





**AP Test Review****BIG IDEA 5: THERMODYNAMICS****Essential Knowledge****5. The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter.**

All changes in matter involve some form of energy change. Thus, the availability or disposition of energy plays a role in virtually all observed chemical processes. Thermodynamics provides a number of tools for understanding this key role, particularly the conservation of energy, including energy transfer in the forms of heat and work. Chemical bonding is central to chemistry, so one key concept associated with energy is that the breaking of a chemical bond inherently requires an energy input, and because bond formation is the reverse process, it will release energy. One key determinant of chemical transformations is the change in potential energy that results from changes in electrostatic forces. In addition to the transfer of energy, the thermodynamic concept of entropy is an important component in determining the direction of chemical or physical change.

**5.A. Two systems with different temperatures that are in thermal contact will exchange energy. The quantity of thermal energy transferred from one system to another is called heat.**

The particles in chemical systems are continually undergoing random motion. The temperature of a system is a direct measure of the average kinetic energy associated with this random motion. When chemical systems that have different temperatures are placed in thermal contact, kinetic energy is transferred from the hotter object to the cooler object until the temperatures become equal. This transfer of kinetic energy is referred to in this course as heat transfer. An understanding of heat as the transfer of energy between a system at higher temperature and a system at lower temperature is fundamental. Many practical applications exist, such as weather prediction, design of heating and cooling systems, and regulation of the rates of chemical reactions.

**5.A.1. Temperature is a measure of the average kinetic energy of atoms and molecules.**

- All of the molecules in a sample are in motion.
- The Kelvin temperature of a sample of matter is proportional to the average kinetic energy of the particles in the sample. When the average kinetic energy of the particles in the sample doubles, the Kelvin temperature is doubled. As the temperature approaches 0 K (zero Kelvin), the average kinetic energy of a system approaches a minimum near zero.
- The Maxwell-Boltzmann distribution shows that the distribution of kinetic energies becomes greater (more disperse) as temperature increases.

**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.**

- On average, molecules in the warmer body have more kinetic energy than the molecules in the cooler body.
- Collisions of molecules that are in thermal contact transfer energy.
- Scientists describe this process as “energy is transferred as heat.”
- Eventually, thermal equilibrium is reached as the molecular collisions continue. The average kinetic energy of both substances is the same at thermal equilibrium.
- 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.
- 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.B. Energy is neither created nor destroyed, but only transformed from one form to another.

The conservation of energy plays an important role in reasoning about the transfer of energy in chemical systems. A molecular system has energy that is a function of its current state. The energy of a system changes when the state of the system changes; for instance, when the temperature of the system changes, when a substance melts or boils, or when a chemical reaction occurs, the energy changes. Conservation of energy implies that any change in the energy of a system must be balanced by the transfer of energy either into or out of the system. This energy transfer can take the form of either heat transfer or work. Work includes all forms of energy transfer other than heat transfer. Examples of mechanical work include the expansion of a gas against a piston in engines. The change in energy associated with a chemical process is an important aspect of such processes characterizing, for instance, the amount of energy that can be obtained from a fuel system. Because the change in energy associated with a given process is proportional to the amount of substance undergoing that process, this change is best described on a per mole (or per gram) basis, as in heat capacities (for heating/cooling), enthalpies of fusion or vaporization (for physical transformations), and enthalpies of reaction (for chemical transformations). Calorimetry provides a convenient means to measure changes in energy, and thus is used experimentally to determine heat capacities or enthalpies of physical and chemical transformations.

- 5.B.1. Energy is transferred between systems either through heat transfer or through one system doing work on the other system.
- 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.
  - An additional form of energy transfer is through work. Work is described by other scientific frameworks, such as Newtonian Mechanics or electromagnetism.
  - 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.
- 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.
- 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.
  - 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.3. Chemical systems undergo three main processes that change their energy: heating/cooling, phase transitions, and chemical reactions.
- 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.
  - The amount of energy needed to heat one gram of a substance by 1°C is the specific heat capacity of that substance.
  - 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.4. Calorimetry is an experimental technique that is used to determine the heat exchanged/transferred in 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.C. **Breaking bonds requires energy, and making bonds releases energy.**

Chemical bonds arise from attractive interactions between negatively charged electrons and the positively charged nuclei of the atoms that make up the bond. As electrons approach a positive charge, the potential energy of a system is lowered. Therefore, having electrons shared between atoms results in the system being in a lower energy state, which can only happen if energy is somehow released. Thus, making chemical bonds releases energy. The converse is true for the opposing process. In order to break a chemical bond, energy must be put into the system to overcome the attractive interaction between the shared electrons and the nuclei of the bonded atoms. When considering chemical reactions, however, it is important to recognize that in most cases both bond breaking and bond formation occurs. The overall energy change is determinable from looking at all the energy inputs (to break bonds) and the energy outputs (from the formation of bonds). There are several ways to calculate energy changes for reactions, including traditionally used methods involving enthalpy of formation. One compelling conceptual model for this calculation is to use average bond energies or enthalpies to determine the energy change of a reaction. Many practical examples of chemistry take place in solvents (often water); thus, the determination of overall changes in energy for a reaction must include consideration of any solvent interactions with reactants and products. Energy may appear in different forms, such as potential energy or kinetic energy. In chemical systems, the stored energy is called chemical energy, and the energy of motion (translational, rotational, or vibrational) is called thermal energy. Chemical energy is the potential energy associated with chemical systems. The amount of chemical energy in a system changes when the chemicals are allowed to react. The energy transferred to or from the surroundings when a chemical system undergoes a reaction is often in the form of thermal energy.

- 5.C.1. Potential energy is associated with a particular geometric arrangement of atoms or ions and the electrostatic interactions between them.
- 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.
  - 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.
  - 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.
  - 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.
  - Stronger bonds tend to be shorter bonds.
- 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.
- During a chemical reaction, bonds are broken and/or formed, and these events change the potential energy of the reaction system.
  - 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.
  - 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.
  - 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.
  - 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.
  - 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.
  - 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.D. Electrostatic forces exist between molecules as well as between atoms or ions, and breaking the resultant intermolecular interactions requires energy.**

The same essential interaction that forms chemical bonds, electrostatic attraction, also explains the attractive forces as non-bonded atoms draw near each other. When atoms approach each other, there is always an electrostatic attraction between the positive charges of the nucleus in each atom and the electrons of the approaching atom. When a chemical bond does not form between the two atoms, this attraction is described as an intermolecular force. For molecular systems, these intermolecular forces are understood in terms of charge distributions leading to dipoles (permanent or induced) that then attract each other. The most common categories for these interactions are (a) dipole-dipole, (b) dipole-induced dipole, and (c) induced dipole-induced dipole (dispersion) forces. Hydrogen bonding is an important, specialized form of dipole-dipole interactions. These forces may occur (a) between small molecules, (b) between different large molecules, or (c) between different regions of the same large molecule. The distinction at the particulate level between electrostatic interactions of non-bonded atoms and those of chemically bonded atoms provides the cleanest distinction between a chemical and physical process. A physical process generally involves non-bonded interactions, and a chemical process involves breaking and/or forming covalent bonds. In many systems involving large molecules (both biochemical systems and synthetic polymer systems), the non-bonded interactions play important roles in the observed functions of the systems.

- 5.D.1. Potential energy is associated with the interaction of molecules; as molecules draw near each other, they experience an attractive force.
- Chemists categorize intermolecular forces in terms of the nature of the charge distributions in the molecules involved. Thus, dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole (dispersion) can be defined.
  - All substances will manifest dispersion forces, and these forces tend to be larger when the molecules involved have more electrons or have a larger surface area.
  - Hydrogen bonding is a relatively strong type of intermolecular interaction that occurs when hydrogen atoms that are covalently bonded to the highly electronegative atoms (N, O, and F) are also attracted to the negative end of a dipole formed by the electronegative atom (N, O, and F) in a different molecule, or a different part of the same molecule. When hydrogen bonding is present, even small molecules may have strong intermolecular attractions.
- 5.D.2. At the particulate scale, chemical processes can be distinguished from physical processes because chemical bonds can be distinguished from intermolecular interactions.
- The distinction between chemical and physical processes relates to the nature of the change in molecular interactions. Processes that involve the breaking and/or formation of chemical bonds are classified as chemical processes. Processes that involve only changes in weak intermolecular interactions, such as phase changes, are classified as physical processes.
  - A gray area exists between these two extremes. For instance, the dissolution of a salt in water involves breaking of ionic bonds and the formation of interactions between ions and solvent. The magnitude of these interactions can be comparable to covalent bond strengths, and so plausible arguments can be made for classifying dissolution of a salt as either a physical or chemical process.

- 5.D.3. Non-covalent and intermolecular interactions play important roles in many biological and polymer systems.
- In large biomolecules, non-covalent interactions may occur between different molecules or between different regions of the same large biomolecule.
  - The functionality and properties of molecules depend strongly on the shape of the molecule, which is largely dictated by non-covalent interactions. For example, the function of enzymes is dictated by their structure, and properties of synthetic polymers are modified by manipulating their chemical composition and structure.

**5.E. Chemical or physical processes are driven by a decrease in enthalpy or an increase in entropy, or both.**

One of the most powerful applications of thermodynamic principles is the ability to determine whether a process corresponding to a physical or chemical change will lie toward the reactant or product side when the process reaches a steady equilibrium state. The standard change in Gibbs free energy,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , is used to make this determination. If  $\Delta G^\circ < 0$ , then products are favored at equilibrium, and the forward process is considered to be “thermodynamically favored.” Conversely, if  $\Delta G^\circ > 0$ , then reactants are favored at equilibrium, and the reverse process is considered to be “thermodynamically favored.” Both the enthalpy change ( $\Delta H^\circ$ ) and the entropy change ( $\Delta S^\circ$ ) are closely related to the structure and nature of the components of the system; for this reason, it is often possible to make qualitative determinations concerning the sign (and magnitude) of  $\Delta G^\circ$  without explicit calculation. Enthalpy changes are closely related to the relative bond energies (and relative strengths of intermolecular interactions) of the reactants and products; entropy changes are generally related to the states of the components and the number of individual particles present. In this way, the Gibbs free energy provides a framework based on molecular structure and intermolecular interactions for understanding why some chemical reactions are observed to proceed to near completion, while others reach equilibrium with almost no products being formed. Some processes that are not thermodynamically favored (for example, the recharging of a battery) can be driven to occur through the application of energy from an external source — in this case, an electrical current. Importantly, in biochemical systems, some reactions that oppose the thermodynamically favored direction are driven by coupled reactions. Thus, a cell can use energy to create order (a direction that is not thermodynamically favored) via coupling with thermodynamically favored reactions. For example, many biochemical syntheses are coupled to the reaction in which ATP is converted to ADP + phosphate. In some cases, processes that are thermodynamically favored are not observed to occur because of some kinetic constraint; quite often there is a high activation energy to overcome in order for the process to proceed. Thus, although Gibbs free energy can be used to determine which direction of a chemical process is thermodynamically favored, it provides no information about the rate of the process, or the nature of the process on the microscopic scale.

- 5.E.1. Entropy is a measure of the dispersal of matter and energy.
- 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,  $\Delta S^\circ$ , for many typical chemical and physical processes.
  - 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.



- c. Entropy increases when energy is dispersed. From KMT, we know that the distribution of kinetic energy among the particles of a gas broadens as the temperature increases. This is an increase in the dispersal of energy, as the total kinetic energy of the system becomes spread more broadly among all of the gas molecules. Thus, as temperature increases, the entropy increases.
- 5.E.2. Some physical or chemical processes involve both a decrease in the internal energy of the components ( $\Delta H^\circ < 0$ ) under consideration and an increase in the entropy of those components ( $\Delta S^\circ > 0$ ). These processes are necessarily “thermodynamically favored” ( $\Delta G^\circ < 0$ ).
- For the purposes of thermodynamic analysis in this course, the enthalpy and the internal energy will not be distinguished.
  - The phrase “thermodynamically favored” means that products are favored at equilibrium ( $K > 1$ ).
  - Historically, the term “spontaneous” has been used to describe processes for which  $\Delta G^\circ < 0$ . 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.”
  - For many processes, students will be able to determine, either quantitatively or qualitatively, the signs of both  $\Delta H^\circ$  and  $\Delta S^\circ$  for a physical or chemical process. In those cases where  $\Delta H^\circ < 0$  and  $\Delta S^\circ > 0$ , there is no need to calculate  $\Delta G^\circ$  in order to determine that the process is thermodynamically favored.
  - 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.
  - Any process in which both  $\Delta H^\circ > 0$  and  $\Delta S^\circ < 0$  are not thermodynamically favored, ( $\Delta G^\circ > 0$ ) and the process must favor reactants at equilibrium ( $K < 1$ ). Because the signs of  $\Delta S^\circ$  and  $\Delta H^\circ$  reverse when a chemical or physical process is reversed, this must be the case.
- 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.
- Some exothermic reactions involve decreases in entropy.
  - When  $\Delta G^\circ > 0$ , the process is not thermodynamically favorable. When  $\Delta G^\circ < 0$ , the process is thermodynamically favorable.
  - 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.4. External sources of energy can be used to drive change in cases where the Gibbs free energy change is positive.
- 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.
  - Light may also be a source of energy for driving a process that in isolation is not thermodynamically favored. Useful examples are as follows:
    - 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
    - The overall conversion of carbon dioxide to glucose through photosynthesis, for which  $6 \text{ CO}_2(\text{g}) + 6 \text{ H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) + 6 \text{ O}_2(\text{g})$  has  $\Delta G^\circ = +2880 \text{ kJ/mol}_{\text{rxn}}$ , 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  $\Delta G^\circ$ .
- 5.E.5. A thermodynamically favored process may not occur due to kinetic constraints (kinetic vs. thermodynamic control).
- Many processes that are thermodynamically favored do not occur to any measurable extent, or they occur at extremely slow rates.
  - 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  $\Delta H^\circ$  and  $\Delta S^\circ$ ), and yet it is not occurring at a measurable rate, then the conclusion is that the process is under kinetic control.

## Learning Objectives

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|---|--------------------------|
| 5.1 The student is able to create or use graphical representations in order to connect the dependence of potential energy to the distance between atoms and factors, such as bond order (for covalent interactions) and polarity (for intermolecular interactions), which influence the interaction strength.   | Big Idea 5               |
| 5.2 The student is able to relate temperature to the motions of particles, either via particulate representations, such as drawings of particles with arrows indicating velocities, and/or via representations of average kinetic energy and distribution of kinetic energies of the particles, such as plots of the Maxwell- Boltzmann distribution.   | EK 5.A.1                 |
| 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.   | EK 5.A.2                 |
| 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.   | EK 5.B.1 and<br>EK 5.B.2 |
| 5.5 The student is able to use conservation of energy to relate the magnitudes of the energy changes when two non-reacting substances are mixed or brought into contact with one another.   | EK 5.B.1 and<br>EK 5.B.2 |
| 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. | EK 5.B.3                 |
| 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.  | EK 5.B.4                 |

- 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. EK 5.C.2
- 5.9 The student is able to make claims and/or predictions regarding relative magnitudes of the forces acting within collections of interacting molecules based on the distribution of electrons within the molecules and the types of intermolecular forces through which the molecules interact. EK 5.D.1
- 5.10 The student can support the claim about whether a process is a chemical or physical change (or may be classified as both) based on whether the process involves changes in intramolecular versus intermolecular interactions. EK 5.D.2
- 5.11 The student is able to identify the non-covalent interactions within and between large molecules, and/or connect the shape and function of the large molecule to the presence and magnitude of these interactions. EK 5.D.3
- 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. EK 5.E.1
- 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  $\Delta H^\circ$  and  $\Delta S^\circ$ , and calculation or estimation of  $\Delta G^\circ$  when needed. EK 5.E.2
- 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. EK 5.E.3
- 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. EK 5.E.4
- 5.16 The student can use Le Chatelier's principle to make qualitative predictions for systems in which coupled reactions that share a common intermediate drive formation of a product. EK 5.E.4
- 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. EK 5.E.4
- 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. EK 5.E.5



## AP Test Review

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### FREE RESPONSE PRACTICE

Abide by the time guidelines. Use only (1) a black or blue pen or No. 2 pencil, (2) a scientific or graphing calculator, and (3) the provided Periodic Table and list of Equations and Constants.

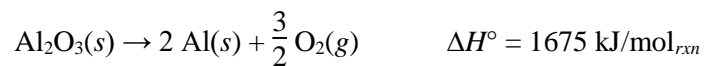
Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved at arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

Write clearly and legibly. Cross out any errors you make; erased or crossed-out work will not be scored.

**2015 AP Chemistry #7** (9 minutes)

Aluminum metal can be recycled from scrap metal by melting the metal to evaporate impurities.

- (a) Calculate the amount of heat needed to purify 1.00 mole of Al originally at 298 K by melting it. The melting point of Al is 933 K. The molar heat capacity of Al is  $24 \text{ J}/(\text{mol}\cdot\text{K})$ , and the heat of fusion of Al is  $10.7 \text{ kJ}/\text{mol}$ .
- (b) The equation for the overall process of extracting Al from  $\text{Al}_2\text{O}_3$  is shown below. Which requires less energy, recycling existing Al or extracting Al from  $\text{Al}_2\text{O}_3$ ? Justify your answer with a calculation.



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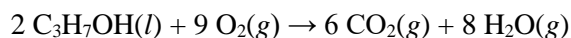
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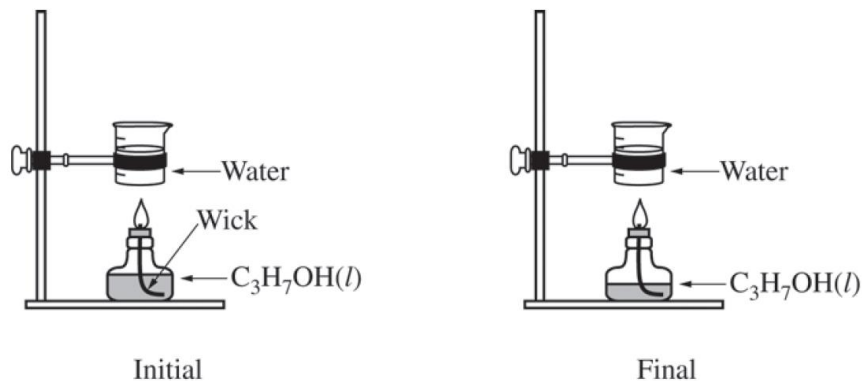
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**2017 AP Chemistry #5** (9 minutes)

A student performs an experiment to determine the enthalpy of combustion of 2-propanol,  $\text{C}_3\text{H}_7\text{OH}(l)$ , which combusts in oxygen according to the equation above. The student heats a sample of water by burning some of the  $\text{C}_3\text{H}_7\text{OH}(l)$  that is in an alcohol burner, as represented below. The alcohol burner uses a wick to draw liquid up into the flame. The mass of  $\text{C}_3\text{H}_7\text{OH}(l)$  combusted is determined by weighing the alcohol burner before and after combustion.



Data from the experiment are given in the table below.

Mass of $\text{C}_3\text{H}_7\text{OH}(l)$ combusted	0.55 g
Mass of water heated	125.00 g
Initial temperature of water	$22.0^\circ\text{C}$
Final temperature of water	$51.1^\circ\text{C}$
Specific heat of water	$4.18 \text{ J}/(\text{g}\cdot^\circ\text{C})$

- (a) Calculate the magnitude of the heat energy, in kJ, absorbed by the water. (Assume that the energy released from the combustion is completely transferred to the water.)
- (b) Based on the experimental data, if one mole of  $\text{C}_3\text{H}_7\text{OH}(l)$  is combusted, how much heat, in kJ, is released? Report your answer with the correct number of significant figures.
- (c) A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing  $\text{C}_3\text{H}_7\text{OH}(l)$  that is contaminated with water, which is miscible with  $\text{C}_3\text{H}_7\text{OH}(l)$ . The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.

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