Chapter 6
Energy and Chemical Reactions

Energy and Energy Changes

• Capacity to do work
  –chemical, mechanical, thermal, electrical, radiant, sound, nuclear
• Energy may affect matter
  – e.g. raise its temperature, eventually causing a state change
  – All physical changes and chemical changes involve energy changes

Heat Transfer and The Measurement of Heat

• SI unit J (Joule)
• calorie
  1 calorie = 4.184 J
• English unit = BTU
• Specific Heat
  amount of heat required to raise the T of 1g of a substance by 1°C
  $SH = \text{units} = \text{J/g}^\circ\text{C}$
Example - Converting Calories to Joules

Convert 60.1 cal to joules

\[ 1 \text{ cal} = 4.184 \text{ joules} \]

\[ 60.1 \text{ cal} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 251 \text{ J} \]

Energy and the Temperature of Matter

• The amount the temperature of an object increases depends on the amount of heat added (q).
  – If you double the added heat energy the temperature will increase twice as much.

• The amount the temperature of an object increases depends on its mass
  – If you double the mass it will take twice as much heat energy to raise the temperature the same amount.

Heat Transfer and the Measurement of Heat

• Heat capacity
  amount of heat required to raise the T of a substance by 1°C
  \[ HC = \frac{J}{\degree C} \]
Heat Transfer and the Measurement of Heat

- Heat transfer equation necessary to calculate amounts of heat
- amount of heat = amount of substance x specific heat x $\Delta T$

$$q = m \times SH \times \Delta T$$

**Example** – Calculate the amount of heat to raise the temperature of 200 g of water from 10.0 °C to 55.0 °C

\[ ?J = 200 \text{g H}_2\text{O} \times \frac{4.184 \text{J}}{1 \text{g H}_2\text{O}} \times (55.0 \degree \text{C} - 10.0 \degree \text{C}) \]

\[ = 3.76 \times 10^4 \text{ J} \text{ or } 37.6 \text{ kJ} \]

Specific Heat Capacity

- Specific Heat (s) is the amount of energy required to raise the temperature of one gram of a substance by one Celsius degree

By definition, the specific heat of water is $4.184 \frac{\text{J}}{\text{g} \ \degree \text{C}}$

Amount of Heat = Specific Heat x Mass x Temperature Change

\[ Q = SH \times m \times \Delta T \]
Example – Calculate the amount of heat energy (in joules) needed to raise the temperature of 7.40 g of water from 29.0°C to 46.0°C

Specific Heat of Water = $\frac{4.184 \text{ J}}{\text{g} \cdot \text{°C}}$

Mass = 7.40 g

Temperature Change = 46.0°C – 29.0°C = 17.0°C

$$Q = \text{SH} \times m \times \Delta T$$

Heat = $\frac{4.184 \text{ J}}{\text{g} \cdot \text{°C}} \times 7.40 \text{ g} \times 17.0 \text{ °C} = 526 \text{ J}$

Example – A 1.6 g sample of metal that appears to be gold requires 5.8 J to raise the temperature from 23°C to 41°C. Is the metal pure gold?

$$Q = \text{SH} \times m \times \Delta T$$

$$\text{SH} = \frac{Q}{m \times \Delta T}$$

$$\Delta T = 41 \text{ °C} - 23 \text{ °C} = 18 \text{ °C}$$

$$s = \frac{5.8 \text{ J}}{1.6 \text{ g} \times 18 \text{ °C}} = 0.20 \text{ J} \text{ g}^{-1} \text{ °C}^{-1}$$

Specific heat of gold is 0.13 $\text{ J} \text{ g}^{-1} \text{ °C}^{-1}$

Therefore the metal cannot be pure gold.

The First Law of Thermodynamics

- Thermodynamics is the study of the changes in energy and transfers of energy that accompany chemical and physical processes.

1. Will two (or more) substances react when they are mixed under specified conditions?
2. If they do react, what energy changes and transfers are associated with their reaction?
3. If a reaction occurs, to what extent does it occur?
The First Law of Thermodynamics

- Exothermic reactions release energy in the form of heat.
- For example, the combustion of propane is exothermic.
  \[ C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) + 2.22 \times 10^5 \text{kJ} \]
- The combustion of n-butane is also exothermic.
  \[ 2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l) + 5.78 \times 10^5 \text{kJ} \]
The First Law of Thermodynamics

2. Chemical systems tend toward a state of **maximum disorder**.
   • Common examples of this are:
     – A mirror shatters when dropped and does not reform.
     – It is easy to scramble an egg and difficult to unscramble it.
     – Food dye when dropped into water disperses.

The First Law of Thermodynamics

• This law can be stated as, “The combined amount of energy in the universe is constant.”
• The first law is also known as the **Law of Conservation of Energy**.
  – Energy is neither created nor destroyed in chemical reactions and physical changes.

Some Thermodynamic Terms

• The substances involved in the chemical and physical changes under investigation are called the **system**.
  – In chemistry lab, the system is the chemicals inside the beaker.
• The environment around the system is called the **surroundings**.
  – The surroundings are outside the beaker.
• The system plus the surroundings is called the **universe**.
Some Thermodynamic Terms

• The set of conditions that specify all of the properties of the system is called the **thermodynamic state of a system**.

• For example the thermodynamic state could include:
  – The number of moles and identity of each substance.
  – The physical states of each substance.
  – The temperature of the system.
  – The pressure of the system.

Some Thermodynamic Terms

• The properties of a system that depend only on the state of the system are called **state functions**.
  – State functions are always written using capital letters.

• The value of a state function is independent of pathway.

• An analog to a state function is the energy required to climb a mountain taking two different paths.
  – \( E_1 \) = energy at the bottom of the mountain
  – \( E_2 \) = energy at the top of the mountain
  – \( E_2 - E_1 = mgh_2 - mgh_1 = mg(\Delta h) \)

Some Thermodynamic Terms

• Notice that the energy change in moving from the top to the bottom is independent of pathway but the work required may not be!

• Some examples of state functions are:
  – \( T, P, V, \Delta E, \Delta H, \text{ and } S \)

• Examples of non-state functions are:
  – \( n, q, w \)
Some Thermodynamic Terms

- In thermodynamics we are often interested in changes in functions.
  - We will define the change of any function $X$ as:
  - $\Delta X = X_{\text{final}} - X_{\text{initial}}$
- If $X$ increases $\Delta X > 0$
- If $X$ decreases $\Delta X < 0$.

Enthalpy Change

- Chemistry is commonly done in open beakers on a desk top at atmospheric pressure.
  - Because atmospheric pressure only changes by small increments, this is almost at constant pressure.
- The enthalpy change, $\Delta H$, is the change in heat content at constant pressure.
  - $\Delta H = q_p$

$\Delta H_{\text{rxn}}$ is the heat of reaction.
- This quantity will tell us if the reaction produces or consumes heat.
  - If $\Delta H_{\text{rxn}} < 0$ the reaction is exothermic.
  - If $\Delta H_{\text{rxn}} > 0$ the reaction is endothermic.
- $\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$
  - $\Delta H_{\text{rxn}} = H_{\text{substances produced}} - H_{\text{substances consumed}}$
  - Notice that this is $\Delta H_{\text{rxn}} = H_{\text{final}} - H_{\text{initial}}$
Calorimetry

- A coffee-cup calorimeter is used to measure the amount of heat produced (or absorbed) in a reaction at constant P.
  - This is one method to measure $q_p$ for reactions in solution.

Calorimetry

- If an exothermic reaction is performed in a calorimeter, the heat evolved by the reaction is determined from the temperature rise of the solution.
  - This requires a two part calculation.

\[
\left( \frac{\text{Amount of heat released by reaction}}{\text{Amount of heat absorbed by calorimeter}} \right) = \left( \frac{\text{Amount of heat absorbed by solution}}{\text{solution by absorbed heat of reaction by calorimeter}} \right)
\]

- Amount of heat gained by calorimeter is called the heat capacity of the calorimeter or calorimeter constant.
  - The value of the calorimeter constant is determined by adding a specific amount of heat to calorimeter and measuring the temperature rise.

Calorimetry

- Example 15-1: When 3.425 kJ of heat is added to a calorimeter containing 50.00 g of water the temperature rises from 24.00°C to 36.54°C. Calculate the heat capacity of the calorimeter in J/°C. The specific heat of water is 4.184 J/g °C.
  - This is a four part calculation.
Calorimetry

1. Find the temperature change.

\[ \Delta T = (36.54 - 24.00)^\circ C = 12.54^\circ C \]

2. Find the heat absorbed by the water in going from 24.00°C to 36.54°C.

\[ q_p = mC\Delta T \]
\[ = (50.00 \text{ g})(4.184 \text{ J/g}\cdot^\circ C)(12.54^\circ C) \]
\[ = 2623.37 \text{ J} \approx 2623 \text{ J} \]

Calorimetry

3. Find the heat absorbed by the calorimeter.
   - Take the total amount of heat added to calorimeter and subtract the heat absorbed by the water.

\[ 3.425 \text{ kJ} = 3425 \text{ J} \]
\[ (3425 \text{ J} - 2623 \text{ J}) = 802 \text{ J} \]

4. Find the heat capacity of the calorimeter.
   - \( \frac{802 \text{ J}}{12.54^\circ C} = 63.955 \text{ J/}^\circ C \approx 64 \text{ J/}^\circ C \)

Calorimetry

- Example 15-2: A coffee-cup calorimeter is used to determine the heat of reaction for the acid-base neutralization

\[ \text{CH}_3\text{COOH}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{NaCH}_3\text{COO}_{(aq)} + \text{H}_2\text{O}_{(l)} \]

When we add 25.00 mL of 0.500 M NaOH at 23.00°C to 25.00 mL of 0.600 M CH₃COOH already in the calorimeter at the same temperature, the resulting temperature is observed to be 25.947°C.
Calorimetry

The heat capacity of the calorimeter has previously been determined to be 27.8 J/°C. Assume that the specific heat of the mixture is the same as that of water, 4.18 J/g°C and that the density of the mixture is 1.02 g/mL.

Calorimetry

• This is a three part calculation.

1. Calculate the amount of heat given off in the reaction.

   temperature change
   \[ \Delta T = (25.947 - 23.000)°C = 2.947°C \]

   heat absorbed by calorimeter
   \[ q = (2.947°C)(278 J/°C) = 819 J \]

Calorimetry

\[ \Delta T = (25.947 - 23.000)°C = 2.947°C \]

heat absorbed by calorimeter
\[ q = (2.947°C)(278 J/°C) = 819 J \]

mass of solution in calorimeter
\[ \frac{(25.00 \text{ mL} + 25.00 \text{ mL})\cdot 102 \text{ g}}{2 \text{ mL}} = 510 \text{ g} \]
Calorimetry

heat absorbed by solution
\[ q = mC\Delta T \]
\[ q = (51.0 \text{ g})(418 \text{ J/}^\circ\text{C})(2.947^\circ\text{C}) = 628 \text{ J} \]

total amount of heat produced by reaction
\[ q = 81.9 \text{ J} + 628 \text{ J} = 709.9 \text{ J} \]

Calorimetry

2. Determine \( \Delta H \) for the reaction under the conditions of the experiment.
   - We must determine the number of moles of reactants consumed which requires a limiting reactant calculation.

\[
\begin{align*}
\text{CH}_3\text{COOH}_{(aq)} + \text{NaOH}_{(aq)} & \rightarrow \text{NaCH}_2\text{COO}_{(aq)} + \text{H}_2\text{O}_{(l)} \\
(25.00 \text{ mL NaOH})(0.500 \text{ mmol NaOH}) & \times \\
\left( \frac{1 \text{ mmol NaCH}_2\text{COO}}{1 \text{ mmol NaOH}} \right) & = 12.5 \text{ mmol NaCH}_2\text{COO} \\
\end{align*}
\]

Calorimetry
Calorimetry

3. Finally, calculate the $\Delta H_{\text{rxn}}$ based on the limiting reactant calculation.

\[ 12.5 \text{ mmol} = 0.0125 \text{ mol} \]
\[ \Delta H_{\text{rxn}} = \frac{7099 \text{ J}}{0.0125 \text{ mol}} = 56792 \text{ J/mol} = 56.8 \text{ kJ/mol} \]

Thermochemical Equations

- **Thermochemical equations** are a balanced chemical reaction plus the $\Delta H$ value for the reaction.

\[ \text{C}_4\text{H}_{12(s)} + 8 \text{ O}_{2(g)} \rightarrow 5 \text{ CO}_{2(g)} + 6 \text{ H}_2\text{O}_2(l) \quad \Delta H_{\text{rxn}}^\circ = -3523 \text{ kJ} \]
- $\Delta H < 0$ designates an **exothermic** reaction.
- $\Delta H > 0$ designates an **endothermic** reaction

Standard States and Standard Enthalpy Changes

- **Thermochemical standard state conditions**
  - The thermochemical standard $T = 298.15 \text{ K}$.
  - The thermochemical standard $P = 1.0000 \text{ atm}$.
    - Be careful not to confuse these values with STP.
- **Thermochemical standard states of matter**
  - For pure substances in their liquid or solid phase the standard state is the pure liquid or solid.
  - For gases the standard state is the gas at 1.00 atm of pressure.
    - For gaseous mixtures the partial pressure must be 1.00 atm.
  - For aqueous solutions the standard state is 1.00 M concentration.
Standard Molar Enthalpies of Formation, $\Delta H^\circ_f$

- The standard molar enthalpy of formation is defined as the enthalpy for the reaction in which one mole of a substance is formed from its constituent elements.
  - The symbol for standard molar enthalpy of formation is $\Delta H^\circ_f$.
- The standard molar enthalpy of formation for MgCl$_2$ is:
  $$\text{Mg(s)} + \text{Cl}_2(g) \rightarrow \text{MgCl}_2(s) + 641.8 \text{ kJ}$$
  $$\Delta H^\circ_{f, \text{MgCl}_2(s)} = -641.8 \text{ kJ/mol}$$

Standard Molar Enthalpies of Formation, $\Delta H^\circ_f$

- Standard molar enthalpies of formation have been determined for many substances and are tabulated in Appendix L.
- Standard molar enthalpies of elements in their most stable forms at 298.15 K and 1.000 atm are zero.
- The standard molar enthalpy of formation for phosphoric acid is -1281 kJ/mol. Write the equation for the reaction for which $\Delta H^\circ_{\text{rxn}} = -1281$ kJ.
  - P in standard state is P$_s$
  - Phosphoric acid in standard state is H$_3$PO$_4(s)$

Standard Molar Enthalpies of Formation, $\Delta H^\circ_f$

$$\frac{3}{2} \text{H}_2(g) + 2 \text{O}_2(g) + \frac{1}{4} \text{P}_4(s) \rightarrow \text{H}_3\text{PO}_4(s) + 1281 \text{ kJ}$$
  $$\Delta H^\circ_{f, \text{H}_3\text{PO}_4(s)} = -1281 \text{ kJ/mol}$$
Standard Molar Enthalpies of Formation, $\Delta H_f^o$

- Calculate the enthalpy change for the reaction of one mole of $H_2(g)$ with one mole of $F_2(g)$ to form two moles of $HF(g)$ at 25°C and one atmosphere.

\[
H_2(g) + F_2(g) \rightarrow 2HF(g)
\]

std. state std. state std. state

for this rxn. $\Delta H_f^o = 2 \times \Delta H_f^r$

from Appendix K, $\Delta H_f^r = -271 \text{ kJ} / \text{mol}$

$\Delta H_f^o = (2 \text{ mol})(-271 \text{ kJ} / \text{mol}) = -542 \text{ kJ}$

---

Standard Molar Enthalpies of Formation, $\Delta H_f^o$

- Example 15-6: Calculate the enthalpy change for the reaction in which 15.0 g of aluminum reacts with oxygen to form $Al_2O_3$ at 25°C and one atmosphere.

\[
4 \text{ Al(s)} + 3 \text{ O}_2(g) \rightarrow 2 \text{ Al}_2\text{O}_3(s)
\]

from Appendix K, $\Delta H_f^{\text{Al}_2\text{O}_3} = -1676 \text{ kJ} / \text{mol}$

\[
? \text{ kJ} = 15.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \times \frac{2 \text{ mol Al}_2\text{O}_3}{4 \text{ mol Al}} \times \frac{-1676 \text{ kJ}}{1 \text{ mol Al}_2\text{O}_3} = -466 \text{ kJ}
\]
Hess’s Law

- Hess’s Law of Heat Summation states that the enthalpy change for a reaction is the same whether it occurs by one step or by any (hypothetical) series of steps.
  - Hess’s Law is true because $\Delta H$ is a state function.
- If we know the following $\Delta H^0$'s
  
  \[
  \begin{align*}
  [1] & 4 \text{FeO}_3(s) + O_2(g) \rightarrow 2 \text{Fe}_2\text{O}_3(s) & \Delta H^0 = -560 \text{ kJ} \\
  [2] & 2 \text{Fe}_{(s)} + O_{2(g)} \rightarrow 2 \text{FeO}_{(g)} & \Delta H^0 = -544 \text{ kJ} \\
  [3] & 4 \text{Fe}(s) + 3 O_2(g) \rightarrow 2 \text{Fe}_2\text{O}_3(s) & \Delta H^0 = -1648 \text{ kJ}
  \end{align*}
  \]

Hess’s Law

- For example, we can calculate the $\Delta H^0$ for reaction [1] by properly adding (or subtracting) the $\Delta H^0$'s for reactions [2] and [3].
- Notice that reaction [1] has FeO and O$_2$ as reactants and Fe$_2$O$_3$ as a product.
  - Each reaction can be doubled, tripled, or multiplied by half, etc.
  - The $\Delta H^0$ values are also doubled, tripled, etc.
  - If a reaction is reversed the sign of the $\Delta H^0$ is changed.
  
  \[
  \begin{align*}
  2 \times \left[ -2 \right] & 2(2 \text{FeO}_3(s) \rightarrow 2 \text{Fe}_{(s)} + O_{2(g)}) & 2(-544) \text{ kJ} \\
  [3] & 4 \text{Fe}_{(s)} + 3 O_{2(g)} \rightarrow 2 \text{Fe}_2\text{O}_3(s) & -1648 \text{ kJ} \\
  [1] & 4 \text{FeO}_{(s)} + O_{2(g)} \rightarrow 2 \text{Fe}_2\text{O}_3 & -560 \text{ kJ}
  \end{align*}
  \]

Hess’s Law

- Example 15-7: Given the following equations and $\Delta H^0$ values
  
  \[
  \begin{array}{c|c}
  \text{Equation} & \Delta H^0 \text{ (kJ)} \\
  \hline
  [1] & 2 \text{N}_2(g) + O_{2(g)} \rightarrow 2 \text{N}_2\text{O}_2(g) & 164.1 \\
  [2] & \text{N}_2(g) + O_{2(g)} \rightarrow 2 \text{NO}_{(g)} & 180.5 \\
  [3] & \text{N}_2(g) + 2 O_{2(g)} \rightarrow 2 \text{NO}_2(g) & 66.4
  \end{array}
  \]

  calculate $\Delta H^0$ for the reaction below.
  
  \[
  \text{N}_2\text{O}_{(s)} + \text{NO}_{2(s)} \rightarrow 3 \text{NO}_{(s)} \quad \Delta H^0 = ?
  \]

  \text{You do it!}
Hess’s Law

- Use a little algebra and Hess’s Law to get the appropriate $\Delta H^\circ$ values

\[
\frac{1}{2} \times \left[ \frac{1}{2} \right] N_2(g) + \frac{1}{2} O_2(g) \rightarrow \frac{1}{2} N_2O_2(g) \quad \Delta H^\circ = -82.05 \\
\frac{1}{2} \times \left[ 2 \right] \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow 3 NO(g) \quad 270.75 \\
\frac{1}{2} \times \left[ -3 \right] NO_2(g) \rightarrow \frac{1}{2} N_2(g) + O_2(g) \quad -33.2 \\
N_2O(g) + NO_2(g) \rightarrow 3 NO(g) \quad 155.5
\]

Hess’s Law

- The sign of the $\Delta H^\circ$ value tells us that the reaction is endothermic.
- The reverse reaction is exothermic, i.e.,

\[
3 NO(g) \rightarrow N_2O(g) + NO_2(g) \quad \Delta H^\circ = -155.5 \text{ kJ}
\]

Hess’s Law

- Hess’s Law in a more useful form.
  - For any chemical reaction at standard conditions, the standard enthalpy change is the sum of the standard molar enthalpies of formation of the products (each multiplied by its coefficient in the balanced chemical equation) minus the corresponding sum for the reactants.

\[
\Delta H^{\text{rxn}} = \sum_n n \Delta H^\circ_{\text{products}} - \sum_n n \Delta H^\circ_{\text{reactants}}
\]

\[ n = \text{stoichiometric coefficients} \]
Hess’s Law

• Calculate the $\Delta H^0_{298}$ for the following reaction from data in Appendix L.

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

Hess’s Law

$\Delta H^0_{298}$ for the following reaction from data in Appendix L.

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

$$\Delta H^0_{298} = \left[3 \Delta H^0_{CO_2(l)} + 4 \Delta H^0_{H_2O(l)}\right] - \left[\Delta H^0_{C_3H_8(g)} + 5 \Delta H^0_{O_2(g)}\right]$$

$$= \left[\left((-393.5) + 4(-2858)\right) - \left((-1038) + 5(0)\right)\right] \text{kJ}$$
Hess’s Law

• Calculate $\Delta H_{298}^{\circ}$ for the following reaction from data in Appendix L.

$$C_3H_6(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(l)$$

$$\Delta H_{298}^{\circ} = \left[3 \Delta H_f^{\circ}(CO_2, g) + 4 \Delta H_f^{\circ}(H_2O, l)\right] - \left[\Delta H_f^{\circ}(C_3H_6, g) + 5 \Delta H_f^{\circ}(O_2, g)\right]$$

$$= \left[\left\{3 \times -393.5 + 4 \times -285.8\right\} - \left\{-1038 + 5 \times 0\right\}\right] \text{kJ}$$

$$= -2211.9 \text{kJ}$$

$\Delta H_{298}^{\circ} = -2211.9 \text{kJ}$, and so the reaction is exothermic.

---

Hess’s Law

• Application of Hess’s Law and more algebra allows us to calculate the $\Delta H_f^{\circ}$ for a substance participating in a reaction for which we know $\Delta H_{\text{rxn}}^{\circ}$, if we also know $\Delta H_f^{\circ}$ for all other substances in the reaction.

• Example 15-9: Given the following information, calculate $\Delta H_f^{\circ}$ for $H_2S(g)$.

$$2 H_2(g) + 3 O_2(g) \rightarrow 2 SO_2(g) + 2 H_2O(l) \quad \Delta H_{298}^{\circ} = -1124 \text{kJ}$$

$\Delta H_f^{\circ}$ ? 0 -296.8 -285.8

(kJ/mol)

You do it!

---

Hess’s Law

$$\Delta H_{298}^{\circ} = \left[2 \Delta H_f^{\circ}(SO_2, g) + 2 \Delta H_f^{\circ}(H_2O, l)\right] - \left[2 \Delta H_f^{\circ}(H_2, g) + 3 \Delta H_f^{\circ}(O_2, g)\right]$$

$$= \left[\left\{2 \times -296.8 + 2 \times -285.8\right\} - \left\{2 \times 0 + 3 \times 0\right\}\right] \text{kJ}$$

$$= -1124 \text{kJ}$$

now we solve for $\Delta H_f^{\circ}(H_2S, g)$

$2 \Delta H_f^{\circ}(H_2S, g) = -41.2 \text{kJ}$

$\Delta H_f^{\circ}(H_2S, g) = -20.6 \text{kJ}$
Bond Energies

- Bond energy is the amount of energy required to break the bond and separate the atoms in the gas phase.
  - To break a bond always requires an absorption of energy!

\[ \text{A - B}_\text{(g)} + \text{bond energy} \rightarrow \text{A}_\text{(g)} + \text{B}_\text{(g)} \]

\[ \text{H - Cl}_\text{(g)} + 432 \text{ kJ/mol} \rightarrow \text{H}_\text{(g)} + \text{Cl}_\text{(g)} \]

Bond Energies

- Table of average bond energies

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(_2)</td>
<td>159</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>243</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>192</td>
</tr>
<tr>
<td>O(_2) (double bond)</td>
<td>498</td>
</tr>
<tr>
<td>N(_2) (triple bond)</td>
<td>946</td>
</tr>
</tbody>
</table>

Bond Energies

- Bond energies can be calculated from other \(\Delta H^{\circ}_{298}\) values.
• Bond energies can be calculated from other $\Delta H^\circ_{298}$ values.

**Example 15-9:** Calculate the bond energy for hydrogen fluoride, HF.

- $\text{H} - \text{F} (g) + \text{BE} \rightarrow \text{H} (g) + \text{F} (g)$, atoms NOT ions
- $\Delta H^\circ_{298} = \text{BE}_{\text{HF}}$

\[
\Delta H^\circ_{298} = \left[ \Delta H^\circ_{\text{H} (g)} + \Delta H^\circ_{\text{F} (g)} \right] - \left[ \Delta H^\circ_{\text{HF}_{(g)}} \right]
\]

- $\text{BE for HF}$
- $\Delta H^\circ_{298} = 568.0 \text{ kJ} \leftarrow \text{BE for HF}$

---

- *Example 15-10:* Calculate the average N-H bond energy in ammonia, NH$_3$.

  *You do it!*
Bond Energies

\[ \text{NH}_3(g) \rightarrow \text{N}(g) + 3 \text{H}(g) \quad \Delta H_{298}^o = 3 \text{BE}_{\text{N-H}} \]

\[ \Delta H_{298}^o = \left[ \Delta H_{f}^o(\text{N}(g)) + 3 \Delta H_{f}^o(\text{H}(g)) \right] - \left[ \Delta H_{f}^o(\text{NH}_3(g)) \right] \]

\[ \Delta H_{298}^o = \left[ (472.7) + 3(218) \right] - \left[ -46.11 \right] \text{kJ} \]

\[ \Delta H_{298}^o = 1173 \text{ kJ} \]

average BE \(_{\text{N-H}} = \frac{1173 \text{ kJ}}{3} = 391 \text{ kJ/mol N-H bonds} \]

Changes in Internal Energy, \( \Delta E \)

• The internal energy, \( E \), is all of the energy contained within a substance.
  – This function includes all forms of energy such as kinetic, potential, gravitational, electromagnetic, etc.
  – The First Law of Thermodynamics states that the change in internal energy, \( \Delta E \), is determined by the heat flow, \( q \), and the work, \( w \).

Changes in Internal Energy, \( \Delta E \)

\[ \Delta E = E_{\text{products}} - E_{\text{reactants}} \]

\[ \Delta E = q + w \]

\( q > 0 \) if heat is absorbed by the system.

\( q < 0 \) if heat is absorbed by the system.

\( w > 0 \) if the surroundings do work on the system.

\( w < 0 \) if the system does work on the surroundings.
Changes in Internal Energy, $\Delta E$

- $\Delta E$ is **negative** when energy is released by a system undergoing a chemical or physical change.
  - Energy can be written as a product of the process.

$$C_3H_8(g) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l) + 3.516 \times 10^3 \text{ kJ}$$

$$\Delta E = -3.516 \times 10^3 \text{ kJ}$$

Changes in Internal Energy, $\Delta E$

- $\Delta E$ is **positive** when energy is absorbed by a system undergoing a chemical or physical change.
  - Energy can be written as a reactant of the process.

$$5CO_2(g) + 6H_2O(l) + 3.516 \times 10^3 \text{ kJ} \rightarrow C_3H_8(g) + 8O_2(g)$$

$$\Delta E = +3.516 \times 10^3 \text{ kJ}$$

Changes in Internal Energy, $\Delta E$

- Example 15-12: If 1200 joules of heat are added to a system in energy state $E_1$, and the system does 800 joules of work on the surroundings, what is the:

1. energy change for the system, $\Delta E_{ SYS}$?

$$\Delta E = E_2 - E_1 = q + w$$

$$\Delta E = 1200 \text{ J} + (-800 \text{ J})$$

$$\Delta E = 400 \text{ J}$$

$$\Delta E_{SYS} = + 400 \text{ J}$$
Changes in Internal Energy, $\Delta E$

2. energy change of the surroundings, $\Delta E_{\text{surr}}$?

\[ \Delta E_{\text{surr}} = -400 \text{ J} \]

3. energy of the system in the new state, $E_2$?

\[ \Delta E_{\text{sys}} = E_2 - E_1 \]

\[ E_2 = E_1 + \Delta E_{\text{sys}} \]

\[ = E_1 + 400 \text{ J} \]

• In most chemical and physical changes, the only kind of work is pressure-volume work.

• Pressure is force per unit area.

\[ P = \frac{\text{force}}{\text{area}} = \frac{F}{d^2} \]
Changes in Internal Energy, $\Delta E$

- Volume is distance cubed.
  \[ V = d^3 \]
- $P \Delta V$ is a work term, i.e., the same units are used for energy and work.
  \[ P \Delta V = \left( \frac{F}{d^2} \right) \left( d^3 \right) = F \times d \quad \text{which is work} \]

Relationship of $\Delta H$ and $\Delta E$

- The total amount of heat energy that a system can provide to its surroundings at constant temperature and pressure is given by
  \[ \Delta H = \Delta E + P \Delta V \]
  - which is the relationship between $\Delta H$ and $\Delta E$.
- $\Delta H$ = change in enthalpy of system
- $\Delta E$ = change in internal energy of system
- $P \Delta V$ = work done by system

Relationship of $\Delta H$ and $\Delta E$

- At the start of Chapter 6 we defined $\Delta H = q_p$.
- Here we define $\Delta H = \Delta E + P \Delta V$.
  - Are these two definitions compatible?
- Remember $\Delta E = q + w$.
- We have also defined $w = -P \Delta V$.
  - Thus $\Delta E = q + w = q - P \Delta V$.
- Consequently, $\Delta H = q - P \Delta V + P \Delta V = q$.
  - At constant pressure $\Delta H = q_p$. 
Relationship of $\Delta H$ and $\Delta E$

• For reactions in which the volume change is very small or equal to zero.
  
  For small volume changes,
  
  $\Delta V \approx 0$ and $P \Delta V \approx 0$.
  
  Since $\Delta H = \Delta E + P \Delta V$ then
  
  $\Delta H \approx \Delta E$.
  
  For no volume change,
  
  $\Delta H = \Delta E$.

Relationship of $\Delta H$ and $\Delta E$

• Change in enthalpy, $\Delta H$, or heat of reaction is amount of heat absorbed or released when a reaction occurs at constant pressure.

• The change in energy, $\Delta E$, is the amount of heat absorbed or released when a reaction occurs at constant volume.

• How much do the $\Delta H$ and $\Delta E$ for a reaction differ?
  
  The difference depends on the amount of work performed by the system or the surroundings.

Relationship of $\Delta H$ and $\Delta E$

$\Delta H^o = -3523 \text{ kJ/mol}$ for the combustion of n-pentane, $n$-C$_5$H$_{12}$. Combustion of one mol of n-pentane at constant pressure releases 3523 kJ of heat. What are the values of the work term and $\Delta E$ for this reaction?

$$C_5H_{12(g)} + 8 O_{2(g)} \rightarrow 5 CO_{2(g)} + 6 H_2O_{(l)}$$
Relationship of $\Delta H$ and $\Delta E$

- Determine the work done by this reaction. **You do it!**

$$C_6H_{12}(l) + 8 O_2(g) \rightarrow 5 CO_2(g) + 6 H_2O(l)$$

Since $\Delta H^\circ = -3523 \text{ kJ/mol}$, we know that $T = 298 \text{ K}$.

$w = -P\Delta V = -(\Delta n_g)RT$

$\Delta n_g = 5 - 8 \text{ mol} = -3 \text{ mol}$

$w = -(3 \text{ mol})(8.314 \text{ J/mol K})(298 \text{ K}) = 7433 \text{ J} = 7.433 \text{ kJ}$

Relationship of $\Delta H$ and $\Delta E$

- Now calculate the $\Delta E$ for this reaction from the values of $\Delta H$ and $w$ that we have determined.

$\Delta H = \Delta E + P\Delta V \therefore \Delta E = \Delta H - P\Delta V$

since $w = -P\Delta V = 7.433 \text{ kJ}$

then $P\Delta V = -7.433 \text{ kJ}$

$\Delta E = -3523 \text{ kJ} - (-7.433 \text{ kJ}) = -3516 \text{ kJ}$