### 6.1 Endothermic and Exothermic Processes

Essential knowledge statements from the AP Chemistry CED:

- Temperature changes in a system indicate energy changes.
- Energy changes in a system can be described as endothermic and exothermic processes such as the heating or cooling of a substance, phase changes, or chemical transformations.
- When a chemical reaction occurs, the energy of the system either decreases (exothermic reaction), increases (endothermic reaction), or remains the same. For exothermic reactions, the energy lost by the reacting species (system) is gained by the surroundings, as heat transfer from or work done by the system. Likewise, for endothermic reactions, the system gains energy from the surroundings by heat transfer to or work done on the system.
- The formation of a solution may be an exothermic or endothermic process, depending on the relative strengths of intermolecular/interparticle interactions before and after the dissolution process.

When studying energy changes and the flow of heat, it is helpful to differentiate between the system, which represents the portion of the universe that we choose to focus on, and the surroundings, which represents everything else. When a chemical reaction occurs, the system is often the portion of the universe where attractive forces between particles are broken and/or formed.


1. A sample of water at room temperature is added to a beaker and placed on a hot plate. The initial temperature of the water is recorded. The hot plate is turned on, and the temperature of the water is monitored over time.

Would you describe the change that occurred in this experiment as an endothermic process or an exothermic process? Justify your answer by indicating the direction of heat flow. Use the terms system and surroundings in your answer.

2. Two different solutions, $\mathrm{HCl}(a q)$ and $\mathrm{NaOH}(a q)$, occupy separate beakers at room temperature. The initial temperature of each solution is recorded, and the solutions are combined in a Styrofoam cup. The temperature of the solution is monitored over time.

Would you describe the change that occurred in this experiment as an endothermic process or an exothermic process? Justify your answer by indicating the direction of heat flow. Use the terms system and surroundings in your answer.

$$
\mathrm{KOH}(s) \rightarrow \mathrm{K}^{+}(a q)+\mathrm{OH}^{-}(a q) \quad \text { or } \quad \mathrm{CaCl}_{2}(s) \rightarrow \mathrm{Ca}^{2+}(a q)+2 \mathrm{Cl}^{-}(a q)
$$

3. Consider the process of dissolving an ionic solid such as $\mathrm{KOH}(s)$ or $\mathrm{CaCl}_{2}(s)$ in water, as represented by the equations above. The particle diagram below represents the dissolution of an ionic solute in a polar solvent such as water. The dissolution process can be imagined as occurring in three steps.

4. (continued)

Fill in the missing information in the table below, regarding the particle diagram.

| Step | Endothermic <br> or <br> Exothermic? | Are Attractive Forces <br> Between Particles <br> Broken or Formed? |
| :---: | :---: | :---: |
| 1 |  |  |
| 2 |  |  |
| 3 |  |  |

Two examples of experiments during which a change in temperature may be observed are the following.

- A solute is dissolved in a solvent, forming a solution.
- A chemical reaction occurs, forming a new substance.

If temperature changes are detected in these types of experiments, it is related to energy changes in the system. At the particle level, energy changes are associated with attractive forces between particles.

- Breaking attractive forces between particles is an endothermic process; energy is absorbed.
- Forming attractive forces between particles is an exothermic process; energy is released.

Information about breaking and forming chemical bonds is included in Topic 6.7 (Bond Enthalpies).
If a temperature change occurs during the process of forming a solution or during a chemical reaction, it is important to understand the direction of heat flow between the system and the surroundings. This information is summarized in the following table.
Note that the thermometer is usually considered to be part of the surroundings and not the system.

| Temperature Changes and Heat Flow that Occur During the Process of Solution Formation or During a Chemical Reaction |  |  |  |
| :---: | :---: | :---: | :---: |
| How Does the Temperature Change During the Process? | Direction of Heat Flow | Diagram to Illustrate Heat Flow | Classification of the Process |
| It decreases. | Heat flows from the surroundings into the system. |  | endothermic |
| It increases. | Heat flows from the system into the surroundings. |  | exothermic |

In Topic 6.3 (Heat Transfer and Thermal Equilibrium), you will study a different type of experiment in which heat flows from a warmer object to a cooler object. One example involves adding a hot piece of metal to a sample of water at room temperature. This situation involves a difference in kinetic energy, but it does NOT usually involve breaking or forming attractive forces between particles.

### 6.2 Energy Diagrams

Essential knowledge statement from the AP Chemistry CED:

- A physical or chemical process can be described with an energy diagram that shows the endothermic or exothermic nature of that process.

In Topic 5.6, you learned about reaction energy profiles.


4. The left diagram shown above represents the energy profile for a chemical reaction.
(a) Fill in the following information based on the left diagram.

Activation energy for the forward reaction: $\qquad$ kJ

Energy difference between reactants and products: $\qquad$ kJ

Is the chemical reaction classified as endothermic or exothermic? $\qquad$
(b) On the diagram on the right, draw an energy profile for a different chemical reaction with the following features.

- The potential energy of the reactants should be the same in each diagram.
- The activation energy for the forward reaction should be the same in each diagram.
- The absolute value of the energy difference between reactants and products should be the same in each diagram.
- The reaction represented by the diagram on the right should show the opposite change in energy. In other words, if the left diagram represents an endothermic reaction, the right diagram should represent an exothermic reaction (or vice versa.)


### 6.3 Heat Transfer and Thermal Equilibrium

Essential knowledge statements from the AP Chemistry CED:

- The particles in a warmer body have a greater average kinetic energy than those in a cooler body.
- Collisions between particles in thermal contact can result in the transfer of energy. This process is called "heat transfer," "heat exchange," or "transfer of energy as heat."
- Eventually, thermal equilibrium is reached as the particles continue to collide. At thermal equilibrium, the average kinetic energy of both bodies is the same, and hence, their temperatures are the same.


5. In a certain experiment, a piece of metal is heated to a temperature of $100^{\circ} \mathrm{C}$ in a boiling water bath. Then the hot metal is quickly transferred to a sample of water at $20^{\circ} \mathrm{C}$ in an insulated container.
(a) Describe the direction of heat flow at the moment that the sample of metal is added to the sample of water at $20^{\circ} \mathrm{C}$.
(b) At what point during the experiment will the transfer of heat between the metal and the water be complete?

### 6.4 Heat Capacity and Calorimetry

Essential knowledge statements from the AP Chemistry CED:

- The heating of a cool body by a warmer body is an important form of energy transfer between two systems. The amount of heat transferred between two bodies may be quantified by the heat transfer equation $(q=m c \Delta T)$. Calorimetry experiments are used to measure the transfer of heat.
- The first law of thermodynamics states that energy is conserved in chemical and physical processes.
- The transfer of a given amount of thermal energy will not produce the same temperature change in equal masses of matter with differing specific heat capacities.
- Heating a system increases the energy of the system, while cooling a system decreases the energy of the system.
- The specific heat capacity of a substance and the molar heat capacity are both used in energy calculations.
- Chemical systems change their energy through three main processes: heating/cooling, phase transitions, and chemical reactions.

The amount of heat required to raise the temperature of one gram of a substance by $1^{\circ} \mathrm{C}$ (or by 1 K ) is defined as the specific heat capacity (also known as the specific heat).
$q=m c \Delta T$
$q=$ heat
$m=$ mass
$c=$ specific heat capacity
$\Delta T=$ change in temperature

The units of $c$ are usually one of the following.

$$
\mathrm{J} /\left(\mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right) \quad \text { or } \quad \mathrm{J} /(\mathrm{g} \cdot \mathrm{~K})
$$

$\Delta T$ has the same magnitude in either ${ }^{\circ} \mathrm{C}$ or K . For example, if the temperature changes from $20^{\circ} \mathrm{C}$ to $25^{\circ} \mathrm{C}$, this would be a change from 293 K to $298 \mathrm{~K} . \Delta T=5^{\circ} \mathrm{C}$ or 5 K .

| Substance | Specific Heat Capacity <br> $\mathrm{J} /\left(\mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)$ |
| :---: | :---: |
| $\mathrm{Fe}(s)$ | 0.46 |
| $\mathrm{H}_{2} \mathrm{O}(l)$ | 4.18 |

6. The specific heat capacity of $\mathrm{Fe}(s)$ and $\mathrm{H}_{2} \mathrm{O}(l)$ are listed in the table above.
(a) Calculate the amount of heat that is required to raise the temperature of a pure sample of 25.0 g $\mathrm{H}_{2} \mathrm{O}(l)$ from $20.0^{\circ} \mathrm{C}$ to $75.0^{\circ} \mathrm{C}$. Include units in your answer.
7. (continued)
(b) A pure sample of $125 \mathrm{~g} \mathrm{Fe}(\mathrm{s})$ absorbs 5.32 kJ of heat. The initial temperature of the $\mathrm{Fe}(s)$ sample is $21.0^{\circ} \mathrm{C}$. Calculate the final temperature of the $\mathrm{Fe}(s)$. Include units in your answer.
(c) Calculate the molar heat capacity of $\mathrm{H}_{2} \mathrm{O}(l)$ in units of $\mathrm{J} /\left(\mathrm{mol}^{\circ}{ }^{\circ} \mathrm{C}\right)$.

| Substance | Specific <br> Heat <br> Capacity <br> $\mathrm{J} /\left(\mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)$ | Mass of <br> Sample <br> $(g)$ | Amount <br> of Heat <br> Absorbed by <br> the Sample <br> $(\mathrm{kJ})$ | Initial <br> Temperature <br> of Sample <br> $\left({ }^{\circ} \mathrm{C}\right)$ | Final <br> Temperature <br> of Sample <br> $\left({ }^{\circ} \mathrm{C}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Fe}(s)$ | 0.46 | 100.0 | 1.00 | 25.0 | $?$ |
| $\mathrm{H}_{2} \mathrm{O}(l)$ | 4.18 | 100.0 | 1.00 | 25.0 | $?$ |

In a certain experiment, a sample of $\mathrm{Fe}(s)$ and a sample of $\mathrm{H}_{2} \mathrm{O}(l)$ each absorb a certain amount of heat. Data from the experiment is listed in the table above.
(d) A student makes the claim that the final temperature of the $\mathrm{H}_{2} \mathrm{O}(l)$ will be the same as the final temperature of the $\mathrm{Fe}(s)$ because each sample has the same mass and absorbed the same quantity of heat. Do you agree or disagree with the student's claim? Justify your answer with a calculation to support your choice.

A calorimeter is a device used to record the flow of heat during a physical or chemical process. A simple version of this piece of equipment involves a Styrofoam coffee cup and a thermometer. Sometimes a lid is used on the cup to minimize the loss of heat to the surroundings.
7. A pure sample of $\mathrm{Cu}(s)$ with a mass of 100.0 g is placed in a boiling water bath at $100.0^{\circ} \mathrm{C}$ for several minutes. Then the hot $\mathrm{Cu}(s)$ sample is quickly transferred to a sample of $100.0 \mathrm{~g} \mathrm{of}_{\mathrm{H}} \mathrm{O}(l)$ at room temperature in a coffee-cup calorimeter. The initial temperature of the $\mathrm{H}_{2} \mathrm{O}(l)$ in the calorimeter is $22.0^{\circ} \mathrm{C}$. Eventually, thermal equilibrium is reached when the temperature of the mixture of $\mathrm{Cu}(s)$ and $\mathrm{H}_{2} \mathrm{O}(l)$ reaches a maximum value. The final temperature of the mixture is $28.7^{\circ} \mathrm{C}$. Assume that no heat is lost to the container or the surroundings outside the container. The specific heat capacity of $\mathrm{H}_{2} \mathrm{O}(l)$ is $4.18 \mathrm{~J} /\left(\mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)$.
(a) The magnitude of $\Delta T$ for the $\mathrm{H}_{2} \mathrm{O}(l)$ in this experiment is equal to $28.7^{\circ} \mathrm{C}-22.0^{\circ} \mathrm{C}=6.7^{\circ} \mathrm{C}$. Calculate the magnitude of $\Delta T$ for the $\mathrm{Cu}(s)$.
(b) A student makes the claim that the amount of heat energy lost by $\mathrm{Cu}(s)$ is greater than the amount of heat energy gained by $\mathrm{H}_{2} \mathrm{O}(l)$ in this experiment. Do you agree or disagree with the student's claim? Justify your answer.
(c) Use the information from this experiment to calculate the value of the specific heat capacity of $\mathrm{Cu}(s)$. Include units in your answer.
8. The specific heat capacity of $\mathrm{Al}(s)$ is $0.91 \mathrm{~J} /\left(\mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)$, and the specific heat capacity of $\mathrm{H}_{2} \mathrm{O}(l)$ is $4.18 \mathrm{~J} /\left(\mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)$. A pure sample of $\mathrm{Al}(\mathrm{s})$ with a mass of 100.0 g is placed in a boiling water bath at $100.0^{\circ} \mathrm{C}$ for several minutes. Then the hot $\mathrm{Al}(s)$ sample is quickly transferred to a sample of 100.0 g of $\mathrm{H}_{2} \mathrm{O}(l)$ in a coffee-cup calorimeter. The initial temperature of the $\mathrm{H}_{2} \mathrm{O}(l)$ in the calorimeter is $22.0^{\circ} \mathrm{C}$. Eventually, thermal equilibrium is reached when the temperature of the mixture of $\operatorname{Al}(s)$ and $\mathrm{H}_{2} \mathrm{O}(l)$ reaches a maximum value. Assume that no heat is lost to the container or the surroundings outside the container.

Calculate the final temperature of the mixture when thermal equilibrium is reached.

### 6.5 Energy of Phase Changes

Essential knowledge statements from the AP Chemistry CED:

- Energy must be transferred to a system to cause a substance to melt (or boil). The energy of the system therefore increases as the system undergoes a solid-to-liquid (or liquid-to-gas) phase transition. Likewise, a system releases energy when it freezes (or condenses). The energy of the system decreases as the system undergoes a liquid-to-solid (or gas-to-liquid) phase transition. The temperature of a pure substance remains constant during a phase change.
- The energy absorbed during a phase change is equal to the energy released during a complementary phase change in the opposite direction. For example, the molar heat of condensation of a substance is equal to the negative of its molar heat of vaporization.

9. The diagram shown at right represents a heating curve for a pure substance. The experiment begins with a sample of a pure solid.

Heated is added at a constant rate. The temperature of the substance is monitored over time.

Fill in the missing information in the table below.


Heat Added

| Curve Segment | Change that Occurs During this Part of the Experiment |
| :---: | :---: |
| AB |  |
| BC |  |
| CD |  |
| DE |  |
| EF |  |

10. Fill in the missing information in the table below.

| Phase Change | Endothermic or <br> Exothermic? | Are Attractive Forces <br> Between Particles <br> Broken or Formed? |
| :--- | :--- | :--- |
| melting (solid $\rightarrow$ liquid) |  |  |
| evaporation (liquid $\rightarrow$ gas) |  |  |
| sublimation (solid $\rightarrow$ gas) |  |  |
| freezing (liquid $\rightarrow$ solid) |  |  |
| condensation (gas $\rightarrow$ liquid) |  |  |
| deposition (gas $\rightarrow$ solid) |  |  |

The molar heat of fusion is defined as the amount of heat required to convert 1 mole of a pure substance from a solid to a liquid at its melting point.

The molar heat of vaporization is defined as the amount of heat required to convert 1 mole of a pure substance from a liquid to a gas at its boiling point.

| Boiling Point of $\mathrm{CH}_{4}$ | 112 K |
| :---: | :---: |
| Molar Heat of Vaporization for $\mathrm{CH}_{4}$ | $8.17 \mathrm{~kJ} / \mathrm{mol}$ |

11. Information about $\mathrm{CH}_{4}$ is listed in the table above. Which of the following statements accurately describes the net flow of thermal energy when $32.08 \mathrm{~g} \mathrm{CH}_{4}$ is converted from a gas to a liquid at 112 K ?
(A) 8.17 kJ of thermal energy flows from the sample of $\mathrm{CH}_{4}$ to the surroundings.
(B) 8.17 kJ of thermal energy flows from the surroundings to the sample of $\mathrm{CH}_{4}$.
(C) 16.34 kJ of thermal energy flows from the sample of $\mathrm{CH}_{4}$ to the surroundings.
(D) 16.34 kJ of thermal energy flows from the surroundings to the sample of $\mathrm{CH}_{4}$.

| Substance | Specific Heat <br> Capacity | Melting Point | Molar Heat of <br> Fusion |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{O}_{3}(s)$ | $1.17 \mathrm{~J} /\left(\mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)$ | $159^{\circ} \mathrm{C}$ | $27.1 \mathrm{~kJ} / \mathrm{mol}$ |


| Substance | Specific Heat <br> Capacity | Boiling Point | Molar Heat of <br> Vaporization |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}(l)$ | $2.46 \mathrm{~J} /\left(\mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)$ | $78^{\circ} \mathrm{C}$ | $42.3 \mathrm{~kJ} / \mathrm{mol}$ |

12. Information about two different substances is listed in the tables above.
(a) Calculate the quantity of heat that must be absorbed to increase the temperature of a pure sample of 0.375 g of $\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{O}_{3}(s)$ from $25^{\circ} \mathrm{C}$ to the melting point of $159^{\circ} \mathrm{C}$ and melt the solid completely. Include units in your answer.
(b) Calculate the quantity of heat that must be absorbed to increase the temperature of a pure sample of 0.375 g of $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}(l)$ from $25^{\circ} \mathrm{C}$ to the boiling point of $78^{\circ} \mathrm{C}$ and evaporate the liquid completely. Include units in your answer.
