605679E-13-2.32831259E+04 1.66340885E+01</td>
</tr>
</tbody>
</table>

**column numbers:**

```
1 10 20 30 40 50 60 70 80
23456789 123456789 123456789 123456789 123456789 123456789 123456789 123456789
```

-E.R. Ritter J.W. Bozzelli

Thermochemical databases


Tables TRC (Thermodynamics Research Center) Thermodynamic Tables - Hydrocarbons - Department of Chemistry, Texas A&M University

Online databases:
NIST Webbook: http://webbook.nist.gov/

Computational Chemistry Comparison and Benchmark Data Base http://webbook.nist.gov/chemistry/


Active Thermochemical Tables (Branco Ruscic Argonne National Lab.) https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php