Topic 3: Energy

\[ \Delta G_{AB}^\circ = -RT \ln \frac{[A]}{[B]} \]


Reference:
NIST Webbook has lots of thermochemical enthalpy data (Hf): http://webbook.nist.gov/cgi/cbook.cgi?Name=toluene&Units=SI
Exponentials and Logarithms are NOT INTUITIVE

■ How much would you rather owe?

$100 \quad \text{vs.} \quad \ln 9132$

■ How many liters of gas will fill your tank?

$e^4 \quad \text{vs.} \quad e^6$
RATIOS are Intuitive: Free Energy is a Predictor of Ratios

- You’ll gain insight into chemical phenomena by converting energy (in kcal/mol or kJ/mol) into numerical ratios. Even a child can think in factors of 10. Recall the Gibbs relationship: \[ \Delta G^\circ = -RT \ln K_{eq} \].

<table>
<thead>
<tr>
<th>A : B</th>
<th>( \Delta G^\circ ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1000</td>
<td>-4.2</td>
</tr>
<tr>
<td>1 : 100</td>
<td>-2.8</td>
</tr>
<tr>
<td>1 : 10</td>
<td>-1.4</td>
</tr>
<tr>
<td>1 : 1</td>
<td>0</td>
</tr>
<tr>
<td>10 : 1</td>
<td>1.4</td>
</tr>
<tr>
<td>100 : 1</td>
<td>2.8</td>
</tr>
</tbody>
</table>

**RULE:**

\[ \Delta G^\circ = +4.2 \text{ kcal/mol} \]

\[ \begin{align*}
\text{I} & \quad \text{factor of 10 in } K_{eq} \text{ or } k \\
\text{II} & \quad \text{factor of 2 in } K_{eq} \text{ or } k
\end{align*} \]

- Predict the yield for the following (equilibrium) reaction.

- Estimate the difference in energy of the transition states.

You don’t know how EXACTLY how much of the equatorial product was present, but you do know that it was \( \leq 5\% \). **Use that information.** Therefore the ratio of products was 95: \(<5 \text{ or } >20:1\) and \( \Delta G^\ddagger > 1.8 \text{ kcal/mol} \).
Using BDEs to Estimate Enthalpy Differences

Drilling for oil often releases CH₄. It is cheaper to burn than ship the gas. Why can’t we convert CH₄ gas into a useful liquid?

\[ \text{HO—OH} + \text{H₃C—H} \rightarrow \text{HO—H} + \text{H₃C—OH} \]

Hard to estimate \( \Delta G = \Delta H - T \Delta S \)

Easy to estimate \( \Delta H \)

We can ignore \( T \Delta S \) as long as we compare similar things: 2 reactants vs 2 products similar transition states etc.

Easy Hess’ Law: \( \Delta H = E(\text{bonds broken}) - E(\text{bonds formed}) \)

\[ \text{HO—OH} + \text{H₃C—H} \rightarrow \text{HO—H} + \text{H₃C—OH} \]

\[ \text{HO•} + \text{•OH} + \text{H₃C•} + \text{•H} \]

Reactions are favorable if you break weak bonds and/or form strong bonds

Hess: The enthalpy change accompanying a chemical transformation is independent of the mechanism or number of steps.
Bond Dissociation Energies - Memorize

- Bond STRENGTH refers to B.DE. = homolysis
  \[ \text{R–H} \rightarrow \text{R}^\cdot + \cdot\text{H} \quad \Delta H^\circ = \text{BDE} \]
- Covalent bonds *between* electronegative atoms will be weak.
- BDEs for X-H bonds correlate with X\(^\cdot\) radical stability
- Longer bonds are weaker
- \(\pi_{\text{C=C}}\) is weak … but \(\pi_{\text{C=O}}\) is strong

**COMMON BONDS**
- C–C–H 98
- C=\(\text{C}–\text{H}\) 110
- C≡\(\text{C}–\text{H}\) 131
- Bn–H 85

**STRONG SINGLE BONDS**  (>100 kcal/mol)
- RO–H 110
- C≡\(\text{C}–\text{H}\) 131
- Si–F 141
- Ph\(_3\text{P}\)–O 136

**WEAK SINGLE BONDS**  (<70 kcal/mol)
- C–Si 69
- C–Br 67
- C–I 57
- O–Br 53
- N–Cl 48

**X–X BONDS** = **ALWAYS WEAK**
- H\(_3\text{C}–\text{CH}_3\) 88
- H\(_2\text{N}–\text{NH}_2\) 65
- HO–OH 51
- F–F 38
- Cl–Cl 58
- Br–Br 46
- I–I 36
Estimating $\Delta H_{\text{rxn}}$ using Hess' Law

- We can’t make methanol from methane, but why not? Is it a thermodynamic problem?

$$\text{H}_2\text{O} + \text{H}_2\text{C} = \rightarrow \text{HOH} + \text{H}_3\text{C}$$

- Hess' Law: $\Delta H^\circ_{\text{rxn}} = \Sigma \text{BDE(bonds broken)} - \Sigma \text{BDE(bonds formed)}$

$$\Delta H^\circ?$$

$\text{H}_3\text{C} = \text{H}_2\text{O} \rightarrow \text{H}_3\text{C}\text{OH} + \text{HOH}$

<table>
<thead>
<tr>
<th>Broken</th>
<th>Formed</th>
<th>$\Delta H \approx 134 - 189$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H 98</td>
<td>C–O 79</td>
<td>= - 65 kcal/mol</td>
</tr>
<tr>
<td>O–O 36</td>
<td>O–H 110</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>189</td>
<td>$\Delta H^\circ_{\text{gas}} = -55$ kcal/mol</td>
</tr>
</tbody>
</table>

- Caveats:
  Hess' law is only as good as your BDEs.
  Doesn't account for strain & aromaticity
  Doesn't account for entropic costs; e.g., A+B -> C vs A -> D
Electronic structure calculations give you the energy difference between nuclei and electrons and infinite separation versus nuclei at specified positions with electrons in optimized molecular orbital configurations. Use $\Delta E$ from electronic structure calculations is similar to $\Delta H^\circ$.

\[
\begin{array}{ccc}
\text{nuclei (+)} & \text{e-} \\
\text{H}_3\text{C}\text{H} & + & \text{HO-}\text{OH} \\
\rightarrow & & \rightarrow \\
\text{H}_3\text{C-OH} & + & \text{HO-}\text{H}
\end{array}
\]

\[
\begin{array}{c}
-25,222.572382 \\
-94,606 \\
-71,253 \\
-47,042
\end{array}
\]

\[
\Delta H^\circ \approx \Delta E \text{ (products - reactants)} = -55 \text{ kcal/mol}
\]

Natural gas (CH\textsubscript{4}) is a by-product of most oil wells. It is usually cheaper to burn CH\textsubscript{4} at the well than to transport it somewhere useful. While it is thermally favorable to oxidize methane to methanol, there is no easy way to stop the oxidation from going all the way to CO\textsubscript{2}.

Electronic structure calculations can help you rationalize and predict regiochemistry, stability, etc.

Which is more stable?

\[
\begin{array}{c}
\text{O} \\
\text{H}$\text{H}$
\end{array}
\quad
\begin{array}{c}
\text{H-}$^+$\text{H} \\
\text{H}$\text{H}$
\end{array}
\]
Entropy: \(-T \Delta S\)

In order to conceptualize entropy, one must simultaneously visualize all possible states of a system:

\[
\frac{\Delta H_{298} - T \Delta S_{298}}{\text{kJ/mol}} = -4.6 \text{ kcal/mol} \quad +6.3 \text{ kcal/mol}
\]

Only 1 out of 16 $H_2O$ molecules exists as an ideal H-bond at equilibrium.

Pairing up molecules costs energy, up to 14 kcal/mol. If you take a random solution of two compounds, both at 1 M concentration, and pair the molecules up like ballroom dancers (no bonding) it will cost up to +14 kcal/mol.

A Diels-Alder reaction looks massively favorable, until you consider the entropic cost in the T.S.

\[
\Delta H^\circ -19.3 \text{ kcal/mol} \quad \Delta H^\circ \quad \Delta S^\circ +14.39 \text{ kcal/mol} \quad (\Delta S^\circ -48.31 \text{ eu})
\]

\[
\Delta G^\circ 4.9 \text{ kcal/mol}
\]


The entropy term, \(-T \Delta S\), is temperature dependent.

As one raises the temp., molecules will begin to adopt less favorable trajectories, positions, and shapes.

Intramolecular reactions involving 5 and 6 membered rings T.S.s are often fast.