Enthalpies of Reaction

- Enthalpy is an *extensive property*
  - Magnitude of ΔH is directly related to the amount of reactant used up in a process.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890\ \text{kJ}$$

$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \qquad \Delta H = -1780\ \text{kJ}$$

Enthalpies of Reactions

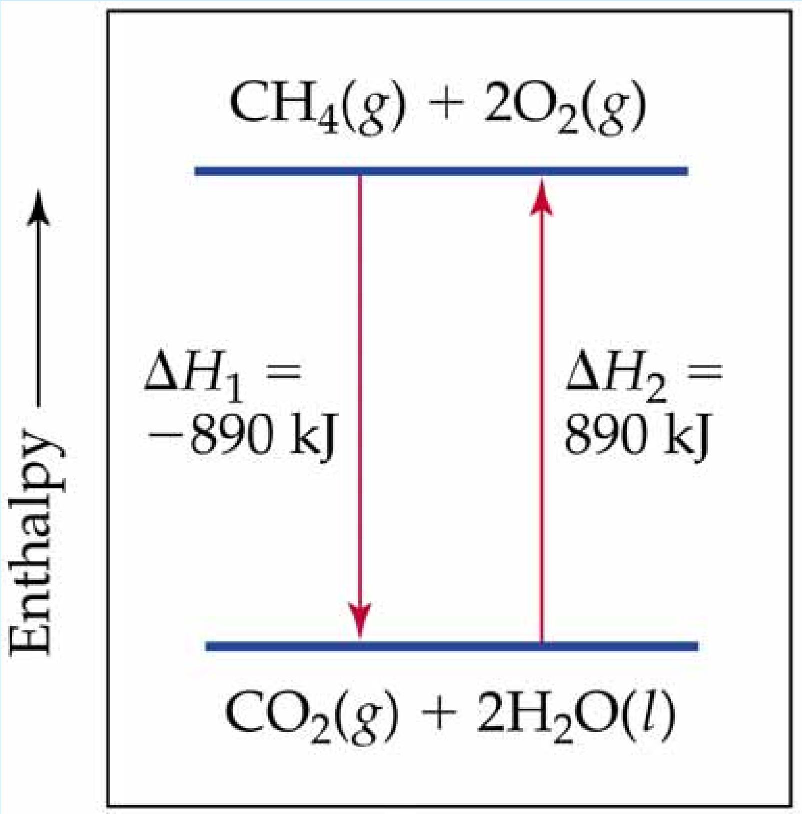
The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.

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

$\Delta H = -890$ kJ

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

$\Delta H = 890$ kJ



Enthalpies of Reaction

- The enthalpy of reaction is dependant on the states of the reactants and products.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H = -802 \text{ kJ}$$

$$2H_2O(l) \rightarrow 2H_2O(g) \quad \Delta H = +88 \text{ kJ}$$

Hess's Law

Result of enthalpy being a state function

Hess's law: if a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of ΔH for each individual step.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + \cancel{2H_2O(g)} \qquad \Delta H = -802\text{ kJ}$$

$$\cancel{2H_2O(g)} \rightarrow 2H_2O(l) \qquad \Delta H = -88\text{ kJ}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890\text{ kJ}$$

Hess's Law
Examples

- Calculate ΔH for the reaction

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$

$$C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2CO_2(g) + H_2O(l) \qquad \Delta H = -1299.6\ \text{kJ}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5\ \text{kJ}$$

$$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -285.8\ \text{kJ}$$

Hess's Law
Examples

- Calculate ΔH for the reaction

$$NO(g) + O(g) \rightarrow NO_2(g)$$

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \qquad \Delta H = -198.9 \text{ kJ}$$

$$O_3(g) \rightarrow 3/2\ O_2(g) \qquad \Delta H = -142.3 \text{ kJ}$$

$$O_2(g) \rightarrow 2\ O(g) \qquad \Delta H = +495.0 \text{ kJ}$$

Enthalpy of Formation

- The enthalpy of formation (or heat of formation) ΔH_f is the enthalpy change associated with forming 1 mole of a compound from its constituent elements.

$$2C(\text{graphite}) + 3H_2(g) + 1/2O_2(g) \rightarrow C_2H_5OH(l)$$

$$\Delta H_{rxn} = \Delta H_f = -277.7 \text{ kJ}$$

Note: only one mole of product formed!

  - If there is more than one state for a substance, the more stable one is used.
    - C(graphite) is more stable than C(diamond).

Standard Enthalpies

- Standard enthalpy, ΔH^{o}, is the enthalpy measured when everything is in its standard state.
  - ΔH_f^{o} - standard enthalpy of formation: ΔH for forming one mole of product directly from its reactants with products and reactants in standard states.
    - The standard enthalpy of formation of the most stable form of any element is zero.
  - ΔH_{vap}^{o} – standard enthalpy of vaporization: ΔH for converting liquids to gases with products and reactants in standard states.
  - ΔH_{fus}^{o} – standard enthalpy of fusion: ΔH for melting solids.
  - ΔH_{sub}^{o} – standard enthalpy of sublimation: ΔH for converting solids to gases
  - ΔH_{comb}^{o} – enthalpy of combustion: ΔH for combusting a substance with oxygen)

Enthalpies of Reaction
from enthalpies of formation

- We can use Hess' Law to calculate enthalpies of a reaction from enthalpies of formation.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

$$\Delta H^\circ_{\text{rxn}} = \sum n\Delta H^\circ_f(\text{products}) - \sum m\Delta H^\circ_f(\text{reactants})$$

Heat Capacity and Specific Heat

- Objects can emit or absorb heat, which causes an object to change temperature.
  - An objects heat capacity is the amount of energy required to raise its temperature by 1 K (or 1^{0}C).
  - The greater the heat capacity, the greater the heat required to produce a given rise in temperature.

Heat Capacity and Specific Heat

- For a pure substance, the heat capacity is usually given for a specified amount of ‘stuff’.
  - The heat capacity of 1 mol of a substance is the molar heat capacity.
  - The heat capacity of 1 g of a substance is the specific heat capacity, or the specific heat.
- The specific heat is determined experimentally by measuring the temperature change, ΔT, that a known mass, m, of the substance undergoes when it gains or loses a specific quantity of heat, q:

$$\text{Specific heat} = \frac{(\text{quantity of heat transferred})}{(\text{grams of substance}) \times (\text{temperature change})}$$

$$= \frac{q}{m \times \Delta T}$$

Specific Heat
Example

- Calculate the specific heat of water if it takes 209 J of heat to increase the temperature of 50.0 g of water by 1.00 K.

Specific Heat
Example

- If we know the specific heat of a substance (a physical property), then we can calculate the quantity of heat that a substance has gained or lost by using its specific heat together with its measured mass and temperature change.

$$q = (\text{specific heat}) \times (\text{grams of substance}) \times T$$

- How much heat is needed to warm 1 cup (250 g) of water from room temperature (22 ^{o}C) to near its boiling point (100 ^{o}C).
- What is the molar heat capacity of water?

Calorimetry

- Calorimetry is the measurement of heat flow. Calorimetry is done in a calorimeter, an apparatus that measures heat flow.
  - Constant pressure calorimetry – pressure is held constant, usually open to atmosphere.
  - Constant volume calorimetry – volume is held constant, used to study combustion reactions in a bomb calorimetry.

Constant Pressure Calorimetry

$$\Delta H_{\mathrm{rxn}} = q_{\mathrm{rxn}} = -q_{\mathrm{soln}}$$

$$q_{\mathrm{soln}} = (\text{specific heat of solution}) \times (\text{grams of solution}) \times \Delta T$$

- Mixing 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH, the temperature changes from 21.0ºC to 27.5ºC. Calculate ΔH_{rxn}. Assume the calorimeter does not lose any heat, take the density of the solution to be 1.0 g/mL, and take the specific heat of the solution to be 4.18 J/g-K.

Constant Volume (Bomb) Calorimetry

$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T$$

- Used to measure heats of combustion.

1. Determine the heat capacity of the calorimeter C_{cal} by measuring the ΔT rise for a substance with a known heat of combustion (usually benzoic acid).
2. Repeat the experiment with an unknown.