Key points of the last lecture

- H is a state function

- Method of alternate paths to find unknown $\Delta H$

\[
\Delta H_{\text{rxn}} = \Delta H_A + \Delta H^\circ_{\text{rxn}} + \Delta H_B
\]
Key points of today’s last lecture

- Heats of formation
- Bond Energies
- Experimental measurement of $\Delta H$
Hess’s Law using Enthalpies of formation, $\Delta H^\circ_f$

The standard enthalpy per mole of a compound is defined as the enthalpy of formation of 1 mole of the compound at 1 atm (1 bar) from its elements in their standard state.

$$\Delta H^\circ_{rxn} = c \Delta H^\circ_{f,C} + d \Delta H^\circ_{f,D} - a \Delta H^\circ_{f,A} - b \Delta H^\circ_{f,B}$$

$$\Delta H^\circ_{rxn} = \sum_{k=1}^{N \_ \text{Species}} v_k \Delta H^\circ_{f,k}$$

$$\Delta H^\circ = n_X \Delta H^\circ_{rxn}$$

$\Delta H^\circ_f = 0$ for elements in their standard state

Values of $\Delta H^\circ_f$ are tabulated in Appendix B of the text.
Using bond dissociation energies to calculate $\Delta H^\circ_f$

For many compounds, the $\Delta H^\circ_f$ can be found by using bond dissociation energies, $D$ (kJ/mole).

Bond dissociation energies are average values, therefore it is not always the case that the $\Delta H^\circ_f$ of a molecule is equal to the sum of its bond dissociation energies.

Example: Calculate the heat of formation of gaseous benzene using bond dissociation energies at 25 °C and constant pressure.

Bond dissociation energies

\[
\begin{align*}
C - C &= 346 \text{ kJ/mole} \\
C = C &= 602 \text{ kJ/mole} \\
C - H &= 415 \text{ kJ/mole} \\
H - H &= 432 \text{ kJ/mole}
\end{align*}
\]

$C(g), \Delta H^\circ_f = 716.7$ kJ/mole
\[6C(s) + 3H_2(g) \rightarrow C_6H_6(g)\]

\[6C(s) \rightarrow 6C(g) \quad \Delta H_I = 6(716.7 \text{ kJ/mole}) = 4.3 \times 10^3 \text{ kJ/mole}\]

\[3(H-H)(g) \rightarrow 6H(g) \quad \Delta H_{II} = 3(432.0 \text{ kJ/mole}) = 1.3 \times 10^3 \text{ kJ/mole}\]

\[3(C-C)(g) \quad \Delta H_{III} = 3(-346.0 \text{ kJ/mole}) = -1.04 \times 10^3 \text{ kJ/mole}\]

\[3(C=C)(g) \quad \Delta H_{IV} = 3(-602.0 \text{ kJ/mole}) = -1.81 \times 10^3 \text{ kJ/mole}\]

\[6(C-H)(g) \quad \Delta H_{V} = 6(-411.0 \text{ kJ/mole}) = -2.47 \times 10^3 \text{ kJ/mole}\]

\[\Delta H_{\text{total}} = \Delta H_I + \Delta H_{II} + \Delta H_{III} + \Delta H_{IV} + \Delta H_V\]

\[= 280 \text{ kJ/mole}\]
\[ \Delta H_f^o = 280 \text{kJ/mole (using dissociation energies)} \]

\[ \Delta H_f^o = 82.93 \text{ kJ/mole (tabulated value)} \]

Resonance energy stabilizes the structure of benzene!
Using calorimetry to determine heats of reactions

Constant volume (bomb) calorimeter

Container with outer water bath maintained at the same temperature as the inner water bath

\[ dV = 0 \]

\[ w = 0 \]

\[ \Delta U = q_v \]

\[ \Delta U = 0 \]
Use method of alternate paths to find the heats of reactions

\[
\begin{align*}
\Delta U_{rxn,T_i} & \\
Reactants(T_i, V) + Cal(T_i) & \rightarrow Products(T_i, V) + Cal(T_i) \\
\end{align*}
\]

\[
\begin{align*}
\Delta U_{R+cal} & \\
\end{align*}
\]

\[
\begin{align*}
\Delta U_{P+cal} & \\
\end{align*}
\]

\[
\begin{align*}
\Delta U_{rxn,T_f} & \\
Reactants(T_f, V) + Cal(T_f) & \rightarrow Products(T_f, V) + Cal(T_f) \\
\end{align*}
\]

\[
\begin{align*}
\Delta H_{rxn,T} = \Delta U_{rxn,T} + \Delta (PV)_{rxn,T} \\
\end{align*}
\]
\[ \Delta H_{rxn,T} = \Delta U_{rxn,T} + \Delta(PV)_{rxn,T} \]

Assume reaction occurs at constant pressure and the volume change of the solid and liquid reactants is negligible. Also assume that the gaseous reactants and products are ideal.

\[ \Delta H_{rxn,T} = \Delta U_{rxn,T} + RT\left( \sum v_{g,products} - \sum v_{g,reactants} \right)_T \]

Stoichiometric numbers in a balanced equation
Using calorimetry to determine heats of reactions

Constant pressure

\[ dP = 0 \]

\[ \Delta H = q_p \]

\[ \Delta H = 0 \]
\[
\text{Reactants}(T_i, P) + \text{Cal}(T_i) \rightarrow \text{Products}(T_i, P) + \text{Cal}(T_i)
\]

\[
\Delta H_{\text{rxn}, T_i}
\]

\[
\Delta H_{R+\text{cal}}
\]

\[
\text{Reactants}(T_f, P) + \text{Cal}(T_f) \rightarrow \text{Products}(T_f, P) + \text{Cal}(T_f)
\]

\[
\Delta H_{\text{rxn}, T_f}
\]

\[
\Delta H_{P+\text{cal}}
\]
Example:

(a) In an adiabatic bomb calorimeter, the combustion of 0.5173 g of ethanol causes the temperature to rise from 25.0 to 29.289 °C. The heat capacity of the bomb, the products and other contents is 3576 J/K. What is the molar internal energy of combustion of ethanol at 25.0 °C?

(a) Calculate the molar enthalpy of combustion of ethanol at 25.0 °C?

\[ \text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) + \text{Cal} \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) + \text{Cal} \]

\( (T=25^\circ \text{C}, \text{ V}) \)

\( (T=29.289^\circ \text{C}, \text{ V}) \)
\[ \Delta U_{rxn,25^\circ C} = \Delta U_{P+cal} = 0 \]

\[ \Delta U_{rxn,25^\circ C} = C_v(Products+Cal)\Delta T \]

\[ = 3576 \text{JK}^{-1}(-4.289 K) \]

\[ = -1.534 \times 10^4 J \]

\[ \Delta U^\circ_{rxn} = \Delta U^\circ_{rxn} \left( \frac{M_{\text{ethanol}}}{m_{\text{ethanol}}} \right) \]

\[ = -1.5434 \times 10^4 J \left( \frac{46.0 \text{g/mole}}{0.5173 \text{g}} \right) \]

\[ = -1.37 \times 10^6 J/\text{mole} \]
Calculate the molar enthalpy of combustion of ethanol at 25.0 °C?

\[ \Delta H_{rxn}^\circ = \Delta U_{rxn,T}^\circ + RT\left( \sum \nu_{g,products} - \sum \nu_{g,reactants} \right) \]

\[ C_2H_5OH(l) + 3O_2(g) + Cal \rightarrow 2CO_2(g) + 3H_2O(l) + Cal \]

\[ (T=25^\circ C, V) \]

\[ (T=29.289^\circ C, V) \]

\[ \Delta H_{rxn}^\circ = -1.37 \times 10^6 \text{ J/mole} + (8.314 \text{ JK}^{-1} \text{ mole}^{-1}) (298.15 \text{ K}) (2 - 3) \]

\[ = -1.373 \times 10^6 \text{ J/mole} \]