What was the purpose of Problem 8.74?

- Practice the following concepts:
  - Energy balances
  - Mass balances
  - Psychrometric chart
  - Recycle
  - Dry air as a constant quantity in balances

Heats of Reaction

1. Definition

- \( \Delta H_e \) = heat of reaction (kJ/mol or Btu/lbmol or cal/mol)
  - \( \Delta H_e < 0 \), exothermic (gives off heat)
  - \( \Delta H_e > 0 \), endothermic (needs heat)
- \( \Delta H_e^0 \) = standard heat of reaction (i.e., at 25°C)
- Heat of reaction always defined by complete reaction (i.e., \( X_a = 1 \))
  - Heat absorbed per mole reacted
- Remember for a single reaction, \( \xi = \frac{n_{\text{actual}} - n_{\text{actual, reactant}}}{n_{\text{actual, reactant}}} \)
- Therefore \( \Delta H_{\text{system}} = \xi \Delta H_e \)

\[ \text{(moles reacted)} \times \left( \frac{\text{kJ of energy}}{\text{moles reacted}} \right) \]

Heats of Reaction

2. From Heats of Reaction

- \( \Delta H_f^0 \) = heat required to form species at 1 atm, 25°C
  - Tabulated in Table B.1, 2nd to last column
  - Assumes all reactants and products at 25°C
- \( \Delta H_p = \sum \nu_i \Delta H_f^0 \)
  - Remember negative sign for reactants
  - Like products minus reactants
- Example: Gasification of carbon

\[ C(s) + H_2O(g) \Rightarrow CO(g) + H_2(g) \]

\begin{array}{c|c|c|c}
\text{Species} & \nu_i & \Delta H_f^0 \text{ (kJ/mol)} & \text{Endothermic} \\
\hline
C(s) & -1 & 0.0 & \\
H_2O & -1 & -241.83 & \\
CO & 1 & -110.52 & \end{array}

\[ \Delta H_p = -110.52 - 0 - (-241.83) = +131.31 \text{ kJ/mol} \]

Schedule

- Today – Heats of Reaction, Heat of Combustion
- Fri – Energy Balance with Reaction
  - WARNING on Reading:
    - Skip Heat of reaction method on pages 450-451, Skip Examples 9.5-1 and 9.5-3
- Mon – Practice Energy Balance with Reaction
- Wed – Adiabatic Flame Temperature
- Fri – Transient Balances
- Mon – Review for Exam 3
  (Tues, Apr 4 thru Fri, Apr 7 (due in class at 10 am)
Heats of Reaction

3. Path Independent

- C(s) + O\(_2\) \(\rightarrow\) CO\(_2\) \(\Delta H^\circ\) = -393.51 kJ/mol
- C(s) + \(\frac{1}{2}\)O\(_2\) \(\rightarrow\) CO \(\Delta H^\circ\) = -110.52 kJ/mol
- CO + \(\frac{1}{2}\)O\(_2\) \(\rightarrow\) CO\(_2\) \(\Delta H^\circ\) = -282.99 kJ/mol
- C(s) + O\(_2\) \(\rightarrow\) CO\(_2\) \(\Delta H^\circ\) = -393.51 kJ/mol

Hess’s Law:
- Add or subtract reactions to get correct \(\Delta H^\circ\)

Heats of Reaction

4. Heat of Combustion

- \(\Delta H^\circ_c\) = heat of combustion at 1 atm, 25°C
- Tabulated in Table B.1, 2nd to last column
- Assumes all reactants and products at 25°C
- All C \(\rightarrow\) CO\(_2\) (g)
- All H \(\rightarrow\) H\(_2\)O (liq) (for “high heating value”)
- All S \(\rightarrow\) SO\(_2\) (g)
- All N \(\rightarrow\) N\(_2\) (g)

- Heating value = - \(\Delta H^\circ_c\)
- Example: \(\text{NH}_3 + \frac{3}{2}\text{O}_2 \rightarrow \frac{3}{2}\text{H}_2\text{O}(\text{liq}) + \frac{1}{2}\text{N}_2\)

\[\Delta H^\circ_f,\text{i} (\text{kJ/mol}) : -46.19 \quad 0.0 \quad -285.84 \quad 0.0\]

\[\Delta H^\circ_r = \frac{3}{2}(\Delta H^\circ_f,\text{i} + \frac{3}{2}) = -382.57 \text{ kJ/mol}\]

(same as \(\Delta H^\circ_c\) in Table B.1)

Heats of Reaction

6. Review

- How do you find \(r_{\text{f}}\) at different temperatures?
  \[\Delta r_{\text{f}} = \Delta r_{\text{f}}^\circ + \int_{25}^{25} C_{\text{p,m}} dT\]

- Suppose \(C_{\text{p,methane}} = 0.079 \text{ kJ/mol/°C}\)
  and \(\Delta C_{\text{p,methane}} = -74.85 \text{ kJ/mol/°C}\)

- Find \(r_{\text{f,methane}}\) at 400°C
  \[\Delta r = -74.85 \frac{\text{kJ}}{\text{mol}} + \int_{25}^{400} 0.079 \frac{\text{kJ}}{\text{mol/°C}} dT\]
  \[= -74.85 + 0.079 \times (400 - 25) = -45.22 \frac{\text{kJ}}{\text{mol CH}_4}\]

Multiple Species

- Calculate the energy required to raise a mixture from 25°C to 400°C.
  \[\Delta H = \sum n_i \Delta H_i\]

- Suppose \(\Delta H_{\text{O}_2} = \sum a_{\text{O}_2} \Delta H_{\text{O}_2}\)
  \[\Delta H_{\text{O}_2} = \int_{25}^{400} C_{\text{p,O}_2} dT\]
  \[= a_{\text{O}_2}(400 - 25) + \frac{b_{\text{O}_2}}{2}(400^2 - 25^2) + \frac{c_{\text{O}_2}}{3}(400^3 - 25^3) + \frac{d_{\text{O}_2}}{4}(400^4 - 25^4)\]

Multiple Species

- Now get \(\Delta H = \sum n_i \Delta H_i\)
  \[0.05 \times \left(a_{\text{O}_2}(400 - 25) + \frac{b_{\text{O}_2}}{2}(400^2 - 25^2) + \frac{c_{\text{O}_2}}{3}(400^3 - 25^3) + \frac{d_{\text{O}_2}}{4}(400^4 - 25^4)\right)\]
  \[1.0 \times \left(a_{\text{CO}_2}(400 - 25) + \frac{b_{\text{CO}_2}}{2}(400^2 - 25^2) + \frac{c_{\text{CO}_2}}{3}(400^3 - 25^3) + \frac{d_{\text{CO}_2}}{4}(400^4 - 25^4)\right)\]
  \[0.30 \times \left(a_{\text{H}_2\text{O}(\text{liq})}(400 - 25) + \frac{b_{\text{H}_2\text{O}(\text{liq})}}{2}(400^2 - 25^2) + \frac{c_{\text{H}_2\text{O}(\text{liq})}}{3}(400^3 - 25^3) + \frac{d_{\text{H}_2\text{O}(\text{liq})}}{4}(400^4 - 25^4)\right)\]

- Define new variables:
  \[a' = \sum a_{\text{O}_2} \quad b' = \sum a_{\text{O}_2} \frac{b_{\text{O}_2}}{2} \quad c' = \sum a_{\text{O}_2} \frac{c_{\text{O}_2}}{3} \quad d' = \sum a_{\text{O}_2} \frac{d_{\text{O}_2}}{4}\]

- Now \(\Delta H\) becomes:
  \[\Delta H = a'(400 - 25) + b'(400^2 - 25^2) + c'(400^3 - 25^3) + d'(400^4 - 25^4)\]
Two Methods to Find $\Delta H_{\text{rxn}}$

- **Path Method** ($A \rightarrow B$)

- **Heat of Formation**

  $$\Delta H_{\text{rxn}} = \sum n_i \Delta H_{f_i}^{25°C}$$

  where $I$ is negative for reactants and positive for products

Example

- $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$

  - Find the heat of reaction at 1200°C
    
    A. $\Delta C_p$ approach (path method)
    
    B. $H_{\text{out}} - H_{\text{in}}$ ($\Delta H_f^0$ approach)

  See spreadsheet