Unit 5 Thermodynamics - The Warm-Up

Content Area: **Science**
Course(s): **AP Chemistry**
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Transfer Skills

The Warm-Up: Thermodynamics:

Thermodynamic properties of entropy and enthalpy drive reactions.

Enduring Understandings

There are two driving forces in nature- entropy and enthalpy.

Entropy of the universe is always increasing.

Essential Questions

How do enthalpy and entropy drive natural events?

To what extent does temperature predict the spontaneity of a reaction?

Content

Vocabulary:

System, surroundings, state function, work, heat, enthalpy, calorimetry, heat capacity, specific heat capacity, Hess's Law, entropy, Gibbs free energy

Skills

Relate changes in entropy to a change in state, change in temperature, and/or change in the number of product particles compared to reactant particles.

Use standard tables of entropies, enthalpies and free energies to calculate the change in entropy, enthalpy and/or free energy of a reaction.

Use calorimetry to calculate the energy/heat transfer in reactions.

Explain how changes in enthalpy and entropy both influence the spontaneity of a reaction.

Determine the spontaneity of a reaction by calculating the change in free energy of the reaction (from tables of standard free energies or form the Gibbs equation).

Resources

Standards

Big Idea 3: Changes in matter involve the rearrangement and/or reorganization of atoms and/or the transfer of electrons.
Essential knowledge 3.C.2: Net changes in energy for a chemical reaction can be endothermic or exothermic.
a. Macroscopic observations of energy changes when chemicals react are made possible by measuring temperature changes.

b. These observations should be placed within the context of the language of exothermic and endothermic change.

c. The ability to translate observations made at the macroscopic level in the laboratory to a conceptual framework is aided by a graphical depiction of the process called an energy diagram, which provides a visual representation of the exothermic or endothermic nature of a reaction.

d. It is important to be able to use an understanding of energy changes in chemical reactions to identify the role of endothermic and exothermic reactions in real-world processes.

3.C.2 Learning Objective:
LO 3.11 The student is able to interpret observations regarding macroscopic energy changes associated with a reaction or process to generate a relevant symbolic and/or graphical representation of the energy changes. [See SP 1.5, 4.4]

Big Idea 5: The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter.

Essential knowledge 5.A.2: The process of kinetic energy transfer at the particulate scale is referred to in this course as heat transfer, and the spontaneous direction of the transfer is always from a hot to a cold body.
a. On average, molecules in the warmer body have more kinetic energy than the molecules in the cooler body.

b. Collisions of molecules that are in thermal contact transfer energy.

c. Scientists describe this process as "energy is transferred as heat."

d. Eventually, thermal equilibrium is reached as the molecular collisions continue. The average kinetic energy of both substances is the same at thermal equilibrium.

e. Heat is not a substance, i.e., it makes no sense to say that an object contains a certain amount of heat. Rather, "heat exchange" or "transfer of energy as heat" refers to the process in which energy is transferred from a hot to a cold body in thermal contact.

f. 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.

5.A.2 Learning Objective:
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. [See SP 7.1]

Enduring understanding 5.B: Energy is neither created nor destroyed, but only transformed from one form to another. Essential knowledge 5.B.1: Energy is transferred between systems either through heat transfer or through one system doing work on the other system.
a. Heating a cold body with a hot body is a form of energy transfer between two systems. The transfer of thermal energy is an important concept in thermodynamics.

b. An additional form of energy transfer is through work. Work is described by other scientific frameworks, such as Newtonian Mechanics or electromagnetism.

c. In this course, calculations involving work are limited to that associated with changes in volume of a gas. An example of the transfer of energy between systems through work is the expansion of gas in a steam engine or car piston. Reasoning about this energy transfer can be based on molecular collisions with the piston: The gas is doing work on the piston, and energy is transferred from the gas to the piston.

Essential knowledge 5.B.2: When two systems are in contact with each other and are otherwise isolated, the energy that comes out of one system is equal to the energy that goes into the other system. The combined energy of the two systems remains fixed. Energy transfer can occur through either heat exchange or work.
a. When energy is transferred from system 1 to system 2, the energy transferred from system 1 is equal in magnitude to the energy transferred to system 2.

b. If a system transfers energy to another system, its energy must decrease. Likewise, if energy is transferred into a system, its energy must increase.

5.B.2 Learning Objectives:
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. [See SP 1.4, 2.2, connects to 5.B.1, 5.B.2]

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. [See SP 2.2, connects to 5.B.1, 5.B.2]

Essential knowledge 5.B.3: Chemical systems undergo three main processes that change their energy: heating/cooling, phase transitions, and chemical reactions.
a. Heating a system increases the energy of the system, while cooling a system decreases the energy. A liter of water at 50°C has more energy than a liter of water at 25°C.

b. The amount of energy needed to heat one gram of a substance by 1°C is the specific heat capacity of that substance.

c. Energy must be transferred to a system to cause it to melt (or boil). The energy of the system therefore increases as the system undergoes a solid-liquid (or liquid-gas) phase transition. Likewise, a system gives off energy when it freezes (or condenses). The energy of the system decreases as the system undergoes a liquid-solid (or gas-liquid) phase transition.

d. The amount of energy needed to vaporize one mole of a pure substance is the molar enthalpy of vaporization, and the energy released in condensation has an equal magnitude. The molar enthalpy of fusion is the energy absorbed when one mole of a pure solid melts or changes from the solid to liquid state and the energy released when the liquid solidifies has an equal magnitude.

e. When a chemical reaction occurs, the energy of the system decreases (exothermic reaction), increases (endothermic reaction), or remains the same. For exothermic reactions, the energy lost by the reacting molecules (system) is gained by the surroundings. The energy is transferred to the surroundings by either heat or work. Likewise, for endothermic reactions, the system gains energy from the surroundings by heat transfer or work done on the system.

f. The enthalpy change of reaction gives the amount of energy released (for negative values) or absorbed (for positive values) by a chemical reaction at constant pressure.

5.B.3 Learning Objective:
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 $P\Delta V$ work. [See SP 2.2, 2.3]

Essential knowledge 5.B.4: Calorimetry is an experimental technique that is used to measure the change in energy of a chemical system.
a. The experimental setup for calorimetry is the following: A chemical system is put in thermal contact with a heat bath. The heat bath is a substance, such as water, whose heat capacity has been well established by previous experiments. A process is initiated in the chemical system (heating/cooling, phase transition, or chemical reaction), and the change in temperature of the heat bath is measured.

b. Because the heat capacity of the heat bath is known, the observed change in temperature can be used to determine the amount of energy exchanged between the system and the heat bath.

c. The energy exchanged between the system and the heat bath is equal in magnitude to the change in energy of the system. If the heat bath increased in temperature, its energy increased, and the energy of the system decreased by this amount. If the heat bath decreased in temperature, and therefore energy, the energy of the system increased by this amount.

d. Because calorimetry measures the change in energy of a system, it can be used to measure the heat associated with each of the processes listed in 5.B.3. In this manner, calorimetry may be used to measure heat capacities, enthalpies of vaporization, enthalpies of fusion, and enthalpies of reactions. Only constant pressure calorimetry is required in the course.

5.B.4 Learning Objective:
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. [See SP 4.2, 5.1]

Enduring understanding 5.C: Breaking bonds requires energy, and making bonds releases energy. Essential knowledge 5.C.1: Potential energy is associated with a particular geometric arrangement of atoms or ions and the electrostatic interactions between them.
a. The attraction between the electrons of one atom and the protons of another explains the tendency for the atoms to approach one another. The repulsion between the nuclei (or core electrons) explains why the atoms repel one another at close distance. The distance at which the energy of interaction is minimized is called the bond length, and the atoms vibrate about this minimum energy position.

b. A graph of energy versus the distance between atoms can be plotted and interpreted. Using this graph, it is possible to identify bond length and bond energy.

c. Conceptually, bond making and bond breaking are opposing processes that have the same magnitude of energy associated with them. Thus, convention becomes important, so we define the bond energy as the energy required to break a bond.

d. Because chemical bonding arises from electrostatic interaction between electrons and nuclei, larger charges tend to lead to larger strengths of interaction. Thus, triple bonds are stronger than double or single bonds because they share more pairs of electrons.

e. Stronger bonds tend to be shorter bonds.

Essential knowledge 5.C.2: The net energy change during a reaction is the sum of the energy required to break the bonds in the reactant molecules and the energy released in forming the bonds of the product molecules. The net change in energy may be positive for endothermic reactions where energy is required, or negative for exothermic reactions where energy is released.
a. During a chemical reaction, bonds are broken and/or formed, and these events change the potential energy of the reaction system.

b. The average energy required to break all of the bonds in the reactant molecules can be estimated by adding up the average bond energies or bond enthalpies for all the bonds in the reactant molecules. Likewise, the average energy released in forming the bonds in the products can be estimated. If the energy released is greater than the energy required, then the reaction is exothermic. If the energy required is greater than the energy released, then the reaction is endothermic.

c. For an exothermic reaction, the products are at a lower potential energy compared with the reactants. For an endothermic reaction, the products are at a higher potential energy than the reactants.

d. In an isolated system, energy is conserved. Thus, if the potential energy of the products is lower than that of the reactants, then the kinetic energy of the products must be higher. For an exothermic reaction, the products are at a higher kinetic energy. This means that they are at a higher temperature. Likewise, for an endothermic reaction, the products are at a lower kinetic energy and, thus, at a lower temperature.

e. Because the products of a reaction are at a higher or lower temperature than their surroundings, the products of the reaction move toward thermal equilibrium with the surroundings. Thermal energy is transferred to the surroundings from the hot products in an exothermic reaction. Thermal energy is transferred from the surroundings to the cold products in an endothermic reaction.

f. Although the concept of "state functions" is not required for the course, students should understand these Hess's Law ideas: When a reaction is reversed, the sign of the enthalpy of the reaction is changed; when two (or more) reactions are summed to obtain an overall reaction, the enthalpies of reaction are summed to obtain the net enthalpy of reaction.

g. Tables of standard enthalpies of formation can be used to calculate the standard enthalpy of reactions. Uses should go beyond algorithmic calculations and include, for instance, the use of such tables to compare related reactions, such as extraction of elemental metals from metal oxides.

5.C.2 Learning Objective:
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. [See SP 2.3, 7.1, 7.2]

Enduring understanding 5.E: Chemical or physical processes are driven by a decrease in enthalpy or an increase in entropy, or both. Essential knowledge 5.E.1: Entropy is a measure of the dispersal of matter and energy.
a. Entropy may be understood in qualitative terms rather than formal statistical terms. Although this is not the most rigorous approach to entropy, the use of qualitative reasoning emphasizes that the goal is for students to be able to make predictions about the direction of entropy change, $\Delta S°$, for many typical chemical and physical processes.

b. Entropy increases when matter is dispersed. The phase change from solid to liquid, or from liquid to gas, results in a dispersal of matter in the sense that the individual particles become more free to move, and generally occupy a larger volume. Another way in which entropy increases in this context is when the number of individual particles increases when a chemical reaction precedes whose stoichiometry results in a larger number of product species than reacting species. Also, for a gas, the entropy increases when there is an increase in volume (at constant temperature), and the gas molecules are able to move within a larger space.

5.E.1 Learning Objective:
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. [See SP 1.4]

Essential knowledge 5.E.2: Some physical or chemical processes involve both a decrease in the internal energy of the components ($\Delta H° < 0$) under consideration and an increase in the entropy of those components ($\Delta S° > 0$). These processes are necessarily "thermodynamically favored" ($\Delta G° < 0$).
a. For the purposes of thermodynamic analysis in this course, the enthalpy and the internal energy will not be distinguished.

b. The phrase "thermodynamically favored" means that products are favored at equilibrium ($K > 1$).

c. Historically, the term "spontaneous" has been used to describe processes for which $\Delta G° < 0$. The phrase "thermodynamically favored" is used here to avoid misunderstanding and confusion that can occur because of the common connotation of the term "spontaneous," which students may believe means "immediately" or "without cause."

d. For many processes, students will be able to determine, either quantitatively or qualitatively, the signs of both $\Delta H°$ and $\Delta S°$ for a physical or chemical process. In those cases where $\Delta H° < 0$ and $\Delta S° > 0$, there is no need to calculate $\Delta G°$ in order to determine that the process is thermodynamically favored.

e. As noted below in 5.E.5, the fact that a process is thermodynamically favored does not mean that it will proceed at a measurable rate.

f. Any process in which both ΔH° > 0 and ΔS° < 0 are not thermodynamically favored, (ΔG° > 0) and the process must favor reactants at equilibrium (K < 1). Because the signs of ΔS° and ΔH° reverse when a chemical or physical process is reversed, this must be the case.

5.E.2 Learning Objective:
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 ΔH° and ΔS°, and calculation or estimation of ΔG° when needed. [See SP 2.2, 2.3, 6.4, connects to 5.E.3]

Essential knowledge 5.E.3: If a chemical or physical process is not driven by both entropy and enthalpy changes, then the Gibbs free energy change can be used to determine whether the process is thermodynamically favored.
a. Some exothermic reactions involve decreases in entropy.

b. When ΔG° > 0, the process is not thermodynamically favorable. When ΔG° < 0, the process is thermodynamically favorable.

c. In some reactions, it is necessary to consider both enthalpy and entropy to determine if a reaction will be thermodynamically favorable. The freezing of water and the dissolution of sodium nitrate in water provide good examples of such situations.

5.E.3 Learning Objective:
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. [See SP 2.2, connects to 5.E.2]

Essential knowledge 5.E.4: External sources of energy can be used to drive change in cases where the Gibbs free energy change is positive.
a. Electricity may be used to cause a process to occur that is not thermodynamically favored. Useful examples are charging of a battery and the process of electrolysis.

b. Light may also be a source of energy for driving a process that in isolation is not thermodynamically favored. Useful examples are as follows: 1. The photoionization of an atom, because although the separation of a negatively charged electron from the remaining positively charged ion is highly endothermic, ionization is observed to occur in conjunction with the absorption of a photon 2. The overall conversion of carbon dioxide to glucose through photosynthesis, for which 6 CO2(g) + 6 H2O(l) → C6H12O6(aq) + 6 O2(g) has ΔG° = +2880 kJ/ molrxn, yet is observed to occur through a multistep process that is initiated by the absorption of several photons in the range of 400–700 nm

c. A thermodynamically unfavorable reaction may be made favorable by coupling it to a favorable reaction, such as the conversion of ATP to ADP in biological systems. In this context, coupling means the process involves a series of reactions with common intermediates, such that the reactions add up to produce an overall reaction with a negative ΔG°.

5.E.4 Learning Objectives:
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. [See SP 6.2]

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. [See SP 6.4, connects to

6.B.1]

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. [See SP 6.4, connects to 6.A.2]

Essential knowledge 5.E.5: A thermodynamically favored process may not occur due to kinetic constraints (kinetic vs. thermodynamic control).
a. Many processes that are thermodynamically favored do not occur to any measurable extent, or they occur at extremely slow rates.

b. Processes that are thermodynamically favored, but do not proceed at a measurable rate, are said to be under "kinetic control." High activation energy is a common reason for a process to be under kinetic control. The fact that a process does not proceed at a noticeable rate does not mean that the chemical system is at equilibrium. If a process is known to be thermodynamically favored (through qualitative and/or quantitative analysis of ΔH° and ΔS°), and yet it is not occurring at a measurable rate, then the conclusion is that the process is under kinetic control.

5.E.5 Learning Objective:
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. [See SP 1.3, 7.2, connects to 6.D.1]

Big Idea 6: Any bond or intermolecular attraction that can be formed can be broken. These two processes are in a dynamic competition, sensitive to initial conditions and external perturbations.
Enduring understanding 6.D: The equilibrium constant is related to temperature and the difference in Gibbs free energy between reactants and products. Essential knowledge 6.D.1: When the difference in Gibbs free energy between reactants and products (ΔG°) is much larger than the thermal energy (RT), the equilibrium constant is either very small (for $\Delta G^\circ > 0$) or very large (for $\Delta G^\circ < 0$). When ΔG° is comparable to the thermal energy (RT), the equilibrium constant is near 1.
a. The free energy change for a chemical process in which all of the reactants and products are present in a standard state (as pure substances, as solutions of 1 molar concentration, or as gases at a pressure of 1 bar, or 1 atm) is given a particular symbol, ΔG°.

b. The equilibrium constant is related to free energy by $K = e\ –\Delta G^\circ/RT$. This relation may be used to connect thermodynamic reasoning about a chemical process to equilibrium reasoning about this process. This reasoning can be done quantitatively through numerical examples or qualitatively through estimation. For example, the thermal energy (RT) at room temperature is 2.4 kJ/mol. This sets the energy scale for relating the enthalpy and entropy changes to the magnitude of K, since when the magnitude of ΔG° is large compared to the thermal energy, then K deviates strongly from 1.

c. The relation $K = e\ –\Delta G^\circ/RT$ provides a refinement of the statement in 5.E that processes with $\Delta G^\circ < 0$ favor products, while those with $\Delta G^\circ > 0$ favor reactants. If $\Delta G^\circ < 0$, then $K > 1$, while if $\Delta G^\circ > 0$, then $K < 1$. The phrase "favors products" in 5.E is therefore more precisely stated as $K > 1$, while "favors reactants" in 5.E is more precisely stated as $K < 1$.

d. Since K is directly related to free energy, when the magnitude of K is of primary interest, it is useful to consider whether a reaction is exergonic ($\Delta G^\circ < 0$) or endergonic ($\Delta G^\circ > 0$). (Exothermic versus endothermic is the useful distinction when the issue of interest is whether a reaction releases or consumes energy.) In many biological applications, the magnitude of K is of central importance, and so the exergonic/endergonic distinction is useful.

6.D.1 Learning Objective:
LO 6.25 The student is able to express the equilibrium constant in terms of ΔG° and RT and use this relationship to estimate the magnitude of K and, consequently, the thermodynamic favorability of the process. [See SP 2.3]