

Chemistry

Thermochemistry

Lesson 10

Lesson Plan

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The Flow of Energy-Heat

Objectives: Explain the relationship between energy and heat; Distinguish between heat capacity and specific heat.

- Energy and Heat
 - **Thermochemistry** is concerned with the heat changes that occur during chemical reactions
 - **Energy** is the capacity for doing work or supplying heat.
 - **Work** is a force times a distance.
 - Energy is not visible – it is odorless and tasteless. Energy can only be detected because of its results.
 - Energy stored within the chemical structure units of chemical substances is called **chemical potential energy**.
 - Gasoline is a form of stored potential energy, so is sugar.
 - The amount of energy stored in a chemical depends on the elements and their arrangements.
 - **Heat**, represented by q , is energy that transfers from one object to another due to a temperature difference between them.
 - As with energy, heat itself cannot be detected, only the affects of adding or subtracting heat can be detected.
 - An effect of adding heat is a rise in temperature of an object.
 - Heat always flows from a warmer object to a cooler object.
- Exothermic and Endothermic Processes
 - Almost all chemical reactions and changes in state involve the release or absorption of heat.
 - When looking at the process, we define the **system** as those objects you are focusing on.
 - The **surroundings** are everything else.
 - Together, the system and the surroundings make up the **universe**.
 - A major study of Thermochemistry is to examine the flow of heat from a system to the surroundings or from the surroundings to the system
 - The **Law of Conservation of Energy** states that in any chemical or physical process that energy is neither created nor destroyed.
 - All energy in a process can be accounted for as work, stored energy or heat.
 - When a reaction releases heat into it's surrounding, it is termed an **exothermic process** – q is defined as negative.
 - When a reaction absorbs heat from its surroundings, it is termed an **endothermic process** – q is defined as positive.
 - Examples

- When standing around a camp fire
 - The fire is exothermic
 - The people are endothermic
 - A person who has been running a race is exothermic
- Heat Capacity and Specific Heat
 - Often when dieting, a person will count their calorie intake, or when exercising they will speak of burning calories.
 - As food is broken down in your body, heat is generated. If you ingest 10g of sugar, then as it is chemically processed into CO₂ and H₂O, a certain amount of heat is produced. This is the same amount of heat that would be produced if 10g of sugar were burned in a fire.
 - A **calorie** is the amount heat needed to raise one gram of pure water by one degree Centigrade. It is abbreviated as *c*.
 - *c* refers to energy due to chemical/physical reactions (such as in the definition) – but not the energy in food. *C* is used to refer to energy in food.
 - One Calorie = 1000 calories = 1 kilocalorie
 - So if you state that 10g of sugar has 41 Calories, then that is equivalent to 41 kilocalories of heat when completely burned to produce CO₂ and H₂O.
 - The calorie is also related to the **joule** – which is the SI unit of heat and energy. A joule is just less than ¼ of a calorie.
 - 1J = 0.2390 cal 4.184J = 1cal
 - The amount of heat needed to raise the temperature of an object by 1°C is the **heat capacity** of that object.
 - Heat capacity depends on the mass of the object and the chemical composition of the object. Items of the same composition, but different masses will have different heat capacity.
 - **Specific heat capacity** or **specific heat** is the heat required to raise 1g of a substance by 1°C. The symbol for specific heat is *C*. Specific heat is expressed in cal/g · °C or J/g · °C
 - Water has a heat capacity of 1.00 cal/g whereas iron is .11 cal/g. This means that for the same mass, iron will heat up 9 times faster than water when given the same amount of heat.
 - Specific heat can be calculated for a substance using the equation

$$C = \frac{q}{m \cdot \Delta t} = \frac{\text{heat (joules or calories)}}{\text{mass (grams)} \times \text{change in temperature (}^\circ\text{C)}}$$

Sample Problem

The temperature of a piece of copper with a mass of 95.4 g increases from 25.0°C to 48.0°C when the metal absorbs 849J of heat. What is the specific heat of the copper?

$$C = \frac{q}{m \cdot \Delta t} = \frac{849J}{95.4g \times (48.0^\circ C - 25.0^\circ C)} = \frac{849J}{2194.2g^\circ C} = .387J / g^\circ C$$

Measuring and Expressing Heat Changes

Objectives: Construct equations that show the heat change for chemical and physical processes; Calculate heat changes in chemical and physical processes.

- Calorimetry
 - In order to impress your date with a candle light dinner, you light a match – you suddenly are struck by how much heat that little match is putting off and wonder “How would I go about measuring how much heat the match releases as it flares up”? Forgetting about your date, you head off to the lab to see if you can figure out the answer. No wonder scientists are such a lonely bunch of people!
 - Heat that is released or absorbed during many chemical reactions can be measured by calorimetry. **Calorimetry** is the accurate and precise measurement of heat exchange for chemical and physical processes.
 - Using the concept from the Law of Conservation of Energy, we know that energy released by a reaction is absorbed by its surroundings, and energy absorbed by a reaction is taken from its surroundings.
 - To measure these changes, a device called a **calorimeter** is used.
 - The simplest calorimeter is a well-insulated foam cup with a loose fitting cup filled with water. A thermometer measures the change of the temperature of the water, and a stirring stick to make sure of uniform water temperature.
 - A second type of calorimeter is called a **bomb calorimeter**. In a bomb calorimeter, the reaction takes place in a sealed metal container surrounded by water. Again a stirrer assures of uniform water temperature, which a thermometer measures. The inner container is filled with oxygen and ignited with a heating element. The substance burns rapidly in the pure oxygen atmosphere, thus the name bomb calorimeter.
 - One primary difference between the two types of calorimeters is that with the first the reaction takes place at atmospheric pressure. In the bomb calorimeter, the reaction takes place in constant volume, and being closed, the mass is constant.
- In constant pressure (such as open to the atmosphere) the heat content is the same as a property called **enthalpy**, which has the symbol **H**.
 - So we can state that for constant pressure reactions that the change in enthalpy (ΔH) is equal to the heat change, or $q = \Delta H$
 - Combining this with our definition of specific heat
$$C = \frac{q}{m \cdot \Delta t} \text{ or } q = C \cdot m \cdot \Delta t$$
, we can state that $q = \Delta H = C \cdot m \cdot \Delta t$
 - For endothermic reactions ΔH is positive and negative for exothermic reactions.

Sample Problem

When acids are neutralized by the addition of a base, heat is produced. 25.0ml of water containing 0.025mol HCl is added to 25.0ml of water containing 0.025mol of NaOH in a foam cup calorimeter. At the start the solutions and the container are all at 25.0°C. During the reaction, the highest temperature observed is 32.0°C.

Calculate the heat (in kJ) released during this reaction. Assume the densities of the solutions are 1.00g/mL.

The equation to use is $q = C \cdot m \cdot \Delta t$. It requires three unknowns, the specific heat (which we know to be 4.18 J/g°C), the change in temperature (which we know to be 32.0°C-25.0°C = 7.00°C) and the mass of the water – which we do not know.

Finding the mass of the water:

We are given that we have 25.0mL of water with 0.025mol HCl and 25.0mL of water with 0.025mol NaOH, so the total volume of water = 50.0mL. We are also given that the density of water is 1.00g/mL, so we set up a conversion:

$$m = 50.0\text{mL} \times \frac{1.00\text{g}}{\text{ml}} = 50.0\text{g}$$

Now that we have everything:

$$q = C \cdot m \cdot \Delta t = (4.18\text{J} / \text{g}^\circ\text{C})(50.0\text{g})(7.0^\circ\text{C}) = 1464\text{J}$$

$$1464\text{J} \times \frac{1\text{kJ}}{1000\text{J}} = 1.5\text{kJ}$$

- Thermochemical Equations

- When we learned to write chemical equations, we indicated if heat was applied as part of the reaction. As it turns out, we can include heat released in an equation as well.
- One of the components of concrete is calcium oxide. When it mixes with water an exothermic reaction occurs. This is why freshly poured concrete is warm. When 1mol of calcium oxide reacts with 1mol of water, then 1 mol of calcium hydroxide forms and 65.2kJ of heat is released. This can be written as $\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s) + 65.2\text{kJ}$
- An equation, which includes the heat change, is called a **thermochemical equation**.
- A **heat of reaction** is the heat change for the equation, exactly as it is written. The physical state of the reactants and products must also be given. Usually these will be reported as ΔH , indicating that the reaction took place at constant pressure – usually 101.3 kPa at 25°C. If the change in heat is not given in ΔH , but as part of the equation, the value shown is the absolute value.
- So for the example we just did of calcium oxide reacting with water, the equation would be $\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s) \Delta H = -65.2\text{kJ}$, since heat was released. In the case of the decomposition of sodium hydrogen carbonate, which is an endothermic reaction, we would have $2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g) \Delta H = 129\text{kJ}$, indicating that heat was absorbed by the reaction. Notice that in these two examples that the enthalpy is higher for the calcium oxide than for the sodium hydrogen carbonate, since the CaO released heat and the NaHCO₃ absorbed heat during their reactions.

Sample Problem

Using the equation for the decomposition of NaHCO_3 , determine the kJ of heat required to decompose 2.24mol of NaHCO_3 .

Looking at the thermochemical equation, we have

$2\text{NaHCO}_3(s) + 129\text{kJ} \rightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g)$ then we can do a conversion using the fact that 2mol of NaHCO_3 , requires 129kJ of heat.

$$2.24\text{mol NaHCO}_3 \times \frac{129\text{kJ}}{2\text{mol NaHCO}_3} = 144.48\text{kJ} = 144\text{kJ}$$

- Notice that we worked this problem very much like we did the mole-mole ratio problems in stoichiometry
- Why is indicating the phase state of the reactants and products important? Look at these two equations of the decomposition of water
 - $\text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta H = 285.8\text{kJ}$
 - $\text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta H = 241.8\text{kJ}$
 - A difference of 44.0kJ
 - Please note that an illegal $\frac{1}{2}$ is used to balance the equation, just so we could examine 1 mol of H_2O in a balanced equation.
- So why the difference? Notice that in the first case that the water is liquid, but in the second case it is a gas. The products in both cases are gases. The difference is that the water had to be converted to from liquid to gas and that takes energy (heat) at 25°C
- Another area of interest in thermochemistry is the **heat of combustion**. This is a measure for the complete combustion of one mole of a substance and is given in kJ/mol. Hydrogen is -286 kJ/mol, methane is -890 kJ/mol, and sucrose is -5645 kJ/mol.

Heat in Changes of States

Objectives: Classify, by type, the heat changes that occur during melting, freezing, boiling, and condensing; Calculate the heat changes that occur during melting, freezing, boiling, and condensing.

- Heats of Fusion and Solidification

- When a cube of ice is set out on a table top in a warm room, what happens to it?
 - The ice is the system, the table and air around it is the surroundings. The ice absorbs heat from it's surroundings and melts.
 - The ice (and surrounding water) remains at 0°C until all the ice has melted.
 - The temperature of the water rises above 0°C after the ice is all melted. Why?
- Heat and the Change of Phase for Solids and Liquids
 - Remember when we spoke in the last chapter about for a solid to melt, that you had to add enough kinetic energy to overcome the forces of the crystal.
 - When a substance melts, there is no change in temperature, only in kinetic energy that is used to overcome the forces binding a solid together.

- Heat added to a solid will raise the temperature and kinetic energy to a certain point – the melting point. Continuing to add energy will raise the kinetic energy, but not the temperature. Once enough energy has been added to raise the kinetic energy of all the particles to break the binding forces, then added heat will raise the temperature, while still continuing to increase the kinetic energy.
- The heat required to overcome the binding forces of one mole of a solid, at constant temperature, is called the **molar heat of fusion**. It is abbreviated as ΔH_{fus} .
- The heat removed from a mole of a liquid to convert it into a solid, at constant temperature, is called the **molar heat of solidification**, and is abbreviated as ΔH_{solid} .
- The amount of heat absorbed by a solid as it melts is exactly the same amount of heat released as the same mass of liquid solidifies.
- $\Delta H_{\text{fus}} = -\Delta H_{\text{solid}}$
- The melting of 1 mol of ice at 0°C to 1 mol of water at 0°C requires the absorption 6.01kJ of heat. Likewise the freezing of 1 mole of water at 0°C to become 1 mole of ice at 0°C requires the release of 6.01kJ of heat
- Since the process of solidification releases heat, it is exothermic and the enthalpy of the substance is reduced.
- Since the process of fusion absorbs heat, it is endothermic and the enthalpy of the substance is increased.

Sample Problems

How many grams of ice at 0°C and 101.3 kPa could be melted by the addition of 2.25kJ of heat?

Looking at the table, we see that the heat of fusion for ice is 6.01kJ/mol, so we have something we do a conversion with

$$2.25\text{kJ} \times \frac{1\text{mol ice}}{6.01\text{kJ}} \times \frac{18.0\text{g ice}}{1\text{mol ice}} = 6.74\text{g ice}$$

- Heats of Vaporization and Condensation
 - We just saw that as a solid changes to a liquid, it takes the addition of heat, but the solid/liquid remains at the same temperature (and of course the same for the removal of heat from liquids to become a solid).
 - The same process holds true for a liquid becoming a gas, or a gas becoming a liquid.
 - When you heat a liquid, its temperature reaches a point and goes no higher. Additional heat is added raises the kinetic energy of the particles until they overcome the intermolecular forces – until all the particles have enough kinetic energy to overcome the intermolecular forces, the substance remains at the same temperature.
 - The heat added to overcome the intermolecular forces for one mole of a substance is called the **molar heat of vaporization**, and is abbreviated as ΔH_{vap} .

- The molar heat of vaporization for water is 40.7kJ/mol – that is 40.7kJ of heat must be supplied to 1 mole of water in a liquid phase at 100°C and 101.3kPa to convert it into one mole of water in a vapor phase at 100°C.
 - The equation for such would be

$$H_2O(l) \rightarrow H_2O(g) \quad \Delta H = 40.7kJ / mol$$
- Diethyl ether (C₄H₁₀O) was once used as an anesthetic. It has a relatively low boiling point (34.6°C). The heat of vaporization is also fairly low – 15.7kJ/mol. If you were to pour some diethyl ether into a beaker on a warm day, it would absorb heat from the beaker and evaporate very rapidly. Enough heat can be absorbed from the walls of the beaker to cause air to condense on the sides of the beaker as frost.
 - Is this an endothermic or exothermic process?
- Condensation is the exact opposite of evaporation, therefore the heat released when a gas converts into a liquid, at constant temperature, is equal to the heat absorbed when the same mass goes from a liquid to a vapor.
- The heat released by 1 mol of a gaseous substance, at constant temperature, to become 1 mol of a liquid substance is called the **heat of condensation** and has the abbreviation of ΔH_{cond} .
- As with $\Delta H_{\text{fus}} = -\Delta H_{\text{solid}}$, it is also true that $\Delta H_{\text{vap}} = \Delta H_{\text{cond}}$.
- Using the same example of 1 mole of steam changing into 1 mole of water

$$H_2O(g) \rightarrow H_2O(l) \quad \Delta H = -40.7kJ / mol$$

Sample Problem

How much heat would be required (in kJ) is absorbed when 24.8g H₂O(l) at 100°C is converted into steam at 100°C?

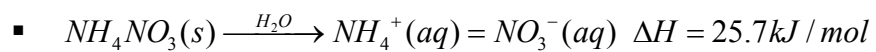
Just another conversion problem!

$$24.8g \text{ H}_2\text{O} \times \frac{1\text{mol H}_2\text{O}}{18.0g \text{ H}_2\text{O}} \times \frac{40.7\text{kJ}}{1\text{mol H}_2\text{O}} = 56.1\text{kJ}$$

- Heat of Solution

- Sometimes when a solute dissolves in a solvent there is a heat change. The heat change caused by dissolving one mole of a substance is the **molar heat of solution**, abbreviated by ΔH_{soln} .
- As an example, when NaOH is dissolved in water, the solution becomes so hot that it steams. This heat is released as the sodium ions and the hydroxide ions separate and interact with the water. The ΔH_{soln} for one mole of NaOH is 445.1kJ.

$$NaOH \xrightarrow{H_2O} Na^+(aq) + OH^-(aq) \quad \Delta H = -445.1kJ / mol$$
- This is how the hot presses that comes out of a box work. Inside the pouch is water and another sealed container of calcium chloride. When the container of calcium chloride is broken and mixes with the water, heat is released.
 - $CaCl_2 \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^-(aq) \quad \Delta H = -82.8kJ / mol$
 - This is an exothermic reaction
- A cold pack can be created with the mixture of ammonium nitrate and water



Sample Problem

How much heat (in kJ) is released when 2.500 mol NaOH(s) is dissolved in water.

Another conversion problem!

$$2.5000mol \ NaOH \times \frac{445.1kJ}{1mol \ NaOH} = 1112.75kJ = 1113kJ$$