Chapter Outline

- 9.1 Energy as a Reactant or Product
- 9.2 Transferring Heat and Doing Work
- 9.3 Enthalpy and Enthalpy Changes
- 9.4 Heating Curves and Heat Capacity
- 9.5 Heats of Reaction and Calorimetry
- 9.6 Hess’s Law and Standard Heats of Reactions
- 9.7 Heats of Reactions from Heats of Formation and Bond Energies
- 9.8 Applications
Definitions

- **Thermodynamics**: The study of energy and its transformation

- **Thermochemistry**: The study of the relation between chemical reactions and changes in energy
  - Thermochemical equation:
    - $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + \text{energy}$

- **Thermochemical Equilibrium**: A condition in which temperature is uniform throughout a material
Energy of Chemical Reactions

$2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) + \text{energy}$

Graph showing the energy change during the reaction with progress of the reaction.
First Law of Thermodynamics

- Law of Conservation of Energy:
  - Energy cannot be created or destroyed
  - It can be converted from one form to another
    - Potential energy $\rightarrow$ kinetic energy
    - Chemical energy $\rightarrow$ heat
** Terminology **

- **System**: The part of the universe that is the focus of a thermodynamic study
  - Isolated / open / closed

- **Surroundings**: Everything in the universe that is not part of the system

- Universe = System + Surroundings
Internal Energy

- **Internal Energy:**
  - **State Function:** Depends only on total KE and PE of all components of the system
  - $\Delta E = E_{\text{final}} - E_{\text{initial}}$

- $\Delta E = q + w$
  - $\Delta E =$ change in system’s internal energy
  - $q =$ heat or thermal energy, $w =$ work
Energy Flow Diagrams

- **Surroundings**
  - Heat in: $q > 0$
  - Heat out: $q < 0$

- **System**
  - Work done on system: $w > 0$
  - Work done by system: $w < 0$

$$\Delta E = q + w$$
### TABLE 9.1 Flows of Heat and Work and Their Impact on $E_{sys}$

<table>
<thead>
<tr>
<th>Processes That Increase $E_{sys}$</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surroundings hotter than the system, so heat flows into the system</td>
<td>$q &gt; 0$</td>
</tr>
<tr>
<td>Surroundings do work on the system</td>
<td>$w &gt; 0$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Processes That Decrease $E_{sys}$</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>System hotter than its surroundings, so heat flows into surroundings</td>
<td>$q &lt; 0$</td>
</tr>
<tr>
<td>System does work on its surroundings</td>
<td>$w &lt; 0$</td>
</tr>
</tbody>
</table>
Types of Molecular Motion

- Types of molecular motion
  a) translational
  b) rotational
  c) vibrational
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• 9.8 Applications
Types of Systems

(a) Isolated system

(b) Closed system

(c) Open system
Heat Flow

- **Exothermic** process: Heat flows out of system to surroundings \((q < 0)\)

- **Endothermic** process: Heat flows into system from surroundings \((q > 0)\)
**P-V Work**

- **Work:**
  - \( w = -P\Delta V \)
    - where \( P \) = pressure, \( \Delta V \) = change in volume
  - Work done by the system = energy lost by the system, \( w < 0 \)
  - Example: Expansion of a gas

- \( \Delta E = q + w \)
  - \( = q + ( -P\Delta V ) \)
  - \( = q - P\Delta V \)
Units of Energy

• Energy = heat and/or work (same units!)

• Calorie (cal)
  • Amount of heat necessary to raise the temperature of 1 g of water by 1°C

• Joule (J)
  • The SI unit of energy
  • 4.184 J = 1 cal
  • 101.32 J = 1 L·atm
Practice: Calculating Work

Calculate the work in L·atm and joules associated with the expansion of a gas in a cylinder from 54 L to 72 L at a constant external pressure of 18 atm.

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:
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- 9.8 Applications
Enthalpy and Enthalpy Changes

- **Enthalpy:** $H = E + PV$
- **Enthalpy change:** $\Delta H = \Delta E + P\Delta V$
- $\Delta H = $ energy absorbed by reactants (endothermic), or energy given off by products (exothermic) for a reaction carried out at constant pressure

$$\Delta H = q_P = \Delta E + P\Delta V$$

- $\Delta H > 0$, endothermic; $\Delta H < 0$, exothermic
- Subscripts for $\Delta H$ indicate specific processes
Enthalpy Change

• Enthalpy of fusion, $\Delta H_{\text{fus}}$: Energy required to convert a given amount (either in mol or g) of solid at its melting point into liquid state

• Enthalpy of vaporization, $\Delta H_{\text{vap}}$: Energy required to convert a given amount (either in mol or g) of liquid at its boiling point into vapor state
Enthalpy Change

Water vapor

Endothermic

\[ \Delta H_{\text{vap}} = +40.67 \text{ kJ/mol} \]

\[ \Delta H_{\text{cond}} = -40.67 \text{ kJ/mol} \]

Liquid water

\[ \Delta H_{\text{fus}} = +6.01 \text{ kJ/mol} \]

\[ \Delta H_{\text{solid}} = -6.01 \text{ kJ/mol} \]

Ice

Exothermic
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- 9.8 Applications
Heating Curve

- **Solid**
- **Solid and liquid**
- **Liquid**
- **Boiling point**
- **Melting point**
- **Liquid and vapor**

Temperature (°C)

Heat added
Heating Curve

Heat in $\rightarrow$ phase change
Heat Capacities

• **Heat capacity** \((C_p)\)
  • Quantity of energy needed to raise the temperature of an object by 1°C (at constant P)

• **Molar heat capacity** \((c_p)\)
  • Quantity of energy required to raise the temperature of 1 mol of a substance by 1°C
    • \(q = n c_p \Delta T \quad (c_p = J / (\text{mol} \cdot ^\circ \text{C})\)

• **Specific heat** \((c_s)\)
  • Quantity of energy required to raise the temperature of 1 g of a substance by 1°C (at constant P)
    • \(q = m c_s \Delta T \quad (c_s = J / (\text{g} \cdot ^\circ \text{C})\)
Heating Curve

Heat in $\rightarrow$ Kinetic energy
<table>
<thead>
<tr>
<th>Sub substance</th>
<th>Phase</th>
<th>$c_p$ [J/(g \cdot °C)]</th>
<th>$c_{p,n}$ [J/(mol \cdot °C)]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>(s)</td>
<td>0.897</td>
<td>24.2</td>
</tr>
<tr>
<td>Carbon (graphite)</td>
<td>(s)</td>
<td>0.71</td>
<td>8.5</td>
</tr>
<tr>
<td>Chromium</td>
<td>(s)</td>
<td>0.449</td>
<td>23.3</td>
</tr>
<tr>
<td>Copper</td>
<td>(s)</td>
<td>0.385</td>
<td>24.5</td>
</tr>
<tr>
<td>Gold</td>
<td>(s)</td>
<td>0.129</td>
<td>25.4</td>
</tr>
<tr>
<td>Iron</td>
<td>(s)</td>
<td>0.45</td>
<td>25.1</td>
</tr>
<tr>
<td>Lead</td>
<td>(s)</td>
<td>0.129</td>
<td>26.7</td>
</tr>
<tr>
<td>Silver</td>
<td>(s)</td>
<td>0.233</td>
<td>25.1</td>
</tr>
<tr>
<td>Tin</td>
<td>(s)</td>
<td>0.227</td>
<td>26.9</td>
</tr>
<tr>
<td>Titanium</td>
<td>(s)</td>
<td>0.523</td>
<td>25.0</td>
</tr>
<tr>
<td>Zinc</td>
<td>(s)</td>
<td>0.387</td>
<td>25.3</td>
</tr>
<tr>
<td><strong>Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>(s)</td>
<td>0.703</td>
<td>42.2</td>
</tr>
<tr>
<td>Water (−10°C)</td>
<td>(s)</td>
<td>2.11</td>
<td>38.0</td>
</tr>
<tr>
<td>Water (25°C)</td>
<td>(ℓ)</td>
<td>4.18</td>
<td>75.3</td>
</tr>
<tr>
<td>Water (102°C)</td>
<td>(g)</td>
<td>1.89</td>
<td>34.1</td>
</tr>
<tr>
<td>Ammonia</td>
<td>(ℓ)</td>
<td>4.75</td>
<td>80.9</td>
</tr>
<tr>
<td><strong>Mixture</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air*</td>
<td>(g)</td>
<td>1.003</td>
<td>29.1</td>
</tr>
</tbody>
</table>

*Dry air at 0°C and 1 atmosphere of pressure.
Heat Transfer Calculations

• Transfer of heat between systems
• Calculated based on the first law of thermodynamics

\[ q_{\text{lost}} = -q_{\text{gained}} \]
Cooling Curves

Heat transfer: Ice
@ -8.0°C to water
@ 0.0 °C

1. Temp change:
   \[ q_1 = n c_p \Delta T \]

2. Phase change:
   \[ q_2 = n \Delta H_{fus} \]
During a strenuous workout, a student generates 2000 kJ of heat energy. What mass of water would have to evaporate from the student’s skin to dissipate this much heat?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:
You heated 500 mL chicken broth to 99°C, which is too hot to consume. How many mL of cold chicken broth (12°C) must you add to the hot broth to get the temperature of the mixture down 37°C? (assume $c_{broth} = 4.184 \text{ J/g}^\circ\text{C}, D = 1.0 \text{ g/mL}$)

- Collect and Organize
- Analyze:
- Solve:
- Think about It:
Chapter Outline

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• 9.4 Heating Curves and Heat Capacity
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• 9.8 Applications
Calorimetry

- **Calorimetry**
  - Experimental measurement of heat transferred during a physical change or chemical change

- **Calorimeter**
  - Device used to measure the absorption or release of heat by a physical change or chemical process
  - Closed system! \[-q_{\text{system}} = q_{\text{calorimeter}}\]
Heat of Reaction

- Bomb calorimeter:
  - Constant-volume device used to measure the energy released during a combustion reaction
  - Heat produced by reaction = heat gained by calorimeter
  - $q_{\text{cal}} = C_{\text{cal}} \Delta T = -\Delta H_{\text{rxn}}$
When 25 mL of 0.100 M reactant A are added to 25 mL of 0.100 M reactant B in a coffee cup calorimeter at 18.5°C, the temperature of the mixture increases to 25.0°C. If the densities of the two solutions are 1.00 g/mL, what is the $\Delta H$ per mol of A reacted? Assume the heat capacity of the calorimeter is 0 J/°C.

\[ \text{A(aq) + B(aq)} \rightarrow \text{products} \]

• Collect and Organize:
• Analyze:
• Solve:
• Think about It:
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• 9.2 Transferring Heat and Doing Work
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• 9.4 Heating Curves and Heat Capacity
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• 9.6 Hess’s Law and Standard Heats of Reactions
• 9.7 Heats of Reactions from Heats of Formation and Bond Energies
• 9.8 Applications
Hess’s Law

• Hess’s Law of Constant Heat of Summation:
  • The $\Delta H^\circ_{\text{rxn}}$ for a reaction that is the sum of two or more reactions is equal to the sum of the $\Delta H^\circ_{\text{rxn}}$ values of the constituent reactions.

1. $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g)$ \hspace{1cm} $\Delta H_1$
2. $\text{CO}(g) + 3\text{H}_2(g) + \text{H}_2\text{O}(g) \rightarrow 4\text{H}_2(g) + \text{CO}_2(g)$ \hspace{1cm} $\Delta H_2$
3. $\text{CH}_4(g) + 2\text{H}_2\text{O}(g) \rightarrow 4\text{H}_2(g) + \text{CO}_2(g)$ \hspace{1cm} $\Delta H_3$

$\Delta H_3 = \Delta H_1 + \Delta H_2$
1. If a reaction is reversed, $\Delta H$ sign changes.

\[ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \quad \Delta H = 180 \text{ kJ} \]

\[ 2\text{NO}(g) \rightarrow \text{N}_2(g) + \text{O}_2(g) \quad \Delta H = -180 \text{ kJ} \]

2. If the coefficients of a reaction are multiplied by an integer, $\Delta H$ is multiplied by the same integer.

\[ 6\text{NO}(g) \rightarrow 3\text{N}_2(g) + 3\text{O}_2(g) \quad \Delta H = 3(-180 \text{ kJ}) \]

\[ \Delta H = -540 \text{ kJ} \]
Using the following data, calculate the $\Delta H_{\text{rxn}}$ for the following reaction.

$$\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$$

Collect and Organize:
- $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(\ell)$ $\Delta H = -285.8 \text{ kJ}$
- $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(\ell) + 2\text{CO}_2(g)$ $\Delta H = -1411 \text{ kJ}$
- $\text{C}_2\text{H}_6(g) + \frac{7}{2}\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(\ell) + 2\text{CO}_2(g)$ $\Delta H = -1560 \text{ kJ}$

Analyze:

Solve:

Think about It:
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• 9.8 Applications
Enthalpy of Formation, $\Delta H_f^o$

- The **standard enthalpy of formation**, $\Delta H_f^o$
  - The enthalpy change for the process of forming 1 mol of a substance from its constituent elements in their **standard states** *
  - e.g., formation reaction for NO:
    - $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO(g)$
    - $\Delta H_{rxn} = \Delta H_f^o (NO)$
  - (*The standard state of an element is its most stable form under 1atm pressure and 25°C.*)
Standard Enthalpy of Reactions

- **Standard enthalpy of reaction** ($\Delta H^\circ_{\text{rxn}}$)
  - Enthalpy change associated with a reaction that takes place under standard conditions
  - Also called standard heat of reaction
- **Calculated from** $\Delta H_f^\circ$ (see Appendix 4)
  - $\Delta H^\circ_{\text{rxn}} = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$
Methods of Determining $\Delta H^o_{\text{rxn}}$

1. From calorimetry experiments:
   - $\Delta H^o_{\text{rxn}} = - C_{\text{cal}} \Delta T$

2. From enthalpies of formation:
   - $\Delta H^o_{\text{rxn}} = \sum n_p \Delta H^o_f(\text{products}) - \sum n_r \Delta H^o_f(\text{reactants})$
   - $\Delta H^o_f$ values listed in Appendix 4.

3. Using Hess’s law (Section 9.6)
Use Table 9.4 to calculate an approximate enthalpy of reaction for
\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:
Bond Energies

• **Bond Energy**: Enthalpy change that occurs when 1 mol of bonds in the gas phase are broken

• Bond energy is also a measure of the bond strength. The larger the bond energy, the stronger the bond.
Bond Energies

\[
\begin{align*}
\text{Energy in} & : 4(+413 \text{ kJ}) + 2(+498 \text{ kJ}) \\
\text{Energy out} & : 2(-799 \text{ kJ}) + 4(-463 \text{ kJ}) \\
\text{Reactants:} & \quad \text{CH}_4 + 2 \text{O}_2 \\
\text{Products:} & \quad \text{CO}_2 + 2 \text{H}_2\text{O} \\
\Delta H_{\text{rxn}} & = -802 \text{ kJ} \\
& \quad -3450 \text{ kJ}
\end{align*}
\]
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• 9.8 Applications
Fuel Values

• **Fuel value** = Energy released during complete combustion of 1 g of a substance
  
  • \( \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \)
  
  • \( \Delta H^\circ_{\text{comb}} = -802.3 \text{ kJ/mol} \)
  
  • Fuel value = \((802.3 \text{ kJ/mol}) \cdot (1 \text{ mol} / 16.04 \text{ g})\)
  
  • = 50.02 kJ/g

• **Fuel density** = Energy released during complete combustion of 1 L of a liquid fuel
# Fuel Values

<table>
<thead>
<tr>
<th>Substance</th>
<th>MW (g/mol)</th>
<th>Fuel Value (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4), methane</td>
<td>16.04</td>
<td>54.0</td>
</tr>
<tr>
<td>C(_3)H(_8), propane</td>
<td>44.09</td>
<td>50.3</td>
</tr>
<tr>
<td>C(<em>5)H(</em>{12}), pentane</td>
<td>72.14</td>
<td>48.8</td>
</tr>
<tr>
<td>C(<em>9)H(</em>{20}), avg. gasoline compound</td>
<td>128.25</td>
<td>47.4</td>
</tr>
<tr>
<td>C(<em>{14})H(</em>{30}), avg. diesel compound</td>
<td>198.37</td>
<td>44.8</td>
</tr>
</tbody>
</table>
Food Values

- Quantity of energy produced when a material consumed by an organism for sustenance is burned completely
  - Determined by bomb calorimetry
  - Nutritional calorie = 1 kcal = 4.184 kJ

<table>
<thead>
<tr>
<th>Food Category</th>
<th>Food Value (Cal or kcal/g)</th>
<th>Food Value (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proteins</td>
<td>4.0</td>
<td>16.7</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>4.0</td>
<td>16.7</td>
</tr>
<tr>
<td>Fats</td>
<td>9.0</td>
<td>37.7</td>
</tr>
</tbody>
</table>
Click here to launch the ChemTours website
This concludes the Lecture PowerPoint presentation for Chapter 9