Lecture 5: Standard Enthalpies

• Reading: Zumdahl 9.6
• Outline
  – What is a standard enthalpy?
  – Defining standard states.
  – Using standard enthalpies to determine $\Delta H^\circ_{\text{rxn}}$
• Problems
Definition of $\Delta H_f^o$

- We saw in the previous lecture the utility of having a series of reactions with known enthalpies.
- It would be nice to have a basic (systematic) set of reactions one could use to determine the heat of a reaction, rather than having to be clever to determine how to add (arbitrary) whole reactions.
- What if one could deal with combinations of compounds directly rather than dealing with whole reactions to determine $\Delta H_{rxn}$?

- Standard Enthalpy of Formation is “The change in enthalpy that accompanies the formation of 1 mole of a compound from its elements with all substances at standard state.”
- We envision taking elements at their standard state, and combining them to make compounds, also at standard state.
What is Standard State?

• Standard State: A precisely defined reference state. It is a common reference point that one can use to compare thermodynamic properties.

• Definitions of Standard State:
  – For a gas: $P_A = 1$ atm.
  – For solutions: $[C_A] = 1$ M (mol/l).
  – For liquids and solids: pure liquid or solid
  – For elements: The form in which the element exists under conditions of 1 atm and 298 K. (i.e. 25°C)

• The text has a nice table summarizing this and a short discussion about using the standard pressure as 1 bar rather than 1 Atm (which differ by 1%). We will not concern ourselves with this distinction.
Sample Standard States

• Standard elemental states (cont.):
  – Hydrogen: \( \text{H}_2 \) (g) (not atomic H)
  – Oxygen: \( \text{O}_2 \) (g)
  – Carbon: C (gr). Graphite, solid, as opposed to diamond

• We will denote the standard state using the superscript “\(^\circ\)”.  
  – Example: \( \Delta H^\circ_{\text{rxn}} \leftarrow \) a reaction carried out under standard state
Importance of Elements

- We will use the elemental forms as a primary reference when examining compounds.

- Pictorially, for chemical reactions we envision taking the reactants to the standard elemental form, then reforming the products.
Example: Combustion of Methane

\[ CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \]

Using Hess’ Law, and the elements as intermediates in reactions. Writing the above (net) reaction as a sum of 4 separate reactions.
Elements and $\Delta H^\circ_f$

- For elements in their standard state:
  \[ \Delta H^\circ_f = 0 \]

- With respect to the graph, we are envisioning chemical reactions as proceeding through elemental forms. In this way we are comparing $\Delta H^\circ_f$ for reactants and products to a common reference (zero)
Tabulated Values of $\Delta H_f^o$

- In Zumdahl, tables of $\Delta H_f^o$ are provided in Appendix 4 (pg A21).
- The tabulated values represent the $\Delta H_f^o$ for forming the compound from elements at standard conditions.

\[
C(\text{gr}) + 2H_2(g) \rightleftharpoons CH_4(g) \quad \Delta H_f^o = -75\text{kJ/mol}
\]
\[
C(\text{gr}) + O_2(g) \rightleftharpoons CO_2(g) \quad \Delta H_f^o = -394\text{kJ/mol}
\]
\[
H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(\ell) \quad \Delta H_f^o = -286\text{kJ/mol}
\]
Burn Methane (Hess’ Law)

- Visual of energy to burn methane going through the standard states.

\[ \text{CH}_4 \rightleftharpoons C(\text{gr}) + 2H_2(g) \quad \text{C(\text{gr})} + 2H_2(g) + 2O_2(g) \rightleftharpoons \text{CO}_2(g) + 2H_2O(\ell) \]
Using $\Delta H^\circ_f$ to determine $\Delta H^\circ_{rxn}$

- Since we have connected the $\Delta H^\circ_f$ to a common reference point, we can now determine $\Delta H^\circ_{rxn}$ by looking at the difference between the $\Delta H^\circ_f$ for products versus reactants.
- Mathematically:
  \[ \Delta H^\circ_{rxn} = \Sigma \Delta H^\circ_f \cdot c(\text{products}) - \Sigma \Delta H^\circ_f \cdot c(\text{reactants}) \]
- Example

\[ CH_4 + 2O_2 (g) \rightleftharpoons CO_2 (g) + 2H_2O (\ell) \]
\[ \Delta H^\circ_{rxn} = 2 \cdot \Delta H^\circ_f (H_2O) + 1 \cdot \Delta H^\circ_f (CO_2) - 2 \cdot \Delta H^\circ_f (O_2) - 1 \cdot \Delta H^\circ_f (CH_4) \]
\[ \Delta H^\circ_{rxn} = 2 \cdot (-286) + 1 \cdot (-394) - 2 \cdot (0) - 1 \cdot (-75) \text{kJ/mol} \]
\[ \Delta H^\circ_{rxn} = -\{2 \cdot (286) + 394 - 0 - 75\} = -890 \text{kJ/mol} \]
How to Calculate $\Delta H^\circ_{\text{rxn}}$

- When a reaction is reversed, $\Delta H_{\text{rxn}}$ changes sign.

- If you multiply a reaction by an integer, $\Delta H_{\text{rxn}}$ is also multiplied (it is an variable).

- Elements in their standard states are not included in calculations because $\Delta H^\circ_f = 0$ for elements.
Example: Burning Methanol

- Determine the $\Delta H^\circ_{\text{rxn}}$ for the combustion of methanol.

\[
\text{CH}_3\text{OH} (l) + 3/2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)
\]

- $\Delta H^\circ_f$ in Appendix 4:
  
<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H^\circ_f$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH(l)</td>
<td>-238.6</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>-393.5</td>
</tr>
<tr>
<td>H$_2$O(l)</td>
<td>-286</td>
</tr>
</tbody>
</table>
Example -- Burning (cont.)

\[ CH_3OH (l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \]

\[ \Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_f * c(\text{products}) - \Sigma \Delta H^\circ_f * c(\text{reactants}) \]
\[ = \Delta H^\circ_f(\text{CO}_2(g)) + 2\Delta H^\circ_f(\text{H}_2\text{O}(l)) - \Delta H^\circ_f(\text{CH}_3\text{OH}(l)) \]
\[ = (-393.5) + (2)(-286) - (-238.6) \text{ kJ/mol} \]
\[ = -728.7 \text{ kJ/mol} \]

Exothermic!
Sample Problem: Z9.63

• Using the following reaction:

\[ 2\text{ClF}_3(\text{g}) + 2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 6\text{HF}(\text{g}) + \text{Cl}_2(\text{g}) \]

\[ \Delta H^\circ_{\text{rxn}} = -1196 \text{ kJ} \]

Determine the \( \Delta H^\circ_f \) for ClF\(_3\)(g)

\[ \Delta H^\circ_f \]
\[ \text{NH}_3(\text{g}) \quad -46 \text{ kJ/mol} \quad \text{HF}(\text{g}) \quad -271 \text{ kJ/mol} \]
Another Example (cont.)

• Given the reaction of interest:

\[ 2\text{ClF}_3(\text{g}) + 2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 6\text{HF}(\text{g}) + \text{Cl}_2(\text{g}) \]

\[ \Delta H^\circ_{\text{rxn}} = -1196 \text{ kJ} \]

\[ \Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_f * c(\text{products}) - \Sigma \Delta H^\circ_f * c(\text{reactants}) \]

\[ \Delta H^\circ_{\text{rxn}} = 6\Delta H^\circ_f(\text{HF}(\text{g})) - 2\Delta H^\circ_f(\text{NH}_3(\text{g})) - 2\Delta H^\circ_f(\text{ClF}_3(\text{g})) \]
Another Example (end)

\[ \Delta H^\circ_{rxn} = 6\Delta H^\circ_f(HF(g)) - 2\Delta H^\circ_f(NH_3(g)) - 2\Delta H^\circ_f(ClF_3(g)) \]

-1196 kJ = (6mol)(-271 kJ/mol) - (2)(-46 kJ/mol) - (2)\(\Delta H^\circ_f(ClF_3(g))\)

-1196 kJ = -1534 kJ - (2)\(\Delta H^\circ_f(ClF_3(g))\)

338 kJ = - (2)\(\Delta H^\circ_f(ClF_3(g))\)

\(\Delta H^\circ_f(ClF_3(g)) = -169 \text{ kJ/mol} \)
A Reaction at non-standard Temperature

• Problem Z9.85  $\Delta H_{vap}$ for water (to steam) at the normal boiling point (373.2 K) is 40.66 kJ/mole. Given the following heat capacity data, what is $\Delta H_{vap}$ at 293.2 K (room temperature) for 1 mol?

• $C_p (H_2O(l)) = 75$ J/mol.K
• $C_p (H_2O(g)) = 36$ J/mol.K
• Energies (such as enthalpies) are path independent, so we need a path for the change from water to steam at a lower temperature than the normal boiling point. (Does water evaporate at room temperature?)
Heating Water– Problem Z9.85

• We know how much energy it takes to increase the temperature from $T$ to the “normal” boiling temperature (100°C), using the molar heat capacity. Assume one mole.

$$q_P = C_p \Delta T = \Delta H_p$$

$$T_b = 100C \quad T = 20C$$

$$\Delta T_{\text{warm}} = T_b - T = 80K$$

• This applies to any substance, so it applies to steam (vapor or gas) as well as the liquid form, water.

• This, of course, works only if the heat capacity is independent of temperature (which it is not, exactly), but the heat capacities over small temperature ranges do not change much.
Diagram the different changes

A (Hess’s Law) diagram of the changes we know and the one we want. Can go directly from water to steam at 67°C or heat water to 100°C let it go to gas (know the heat required for that) and then cool the steam back to 67°C without it condensing to water.

$\Delta H(T_B) = 40.66 \text{ kJ/mol}$

$T_B = 373.2 \text{ K}$

$\Delta H(\ell) = C_p(\ell) \Delta T_{\text{warm}}$

$\Delta H(g) = C_p(g) \Delta T_{\text{cool}}$

$T = 293.2 \text{ K}$

$\Delta H(T) = ?$
Set Up Algebra and Solve

The sum of the heats of the three steps must equal the heat for the single step (which is what we are after)

\[ \Delta H_{\text{vap}}(T) = \Delta H(\text{warm}, \ell) + \Delta H_{\text{vap}}(T_B) + \Delta H(\text{cool}, g) \]

\[ \Delta H_{\text{vap}}(T) = C_p(\ell) \Delta T_{\text{warm}} + \Delta H_{\text{vap}}(T_B) + C_p(g) \Delta T_{\text{cool}} \]

\[ = \Delta H_{\text{vap}}(T_B) + \left\{ C_p(\ell) - C_p(g) \right\} \Delta T_{\text{warm}} \]

\[ = 40.66 \cdot 10^3 + \left\{ 75 - 36 \right\} 80 J / \text{mole} \]

\[ = 40.66 + 3.1 = 43.76 J / \text{mole} \]

This is not a big correction. The process is endothermic at the boiling point and only slightly more endothermic at room temperature. (Why doesn’t water boil at room temperature, too?) Why does water boil at all if it is always so endothermic? See Problem Z9.4. Use the heats of formation to get \( \Delta H_{\text{vap}} \). What number do you get? Why?
A reaction occurs (a review from 142)

- We have a chemical reaction, where a little bit of the material reacts.
- The balanced chemical reaction, written in terms of the species $S_i$, and the stoichiometric coefficients $(C)$ is:
  \[ \sum_{\text{react}} c(i) S(i) \rightleftharpoons \sum_{\text{prod}} c(i) S(i) \]

- Because all species are attached by the balanced reaction, if some of one is used, others are also used and others are generated.
  \[ n(i) = n^0_o(i) \pm c(i) X \]

  \[ \Delta n(i) = n(i) - n^0_o(i) = \pm c(i) X \]

- $X$ is the extent of advancement. If we know $X$, which is the number of moles that change change, then we know how many moles of each species change.

Here, need a minus sign with the coefficients for reactants.
Ammonia as an example of Stoichiometry

- Consider the synthesis of Ammonia: \[3H_2 + N_2 \rightarrow 2NH_3\]
- Given the balanced reaction, and stoichiometric coefficients and initial concentrations, set up ICE Table

<table>
<thead>
<tr>
<th>Initial Conc</th>
<th>Stoic Coeffs</th>
<th>Change</th>
<th>New Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>([H_2]_o) = .1</td>
<td>3(-);react</td>
<td>-3x</td>
<td>([H_2] = .1 - 3x)</td>
</tr>
<tr>
<td>([N_2]_o) = .2</td>
<td>1(-);react</td>
<td>-x</td>
<td>([F_2] = .2 - x)</td>
</tr>
<tr>
<td>([NH_3]_o) = .3</td>
<td>2(+);prod</td>
<td>+2x</td>
<td>([HF] = .3 + 2x)</td>
</tr>
</tbody>
</table>

Problem: Have a mixture of different initial moles of each the substances, and we lose 0.2 moles of ammonia, how much of each species is present at the end?"
Use the relations to solve for all species

• The ammonia change gives X, or delta X.
  \[ \Delta n(NH_3) = c(NH_3) x \]
  \[ -0.2 = 2 \cdot x \]
  \[ x = \frac{-0.2}{2} = -0.1 \text{ moles} \]

• Now we know the advancement of the reaction. (Notice it is negative, meaning the reaction is going from products to reactants, or it is running backward, as written). We can solve for the concentrations of each species.
  \[ n(i) = n_i^0(i) + c(i) x \quad \text{for} \quad i = 1, 2, 3 \]
  \[ x = -0.1 \]
  \[ n_{H_2} = 0.1 + -3 \cdot (-0.1) = 0.4 \]
  \[ n_{N_2} = 0.2 + -1 \cdot (-0.1) = .3 \]
  \[ n_{NH_3} = 0.3 + 2 \cdot (-0.1) = .1 \text{ moles} \]
Application to Reaction Energy

- When a certain amount of one substance is used up (or generated) how much heat (at constant pressure), $q_p$, is released? (The reaction can be either endothermic or exothermic).

$$q_p = \frac{\Delta n(i)}{c(i)} \cdot \Delta H_{rxn} = x \cdot \Delta H_{rxn}$$

- To correctly determine the sign of the heat, one must multiply the coefficient, $c$, for reactants by minus one; and use the coefficients for products as is.

- For ammonia, the heat of formation is: -46 kJ/mole.

$$\Delta n(NH_3) = c(NH_3) \cdot x$$

$$x = \frac{-0.2}{2} = -0.1 \text{ moles}$$

$$\Delta H_{rxn} = 2\Delta H_f^o = -2 \cdot 46 = -98 \text{ kJ / mole}$$

$$q_p = \frac{\Delta n(NH_3)}{c(NH_3)} \cdot \Delta H_{rxn} = x \cdot \Delta H_{rxn} = 9.8 \text{ kJ}$$

Endothermic in this direction.