Big Idea 5: Thermodynamics

The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter.

When all else fails, remember that $\Delta$ means change, final minus initial, or products minus reactants. That will allow you to calculate $\Delta G$, $\Delta H$, $\Delta S$, $\Delta E$, and anything else $\Delta$.

LO 5.1 The student is able to create or use graphical representations in order to connect the dependence of potential energy to the distance between atoms and factors, such as bond order (for covalent interactions) and polarity (for intermolecular interactions), which influence the interaction strength.

Example:

<table>
<thead>
<tr>
<th>$V(R)$</th>
<th>Does the graph on the left show the relationship between like charged particles or oppositely charged particles? Justify your response.</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Graph]</td>
<td>Like charged particles - Potential energy $\uparrow$ as $R$ $\downarrow$</td>
</tr>
</tbody>
</table>

LO 5.2 The student is able to relate temperature to the motions of particles, either via particulate representations, such as drawings of particles with arrows indicating velocities, and/or via representations of average kinetic energy and distribution of kinetic energies of the particles, such as plots of the Maxwell-Boltzmann distribution.

The graph to the right is a Maxwell-Boltzmann distribution for noble gases. Describe how the graph shows which element has the fastest average speed.

Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases

- $^4$He
- $^{20}$Ne
- $^{32}$Ar
- $^{132}$Xe

Probability density ($\Delta v$)

0.001 0.002 0.003 0.004

Speed (m/s)

0 500 1000 1500 2000 2500

- Slowest
- Fastest
LO 5.3 The student can generate explanations or make predictions about the transfer of thermal energy between systems based on this transfer being due to a kinetic energy transfer between systems arising from molecular collisions.

Example:

A student is studying the transfer of heat from a hot piece of metal in a cold cup of water. If the measured amount of heat transferred from the hot metal to the cold water is lower than expected, which of the following is a plausible explanation?

a) The water was stirred after the metal was added  
  b) The calorimeter absorbed heat from the transfer  
  c) The water absorbed too much heat from the metal  
  d) The heat was transferred from the cold water to the hot metal

LO 5.4 The student is able to use conservation of energy to relate the magnitudes of the energy changes occurring in two or more interacting systems, including identification of the systems, the type (heat versus work), or the direction of energy flow.

Example:

According to the first law of thermodynamics, the energy of the universe is constant. Does this mean that \( \Delta E \) is always equal to zero?

a. Yes, \( \Delta E = 0 \) at all times, which is why \( q = -w \)  
   b. No, \( \Delta E \) does not always equal zero, but this is only due to factors like friction and heat.  
   c. No, \( \Delta E \) does not always equal zero because it refers to the system's internal energy, which is affected by heat and work.  
   d. No, \( \Delta E \) never equals zero because work is always being done on the system or by the system

LO 5.5 The student is able to use conservation of energy to relate the magnitudes of the energy changes when two nonreacting substances are mixed or brought into contact with one another.

Example:

You take 243.8 g of a solid at 30.0°C and let it melt in 425 g of water. The water temperature decreases from 85.1°C to 30.0°C. Calculate the heat of fusion of this solid.

\[ q = m \cdot H_f \quad \text{or} \quad m \cdot L \Delta T \]

\( (243.8 \text{ g}) \cdot H_f = (425 \text{ g}) \cdot (4.18 \text{ J/}^\circ \text{C} \cdot \text{g}) \cdot (55.1^\circ \text{C}) \)

\[ L = \frac{1}{401.5^\circ \text{C}} \]
LO 5.6 The student is able to use calculations or estimations to relate energy changes associated with heating/cooling a substance to the heat capacity, relate energy changes associated with a phase transition to the enthalpy of fusion/vaporization, relate energy changes associated with a chemical reaction to the enthalpy of the reaction, and relate energy changes to PΔV work.

Example:

How much heat is required to raise the temperature of a 4.48-g sample of iron (specific heat = 0.450 J/g°C) from 25.0°C to 79.8°C?

a. 198 J
b. 246 J
c. 546 J
d. 661 J

LO 5.7 The student is able to design and/or interpret the results of an experiment in which calorimetry is used to determine the change in enthalpy of a chemical process (heating/cooling, phase transition, or chemical reaction) at constant pressure.

A student is given the task of determining the enthalpy of reaction for the reaction between HCl(aq) and NaOH(aq). A student is given two solutions, 75.0 mL of 1.00 M HCl and 75.0 mL of 1.00 M NaOH, each at 25.0°C. The student pours the solutions into an insulated cup, stirs the mixture, covers the cup, and records the maximum temperature of the mixture. The student calculates the amount of heat evolved in the experiment to be 4.1 kJ. Calculate the student’s experimental value for the enthalpy of reaction, in kJ/mol, as

\[ \frac{0.075 \text{ L} \times 1.00 \text{ mol HCl}}{2} = 0.075 \text{ mol HCl} \]

\[ -4.1 \text{ kJ} \cdot \text{mol}^{-1} \]

LO 5.8 The student is able to draw qualitative and quantitative connections between the reaction enthalpy and the energies involved in the breaking and formation of chemical bonds.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Enthalpy (KJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>+347</td>
</tr>
<tr>
<td>C-H</td>
<td>+423</td>
</tr>
<tr>
<td>O=O</td>
<td>+498</td>
</tr>
<tr>
<td>O-H</td>
<td>+484</td>
</tr>
<tr>
<td>C=O (in CO₂)</td>
<td>+805</td>
</tr>
<tr>
<td>C-O</td>
<td>+358</td>
</tr>
<tr>
<td>H-H</td>
<td>+436</td>
</tr>
<tr>
<td>C=C</td>
<td>+612</td>
</tr>
</tbody>
</table>

Using the table of bond enthalpies to the left, calculate the ΔH° for the following reaction:

\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

\[ \begin{align*}
4(\text{C}-\text{H}) + 2(\text{O}=\text{O}) & - [2(\text{C}=\text{O}) + 4(\text{H}+\text{O})] \\
4(413) + 2(154) & - [2(501) + 4(464)] \\
2618 & - 3466 \\
\Delta H^0 & = -848 \text{ KJmol}^{-1}
\end{align*} \]
LO 5.9 The student is able to make claims and/or predictions regarding relative magnitudes of the forces acting within collections of interacting molecules based on the distribution of electrons within the molecules and the types of intermolecular forces through which the molecules interact.

Example:

The normal vapor pressure of ethyl alcohol (CH₃CH₂OH) is 59.0 mm Hg, while the normal vapor pressure of acetic acid (CH₃COOH) is 12.3 mm Hg. Account for the differences in vapor pressure. You must discuss both of the substances in your answer.

*Acetic acid has lower vapor pressure b/c it has stronger IMFs than ethanol. Acetic acid has 1 lone pair, dipole-dipole, and H-bonding while ethanol has 1 lone pair, one dipole-dipole (C-O), and H-bonding.*

LO 5.10 The student can support the claim about whether a process is a chemical or physical change (or may be classified as both) based on whether the process involves changes in intramolecular versus intermolecular interactions.

Example: *(physical change = intermolecular forces)*

When water boils, steam forms. When baking soda and vinegar are mixed, carbon dioxide gas is formed. Which change is physical and which is chemical? Justify your response by describing the changes in intramolecular forces and intermolecular forces.

*(chemical change = intramolecular bonds)*

LO 5.11 The student is able to identify the noncovalent interactions within and between large molecules, and/or connect the shape and function of the large molecule to the presence and magnitude of these interactions.

In the illustration on the right, there are 2 nucleic acid chains interacting. Describe why Adenine is interacting only with Thymine and why Guanine is only interacting with Cytosine, in terms of intermolecular forces:

*Adenine has 1 lone pair, Tymine has 2 lone pairs.*

*Guanine and Cytosine 0-0 x 3*
LO 5.12 The student is able to use representations and models to predict the sign and relative magnitude of the entropy change associated with chemical or physical processes.

Example:

Using the following data, calculate the $\Delta S^0$ for the reaction: $2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (l)$

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta S^0$ (J/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2 (g)$</td>
<td>130.58</td>
</tr>
<tr>
<td>$\text{O}_2 (g)$</td>
<td>205.0</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} (l)$</td>
<td>69.91</td>
</tr>
</tbody>
</table>

$$2(69.91 \text{ J/K}) - [2(130.58 \text{ J/K}) + 205 \text{ J/K}] = -326.34 \text{ J/K}$$

LO 5.13 The student is able to predict whether or not a physical or chemical process is thermodynamically favored by determination of (either quantitatively or qualitatively) the signs of both $\Delta H^0$ and $\Delta S^0$, and calculation or estimation of $\Delta G^0$ when needed.

Example:

$\text{N}_2 (g) + 3 \text{F}_2 (g) \rightarrow 2 \text{NF}_3 (g)$ \hspace{1cm} $\Delta H^0_{298} = -264 \text{ kJ/mol}$ \hspace{1cm} $\Delta S^0_{298} = -278 \text{ J/K mol}$

(a) Calculate the value of the standard free energy change, $\Delta G^0_{298}$, for the reaction.

(b) Is the reaction spontaneous at 298 K?

$$\Delta G = \Delta H - T \Delta S = (-264 \text{ kJ/mol}) - (298 (0.27 \text{ kJ/K}))$$

LO 5.14 The student is able to determine whether a chemical or physical process is thermodynamically favorable by calculating the change in standard Gibbs free energy.

Example:

For a certain chemical reaction, $\Delta H^0 = -35.4 \text{ kJ}$ and $\Delta S^0 = -85.5 \text{ J/K}$.

a) Is the reaction endothermic or exothermic?

b) Does the reaction lead to an increase or decrease in the randomness or disorder of the system?

c) Calculate $\Delta G^0$ for the reaction at 298 K.

d) Is the reaction spontaneous?

$$\Delta G = \Delta H - T \Delta S = -35.4 \text{ kJ/mol} - (298 \text{ K})(-85.5 \text{ J/K})$$

$$\Delta G = -9.9 \text{ kJ/mol}$$
LO 5.15 The student is able to explain how the application of external energy sources or the coupling of favorable with unfavorable reactions can be used to cause processes that are not thermodynamically favorable to become favorable.

Example:

It is industrially favorable to be able to turn iron(III) oxide into iron, however it is not thermodynamically favored. Below are listed thermochemical equations, with corresponding $\Delta G^0$ values. Rearrange them in a way that will produce a reaction that is thermodynamically favored to convert iron(III) oxide into iron.

$$\text{Fe}_2\text{O}_3(s) \rightarrow 2\text{Fe}(s) + \frac{3}{2} \text{O}_2(g) \quad \Delta G^0 = 740 \text{ kJ/mol}$$

$$3(\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta G^0 = -283 \text{ kJ/mol})$$

$$\text{Fe}_2\text{O}_3(s) + 3(\text{O}_2(g) \rightarrow 2\text{Fe}(s) + 3\text{CO}_2(g) \quad \Delta G = 740 + 3(-283)$$

$$\Delta G = -109 \text{ kJ/mol}$$

LO 5.16 The student can use LeChatelier’s principle to make qualitative predictions for systems in which coupled reactions that share a common intermediate drive formation of a product.

Example:

Consider the following reactions involved in the process of smelting copper from its ore:

$$\text{Cu}_2\text{S}(s) \rightarrow 2\text{Cu}(s) + \text{S}(s) \quad \Delta G^0 = +86.2 \text{ kJ}$$

$$\text{S}(s) + \text{O}_2(g) \rightarrow \text{SO}_2(g) \quad \Delta G^0 = -300.1 \text{ kJ}$$

The first step of the process above is not thermodynamically favored; heat would need to be added to drive the reaction. Describe how LeChatelier’s Principle, along with coupling reactions, can be used to help favor producing Copper from its ore.

If $\text{Cu}_2\text{S}$ is heated in the presence of oxygen, the sulfur produced from the first reaction will be removed by the second, driving the first reaction forward.

LO 5.17 The student can make quantitative predictions for systems involving coupled reactions that share a common intermediate, based on the equilibrium constant for the combined reaction.

Example:

Zinc hydroxide is not very soluble in water. The $K_{sp}$ for $\text{Zn(OH)}_2$ is $5 \times 10^{-17}$. If a strong acid were added to a saturated solution of $\text{Zn(OH)}_2$, the concentration of $\text{Zn}^{2+}$ would increase. Explain this in terms of equilibrium and coupled reactions.

$$2\text{Zn(OH)}_2(s) \rightleftharpoons 2\text{Zn}^{2+}(aq) + 4\text{OH}^-(aq) \quad \text{If H}^+ \text{ added, second reaction removes OH}^{-} \text{ which drives first reaction forward.}$$
LO 5.18 The student can explain why a thermodynamically favored chemical reaction may not produce large amounts of product (based on consideration of both initial conditions and kinetic effects), or why a thermodynamically unfavored chemical reaction can produce large amounts of product for certain sets of initial conditions.

Example:

Hydrogen gas burns in air according to the equation below:

\[ 2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (l) \]

The \( \Delta G^\circ \) for the above reaction is -474 kJ. Explain why a balloon of hydrogen does not spontaneously ignite when exposed to air.

*Activation energy is too high.*