Chapter 5 and Chapter 6.6-6.8

Energy, Thermodynamics, Kinetics and Equilibrium
Energy

- **Heat**: energy contained in an object
  - Sum of kinetic and potential energies
  - Measured by the temperature
    - Relative average amount of heat in the system
    - Fahrenheit, Celsius, Kelvin

- **Kinetic Energy**: energy of motion.
  - Molecules rub together (friction)
  - Get hotter….add heat move faster

- **Potential Energy**: energy contained in stored form
  - Chemical bonds

\[ E = \frac{1}{2} mv^2 \]
The Laws of Thermodynamics

- **Thermodynamics**: study of the production and flow of heat and its conversion to **work** (useful energy)

- **1st law**: Energy can be neither created nor destroyed
  - It can only be moved from one place to another
  - Heat added to a system (+) must be taken from somewhere else (-)

- **2nd law**: Heat flows from high temperature to low temperature naturally until “thermal equilibrium”

- **3rd law**: The temperature of objects cannot reach absolute zero.
  - Absolute zero (0 K or –273 C) is the temperature where all motion ceases.
  - Thus, the universe becomes more disordered
Energy

- Units for Heat—Joule (J) or calorie (cal)
- 1 calorie = the amount of heat required to raise the temperature of 1 g of water by 1°C at 1 atm of pressure
- 1 calorie = 4.186 J
- NUTRITIONAL CALORIES ARE KILOCALORIES!
  - 1 Cal = 1 kcal = 1000 calories = 4.18 kJ = 41,800 J
- The number of Calories that an item (food) contains is measured in a Calorimeter
  - Item is burned inside a steel chamber with water on the outside
  - The change in temperature of the water is used to calculate the number of Calories
Calculations involving Specific Heat and Calorimetry

- Specific Heat: the amount of heat required to raise the temperature of 1 g of a substance 1°C
- Different for every element

\[ S.H. = \frac{\text{amt of heat}}{1 \text{ g} \times 1^\circ \text{C}} \]

Heat (cal) = (mass) \times (Temp. Change) \times S.H.

\[ g \times ^\circ \text{C} \times \frac{\text{cal}}{1 \text{ g} \times 1^\circ \text{C}} \]

Heat (Joules) = (mass) \times (Temp. Change) \times

\[ g \times ^\circ \text{C} \times \frac{\text{Joules}}{1 \text{ g} \times 1^\circ \text{C}} \]

**Table 5.1  Specific Heats of Some Substances**

<table>
<thead>
<tr>
<th>Substance</th>
<th>(cal/g °C)</th>
<th>(J/g °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.00</td>
<td>4.18</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.58</td>
<td>2.4</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.22</td>
<td>0.92</td>
</tr>
<tr>
<td>Sand</td>
<td>0.19</td>
<td>0.79</td>
</tr>
<tr>
<td>Iron</td>
<td>0.11</td>
<td>0.46</td>
</tr>
<tr>
<td>Copper</td>
<td>0.093</td>
<td>0.39</td>
</tr>
<tr>
<td>Silver</td>
<td>0.057</td>
<td>0.24</td>
</tr>
<tr>
<td>Gold</td>
<td>0.031</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Calculations involving Specific Heat and Calorimetry

- Example 5-1: How much heat, in kcal, is required to heat 100.0 g of water from 20°C to 70°C?

Heat (cal) = (mass) x (Temp. Change) x S.H.

\[ g \times °C \times \frac{cal}{1g \times 1°C} \]

Change in temp = 70°C – 20°C = 50°C

\[ \text{Heat} = 100 \, g \times 1 \times \frac{cal}{g \, °C} \times (50°C) \]

\[ \text{Heat} = 5050 \, cal = 5.050 \, kcal \]
Calorimetry and Nutrition

Example 5-2: how many calories are in a piece of cheesecake that contains 20 g of carbs, 22 g of fat and 5 g of protein?

\[
20 \text{ g carbs} \times \frac{4 \text{kcal}}{\text{g}} = 80 \text{kcal}
\]

\[
5 \text{ g protein} \times \frac{4 \text{kcal}}{\text{g}} = 20 \text{kcal}
\]

\[
22 \text{ g fat} \times \frac{9 \text{kcal}}{\text{g}} = 198 \text{kcal}
\]

Total = 298 kcal = 298 Calories

Caloric Value of foods:
- Carbs: 4 kcal per gram
- Fat = 9 kcal per gram
- Protein = 4 kcal per gram
### Table 5.4  Typical Energy Requirements

<table>
<thead>
<tr>
<th>Age (yr)</th>
<th>Weight (lb)</th>
<th>Mass (kg)</th>
<th>Energy (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Young Adult</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Female (13–19)</td>
<td>115</td>
<td>52</td>
<td>2400</td>
</tr>
<tr>
<td>Male (13–19)</td>
<td>130</td>
<td>59</td>
<td>2980</td>
</tr>
<tr>
<td><strong>Adult</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Female</td>
<td>121</td>
<td>55</td>
<td>2200</td>
</tr>
<tr>
<td>Male</td>
<td>143</td>
<td>65</td>
<td>3000</td>
</tr>
</tbody>
</table>
States of Matter

- Solids

Ice is solid $\text{H}_2\text{O}$
States of Matter

- Solids
- Liquids

Liquid

H₂O
States of Matter

- Solids
- Liquids
- Gases

Steam is gaseous H₂O
<table>
<thead>
<tr>
<th>Property</th>
<th>Solid</th>
<th>Liquid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shape</strong></td>
<td>Has a definite shape</td>
<td>Takes the shape of the container</td>
<td>Takes the shape of its container</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>Has a definite volume</td>
<td>Has a definite volume</td>
<td>Fills the volume of the container</td>
</tr>
<tr>
<td><strong>Arrangement of particles</strong></td>
<td>Fixed, very close</td>
<td>Random, close</td>
<td>Random, far apart</td>
</tr>
<tr>
<td><strong>Interaction between particles</strong></td>
<td>Very strong</td>
<td>Strong</td>
<td>Essentially none</td>
</tr>
<tr>
<td><strong>Movement of particles</strong></td>
<td>Very slow</td>
<td>Moderate</td>
<td>Very fast</td>
</tr>
<tr>
<td><strong>Examples</strong></td>
<td>Ice, salt, iron</td>
<td>Water, oil, vinegar</td>
<td>Water vapor, helium, air</td>
</tr>
</tbody>
</table>

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Intermolecular Attractions

- There are four important intermolecular attractions

1. **Ion-ion interactions**
   - The force of attraction between two oppositely charged ions
   - Highest Melting Points
Intermolecular Attractions

2. **Dipole-dipole interactions**
   
   Attraction between a partially negative atom and a partially positive atom.
   
   Consider BrF a polar molecule.
Intermolecular Attractions

3. **Hydrogen bonding**-special type of Dipole-dipole
   Attraction between H (with a slightly positive charge) and a slightly electronegative atom of O, N, F, Cl, Br, P, S, I
   Consider H₂O a very polar molecule.
4. **Dispersion forces**

- They are the weakest of the intermolecular forces.
- This is the only attractive force in nonpolar molecules.
- A temporary dipole in one atom induces a dipole in other atoms.
- Lowest melting points
### Intermolecular Attractions

<table>
<thead>
<tr>
<th>Type of Force</th>
<th>Typical Bond Strength</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ionic Compounds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic bonds</td>
<td>150–3000 kcal/mole</td>
<td>Na⁺ ⋯ Cl⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl⁻ ⋯ Na⁺</td>
</tr>
</tbody>
</table>

| **Molecular Compounds**                |                       |                    |
| Hydrogen bond (X = F, O, or N)        | 5–10 kcal/mole         |                    |
|                                        |                       | O—H ⋯ O—H          |
|                                        |                       | H                   |
| Dipole–dipole                          | 0.1–1 kcal/mole        |                    |
|                                        |                       | Br—Cl ⋯ Br—Cl      |
| Dispersion forces (temporary shift of electrons) | 0.01 kcal/mole |        |
|                                        |                       | F—F ⋯ F—F          |

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Intermolecular Attractions

- Identify the intermolecular attractive force in each of the following:
  - HCl
  - MgBr$_2$
  - PI$_3$
  - CCl$_4$
  - NH$_3$
  - SiF$_4$
  - HF
  - CH$_3$COOH (more than one force)
Phase Changes

Phase changes increase or decrease the intermolecular forces between atoms.

Heat Absorbed-endothermic
Heat released-exothermic
Heating and Cooling Curves

(a) Heating: Solid → Liquid → Gas
    - Melting point
    - Boiling point
    - Heat added

(b) Cooling: Gas → Liquid → Solid
    - Condensation
    - Freezing
    - Heat removed

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Heating and Cooling Curves
Evaporation

- *Evaporation* is the process in which molecules gain enough kinetic energy to escape from the surface of a liquid and become a gas.
- Evaporation is temperature dependent.
- *Heat of Vaporization* is the amount of heat required to change 1.00 g of a liquid substance to a gas at constant temperature.
- Heat of vaporization has units of J/g.
- *Heat of Condensation* is the reverse of heat of vaporization, phase change from gas to liquid.
The Solid State

Normal Melting Point

- The **normal melting point** is the temperature at which the solid melts (liquid and solid in equilibrium) at exactly 1.00 atm of pressure.
- The melting point increases as the strength of the intermolecular attractions increase.
- The reverse of melting is freezing.
Melting and Freezing
Heat Transfer Involving Solids

Heat of Fusion

- **Heat of fusion** is the amount of heat required to melt one gram of a solid at its melting point at constant temperature.

\[
1.00 \text{ g H}_2\text{O}^{(s)} \text{ at } 0^{\circ}\text{C} \xleftrightarrow{+334 \text{ J}} 1.00 \text{ g H}_2\text{O}^{(l)} \text{ at } 0^{\circ}\text{C} \xrightarrow{-334 \text{ J}}
\]

- **Heat of crystallization** is the reverse of the heat of fusion.
In the sublimation process the solid transforms directly to the vapor phase without passing through the liquid phase.

Solid CO₂ or “dry” ice does this well.
Energy and Equilibrium

- **Transfer** of energy accompanies chemical and physical processes.
- Energy is neither created nor destroyed in chemical reactions and physical changes.
- Exothermic reactions release energy in the form of heat. (Heat is a product)
- Endothermic reactions need an input of heat to proceed. (Heat is a reactant)

For example, the combustion of propane is exothermic.

\[
C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) + 2.22 \times 10^3 \text{ kJ}
\]
Exothermic vs. Endothermic

Exothermic reaction:
- Energy of reactants
- Activation energy
- Heat of reaction (released)
- Energy of products

Endothermic reaction:
- Activation energy
- Energy of reactants
- Heat of reaction (absorbed)

Progress of reaction

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The Rate of a Reaction

- **Kinetics** is the study of rates of chemical reactions and the mechanisms by which they occur.
- The **reaction rate** is the increase in product per unit time or decrease reactant per unit time.

\[
\begin{align*}
C_{\text{diamond}} + O_2(g) & \rightarrow CO_2(g) \\
\text{VERY SLOW} \\
H^+(aq) + OH^-(aq) & \rightarrow H_2O(l) \\
\text{INSTANTANEOUS}
\end{align*}
\]
Factors That Affect Reaction Rates

- There are several factors that can influence the rate of a reaction:
  1. The concentration of the reactants.
  2. The temperature of the reaction.
  3. The presence of a catalyst.
Increasing Reaction Rates

**Table 6.6 Factors That Increase Reaction Rate**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>More reactants</td>
<td>More collisions</td>
</tr>
<tr>
<td>Higher temperature</td>
<td>More collisions, more collisions with energy of activation</td>
</tr>
<tr>
<td>Adding a catalyst</td>
<td>Lowers energy of activation</td>
</tr>
</tbody>
</table>
Collision Theory of Reaction Rates

Three basic events must occur for a reaction to occur: the atoms, molecules or ions must:

1. Collide.
2. Collide with enough energy to break and form bonds.
3. Collide with the proper orientation for a reaction to occur.

One method to increase the number of collisions and the energy necessary to break and reform bonds is to heat the molecules.
Catalysts

- Catalysts change reaction rates by providing an alternative reaction pathway with a different activation energy.
Reversible reactions do not go to completion.

- They can occur in either direction
- Symbolically, this is represented as:

\[ a \ A(g) + b \ B(g) \rightleftharpoons c \ C(g) + d \ D(g) \]

A chemical equilibrium is a reversible reaction that the forward reaction rate is equal to the reverse reaction rate.

Molecules are continually reacting, even though the overall composition of the reaction mixture does not change.
Equilibrium

![Diagram of equilibrium reaction between SO₂ and O₂](image)

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Equilibrium
Disturbing a System at Equilibrium: Predictions

- **LeChateliers Principle** - If a change of conditions is applied to a system in equilibrium, the system responds to reduce the stress and reach a new state of equilibrium.

- Some possible stresses to a system at equilibrium are:
  1. Changes in concentration of reactants or products.
  2. Changes in pressure or volume (for gaseous reactions)
  3. Changes in temperature.
### Disturbing a System at Equilibrium

**Table 6.7  Effects of Changes on Equilibrium**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Change (stress)</th>
<th>Reaction Favored to Remove Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>Add more reactant</td>
<td>Forward</td>
</tr>
<tr>
<td></td>
<td>Remove reactant</td>
<td>Reverse</td>
</tr>
<tr>
<td></td>
<td>Add product</td>
<td>Reverse</td>
</tr>
<tr>
<td></td>
<td>Remove product</td>
<td>Forward</td>
</tr>
<tr>
<td>Temperature</td>
<td>Raise $T$ of endothermic reaction</td>
<td>Forward</td>
</tr>
<tr>
<td></td>
<td>Lower $T$ of endothermic reaction</td>
<td>Reverse</td>
</tr>
<tr>
<td></td>
<td>Raise $T$ of exothermic reaction</td>
<td>Reverse</td>
</tr>
<tr>
<td></td>
<td>Lower $T$ of exothermic reaction</td>
<td>Forward</td>
</tr>
</tbody>
</table>
Disturbing a System at Equilibrium: Predictions

\[ 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g}) + 198 \text{ kJ} \]

Heat is a product of this reaction.
Decreasing the reaction temperature stresses the reactants.
This favors the forward reaction.
Disturbing a System at Equilibrium: Predictions

Blood vessels dilate
- sweat production increases
- sweat evaporates
- skin cools

Blood vessels constrict and epinephrine is released
- metabolic activity increases
- muscular activity increases
- shivering occurs
- sweat production stops

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