

Heat and Energy

- Thermochemistry is the study of quantities of heat (q) absorbed or evolved (given off) by a chemical reaction.
- Heat is energy that flows into or out of a system due to a difference between the system's T and the surrounding's T .
- Energy is the capacity to move matter.
- Total Energy is the sum of kinetic, potential, and internal energies.

$$\mathbf{E_{total} = E_k + E_p + U}$$

- Kinetic Energy (E_k) is due to motion. It is a function of mass (m) and velocity (v).

$$\mathbf{E_k = (1/2)mv^2}$$

- Potential Energy (E_p) is due to position in a field of force. The gravitational constant (g) is 9.81 m/s^2 , and the height (h) is in meters.

$$\mathbf{E_p = mgh}$$

- Internal Energy (U) is the combined kinetic and potential energies of particles (molecules) within a system.

Ex 6.01 Calculate the Kinetic Energy of a Basketball in a 2-Point Shot

- $E_k = (1/2)mv^2 = (1/2)(0.624 \text{ kg})(4.47 \text{ m/s})^2 = 6.23 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 6.23 \text{ Joules}$

Law of Conservation of Energy

- Energy may be converted between forms, but total quantity of energy is constant.
- Energy is never created or destroyed, it only changes forms.

Heat of Reaction

- Heat of Reaction is the heat required to keep T of a reacting system constant.
- An Exothermic reaction evolves (releases) heat, so that T increases.

$$\mathbf{q < 0 \text{ and system gives away heat to the surroundings } (\Delta T > 0)}$$

- An Endothermic reaction absorbs heat, so that T decreases.

$$\mathbf{q > 0 \text{ and system draws heat from the surroundings } (\Delta T < 0)}$$

Heat of Reaction at Constant Pressure

- Enthalpy (H) is a measure of a system's heat energy. $H = U + PV$
- Enthalpy is a state function.

That is, it depends only on present state (T and P), not on history.

- For a reaction at constant pressure, the change in enthalpy is equal to the heat of reaction.

$$\mathbf{q_p = \Delta H}$$

- Since $\Delta H = \Delta U + P\Delta V$ we also have $\Delta U = q_p - P\Delta V$

Thermodynamic Equation for a Reaction

- Uses phase subscripts, has molar basis, and ΔH is written after the reaction for the molar amounts as written.
- Rules for writing the equation:
 1. If reaction quantities are multiplied by any factor, then ΔH is as well.
 2. Reverse reaction has opposite sign for ΔH (that is, reaction is multiplied by -1)

Ex 6.02 Write a Thermodynamic Equation for an Exothermic Reaction

- Potassium hydroxide, $\text{KOH}_{(\text{aq})}$, reacts with hydrochloric acid, $\text{HCl}_{(\text{aq})}$.
- The reaction releases 55.9 kJ per mole of KOH.
- The thermodynamic equation is: $\text{KOH}_{(\text{aq})} + \text{HCl}_{(\text{aq})} \rightarrow \text{KCl}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{L})}$ $\Delta H = -55.9 \text{ kJ}$

Ex 6.03 Multiplying a Reaction by Factors

- $2 \times [\text{H}_3\text{O}^{+1}_{(\text{aq})} + \text{OH}^{-1}_{(\text{aq})} \rightarrow 2\text{H}_2\text{O}_{(\text{L})} \quad \Delta H = -55.9 \text{ kJ}]$
 $= 2\text{H}_3\text{O}^{+1}_{(\text{aq})} + 2\text{OH}^{-1}_{(\text{aq})} \rightarrow 4\text{H}_2\text{O}_{(\text{L})} \quad \Delta H = -111.8 \text{ kJ}$
- Multiply by -1 to get the reverse reaction:
 $4\text{H}_2\text{O}_{(\text{L})} \rightarrow 2\text{H}_3\text{O}^{+1}_{(\text{aq})} + 2\text{OH}^{-1}_{(\text{aq})} \quad \Delta H = +111.8 \text{ kJ}$

Stoichiometry and Thermochemistry

- The quantity of heat is proportional to the quantities of reactant and products.
- To determine the amount of heat, first convert mass (g) to moles by dividing by molar mass.

$$\text{Then, total } q = (\text{moles}) \left(\frac{\Delta H}{\text{coefficient}} \right)$$

Ex 6.04 Determine the Amount of Heat Released when 4.536×10^2 g of Ammonia is Produced.

- The thermodynamic equation is: $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightarrow 2\text{NH}_{3(\text{g})} \quad \Delta H = -92.38 \text{ kJ}$
- $q = (4.536 \times 10^2 \text{ g}) \left(\frac{1 \text{ mol NH}_3}{17.03 \text{ g}} \right) \left(\frac{-92.38 \text{ kJ}}{2 \text{ mol NH}_3} \right) = -1.230 \times 10^3 \text{ kJ}$

Heat Capacity

- Heat Capacity (C) is the quantity of heat needed to raise T of an entire system by 1°C .

$$q = C(\Delta T) \quad \text{SI units for C are J}^\circ\text{C}.$$

- Molar Heat Capacity (C_{molar}) is the quantity of heat needed to raise T of one mole by 1°C .

$$q = (C_{\text{molar}})(n)(\Delta T) \quad \text{SI units for } (C_{\text{molar}}) \text{ are J}/(\text{mol } ^\circ\text{C}).$$

- [Specific Heat](#) is the quantity of heat needed to raise T of one gram by 1°C .

$$q = (s)(m)(\Delta T) \quad \text{SI units for s are } \frac{\text{J}}{(\text{g } ^\circ\text{C})}, \text{ but } \frac{\text{calories}}{(\text{g } ^\circ\text{C})} \text{ are sometimes used.}$$

- For H_2O , $s = 1.00 \text{ calories}/(\text{g } ^\circ\text{C}) = 4.18 \text{ J}/(\text{g } ^\circ\text{C})$, where $1 \text{ cal} = 4.18 \text{ J}$

This means 1 cal (or 4.18 J) will raise T of 1 g of H_2O by 1°C .

- [Specific heats and molar heat capacities](#) are measurable physical properties.

Ex 6.05 Find Heat required to increase Temperature of 24.625 g H₂O from 12.2 °C to 27.4 °C

- $\Delta T = T_f - T_i = (27.4 \text{ }^\circ\text{C}) - (12.2 \text{ }^\circ\text{C}) = 15.2 \text{ }^\circ\text{C}$
- $q = (s)(m)(\Delta T) = (4.184 \frac{\text{J}}{\text{g }^\circ\text{C}})(24.625 \text{ g})(15.2 \text{ }^\circ\text{C}) = 1.57 \times 10^3 \text{ J}$
- $q = (1.57 \times 10^3 \text{ J})(1 \text{ kJ} / 1000 \text{ J}) = 1.57 \text{ kJ}$

Calorimeter

- A calorimeter determines ΔH (in kJ/mol) that is absorbed (positive) or released (negative) by measuring ΔT of surroundings (which is often water).
- See Figures [5.12](#) and [5.13](#).

Ex 6.06 Combustion of 4.29 g of hydrogen (H₂) raises calorimeter T from 25.15 to 45.76 °C

- Combustion releases heat, so ΔH of reaction is negative and the reaction is exothermic.
- $C = 25.0 \frac{\text{kJ}}{^\circ\text{C}}$ and $q = -C(\Delta T) = -(25.0 \frac{\text{kJ}}{^\circ\text{C}})(45.76 - 25.15 \text{ }^\circ\text{C}) = -515 \text{ kJ}$
- $(4.29 \text{ g})\left(\frac{1 \text{ mol H}_2}{2.016 \text{ g}}\right) = 2.13 \text{ mol of hydrogen}$
- $\Delta H = \frac{-515 \text{ kJ}}{2.13 \text{ mol}} = -242 \text{ kJ per mole of H}_2$
- $\text{H}_{2(\text{g})} + (\frac{1}{2})\text{O}_{2(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{g})} + 242 \text{ kJ/mol}$ (Heat is a product.)

Hess' Law of Heat Summation

- If a reaction can be written as the sum of other reactions as its components, then the overall ΔH is the sum of the ΔH 's for individual component reactions.

Ex 6.07 Add Reactions and Enthalpies together to determine the Enthalpy of the Sum Reaction

- Reaction 1: $\text{ZnS}_{(\text{s})} \rightarrow \text{Zn}_{(\text{s})} + \text{S}_{(\text{s})} \quad \Delta H = +206.0 \text{ kJ}$
- Reaction 2: $\text{S}_{(\text{s})} + \text{H}_{2(\text{g})} \rightarrow \text{H}_2\text{S}_{(\text{g})} \quad \Delta H = -20.5 \text{ kJ}$

- Sum: $\text{ZnS}_{(\text{s})} + \text{S}_{(\text{s})} + \text{H}_{2(\text{g})} \rightarrow \text{Zn}_{(\text{s})} + \text{S}_{(\text{s})} + \text{H}_2\text{S}_{(\text{g})}$
- Simplify: $\text{ZnS}_{(\text{s})} + \text{H}_{2(\text{g})} \rightarrow \text{Zn}_{(\text{s})} + \text{H}_2\text{S}_{(\text{g})}$
- Enthalpy: $\Delta H = (+206.0 \text{ kJ}) + (-20.5 \text{ kJ}) = +185.5 \text{ kJ overall (endothermic)}$

Ex 6.08 Apply Factors to Reactions prior to Summation

- Double Reaction 1: $2 \times [\text{C}_{(\text{graphite})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})} \quad \Delta H = -393.5 \text{ kJ}]$
- Reverse Reaction 2: $-1 \times [2\text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})} \quad \Delta H = -566.0 \text{ kJ}]$

- Result 1: $2\text{C}_{(\text{graphite})} + 2\text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})} \quad \Delta H = -787.0 \text{ kJ}$
- Result 2: $2\text{CO}_{2(\text{g})} \rightarrow 2\text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \quad \Delta H = +566.0 \text{ kJ}$

- Unsimplified Sum: $2\text{C}_{(\text{graphite})} + 2\text{O}_{2(\text{g})} + 2\text{CO}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})} + 2\text{CO}_{(\text{g})} + \text{O}_{2(\text{g})}$

- Simplified Sum: $2\text{C}_{(\text{graphite})} + 1\text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{(\text{g})}$
- Enthalpy of Sum: $\Delta H = -787.0 \text{ kJ} + 566.0 \text{ kJ} = -221.0 \text{ kJ}$ overall (exothermic)

Standard Enthalpy of Formation (ΔH_f°)

- Determined from reactions which form substances from elements at standard conditions.
- Degree sign ($^\circ$) means reaction is at standard state (298 K and 1 atm).
- Each element is in its reference form, which is the most stable form at standard state.
- Different forms of an element are called allotropes. Graphite and diamond are both allotropes of carbon. Graphite, however, is the reference form because it is more common.

The [Standard Enthalpies of Formation Table](#) has ΔH_f° 's in kJ/mol

- For an element in its reference form, ΔH_f° is zero.
- Note phase subscripts. The enthalpy values are different for different phases. Different phases have different ΔH_f° 's basically because phase changes require heat.
- Values for ions in table are not absolute, but are relative to their ionic reactions with $\text{H}^+_{(\text{aq})}$.
- To find ΔH° for a chemical reaction, use ΔH_f° of reactants and products.

$$\Delta H^\circ_{\text{reaction}} = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

Multiply the ΔH_f° values by stoichiometric coefficients (n and m) in the balanced reaction.

Ex 6.09 Determine an Enthalpy of Vaporization (a physical change only) at Standard State

- We can write the vaporization of water as a reaction (where $n = m = 1$): $1\text{H}_2\text{O}_{(\text{L})} \rightarrow 1\text{H}_2\text{O}_{(\text{g})}$
- $\Delta H^\circ_{\text{vap'n}} = [1 \times \Delta H_f^\circ(\text{H}_2\text{O}_{(\text{g})})] - [1 \times \Delta H_f^\circ(\text{H}_2\text{O}_{(\text{L})})]$
- $\Delta H^\circ_{\text{vap'n}} = [1 \times (-241.83 \text{ kJ/mol})] - [1 \times (-285.84 \text{ kJ/mol})] = +44.01 \text{ kJ}$ (per 1 mol H_2O)
- This means +44.01 kJ are required to vaporize one mole of liquid H_2O at 298 K and 1 atm.

Ex 6.10 Use Enthalpies of Formation (ΔH_f°) to Determine the Enthalpy (ΔH°) of a Chemical Reaction at Standard State (298 K and 1 atm)

- $4\text{NH}_{3(\text{g})} + 5\text{O}_{2(\text{g})} \rightarrow 4\text{NO}_{(\text{g})} + 6\text{H}_2\text{O}_{(\text{g})}$
- $\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$
- $\Delta H^\circ = [4 \times \Delta H_f^\circ(\text{NO}_{(\text{g})}) + 6 \times \Delta H_f^\circ(\text{H}_2\text{O}_{(\text{g})})] - [4 \times \Delta H_f^\circ(\text{NH}_{3(\text{g})}) + 5 \times \Delta H_f^\circ(\text{O}_{2(\text{g})})]$
- $\Delta H^\circ = [4 \times (90.4) + 6 \times (-241.8)] - [4 \times (-46.2) + 5 \times (0.0)] = -904.4 \text{ kJ}$
- This means 904.4 kJ are released when 4 mol $\text{NH}_{3(\text{g})}$ are consumed.
- The thermodynamic conversion factor is $\left(\frac{-904.4 \text{ kJ}}{4 \text{ mol NH}_3}\right)$.