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# AP Chemistry Special Focus: Thermochemistry

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## A Note from the Editor

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To understand why reactions happen and what drives them, one must understand the principles of thermodynamics. This Special Focus set of materials is to help teachers understand these principles so they can help correct the misunderstandings we often see while reading the AP exam. The writers in this Special Focus theme are all esteemed teachers with many years of AP experience in the classroom as well as various levels of AP Exam involvement including: Chief Reader, test development members, questions leaders, and readers. Each has their own style of writing which gives a different perspective when concept overlap occurs. What they have to share will help teachers prepare students for AP questions covering thermochemistry.

AP test conventions of “ $\rightleftharpoons$ ” to represent equilibrium reactions and the use of  $\text{kJ mol}^{-1}$  of reaction will be used.

The chapters are arranged to be in a progressive order. The first chapter begins with basic definitions and explains the concepts. The subsequent chapters then branch into the areas of thermodynamics. How workshop presenters would use these materials depends on if they are teaching a one day workshop, two day workshop or week long institute and on participants needs.

In a one or two day workshop, I would take the time to explain what is in each chapter, the major misconceptions addressed by the chapter and use the practice problems to review the major concepts as the problems are worked.

When completing calculations, students often get lost in the numbers and have no idea which units they should be using. I would emphasize with teachers to always have students include units in their work, even though there are times the units are ignored when reading the test. For example, if the test says to solve in kilojoules, any number written is assumed to be in kJ if no unit is written.

The chapter by Bill Bond introduces and defines the basic terminology as well as addresses the concepts of heat, temperature, state functions, work and internal energy, thermodynamics, enthalpy, heats of reactions, and bond energy. It is crucial everyone understands these basics. Often students can do the “math” problems, but really do not understand the concepts when asked to explain them. To facilitate discussion, I would ask teachers to share methods they use in the classroom to make sure these concepts are clearly understood.

## Special Focus: Thermochemistry

The chapter by Valerie Ferguson covers the concepts of calorimetry. I would make sure to cover the example problems. Valerie addresses heat capacity, specific heat, exothermic and endothermic reactions, enthalpy, heat of neutralization, and Hess's law. Make sure to cover the units of each as this is something students frequently miss.

The chapter by Cheri Smith covers various methods of finding the enthalpy of a reaction including the Law of Hess, heats of formation, and bond energies. There is also a special section where the units of kJ/mol or kJ are discussed. Students often make mistakes on the AP test involving thermodynamics units. There are excellent examples of how to solve enthalpy problems using each method.

The chapter by Linda Kruegel covers free energy and its relationship with both equilibrium and voltage values. If the student understands free energy, the relationships make sense. The AP test always asks about these relationships summarized below.

G	V	K
negative	positive	Greater than 1
zero	zero	1
positive	negative	Less than 1

The chapter by Lew Acampora provides detailed coverage of enthalpy, entropy and free energy. The history behind these concepts is included and gives a unique perspective to this unit. The mathematics of the concepts are clearly explained and cover the misunderstandings students often give in their answers on the AP test. Several example questions are given with solutions.

The chapter by Arden Zip covers the Laws of thermodynamics and their application to chemistry. He discusses all three laws in detail and explains why they can be used to determine what is driving a reaction and if one will occur. This chapter clearly explains the major concepts of thermodynamics and is crucial to student understanding.

The concluding chapter by Adele Mouakad has a sample unit plan with a time line and sample labs that a teacher might use. This is only one approach. Providing time during the workshop for participants to share methods they have found successful is encouraged.

In a week-long institute, I would have the presenter assign readings each night, answer any questions the participants have each day, and then discuss different labs and classroom approaches to teaching the material. This way, one can go more in depth. One might also want to do some of the mentioned labs that reinforce each day's work.

Special thank you's to all the following who helped review this document: Carol Brown, Heather Hattori, David Hostage, Dr. Richard Langley, Dr. George Miller, and Dr. John Moore.

# Introduction to Energy and Chemical Reactions— Including State Functions, Work and Internal Energy, Enthalpy—Heats of Reaction

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Many people think of heat as something that is necessary to change the temperature of a substance, and think of temperature as an instrument of heat measurement. Although there is an intuitive understanding of the concepts of heat and temperature, to go beyond this requires a close examination and quantification of the nature of heat as a form of energy.

Heat can be a tricky concept for students to understand. Kinetic molecular theory tells us that as a substance is heated, molecules gain energy and move faster. We cannot measure the amount of energy in the form of heat a substance contains, but we can measure the flow of heat energy which always moves from a warm to a cold body until temperatures equalize. Temperature change is used to measure this heat flow—including the heat flow which occurs in all chemical reactions. This measurement of heat flow is of great practical importance.

## Energy and Chemical Reactions

Chemical reactions involve not just the conversion of reactants into products, but also involve an energy change in the form of heat—heat released as the result of a reaction, or heat absorbed as a reaction proceeds. Energy changes accompany all chemical reactions and are due to rearranging of chemical bonding. The energy of chemical bonding, a form of chemical potential energy, should be considered in terms of breaking existing bonds and forming new bonds. The term “energy stored in bonds” can be misleading. In fact, addition of energy is always a requirement for the breaking of bonds but the breaking of bonds in and of itself does not release energy. Energy release occurs when new bonds are formed. If more energy is released when new bonds form than was required to break existing bonds, then the difference will result in an overall release of energy. If, on the other hand, more energy is required to break existing bonds than is released when new bonds form, the difference will result overall in energy being absorbed. Whether or not an overall reaction releases or requires energy depends upon the final balance between the breaking and forming of chemical bonds. Now, and later, when students study chemical kinetics, it is important to distinguish “activation energy,” often misleadingly interpreted as energy needed to “start” a reaction, from the thermodynamic “energy of reaction” dealt with here. This latter does not depend on any pathway of how reactants become products. While thermodynamic treatments of an “activated complex” may be used in advanced courses, they are not studied in AP, which maintains a clear distinction between thermodynamic state function changes and kinetic quantities.

## Thermodynamics

*ermodynamics* is the study of energy transformations. A precise definition of energy is difficult. In physics, energy is defined as “the ability to do work”—that is, a force applied over a distance. Although we are unable to see or directly measure energy, we know that energy has the ability to make things happen. Two common forms of energy in chemistry are kinetic energy, the energy of motion, and potential energy, or stored energy.

When studying thermodynamics, it is useful to discuss a process in terms of a *system* and its interaction with its *surroundings*. In a chemistry setting, a system includes all substances undergoing a physical or chemical change. The surroundings would include everything else that is not part of the system.

### Example:

Concentrated sulfuric acid is diluted in water contained in a beaker:



All of the reactants and products in the above equation, along with hydrating water molecules, would be considered the “system.” Everything else—nonhydrating water molecules, the beaker, the air, etc.—would be considered the “surroundings.”

Most commonly, energy is exchanged between a system and its surroundings in the form of heat. Heat will be transferred between objects at different temperatures. *ermochemistry* is the study of thermal energy changes.

Energy is a property that is determined by specifying the condition or “state” (e.g., temperature, pressure, etc.) of a system or substance. Hence, it is referred to as a *state function*—where its value is determined only by its present condition and not on its history. Heat is not a property of a system or substance and is not a state function. Heat is a process—the transfer of energy from a warm to a cold object.

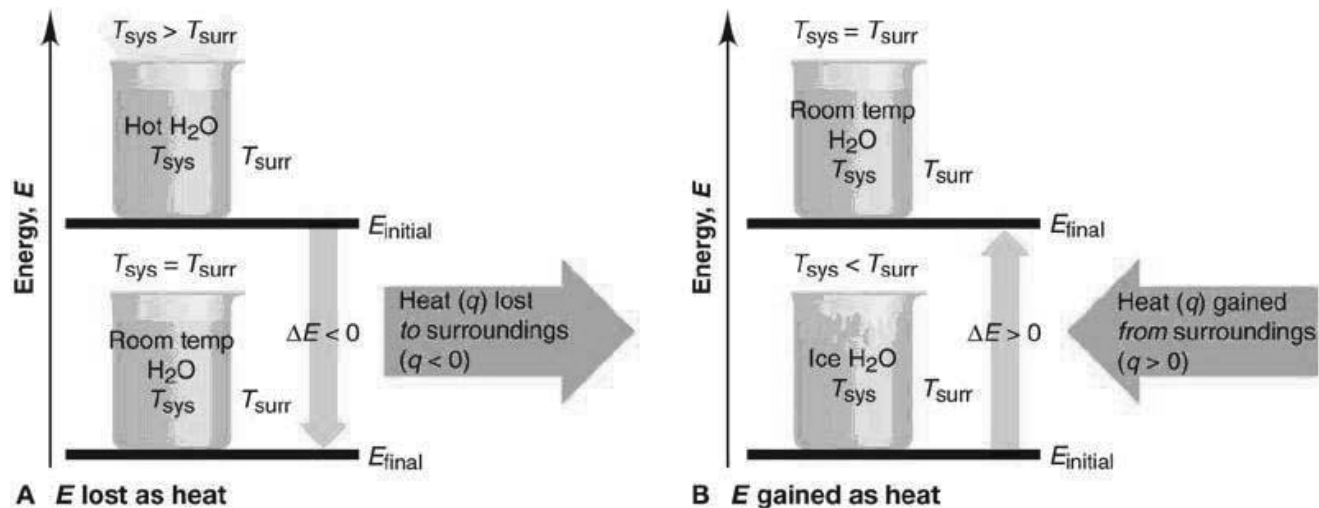
An *exothermic reaction* is one where heat is released from a system to its surroundings. In this case, the temperature of the surroundings will increase.

An *endothermic reaction* is one where heat is absorbed by a system from its surroundings. In this case, the temperature of the surroundings will decrease.

### Examples:

If concentrated sulfuric acid is added to water, an exothermic reaction occurs—the solution increases in temperature.

If solid ammonium nitrate is added to water, an endothermic reaction occurs—the solution decreases in temperature.



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### Sample Question:

- What will be the sign on the value of the heat transferred in the case of an:
  - exothermic reaction.
  - endothermic reaction.

Answer: (a) negative; (b) positive

### Internal Energy:

The term *internal energy* refers to all of the energy contained within a chemical system. For example, in the case of a gas, the kinetic energy of the molecules makes a large contribution to the total internal energy. The flow of heat between a system and its surroundings involves changes in the internal energy of the system.

An increase in the internal energy of a system can take three forms:

- an increase in temperature
- a phase change
- the initiation of a chemical reaction.

A decrease in the internal energy of a system will usually result in:

- a decrease in temperature
- a phase change.

NOTE: It would be unusual for a decrease in internal energy to initiate a chemical reaction.



Often, the outcome of an exothermic reaction is a decrease in internal energy, while the outcome of an endothermic reaction is an increase in internal energy.

While the total internal energy of a system ( $E$ ) cannot be determined, changes in internal energy ( $\Delta E$ ) can be determined. The change in internal energy will be the amount of energy exchanged between a system and its surroundings during a physical or chemical change. This can be summarized by the equation:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Sample Question:

2. What can happen to a system in which an internal energy change is occurring?

Answer: The system can undergo a change in temperature, a phase change can occur, or a chemical reaction can be initiated.

### Heat, Work, and Energy:

The *First Law of Thermodynamics*, sometimes called the Law of Conservation of Energy, states that the energy of the universe is constant and while energy can be converted from one form into another, it cannot be created or destroyed. Considering this, energy exchanged between a system and its surroundings can be considered to offset one another—the same amount of energy leaving a system will enter the surroundings (or vice versa), so the total amount of energy remains constant.

In a chemical system, the energy exchanged between a system and its surroundings can be accounted for by heat ( $q$ ) and work ( $w$ ).

$$\Delta E = q + w$$

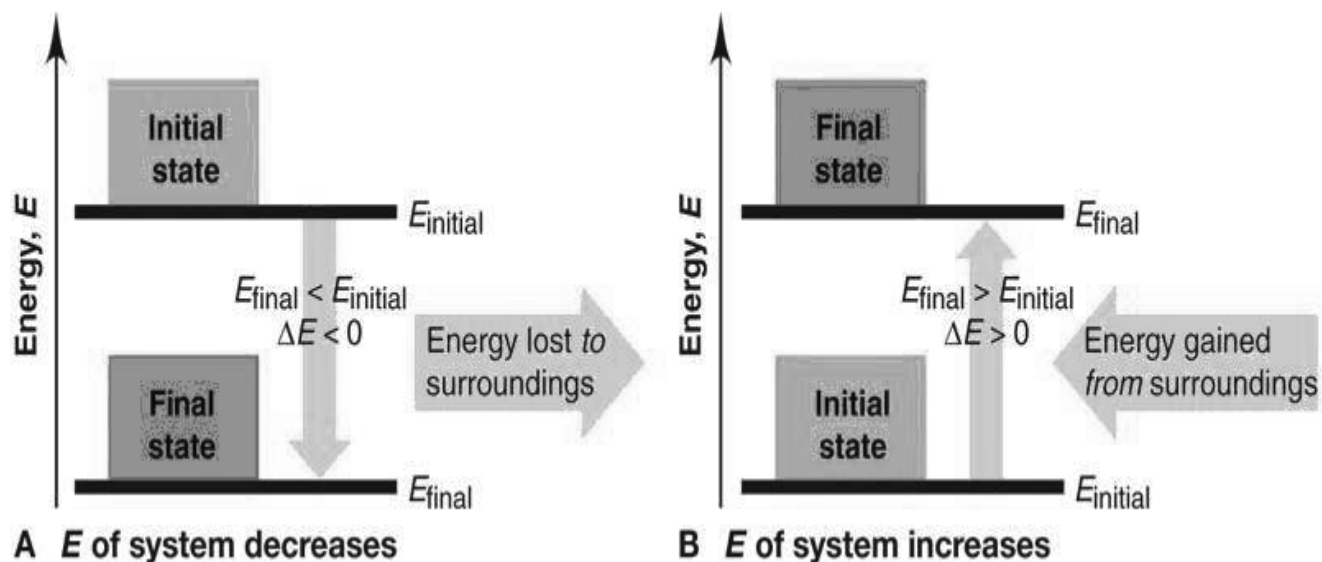
Note: Other than heat, all energy transferred is defined as work.

Although a change in internal energy (mentioned earlier) can assume several different forms, energy can be exchanged between a system and its surroundings only as heat or work.

Whether energy change, heat, and work assume positive or negative values is determined from the perspective of the system. If a system loses energy to its surroundings,  $\Delta E < 0$  (or vice versa).

Heat and work have a similar relationship. If a system loses heat to its surroundings,  $q < 0$  (or vice versa). If a system performs work on its surroundings,  $w < 0$  (or vice versa).

The SI (Metric System) unit for all forms of energy is the joule (J).



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**TABLE 6-1**

### Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	-
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	-

Work refers to a force that moves an object over a distance. Only pressure/volume work (i.e., the expansion/contraction of a gas) is of significance in chemical systems and only when there is an increase or decrease in the amount of gas present.

Example: When, in a chemical reaction, there are more moles of product gas compared to reactant gas, the system can be thought of as performing work on its surroundings (making  $w < 0$ ) because it is “pushing back,” or moving back the atmosphere to make room for the expanding gas. When the reverse is true,  $w > 0$ .

**Table 6.1 The Sign Conventions\* for  $q$ ,  $w$ , and  $\Delta E$**

$q$	+	$w$	=	$\Delta E$
+		+		+
+		-		Depends on <i>sizes</i> of $q$ and $w$
-		+		Depends on <i>sizes</i> of $q$ and $w$
-		-		-

\*For  $q$ : + means system *gains* heat; - means system *loses* heat.  
For  $w$ : + means work done *on* system; - means work done *by* system.

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The expansion/contraction of a gas against constant external pressure can be represented by the equation:

$$w = -P \Delta V$$

where “ $w$ ” represents work done by/on a system; “ $P$ ” represents constant external pressure, and  $\Delta V$  represents the final volume minus the initial volume. This equation will also represent work done on or by a system when the amount of gas changes due to a chemical reaction where gaseous substances are produced or consumed. The student will need to know the conversion factor 101.3 J/L · atm to solve these types of problems.

If there is no change in the total volume of gas before and after a reaction occurs (i.e.,  $\Delta V = 0$ ), there is no significant work done by or on the system.

Note: If the reaction is performed in a rigid container, there may be a change in pressure, but if there is no change in volume, the atmosphere outside the container didn’t “move” and without movement, no work is done by or on the system. If there is no change in volume ( $\Delta V = 0$ ), then no work is done by or on the system ( $w = 0$ ) and the change in internal energy will be entirely due to the heat involved ( $\Delta E = q$ ).

Chemicals commonly react at constant external pressure—often at atmospheric pressure. Consider the mathematics below:

$$\begin{aligned} E &= q + w \\ E &= q + (-P \Delta V) \\ E_{\text{final}} - E_{\text{initial}} &= q + [(-P V_{\text{final}}) - (-P V_{\text{initial}})] \\ q &= (E_{\text{final}} - P V_{\text{final}}) - (E_{\text{initial}} - P V_{\text{initial}}) \end{aligned}$$

The term *enthalpy* ( $H$ ) is used to represent  $E - PV$ , which occurs at constant external pressure. In a way, enthalpy can be considered to be energy with work taken out. Of course, *change in enthalpy* ( $\Delta H$ ) will represent the exchange of heat between a system and its surroundings at constant external pressure.

$$H = E - P V$$

Enthalpy change is then equal to heat exchanged at constant external pressure:

$$\Delta H = q_{\text{constant pressure}}$$

For chemical reactions,  $\Delta H$  can be calculated theoretically and measured directly. Often  $P \Delta V$  is small—even when there is a gas involved, even when there is a change in volume. Theoretically, therefore, work is done by or on the system. If  $P \Delta V$  is sufficiently small, it can be ignored from calculations, and the change in internal energy can be assumed to be the same as the change in enthalpy:

$$\Delta H = \Delta E$$

### Sample Questions:

3. A gas absorbs 28.5 J of heat and then performs 15.2 J of work. The change in internal energy of the gas is:
- 13.3 J
  - 13.3 J
  - 43.7 J
  - 43.7 J
  - none of the above

Answer: (b)  $\Delta E = q + w$ ; 28.5 J - 15.2 J = 13.3 J

4. Which of the following statements correctly describes the signs of  $q$  and  $w$  for the following exothermic process at 1 atmosphere pressure and 370 kelvin?

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- (a)  $q$  and  $w$  are both negative
- (b)  $q$  is positive and  $w$  is negative
- (c)  $q$  is negative and  $w$  is positive
- (d)  $q$  and  $w$  are both positive
- (e)  $q$  and  $w$  are both zero

Answer: c. An exothermic indicates  $q$  is negative and the gas is condensing to a liquid so it is exerting less pressure on its surroundings indicating  $w$  is positive.

5. A system does 130. J of work on its surroundings while 70. J of heat are added to the system. What is the internal energy change for the system?

Answer:  $E = q - w = 70. \text{ J} - 130. \text{ J} = -60. \text{ J}$

6. What will be the volume change if 125 J of work is done on a system containing an ideal gas? The surroundings exert a constant pressure of 5.2 atmospheres.

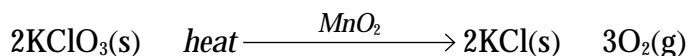
Answer:  $w = -P \Delta V; \Delta V = \frac{125 \text{ J}}{5.2 \text{ atm}} = 24.0 \text{ L}$  e volume will decrease by 0.24 liters.

7. For the following reactions, performed at constant external pressure, is work done on the system by the surroundings, by the surroundings on the system, or is the amount of work negligible?

- (a)  $\text{Sn(s)} + 2\text{F}_2(\text{g}) \rightarrow \text{SnF}_4(\text{s})$
- (b)  $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$
- (c)  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- (d)  $\text{SiI}_4(\text{g}) \xrightarrow{\text{heat}} \text{Si(s)} + 2\text{I}_2(\text{g})$

Answer:

- (a)  $w < 0$ ; work is done on the system as 2 moles of gas reactant decrease to 0 moles of gas product
  - (b)  $w \approx 0$ ; negligible; no change in volume.
  - (c)  $w \approx 0$ ; negligible; 1 mole of gas reactant to 1 mole of gas product indicates a volume change close to zero.
  - (d)  $w > 0$ ; 1 mole of gas reactant expands to 2 moles of gas product thereby doing work on the surroundings.
8. With the addition of heat and manganese dioxide as a catalyst, potassium chlorate at constant pressure will decompose according to the following equation:



Determine whether each of the values  $E$ ,  $H$ ,  $q$ , and  $w$  will be positive, negative, or unable to determine.

Answer:  $H < 0$ ;  $q < 0$ ;  $w < 0$ ;  $E$  cannot be determined from information given. The sign of  $E$  depends upon the magnitudes of  $q$  and  $w$

### Heats of Reaction:

In thermodynamics, a reaction is “complete” when no further changes take place and substances have returned to their original temperature—usually room temperature. The total heat absorbed or released in a complete reaction is called the heat of reaction ( $q_{\text{reaction}}$ ). If the heat of reaction occurs at constant external pressure, the heat of reaction is the same as the enthalpy change ( $H$ ). The value of  $H$  depends upon the specific reaction, amounts of substances, and the temperature. As a result,  $H$  is expressed in terms of quantity of heat (joules) per quantity of substance (usually moles), at a specific temperature. The unit for  $H$  is usually joules/mole or kilojoules/mole.  $H$  for a reaction is given as heat released or absorbed in the reaction according to the molar amounts of reactants and products in the balanced equation. This is referred to as a thermochemical equation and includes the value for  $H$ .

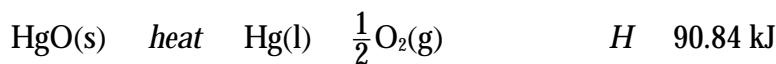
#### Examples:



NOTE: At this point, refer to a table of thermodynamic data including positive and negative values for  $H$ , found in most college-level textbooks, such as Figure 5.16 found on page 168 of *Chemistry: The Central Science* 9th edition by Brown, LeMay, and Bursten published by Pearson/Prentice Hall, 2003.

Thermochemical equations can also be expressed as heat of reaction per mole of reactant or product. This may require fractional coefficients.

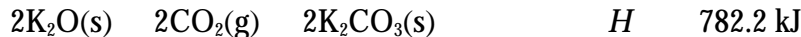
#### Example:



Since  $H$  in a thermochemical equation is always molar amounts in the balanced equation, the unit kJ/mol is unnecessary.

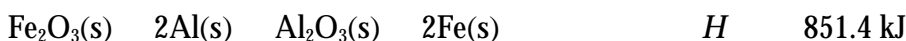
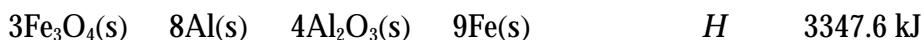
If the amount of reactants changes, the heat of reaction will change proportionally.

Example:



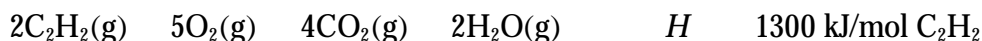
Sample Questions:

9. Compare the quantities of heat released per mole of iron formed when oxides of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  react with aluminum.



Answer for  $\text{Fe}_3\text{O}_4$ : 3347.6 kJ/9 mol      372.0 kJ/mol and for  $\text{Fe}_2\text{O}_3$   
851.4 kJ/2 mol      425.7 kJ/mol

10. The combustion of acetylene in a welding torch liberates intense heat. The equation for this reaction is:



How much heat, in joules, is liberated when 0.260 kg of  $\text{C}_2\text{H}_2$  undergoes complete combustion?

Answer:  $0.260 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol}}{26.04 \text{ g}} \times \frac{1300 \text{ kJ}}{1 \text{ mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 1.30 \times 10^7 \text{ J}$

### Standard State/Standard Enthalpy Change:

To compare heats of reaction for different reactions, it is necessary to know the temperatures at which heats of reaction are measured and the physical states of the reactants and products. Measurements have been made and tables constructed of heats of reaction with reactants in their "standard states". Standard state is the most stable physical state of reactants at 1 atmosphere pressure and a specified temperature—usually 25 °C. For solids which exist in more than one allotropic form, a specific allotrope must be specified.

A standard enthalpy change ( $\Delta H^\circ$ ) is an enthalpy change of reaction where substances in the reaction are in their standard state. If the temperature is other than 25 °C, the temperature must be specified.

For changes in the internal energy of substances in their standard state, the symbol  $\Delta E$  is used.

Sample Question:

11. What would be the standard states at 25 °C of the following substances?

- (a) gold
- (b) water
- (c) oxygen
- (d) ethanol
- (e) helium

Answer: (a) solid; (b) liquid; (c) gas; (d) liquid; (e) gas

Understanding these principles sets the stage for mastering the other concepts of thermochemistry.



## Calorimetry

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**Calorimetry** is the study of the heat released or absorbed during physical and chemical reactions. For a certain object, the amount of heat energy lost or gained is proportional to the temperature change. The initial temperature and the final temperature in the calorimeter are measured and the temperature difference is used to calculate the heat of reaction.

### Heat Capacity and Specific Heat

**Heat capacity**,  $C$ , with units of J/K or J/°C is the amount of energy required to raise the temperature of an object 1 kelvin or 1 °C. Heat capacity is an extensive property, meaning it depends on the amount present—a large amount of a substance would require more heat to raise the temperature 1 K than a small amount of the same substance. Heat capacity depends upon the amount of the substance you have. For pure substances, the heat capacity for one mole of the substance may be specified as the **molar heat capacity**,  $C_{molar}$ .

The **specific heat capacity**,  $c$  or  $s$ , is often used since it is the heat capacity per one gram of the substance with units of J/g·K or J/g·°C. Students often have a difficult time conceptualizing specific heat capacity and remembering the units for the property.

The following is a demonstration that may help student understanding. Have two beakers on the counter.



Ask the students, assuming both beakers are at 20.0°C, if 2000.0 joules of energy are applied to each beaker, will each beaker have the same change in temperature? What factors influence the change in temperature? Have the students do calculations to support their answers.  $2000 \text{ J} (50.0 \text{ g})(\Delta T)(4.18 \text{ J/g} \cdot ^\circ\text{C})$  and  $2000 \text{ J} (100.0 \text{ g})(\Delta T)(4.18 \text{ J/g} \cdot ^\circ\text{C})$ . The results are a 9.57°C and a 4.78°C change respectively. Students need to understand because the density of water is 1.0 g/mL, the volume is also the mass.

Now have the students look at the following set up and answer the same questions.



100.0 g of water  
specific heat =  $4.18 \text{ J/g} \cdot ^\circ\text{C}$



100.0 g of ethanol  
specific heat =  $2.46 \text{ J/g} \cdot ^\circ\text{C}$

If 2000.0 joules of energy are applied to each of these flasks, will the temperature change be the same for each flask? What factors influence the change in temperature? For water,  $2000.0 \text{ J} = (100.0 \text{ g})(\Delta T)(4.18 \text{ J/g} \cdot ^\circ\text{C})$  and for ethanol  $2000.0 \text{ J} = (100.0 \text{ g})(\Delta T)(2.46 \text{ J/g} \cdot ^\circ\text{C})$ , the results are a  $4.78^\circ\text{C}$  and a  $8.13^\circ\text{C}$  change respectively.

### Specific Heat and $q$

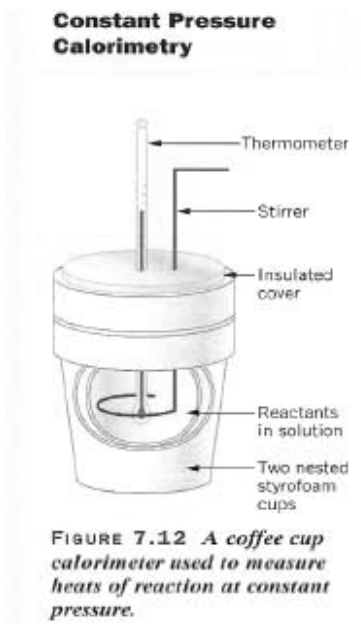
The specific heat capacity of each substance is an intensive property which relates the heat capacity to the mass of the substance. The amount of heat lost or gained is calculated by using the specific heat multiplied by the mass of the sample multiplied by the change in temperature or  $q = cm(\Delta T)$ .

- If a process results in the sample losing heat energy, the loss in heat is designated as  $-q$ . The temperature of the surroundings will increase during this exothermic process.
- If the sample gains heat during the process, then  $q$  is positive. The temperature of the surroundings will decrease during an endothermic process.

The amount of heat that an object gains or loses is directly proportional to the change in temperature.

A **coffee cup calorimeter** measures the temperature change during a reaction when the pressure is constant. This apparatus is used for reactions involving liquids and solids, which occur at constant pressure, atmospheric pressure. Little heat is lost to the calorimeter itself.

This apparatus is used to determine the amount of heat lost or gained during the procedure. Measurements that need to be made include the mass of each reactant, the temperature of each reactant before mixing, and the temperature in the calorimeter after mixing. The results are reported as the amount of heat lost ( $-q$ ) or gained ( $+q$ ).



The following examples show the depth of knowledge expected of students. Students must be able to take raw lab data and communicate how to use the data to calculate different quantities.

### Example 1

If 40.0 g of  $\text{H}_2\text{O}$  at 54.0 °C is added to 60.0 g of  $\text{H}_2\text{O}$  at 20.0 °C, what is the temperature after mixing? Assume that no heat is lost to the calorimeter. (54.0 °C =  $T_1$  and 20.0 °C =  $T_2$ ; specific heat of water is 4.18 J/g °C)

**Strategy:** For this exercise we will assume that the heat lost by the warm water is equal to the heat gained by the cool water.

**Solution:**

Heat lost	Heat gained
$[(T_f - T_1)(40.0 \text{ g})(4.18 \text{ J/g } ^\circ\text{C})]$	$[(T_f - T_2)(60.0 \text{ g})(4.18 \text{ J/g } ^\circ\text{C})]$
$[(T_f - 54.0 \text{ } ^\circ\text{C})(40.0 \text{ g})(4.18 \text{ J/g } ^\circ\text{C})]$	$[(T_f - 20.0 \text{ } ^\circ\text{C})(60.0 \text{ g})(4.18 \text{ J/g } ^\circ\text{C})]$
$(T_f - 54.0 \text{ } ^\circ\text{C})(0.667)$	$(T_f - 20.0 \text{ } ^\circ\text{C})$
$T_f = 33.6 \text{ } ^\circ\text{C}$	

### Example 2

Suppose in Example 1 that the final temperature only reached 31.0 °C instead of the calculated 33.6 °C. The lower final temperature would be due to the heat from the warmer water that is transferred to the calorimeter instead of the cooler water. Determine the heat capacity of the calorimeter.

**Strategy:** The difference between the heat lost and the heat gained can be used to calculate the heat capacity in J/°C.

**Solution:**

Heat lost — Heat gained — Heat gained by calorimeter  
 $(31.0 - 54.0\text{ }^\circ\text{C})(40.0\text{ g})(4.18\text{ J/g }^\circ\text{C}) - (31.0 - 20.0\text{ }^\circ\text{C})(60.0\text{ g})(4.18\text{ J/g }^\circ\text{C})$  Heat  
 gained by calorimeter.

$$3.85 \times 10^3\text{ J} - 2.76 \times 10^3\text{ J} = 1.09 \times 10^3\text{ J}$$

For this procedure,  $1.09 \times 10^3\text{ J}$  are absorbed by the calorimeter when the temperature is increased by  $11.0\text{ }^\circ\text{C}$ , therefore the heat capacity of the calorimeter is  $98.7\text{ J/}^\circ\text{C}$ .

## Heat of Neutralization Worksheet

A calorimetry investigation is to be performed to determine the heat of neutralization when hydrochloric acid and sodium hydroxide solutions are mixed.

- Write the complete chemical equation for the reaction between hydrochloric acid and sodium hydroxide.  


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- Write the net ionic equation for the reaction between hydrochloric acid and sodium hydroxide.  


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- The procedure then calls for measuring 50.00 mL of each 0.10 molar solution. Why is it important to measure the volumes as accurately as possible?  


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- What is the most accurate measuring instrument in your lab for measuring liquid volumes? Explain.  


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- The measured volumes of each solution are put into separate containers and allowed to set for several minutes. The initial temperature of each solution is recorded. The solutions are mixed in the coffee cup calorimeter and the highest temperature is recorded. Assume that the acid and base solutions have the same density and specific heat as water. Explain how the measurements are used to calculate the heat produced during the procedure. Use the equation  $q = mc\Delta T$   


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- Use the net ionic equation from #2 to calculate the number of moles of product formed during the procedure.  


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Special Focus: Thermochemistry

7. Use your answers to #5 and #6 to calculate the value of the heat of reaction,  $H$ , for the procedure in kilojoules per mole.

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8. A follow-up activity uses nitric acid and potassium hydroxide solutions as the reactants. The same amounts and the same concentrations of the reactants are used and the same measurements are made. Write the complete equation for this reaction.

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9. Write the net ionic equation for this reactants given in #8.

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10. Predict how the calculated value for the heat of reaction for nitric acid and potassium hydroxide would compare to the calculated value calculated in #7.

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Sample AP Problem: 2002 AP Examination Free-Response Question 5 a–b



A student is asked to determine the molar enthalpy of neutralization,  $H_{\text{neut}}$ , for the reaction represented above. The student combines equal volumes of 1.0 M HCl and 1.0 M NaOH in an open polystyrene cup calorimeter. The heat released by the reaction is determined by using the equation  $q = mc\Delta T$ .

Assume the following.

Both solutions are at the same temperature before they are combined.

The densities of all the solutions are the same as that of water.

Any heat lost to the calorimeter or to the air is negligible.

The specific heat capacity of the combined solutions is the same as that of water.

- (a) Give the appropriate units for  $q = mc\Delta T$ .

**Solution:**

- $q$  is in joules
  - $m$  is in grams
  - $c$  is in J/g°C
  - $\Delta T$  is in degrees Celsius
- (b) List the measurements that must be made in order to obtain the value of  $q$ .

**Solution:**

- Volume or mass of the HCl or NaOH solutions
- Initial temperature of HCl or NaOH before mixing
- Final (highest) temperature of solution after mixing

A common error on this part of the question was to confuse the calculation of  $T$  with measurements of  $T_i$  and  $T_f$ .

**Enthalpy**

The amount of heat lost or gained during the reaction can be used to determine the enthalpy of reaction. If the system loses energy during the procedure (temperature increase), then the heat lost is reported as  $q$ . This is an exothermic reaction. For the endothermic reactions, the heat gained by the system is reported as  $q$ . This quantity is then divided by the moles of product formed in the procedure as noted in the following example.

Sample AP Problem: 2002 AP Examination Free-Response Questions 5c–d

This part of the question asks the student to explain how to calculate the enthalpy of reaction. This calculation requires knowledge of the quantities measured and an understanding of the term enthalpy of reaction.

5 (c) Explain how to calculate each of the following.

- (i) The number of moles of water formed during the experiment.

**Solution:**

Since there is mixing of equal volumes of the same concentration *and* the reaction has 1:1 stoichiometry, the number of moles of  $\text{H}_2\text{O}$  = moles of HCl = moles NaOH. A common error on this part was to omit the stoichiometric ratio needed for determining the moles of water formed. Students must communicate all reasoning used to answer a question.

- (ii) The value of the molar enthalpy of neutralization,  $H_{neut}$ , for the reaction between  $\text{HCl}_{(aq)}$  and  $\text{NaOH}_{(aq)}$ .

**Solution:**

Determine the quantity of the heat produced,  $q$ , from  $q = mc\Delta T$ , where  $m$  = total mass of solution; divide  $q$  by mol  $\text{H}_2\text{O}$  determined in part (c)(i) to determine  $H_{neut}$ .

## Special Focus: Thermochemistry

- A common misconception in the calculation of  $q$  is to use the mass of one reactant or of the water instead of the sum of the masses of the reactants. The use of the incorrect equation on this part was another common error.
- Students often failed to divide the calculated  $q$  by the moles of water produced.

The next part of this problem asks the student to project how the values of  $q$  and  $H$  will change as reaction conditions change. These questions will probe a student's conceptual understanding of the procedure.

(d) The student repeats the experiment with the same equal volumes as before, but this time uses 2.0 M HCl and 2.0 M NaOH.

(i) Indicate whether the value of  $q$  increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

### Solution:

The  $T$  will be greater, so  $q$  increases. There are more *moles* of HCl and NaOH reacting so the final temperature of the mixture will be higher.

- Common misconceptions on this part included a statement that the mass doubles instead of correctly stating that the number of moles of reactants doubles.

(ii) Indicate whether the value of the molar enthalpy of neutralization,  $H_{neut}$ , increases, decrease, or stays the same when compared to the first experiment. Justify your answer.

### Solution:

Both  $q$  and mol  $H_2O$  increase proportionately. Molar enthalpy is defined as per mole of reaction, therefore  $H_{neut}$  will not change when the number of moles is doubled.

- Students often failed to recognize the proportion of  $q$  to the moles of product to calculate  $H_{neut}$ . Students often focused on a change in mass or molarity instead of moles of product.

As with all lab procedure, students should have a clear understanding of how various errors will affect the calculations. Questions similar to the 5(e) are generally part of every lab question.

(e) Suppose that a significant amount of heat were lost to the air during the experiment. What effect would this have on the calculated value of the molar enthalpy of neutralization,  $H_{neut}$ ? Justify your answer.

**Solution:**

Heat lost to the air will produce a smaller  $T$ . In the equation  $q = mc\Delta T$ , a smaller  $T$  will produce a smaller value for  $q$  than it should. When this smaller value of  $q$  is divided by the correct number of moles of water, the calculated  $H_{neut}$  will be too small. Since the reaction is exothermic,  $q$  will be negative and thus  $H_{neut}$  will be less negative or more positive than it should be.

- Students often failed to completely justify a correct reply that the calculated value for  $H_{neut}$  will be too low. A complete justification needs to begin with the problem with the erroneous measurement and describe how this error affects each calculation that follows.

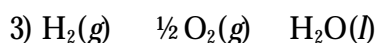
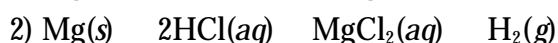
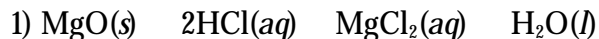
**Hess's Law**

Coffee cup calorimeters are often used to develop an understanding of Hess's Law. The heats of reaction of two or more different reactions are determined. The sum of these enthalpies is equal to the heat of reaction for a target reaction, whose equation is the sum of the equations of the two or more reactions studied.

**Hess's Law Procedure: The Heat of Formation of MgO**

A series of experiments are to be performed with a coffee cup calorimeter. The heat of reaction of each will be determined. The equations will be added together to obtain a target equation. The heats of reaction for each reaction will then be added to obtain the heat of reaction for the target equation.

The heats of reaction for the first two equations will be determined by experiment and the heat of reaction for the third equation will be determined using tables of thermodynamic values. The three reactions are represented by the following equations:

**PROCEDURE:**

**Reaction #1:** Measure 100 mL of a 3.0 M HCl solution into a coffee cup calorimeter. Record the temperature of the liquid to a tenth of a degree. Properly weigh out about 1 g of MgO(s) and record the mass to the nearest centigram. Add the magnesium oxide to the HCl(aq), stir, and record the highest temperature reached during the reaction. Wash out and dry the cup.

**Reaction #2:** Measure 100 mL of 3.0 M HCl solution into the same coffee cup calorimeter. Again record the temperature. This time properly weigh about 0.5 g (about 0.5 meters) of magnesium ribbon. Record the mass. Add the magnesium to the HCl(aq), stir, and record the highest temperature reached during the reaction. Wash out the cup.



CALCULATIONS: For this investigation assume that the density of all solutions is 1.00 g/mL and assume the specific heat of the resulting solutions is 4.18 J/g °C.

1. Which reactant is in excess in reaction number 1? You must show your work to get credit.
2. Which reactant is in excess in reaction number 2? You must show your work to get credit.
3. Calculate the heat, in joules, absorbed by the solutions in both reactions 1 and 2.
4. Calculate the energy, in kilojoules, released per mole of MgO reacted in reaction #1.
5. Calculate the energy, in kilojoules, released per mole of Mg reacted in reaction #2.
6. Combine equations 1, 2, and 3 to obtain the target reaction.
7. Use the answers to #4 and #5 in addition to the heat of formation of water from the table in your text to calculate the heat of formation of MgO. Compare your result for the heat of formation of MgO to that on the table in the textbook. Offer possible explanations for any deviation.

## Conclusion

Students often cannot distinguish between measurements and calculations. Students do not always practice good lab techniques. Most importantly, students often do not have the skill and experience to manipulate raw lab data to obtain a value such as the heat of reaction. Conceptually, students cannot determine the difference between the heat produced during an investigation and the standard enthalpy change for the reaction. Taking the concept to this level of calculation and analysis requires a thorough understanding of the investigation, the balancing of reaction equations involved, and the topic of heat transfer.

Many laboratory books include good investigation procedures to help students develop the skills needed to be successful with this topic. Consult the AP Course Description for some good laboratory books.

## References

I used the following two texts as references. I did not quote from either book specifically. I think many of the texts recommended for the freshman college chemistry course cover this topic quite well.

Brady, James E., and Fred Senese. *Chemistry: Matter and Its Changes*. 4th ed. Hoboken, N.J.: Wiley, 2003

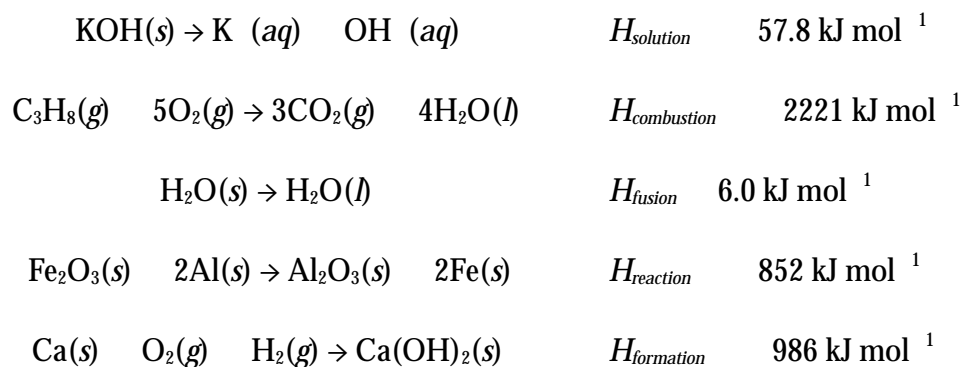
Brown, Theodore E., H. Eugene LeMay, and Bruce E. Bursten. *Chemistry: The Central Science*. 10th ed. Upper Saddle River, N.J.: Pearson/Prentice-Hall, 2006

# The Law of Hess, Heats of Formation, and Bond Energy

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Thermodynamics is the study of heat (the flow of energy from a body at a higher temperature to one at a lower temperature when they are placed in thermal contact) and its conversions from one form of energy to another. One of the core forms of energy considered in thermodynamics is enthalpy. Enthalpy may be thought of as potential energy that may be converted into heat. Potential energy may exist as energy of position or energy of composition. The vast majority of cases dealt with in AP Chemistry involve situations where the pressure remains constant. Examples include reactions occurring in solution or gaseous reactions where the volume is allowed to change. In these cases, enthalpy is virtually synonymous with heat flow. While the absolute enthalpy content of a system is not really important, a change in enthalpy is. Enthalpy changes may be used to heat our homes.

They may be used to move planes, trains, and automobiles. All sorts of processes, both physical and chemical, have an enthalpy change associated with them. A general change in enthalpy is symbolized as  $\Delta H$ . Specific types of enthalpy changes may be symbolized by a subscript attached to this symbol. Some examples include:



It is important to recognize that the  $H_{\text{formation}}$  (abbreviated as  $H_f^\circ$ ) is really just the heat of reaction for a chemical change involving the formation of a compound from its elements in their *standard states*. In this case, *standard state* refers to the state or phase an element exists in under conditions defined, by convention, as *standard*. These conditions are not the same as STP conditions for a gas sample. Rather, they imply a temperature of 25 °C and a pressure of 1 atmosphere.

There are a variety of methods for calculating overall enthalpy changes that an AP Chemistry student should be familiar with. The three most common are the *Law of Hess*, the use of *Heats of Formation*, and the use of *Bond Energies*.

## The Law of Hess:

Enthalpy changes involving a *decrease* in potential energy are said to be *exothermic*. The  $H$  value for an exothermic change is always designated as a *negative* value. Changes involving an *increase* in potential energy are said to be *endothermic* and the  $H$  value for such a change is designated as *positive*. Placement of the correct sign in front of a  $H$  value is an important accounting convention and the signs must be applied consistently through all thermodynamics calculations.

As enthalpy is an *extensive property*, the *magnitude* of an enthalpy change for a chemical reaction *depends upon the quantity of material* that reacts. This means if the amount of reacting material in an exothermic reaction is doubled, twice the quantity of heat energy will be released. Let us for the oxidation of sulfur dioxide gas:



Doubling the reaction results in:

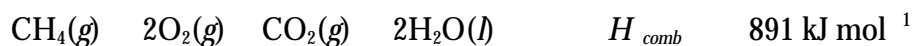


A comparison of the absolute enthalpy content of the reactants and products of a reversible reaction makes it evident that the *magnitude* of  $H$  for an exothermic reaction *remains the same when it is reversed*. There is merely a *sign change* and the reaction becomes endothermic. Hence if the above reaction were reversed:

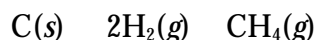


In addition to being an extensive property, enthalpy is also a *state function*. This means an enthalpy change is *completely independent of the pathway followed* to accomplish it.

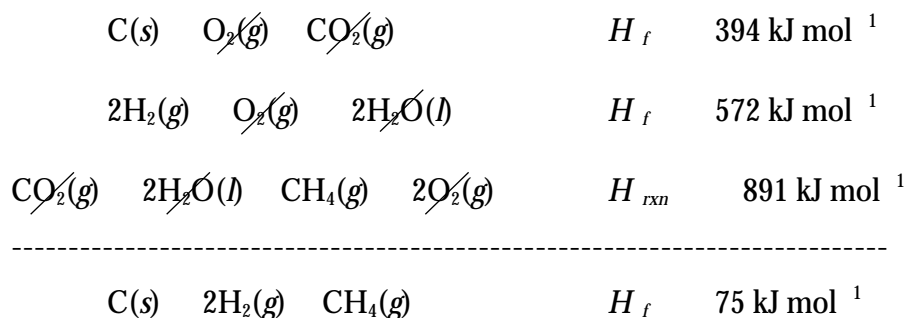
These concepts may be applied to determine the overall enthalpy change for any reaction composed of a series of other reactions combined. The process is known as **The Law of Hess** or **Hess's Law of Heat Summation**. Simply stated: *When a reaction may be expressed as the algebraic sum of other reactions, the enthalpy change of the reaction is the algebraic sum of the enthalpy changes for the combined reactions*. For example, given the following reactions and their enthalpy changes:



It is actually possible to determine the heat of formation for methane. The reaction we are attempting to come up with is:

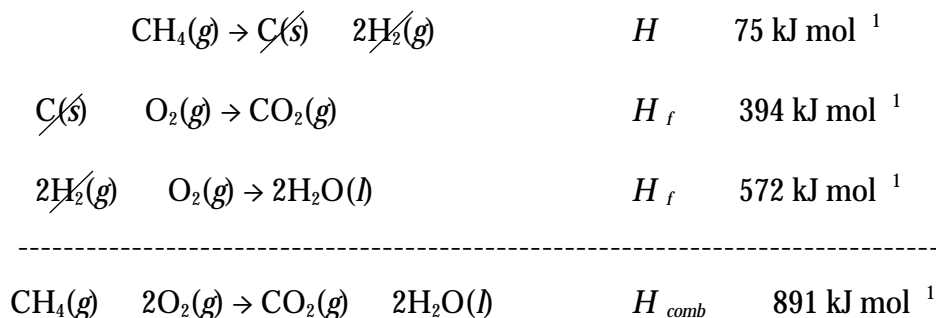


It is always a good idea to begin by looking for species that appear as reactants and products in the overall reaction. This will provide a clue as to whether a reaction needs to be reversed or not. Second, consider the coefficients of species that appear in the overall reaction. This will help determine whether a reaction needs to be multiplied before the overall summation. Leaving the formation of carbon dioxide reaction as is and doubling the formation of water reaction appears to be a good start in that it will provide the reactants desired. The combustion of methane reaction will need to be reversed to provide the desired number of moles of product. Reorganization of the three equations as described with the accompanying change in their  $H$  values results in:



### Using Heats of Formation:

Heats of formation reactions for each of the compounds involved in a chemical change may be rearranged, using the Law of Hess to calculate the overall enthalpy change for the process. Using the heats of formation for methane (which must be reversed in this case), carbon dioxide and liquid water from the previous example, we can determine the overall enthalpy change for the combustion of methane as follows:



Repeated application of this process soon reveals a very useful algorithm that may be used to calculate the overall enthalpy change for any reaction:

$$H_{\text{reaction}} = \sum n H_f(\text{products}) - \sum n H_f(\text{reactants})$$

where “n” is the coefficient of each species in a balanced equation.

It is critical to keep in mind that the  $H_f$  for a pure element in its standard state is always equal to zero. It is also important to note the state of each species in a balanced equation

carefully when using tabular values to complete these calculations as the state of a substance affects its enthalpy of formation value.

The formula above can be used to calculate the overall enthalpy change for the combustion of methane as follows:

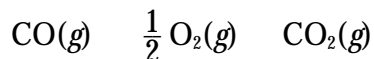
$$H_{\text{reaction}} = [1 H_f \text{CH}_4(g) + 2 H_f \text{O}_2(l)] - [1 H_f \text{CO}_2(g) + 2 H_f \text{H}_2\text{O}(g)]$$

thus:  $H_{\text{comb}} = [1 \text{ mol}(-394 \text{ kJ/mol}) + 2 \text{ mol}(-286 \text{ kJ/mol})] - [1 \text{ mol}(-75 \text{ kJ/mol}) + 2 \text{ mol}(-242 \text{ kJ/mol})]$   
 $= -891 \text{ kJ mol}^{-1}$

### “Per Mole” or “Not Per Mole”

Students and teachers are often confused as to whether to use the unit kJ or kJ mol<sup>-1</sup>. As they are extensive properties, it seems logical to measure enthalpies of formation in kJ mol. Hence, when they are summed using the Law of Hess, it seems correct to express the total enthalpy change in kJ mol<sup>-1</sup> as well. However, as shown above, when the standard heats of formation algorithm is applied, it appears that the mole unit should cancel out due to the multiplication steps. The fact is that many texts simply ignore this quandary. Consequently, Readers of the AP Chemistry exam have traditionally elected to allow students to express their answer in either unit. To be strictly correct however, the overall enthalpy change should always be expressed in kJ mol<sup>-1</sup>. This is a result of considering the total change as the number of kJ *per mole of the entire reaction*. So for the example above, one might calculate a  $H_{\text{comb}}$  value of -891 kJ, then divide by one mole of reaction. Hence,  $H_{\text{comb}} = -891 \text{ kJ mol}^{-1}$  implies that 891 kJ of energy are released for every one mole of methane combusted or for every two moles of oxygen gas consumed in the combustion or for every mole of carbon dioxide formed or for every two moles of liquid water released.

### Sample Question from the 2006 AP Examination



The combustion of carbon monoxide is represented by the equation above.

- (a) Determine the value of the standard enthalpy change,  $H_{\text{rxn}}$ , for the combustion of CO(g) at 298 K using the following information.



Reverse the first equation and add it to second equation to obtain the third equation.	One point is earned for reversing the first equation.
$\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{C}(s) \quad H_{298} = 110.5 \text{ kJ mol}^{-1}$	One point is earned for the correct answer (with sign).
$\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad H_{298} = 393.5 \text{ kJ mol}^{-1}$	
<hr/> $\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad H_{rxn} = 110.5 - (393.5)$ <p style="text-align: center;"><math>283.0 \text{ kJ mol}^{-1}</math></p>	<b>OR</b>
OR	Two points are earned for determining $H_{rxn}$ from the enthalpies of formation.
$H_{rxn} = H_f \text{ of CO}_2(g) - H_f \text{ of CO}(g)$ <p style="text-align: center;"><math>393.55 \text{ kJ mol}^{-1} - (110.5 \text{ kJ mol}^{-1}) = 283.0 \text{ kJ mol}^{-1}</math></p>	(If sign is incorrect, only one point is earned.)

### Bond Energy Calculations:

A third way to calculate enthalpy changes is to use bond energy values. Bond energy is defined as the *energy required to break a bond*. Bond energy values are frequently presented in tables. It is critical to examine such tabular values carefully to see exactly what they represent in terms of *quantity* and *sign*. Most AP Chemistry texts list bond energies as positive values in units of kJ/mole. Such values represent the amount of energy released when one mole of the bond referred to is formed. Although they refer to energy released, the values are listed as positive.

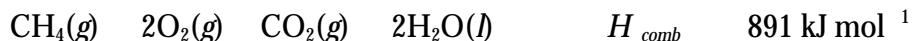
The answer to an enthalpy problem determined using bond energies will not be exactly the same as one calculated using heats of formation, but it will nearly approximate it. There is a simple algorithm available for calculating enthalpy changes using bond energies. It is similar to the one described in the section above, where B.E. stands for Bond Energy.

$$\text{B.E.}_{\text{reaction}} = \text{nB.E.}_{(\text{bonds broken})} - \text{nB.E.}_{(\text{bonds formed})}$$

Because the reactants and products have, in a sense, been reversed, students frequently make errors in the calculation of enthalpy changes using bond energies. The most common incorrect result has the correct magnitude, but the wrong sign. The easiest way to ensure that students fully understand how to determine the overall bond energy change is to make it clear that *bond breaking requires energy, while the formation of bonds releases energy*. Hence, once the structural formulas of all species in a balanced equation have been written down, it is only necessary to determine what bonds have been broken and what new bonds have been formed. Each broken bond is assigned a positive bond energy and each newly

**Special Focus: Thermochemistry**

formed bond is assigned a negative one. Then the bond energies are simply summed. For example, in the combustion of methane reaction from the previous section:



Four C-H bonds ( $414 \text{ kJ mol}^{-1}$ ) and two O=O bonds ( $494 \text{ kJ mol}^{-1}$ ) are broken while two C=O bonds ( $780 \text{ kJ mol}^{-1}$ ) and four H-O bonds ( $463 \text{ kJ mol}^{-1}$ ) are formed. Using these bond energy values, we calculate:

$$\begin{array}{r} 4 \text{ mol}(414 \text{ kJ mol}^{-1}) + 2 \text{ mol}(494 \text{ kJ mol}^{-1}) \\ 4 \text{ mol}(463 \text{ kJ mol}^{-1}) + 2 \text{ mol}(780 \text{ kJ mol}^{-1}) \end{array}$$

While these two values may appear completely different at first glance, they are both exothermic and they are of the same order of magnitude.

**Sample Question from the 1990 AP Examination**

2.

Average Bond Dissociation Energies at 298 K	
Bond	Energy, $\text{kJ mol}^{-1}$
C-H	414
C-C	347
C-Cl	377
Cl-Cl	243
H-Cl	431

The table above contains information for determining thermodynamic properties of the reaction below.

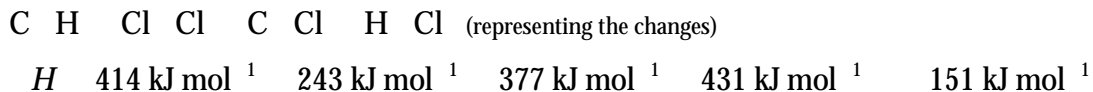


- (a) Calculate the  $H$  for the reaction above, using the table of average bond dissociation energies.

Answer:

$$\begin{aligned} H &= \text{energy of bonds broken} - \text{energy of bonds formed} \\ H &= [\text{C-C} + 5(\text{C-H}) + \text{C-Cl}] - [\text{C-C} + 4(\text{C-H}) + 2(\text{C-Cl}) + \text{H-Cl}] \\ H &= (2794 + 243) \text{ kJ mol}^{-1} - (2757 + 431) \text{ kJ mol}^{-1} = 151 \text{ kJ mol}^{-1} \end{aligned}$$

**OR**



## Enthalpy Demonstrations and Labs

### How Many Thermite Reactions in Your Favorite Burger?

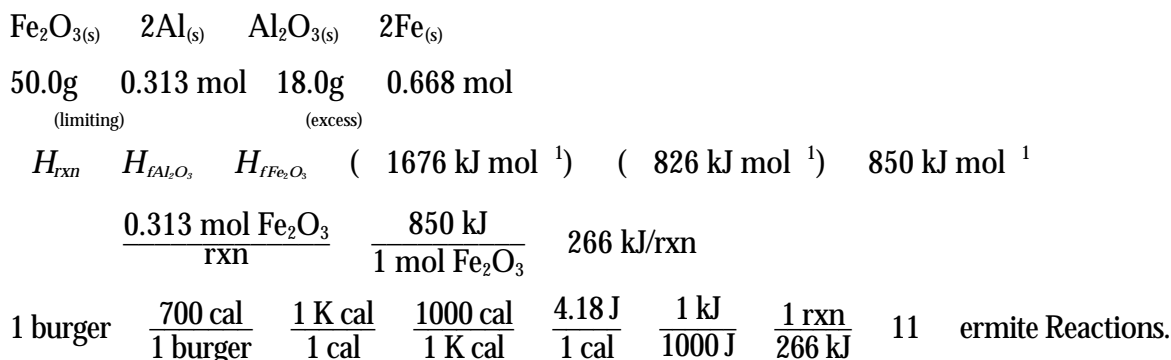
is puts a new spin on the thermite demonstration that is so popular in this unit. Prepare the thermite by thoroughly mixing approximately 50 grams of iron(III) oxide and 18 grams of aluminum powders. Lightly dust a mixture of 10 grams each of sucrose and potassium chlorate over the top of the mixture. is should all be done in a small clay pot or a clean cat food can. In a pinch you can cut a coke can in half and use the bottom half. e mixture should be supported on an iron ring attached to a utility stand some 45 centimeters above the ground. **The demonstration should definitely be performed outside.** Once the students are well back, the **instructor** can ignite the mixture by dropping three or four drops of concentrated sulfuric acid on top. Safety glasses should certainly be worn and the instructor should move clear immediately. is reaction is very exothermic. Enough heat is released to produce white hot molten iron (iron melts at 1535 C and the temperature reached during this reaction exceeds 2000 C). Once the reworks have subsided and everything has cooled down, you may wish to use a strong magnet to pick up the lump of iron produced.

For the demonstration, have your students do the following:

- Write a balanced equation for the thermite reaction.
- Calculate the  $H_{rxn}$  using enthalpy of formation values.
- Given 50.0g of iron(III) oxide and 18.0 of aluminum powder, how much energy is released during this reaction?
- Assuming there are 700 food calories in a double cheeseburger, how many thermite reactions are equivalent to the energy content of a double cheeseburger?

is leads nicely into a discussion of energy absorption as well as release during bond breaking and formation within our bodies, etc.

### Example:





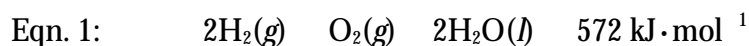
## The Law of Hess

A foolproof lab for the Law of Hess uses coffee cup calorimetry to prove that the enthalpy change when solid pellets of sodium hydroxide and hydrochloric acid neutralize one another is the same as the sum of the changes for the dissolution of sodium hydroxide in water and the neutralization of sodium hydroxide and hydrochloric acid solutions. There are many excellent sources for this lab including *Essential Experiments for Chemistry* by Duncan Morrison and Darrel Scodellaro, SMG Lab Books, 2005; and Experiment 4 in *Laboratory Investigations: AP Chemistry* by David Hostage and Martin Fossett, Peoples Publishing Group, 2005.

## Entropy and Free Energy

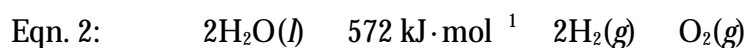
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Many quantities are important in science because they are conserved. That is, in a closed system, the total value of these quantities remains unchanged, regardless of changes that occur within the system. Quantities such as momentum and angular momentum are crucial in the analysis of physical systems. In ordinary, nonnuclear, chemical reactions, conserved quantities of interest include the total mass, total energy, total charge, and the number and type of nuclei and electrons. The conservation of these quantities is reflected in a balanced equation—the “equal” of an equation is the number of each type of nuclei and, if the energy term is included, the total energy on the reactant and the product side of the equation. Thus, the simple equation that describes the burning of hydrogen gas in oxygen:



states that two moles of hydrogen gas will combine with one mole of oxygen gas to form two moles of liquid water. Because the product contains 572 kJ less enthalpy than the reactants, the excess enthalpy is released as heat. Thus,  $H_{\text{R}} = -572 \text{ kJ} \cdot \text{mol}^{-1}$  for the equation given above.<sup>1</sup>

Since a balanced equation contains equal numbers of atoms and electrons, and equal amounts of energy on both sides, the reverse of the equation, corresponding to the reverse reaction, must also be balanced. The reaction,



represents the decomposition of 2 moles of liquid water to form two moles of hydrogen gas and one mole of oxygen gas, and requires the input of 572 kJ of enthalpy. A central question for chemistry, therefore, is to determine the direction in which a chemical reaction will proceed spontaneously<sup>2</sup> and why it does so. Since the total mass and the energy are equal on both sides of the equation, consideration of these quantities cannot answer this question.

1. For notes regarding units in thermochemical equations, see the monograph by Professor James N. Spencer on the AP Chemistry Web site at [http://apcentral.collegeboard.com/apc/members/courses/teachers\\_corner/26124.html](http://apcentral.collegeboard.com/apc/members/courses/teachers_corner/26124.html).

2. The meaning of a reaction occurring “spontaneously” is difficult and counterintuitive for some students. It should be stressed that spontaneity does not imply that a reaction proceeds with any speed, or that a reaction occurs immediately upon combination of reactants. The oxidation of metallic iron at standard temperature is a spontaneous reaction, even though it occurs very slowly. The combustion of hydrogen, as shown above, also occurs spontaneously, even though a mixture of hydrogen and oxygen gases may be preserved indefinitely if it is not sparked. The chemical definition of a spontaneous reaction is a reaction that, once initiated, continues to proceed in the forward direction with no further input of energy. It should also be mentioned that reactions that are nonspontaneous may occur, but will require a continuous source of energy. Important examples of these nonspontaneous reactions are electrolysis reactions such as Equation (2) above.

There is, however, an important chemical quantity that can be used to determine the direction of spontaneous chemical change—entropy, given the symbol  $S$ . Loosely defined, entropy is a measure of the disorder of a system. In chemical systems, the disorder may take on several forms. In terms of the common phases of matter, gases, with particles free to move randomly, generally have greater entropy (disorder) than liquids. Crystalline solids, where particles are constrained to vibrate about a fixed position, generally have lower entropy than liquids. Within a sample of gas, the entropy increases with increased volume (and consequently decreases with increased pressure), as a greater volume allows the particles greater freedom of position and increased disorder. The entropy of a sample also increases with increased temperature, as the kinetic energy of the particles may be distributed over additional accessible modes.<sup>3</sup> Finally, substances that are composed of larger, more complex molecules have greater molar entropies than those that are composed of smaller molecules, largely due to the disorder associated with the degrees of freedom of the molecules. Similarly, mixtures of gases or solids (alloys) have greater entropy than separated samples of pure gases, and solutions often have greater entropies than the pure substances.<sup>4</sup>

It is not readily apparent how the entropy of a system can be quantitatively measured or what units are appropriate to express it. The classical study of heat engines and thermodynamics comes to the rescue. An analysis of the efficiency of the heat engine leads to the relation  $\Delta S = \frac{q}{T}$ , where  $q$  is the heat energy absorbed ( ) or emitted ( ) by a system, and  $T$  represents the absolute temperature of the system. If  $q$  is measured in joules, then the change in entropy of a system will be expressed in  $\text{J} \cdot \text{K}^{-1}$  and will be an extensive property of the system. Chemists (and chemistry problems), preferring to deal with intensive properties based on the mole, often express entropies and changes in entropy in intensive units of  $\text{J} \cdot (\text{mol}^{-1} \text{K}^{-1})$  or  $\text{kJ} \cdot (\text{mol}^{-1} \text{K}^{-1})$ . Chemistry problems are generally presented in these terms.

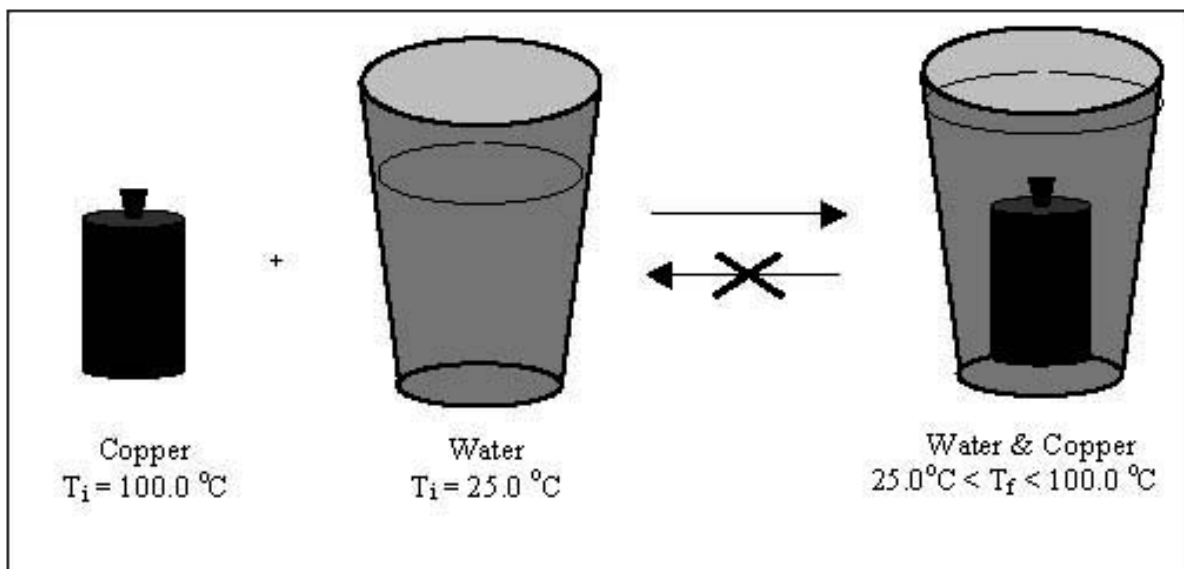
With the concept of entropy, it is now possible to state the direction in which a system will spontaneously evolve. The second law of thermodynamics states that “in any spontaneously occurring process, the total entropy of the universe will increase.” Thus, a chemical reaction or physical change will proceed spontaneously in the direction that increases the total entropy of the universe. This is readily illustrated by the experiment that is commonly performed to determine the specific heat capacity of a substance such as copper. In this experiment, a massed sample of copper is heated to a measured temperature, and is quickly placed in a polystyrene calorimeter containing a massed amount of water whose initial temperature is also known.

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3. The distribution of available energy levels is a quantum-mechanical question and is described by the Boltzmann distribution,

$$\frac{N(E_n)}{N(E_0)} = e^{-E_n/kT}$$

4. Students (and teachers) should be particularly cautious when considering entropy changes when solutes dissolve into aqueous solution. Many solute particles, due to a large ionic charge or to hydrophobic interactions, impose a greater degree of order on the water solvent, therefore decreasing the total entropy of the system. This decrease in the value of  $S$  upon mixing is largely responsible for the immiscibility of nonpolar solutes in water.



The copper-water system is allowed to come to thermal equilibrium and the final common temperature is measured. Given the value of the specific heat capacity of water and the first law of thermodynamics, that total energy is conserved, it is possible to determine the specific heat capacity of the copper. It is a common experience that the copper will lose thermal energy and cool down and that the water will gain thermal energy and heat up until the temperatures are equal. The first law of thermodynamics, though, does not preclude the possibility that the water will cool and the copper will heat up, increasing the temperature differential. However, it is fair to say that this has never been observed and, if such an event were to occur, it would be surprising. The second law of thermodynamics explains this observation. Consider a sample of copper heated to an initial temperature of 100 °C (373 K) and immersed in a calorimeter of water at an initial temperature of 25 °C (298 K). Heat will flow from the copper to the water until the temperatures are equal. Assume that 1 J of heat energy flows from the copper to the water. In this case, the change in entropy of the copper is given by the formula stated earlier:<sup>5</sup>  $\Delta S[\text{Cu}] = \frac{q[\text{Cu}]}{T[\text{Cu}]}$   $\frac{1 \text{ J}}{373 \text{ K}} = 0.00268 \text{ J K}^{-1}$ . Similarly, the change in entropy of the water is determined to be:  $\Delta S[\text{H}_2\text{O}] = \frac{q[\text{H}_2\text{O}]}{T[\text{H}_2\text{O}]}$   $\frac{1 \text{ J}}{298 \text{ K}} = 0.00336 \text{ J K}^{-1}$ . And the total change in entropy of the system is:  $\Delta S_{\text{Tot}} = \Delta S[\text{Cu}] + \Delta S[\text{H}_2\text{O}]$   $(-0.00268 \text{ J K}^{-1}) + (0.00336 \text{ J K}^{-1}) = 0.00067 \text{ J K}^{-1}$ . Though the entropy of the copper has decreased, there was an accompanying increase in the entropy of the water that was greater in magnitude, so that the total entropy change of the universe was positive. A moment's consideration reveals that the transfer of an equal amount of heat energy from the copper to the water will increase the entropy of the system as long as the temperature of the copper is greater than that of the water, and that a transfer of heat energy from the cooler to the hotter substance would result in a decrease in the total entropy of the system, in violation of the second law.

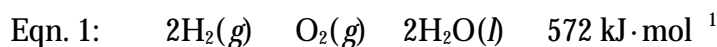
5. It is assumed that the change in temperature of the copper and the water is negligible. By using elementary calculus, this assumption can be eliminated.

us, in the concept of entropy there is a physical quantity that is *not* conserved, and the second law of thermodynamics explains the direction of spontaneous change for any system, physical or chemical. If the entropy of a system is known before and after a change has occurred, the change in entropy can be determined by taking the difference. Qualitatively, students should recognize that changes in which gases are formed from solids or liquids, or reactions that produce a greater number of moles of gas will have an increase in entropy, and conversely, reactions that form solids or liquids from gases will have a negative value of  $\Delta S$ .

Quantitatively, the Absolute Standard Molar Entropy of a substance,  $S$  [Subst], can be determined by precise calorimetric measurements. The details of its measurement are beyond the scope of the AP Chemistry course, but values are tabulated and readily available. There are two important considerations. First, Standard Molar Entropies are absolute quantities and, unlike Standard Enthalpies and Standard Free Energies, are NOT values referenced to pure elements. Consequently, even pure elements in their standard thermodynamic states have nonzero values of  $S$ . Second, units of entropy are commonly expressed in either  $\text{J} \cdot \text{mol}^{-1} \text{K}^{-1}$  or  $\text{kJ} \cdot \text{mol}^{-1} \text{K}^{-1}$ , and students should be aware of the difference, as it is occasionally necessary to convert appropriately.

Because entropy is a state function, for any balanced chemical equation the molar change in entropy of the reaction can be readily determined by subtraction.

That is,  $\Delta S_{\text{Rxn}} = \sum_{\text{Product}} n_i S_i - \sum_{\text{Reactants}} n_i S_i$ , where  $n_i$  are the stoichiometric coefficients of the balanced equation. For example, referring to Equation 1:



and the table of Standard Molar Entropies

Substance	$S$ [Subst], $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$\text{H}_2(g)$	131
$\text{O}_2(g)$	205
$\text{H}_2\text{O}(l)$	70

$$\Delta S_{\text{Rxn}} = \sum_{\text{Product}} n_i S_i - \sum_{\text{Reactants}} n_i S_i$$

$$= [2(70 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1})] - [2(131 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}) + 205 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}]$$

$$= -327 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

Intuitively, the balanced equation reflects the conversion of three moles of highly disordered gases to form two moles of less disordered liquid, it is expected that the change in entropy of the reaction would be negative.

Any chemistry student who has seen a mixture of hydrogen and oxygen gas sparked can attest that the reaction represented by Equation 1 occurs spontaneously and vigorously.

How can the decrease in entropy of the system of Equation 1 be reconciled with the second law of thermodynamics, which states that the entropy of the universe must increase for any spontaneously occurring process? The answer to this lies in the enthalpy term for the reaction,  $H_{\text{Rxn}} = -572 \text{ kJ mol}^{-1}$ . Remember that the system releases 572 kJ of energy per mole of reaction to the surroundings, or  $H_{\text{surr}} = 572 \text{ kJ mol}^{-1}$ . If the surroundings are assumed to be a thermal reservoir at a constant temperature of 298 K, this increase in enthalpy will increase the entropy of the surroundings:

$$S_{\text{surr}} = \frac{H_{\text{surr}}}{T_{\text{surr}}} = \frac{572 \text{ kJ mol}^{-1}}{298 \text{ K}} = 1.919 \text{ kJ mol}^{-1} \text{ K}^{-1} = 1919 \text{ J mol}^{-1} \text{ K}^{-1}. \quad \text{e}$$

total entropy change of the universe associated with this reaction is therefore given by:

$$S_{\text{Tot}} = S_{\text{Rxn}} + S_{\text{surr}} = -327 \text{ J mol}^{-1} \text{ K}^{-1} + 1919 \text{ J mol}^{-1} \text{ K}^{-1} = 1592 \text{ J mol}^{-1} \text{ K}^{-1},$$

a positive value that is expected for a spontaneous process.

When the change in entropy of the surroundings, assumed to be a thermal reservoir at temperature  $T_{\text{surr}}$ , is accounted for, the criterion for spontaneity given by the second law of thermodynamics takes on the following chemically relevant form:

$$S_{\text{Tot}} \geq 0$$

$$S_{\text{Rxn}} + S_{\text{surr}} \geq 0$$

$$S_{\text{Rxn}} + \frac{H_{\text{surr}}}{T_{\text{surr}}} \geq 0$$

$$\text{Since } H_{\text{surr}} = -H_{\text{Rxn}}, \quad S_{\text{Rxn}} + \frac{H_{\text{Rxn}}}{T_{\text{surr}}} \geq 0$$

If the reaction and surroundings are in thermal equilibrium,  $T_{\text{surr}} = T_{\text{Rxn}}$  and

$$S_{\text{Rxn}} + \frac{H_{\text{Rxn}}}{T_{\text{Rxn}}} \geq 0$$

$$T \Delta S_{\text{Rxn}} + H_{\text{Rxn}} \geq 0, \text{ or } H_{\text{Rxn}} - T \Delta S_{\text{Rxn}} \leq 0$$

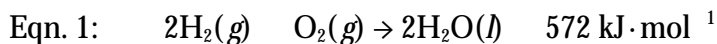
Therefore, the sole condition for a chemical reaction to occur spontaneously is that the expression  $H_{\text{Rxn}} - T \Delta S_{\text{Rxn}}$  takes on a negative value. This quantity has a relevant physical interpretation and is given the name Gibbs Free Energy,  $G_{\text{Rxn}} = H_{\text{Rxn}} - T \Delta S_{\text{Rxn}}$ , after the American thermodynamicist, J. Willard Gibbs. Note that, like the enthalpy change of a reaction, the Free Energy change of a reaction has units of  $\text{kJ mol}^{-1}$  (and that the  $T \Delta S$  term is also expressed in the same units).

Where  $H_{\text{Rxn}}$  represents the enthalpy change of a chemical reaction, or the amount of energy<sup>6</sup> released ( $H_{\text{Rxn}} < 0$ ) or absorbed ( $H_{\text{Rxn}} > 0$ ) as heat,  $G_{\text{Rxn}}$  represents the energy that is

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6. The distinction between energy and enthalpy is that enthalpy accounts for volume expansion. Since chemists generally consider changes that occur at constant pressure, a change in the volume of a system does work ( $P \cdot V$ ) and changes the internal energy of the system. Enthalpy is a state function that accounts for any volume change. For reactions involving only solids and liquids, the change in volume is generally negligible and the distinction between energy and enthalpy can be neglected.

available as useful work.  $\Delta G_{\text{Rxn}}$  is particularly relevant in electrochemical equations, where the  $\Delta G_{\text{Rxn}}$  is related to the standard cell potential of an electrochemical cell. To understand the relationship between  $\Delta H_{\text{Rxn}}$  and  $\Delta G_{\text{Rxn}}$ , consider again the combustion of Hydrogen:



Since the reaction released 572 kJ of energy per mole of reaction, one might suppose that 572 kJ of useful work can be derived from the combustion of two moles of Hydrogen gas (as in a heat engine or fuel cell). However, performing work does not change the entropy of the universe, and if all of the enthalpy change of the reaction were funneled into work, the total change in entropy would be  $-327 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , in violation of the second law of thermodynamics. In order for the reaction to satisfy the requirements of the second law of thermodynamics and to proceed spontaneously, enough energy must be dispersed into the surroundings so that the increase in the entropy of the surroundings offsets the decrease in the entropy of the system. If the temperature of the surroundings is 298 K, then the minimum energy that must be exhausted to the surroundings is derived:

$$\begin{aligned} \Delta S_{\text{Surr}} &= 327 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 0.327 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ \frac{\Delta H_{\text{Surr}}}{298 \text{ K}} &= 0.327 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ \Delta H_{\text{Surr}} &= 0.327 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298 \text{ K} = 97 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

at is, 97 kJ  $\cdot \text{mol}^{-1}$  must be dispersed to the surroundings to satisfy the second law, and the remaining energy is available as useful work:

$$\begin{aligned} \Delta G_{\text{Rxn}} &= \Delta H_{\text{Rxn}} - T \Delta S_{\text{Rxn}} \\ &= 572 \text{ kJ} \cdot \text{mol}^{-1} - [298 \text{ K} \cdot 0.327 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] \\ &= 475 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Of the 572 kJ of enthalpy that is released to the surroundings per mole of reaction, only 475 kJ is available as useful work. Thus, the  $\Delta G_{\text{Rxn}}$  represents the amount of energy that is available as work, and a chemical reaction will be spontaneous if:

$$\Delta G_{\text{Rxn}} = \Delta H_{\text{Rxn}} - T \Delta S_{\text{Rxn}} < 0.$$

Where values of  $\Delta H_{\text{Rxn}}$  and  $\Delta S_{\text{Rxn}}$  are relatively independent of temperature (and, in AP Chemistry problems, they can be considered temperature-independent),  $\Delta G_{\text{Rxn}}$  has an explicit temperature dependence. This can be understood in terms of the requirement that a reaction in which  $\Delta H_{\text{Rxn}}$  and  $\Delta S_{\text{Rxn}}$  are both negative must disperse some energy to the surroundings in order to increase the entropy of the surroundings. The amount of this increase in entropy will depend on the temperature of the surroundings, so that at higher temperatures a greater amount of energy will be needed. While the relationship

$G_{\text{Rxn}} = H_{\text{Rxn}} - T S_{\text{Rxn}}$  is valid at any temperature, it is also convenient to define Standard Free Energies of Formation of substances,  $G_f$  [Subst]. In analogy to Standard Enthalpies of Formation, the  $G_f$  [Subst] is defined as the change in Free Energy of the reaction in which one mole of the substance is formed from the elements in their standard thermodynamic states. By this definition, therefore, the  $G_f$  [Element] = 0, and  $G_{\text{Rxn}} = \sum_{\text{Products}} n_i G_f - \sum_{\text{Reactants}} n_i G_f$ . It should be stressed that values of  $G_f$  [Subst] are conventionally tabulated at the standard temperature of 298 K, therefore this latter relation is only valid at this temperature. Students should be able to calculate values of  $G_{\text{Rxn}}$  from  $H_{\text{Rxn}}$  and  $S_{\text{Rxn}}$  values, and should also be able to calculate them from tabulated values of  $G_f$  [Subst] at 298 K<sup>7</sup>. Students should have a good qualitative understanding of the relationship among  $G_{\text{Rxn}}$ ,  $H_{\text{Rxn}}$ , and  $S_{\text{Rxn}}$ .

As far as we have considered, only reactions occurring under standard concentration or pressure conditions, as indicated by the superscript “°”, have been considered. However, the concentration of each species in the equation does have an effect on the values of the thermodynamic properties of the reaction. An increase in the concentration of the reactant species or a decrease in the concentration of the product species will provide a greater driving force to the reaction and will decrease the value of  $G_{\text{Rxn}}$  from its value at standard concentrations. Similarly, an increase in product concentrations or a decrease in reactant concentrations will have the effect of increasing the value of  $G_{\text{Rxn}}$  from its value at standard concentrations. The extent of this effect on the value of  $G_{\text{Rxn}}$  is expressed by the Gibbs-Helmoltz relation  $G = G^\circ - RT(\ln Q)$ , where  $R$  is the gas constant (usually expressed in units of  $\text{kJ mol}^{-1} \text{K}^{-1}$  to be consistent with the units of  $G_{\text{Rxn}}$ ) and  $Q$  represents the reaction quotient (defined such that for the reaction equation



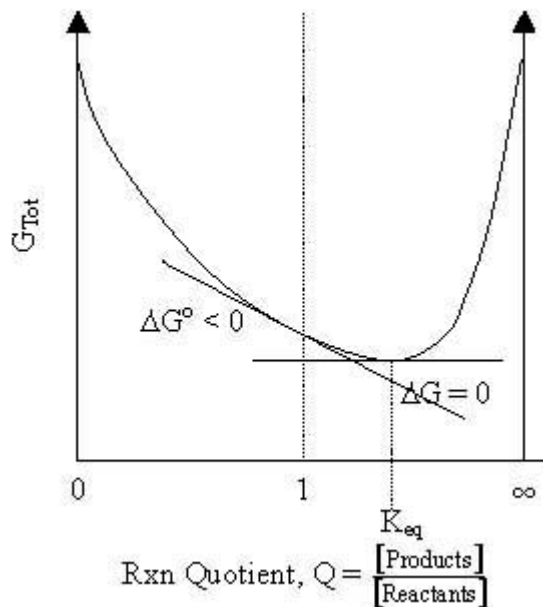
$Q$  has the expression  $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ ).<sup>8</sup> Thus, an increase in the value of  $Q$  above its standard concentration value of unity corresponds to an increase in concentration of product(s) or a decrease in concentration of reactant(s) and will result in an increase in the value of  $G_{\text{Rxn}}$ , or a smaller driving force to the reaction. Thus, reactions that may occur spontaneously under standard concentrations ( $G_{\text{Rxn}}^\circ < 0$ ) may not occur spontaneously at concentrations in which  $Q$  is sufficiently great ( $G = G^\circ - RT(\ln Q) > 0$ ).

$G_{\text{Rxn}}$  can be interpreted as the change in the total free energy of the system due to an infinitesimal progress of reaction leading to an infinitesimal change in reaction quotient,  $Q$ . Students of calculus will be able to understand this as the quantity  $dG_{\text{Tot}}/dQ$ . A general graph of  $G_{\text{Tot}}$  vs.  $Q$  has the shape shown in the diagram on the following page.

7. Note that the relevant equations are provided on the AP Chemistry Exam table of commonly used equations, but is available only for the free-response section of the examination.

8. Again, both the Gibbs-Helmoltz equation and the definition of the reaction quotient,  $Q$ , are included on the table of commonly used formulas provided for the free-response section of the examination.





A system that initially contains only reactants and no products has a reaction quotient of value  $Q = 0$ . As the reaction proceeds, the value of  $Q$  increases, approaching an infinite value if a limiting reactant is exhausted.  $G_{Rxn}$  can be interpreted as the slope of the line tangent to the curve at a given value of  $Q$ .

Two important points deserve mention. When  $Q = 1$  (which is true by definition at standard concentrations, but may also be true for other sets of concentrations),  $G_{Rxn} = G_{Rxn}^\circ$ . Thus,  $G_{Rxn}$  represents the slope of the graph at  $Q = 1$ . If slope is negative, then the total free energy of the system can be decreased if the reaction proceeds in the forward direction, as shown in the diagram above. Conversely, if  $G_{Rxn} > 0$ , then the total free energy can be minimized if the reaction proceeds in the reverse direction. Thus, the criteria that  $G_{Rxn} < 0$  for a reaction that proceeds spontaneously from standard concentrations (and its converse) can be readily understood.

A second important point results from the observation that the graph of  $G_{Tot}$  vs.  $Q$  is concave upward everywhere on its domain and will exhibit a single global minimum. This global minimum corresponds to a position of minimum total free energy, thus the free energy of the system would be increased by a shift in either direction. Since a chemical system at such a position would have no tendency to react, that is  $G_{Rxn} = 0$ , the system is in a state of equilibrium. The value of  $Q$ , the reaction quotient, that corresponds to this equilibrium position, is called the equilibrium constant,  $K_{eq}$ . The relationship between  $G_{Rxn}$  and  $K_{eq}$  can be shown. At equilibrium,  $G_{Rxn} = 0$  and  $Q = K_{eq}$ . Substituting into the Gibbs-Helmholtz relation:

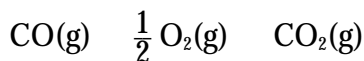
$$\begin{aligned}
 G_{Rxn} &= G_{Rxn}^\circ + R T \ln Q \\
 0 &= G_{Rxn}^\circ + R T \ln K_{eq} \\
 G_{Rxn}^\circ &= -R T \ln K_{eq} \text{ or } K_{eq} = e^{-G_{Rxn}^\circ / R T}
 \end{aligned}$$

From these last equations (and the properties of logarithms), it is clear that  $G_{\text{Rxn}} = 0$  is equivalent to  $K_{\text{eq}} = 1$ . That is, a system that is at standard concentrations will react in the forward direction, and the converse is true for reactions in which  $G_{\text{Rxn}} < 0$ . Furthermore, a reaction will generally proceed in the forward direction if  $G_{\text{Rxn}} < 0$ , which is equivalent to  $Q < K_{\text{eq}}$ . A system that evolves toward the minimum Free Energy ( $G_{\text{Rxn}} = 0$  and therefore  $Q = K_{\text{eq}}$ ) will remain in a state of dynamic equilibrium.

There remains one important limitation of the concepts of Entropy and Free Energy as applied to chemical systems. While they can predict the direction of chemical change, the amount of energy available from a reaction, and the position of the equilibrium of a system, chemical thermodynamics says nothing about the rate at which such a change will occur. In the same way that a boulder poised on the edge of a precipice may remain in the same position for millennia in spite of the lower energy position that may be available at the bottom of the hill, so chemical systems may remain in nonequilibrium states. The availability of a low-energy pathway from the initial state to the equilibrium state that would make such a change occur at a measurable rate remains in the province of chemical kinetics. Many familiar systems are kinetically stable, even if they are not thermodynamically stable. The rate at which pure, dry iron, when exposed to oxygen, forms iron(III) oxide is negligible under normal ambient conditions, even though this change is thermodynamically quite exergonic.  $S$ ,  $H$ , and  $G$  can only predict the direction that a chemical reaction will proceed spontaneously, but cannot predict its rate.

## Examples from Prior AP Chemistry Examinations

1. 2006 AP Examination, Free-Response Question No. 2.

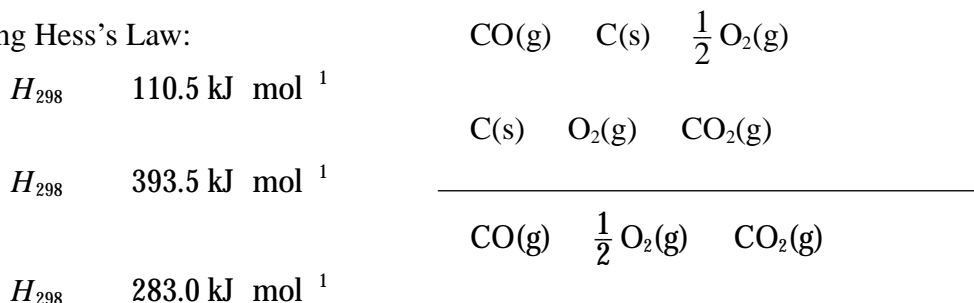


The combustion of carbon monoxide is represented by the equation above.

- (a) Determine the value of the standard enthalpy change,  $H_{\text{Rxn}}$ , for the combustion of  $\text{CO}(g)$  at 298 K using the following information:



Using Hess's Law:



- (b) Determine the value of the standard entropy change,  $S_{\text{Rxn}}$ , for the combustion of  $\text{CO}(g)$  at 298 K using the information in the following table

Substance	$S_f[\text{Subst}], \text{J mol}^{-1} \text{K}^{-1}$
$\text{CO}(g)$	197.7
$\text{CO}_2(g)$	213.7
$\text{O}_2(g)$	205.1

$$S_{\text{Rxn}} = \sum_{\text{Products}} n_i S_f - \sum_{\text{Reactants}} n_i S_f$$

$$= [213.7 \text{ J mol}^{-1} \text{K}^{-1}] - \left[ 197.7 \text{ J mol}^{-1} \text{K}^{-1} + \frac{1}{2} (205.1 \text{ J mol}^{-1} \text{K}^{-1}) \right]$$

$$= 86.6 \text{ J mol}^{-1} \text{K}^{-1} = 0.0866 \text{ kJ mol}^{-1} \text{K}^{-1}$$

- (c) Determine the value of the standard free energy change,  $G_{\text{Rxn}}$ , for the reaction at 298 K. Include units with your answer.

$$G_{\text{Rxn}} = H_{\text{Rxn}} - T S_{\text{Rxn}}$$

$$= 283.0 \text{ kJ mol}^{-1} - 298 \text{ K} (0.0866 \text{ kJ mol}^{-1} \text{K}^{-1})$$

$$= 257.2 \text{ kJ mol}^{-1}$$

- (d) Is the reaction spontaneous under standard conditions at 298 K? Justify your answer.

Yes. Since  $G_{\text{Rxn}} < 0$  the reaction is spontaneous under standard conditions.

- (e) Calculate the value of the equilibrium constant,  $K_{\text{eq}}$ , for the reaction at 298 K.

$$K_{\text{eq}} = e^{-\frac{G_{\text{Rxn}}}{RT}}$$

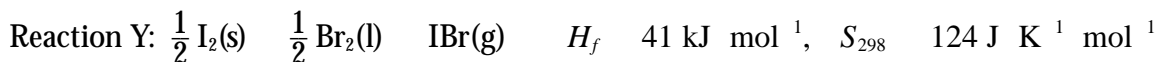
$$= e^{-\frac{(257.2 \text{ kJ mol}^{-1})}{(0.00831 \text{ kJ mol}^{-1} \text{K}^{-1})(298 \text{ K})}}$$

$$= e^{-103.9}$$

$$= 1.28 \times 10^{-45}$$

## 2. 2006 AP Examination Form B, Free-Response Question No. 3

Answer the following questions about the thermodynamics of the reactions represented below.



- (a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation?

$$\begin{aligned} G_{\text{Rxn}} &= H_{\text{Rxn}} - T \Delta S_{\text{Rxn}} \\ &= 18 \text{ kJ mol}^{-1} - (298 \text{ K}) (0.078 \text{ kJ mol}^{-1} \text{ K}^{-1} \\ &\quad - 5 \text{ kJ mol}^{-1}) \end{aligned}$$

Yes, because  $G_{\text{Rxn}} < 0$ , the reaction will occur spontaneously from standard conditions.

- (b) Calculate the value of the equilibrium constant,  $K_{\text{eq}}$ , for reaction X at 25 C.

$$\begin{aligned} K_{\text{eq}} &= e^{-\frac{G_{\text{Rxn}}}{RT}} \\ &= e^{-\frac{(5 \text{ kJ mol}^{-1})}{(0.00831 \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K})}} \\ &= e^2 \\ &= 7 \end{aligned}$$

- (c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

$$K_{\text{eq}} = e^{-\frac{G_{\text{Rxn}}}{RT}} = e^{-\frac{H_{\text{Rxn}}}{RT} - \frac{T \Delta S_{\text{Rxn}}}{RT}} = e^{-\frac{H_{\text{Rxn}}}{RT}} e^{-\frac{\Delta S_{\text{Rxn}}}{R}}$$

The effect of a temperature change on the value of the equilibrium constant will depend on the sign of  $H_{\text{Rxn}}$ . Since  $H_{\text{Rxn}} > 0$  for reaction X, increasing the temperature will increase the value of  $\frac{H_{\text{Rxn}}}{RT}$  and consequently increase the value of  $K_{\text{eq}}$ .

or

LeChatelier's principle states that a system at equilibrium that is subject to a stress will shift to attenuate the effect of the stress. Since reaction X is endothermic, an increase in temperature will shift the equilibrium in the direction that will consume heat energy, which results in a greater value of  $K_{\text{eq}}$ .

- (d) Explain why the standard entropy change is greater for reaction Y than for reaction X. Reaction X represents the conversion of one-half mole of solid reactant and one-half mole of gas-phase reactant to form one mole of gas-phase product, whereas reaction Y represents the conversion of one-half mole of solid reactant and one-half mole of liquid reactant to form one mole of gas-phase product. The important difference is the entropy of the reactants is less in reaction Y than reaction X, due to the one-half mole of liquid

rather than gas. This causes the entropy change of reaction Y to be greater than that of reaction X.

- (e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0? Justify your answer with calculations.

$$K_{\text{eq}} = 1 \text{ if } G_{\text{Rxn}} = 0$$

$$G_{\text{Rxn}} = H_{\text{Rxn}} - T \Delta S_{\text{Rxn}} = 0$$

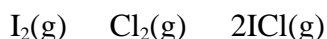
$$41 \text{ kJ mol}^{-1} - (T) (0.124 \text{ kJ mol}^{-1} \text{ K}^{-1}) = 0$$

$$T = \frac{41 \text{ kJ mol}^{-1}}{0.124 \text{ kJ mol}^{-1} \text{ K}^{-1}}$$

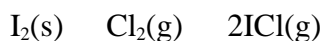
$$T = 331 \text{ K} = 58 \text{ C}$$

The equilibrium constant for reaction Y will be greater than 1.0 for temperatures greater than 58 C.

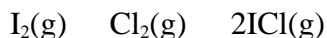
- (f) For the vaporization of solid Iodine,  $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$ , the value of  $H_{298}$  is  $62 \text{ kJ mol}^{-1}$ . Using this information, calculate the value of  $H_{298}$  for the reaction represented below.



Using Hess's Law:  $\text{I}_2(\text{g}) \rightarrow \text{I}_2(\text{s}) \quad H_{298} = 62 \text{ kJ mol}^{-1}$

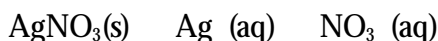


$$H_{298} = 2 (18 \text{ kJ mol}^{-1}) - 36 \text{ kJ mol}^{-1}$$



$$H_{298} = (62 - 36) \text{ kJ mol}^{-1} = 26 \text{ kJ mol}^{-1}$$

3. 2005 AP Examination, Free-Response Question No. 8a–c, d(iv)



The dissolving of  $\text{AgNO}_3(\text{s})$  in pure water is represented by the equation above.

- (a) Is  $G$  for the dissolving of  $\text{AgNO}_3(\text{s})$  positive, negative, or zero? Justify your answer. Because the equation represents a spontaneous dissolving of solid  $\text{AgNO}_3$ , the value of  $G$  for the process is negative.
- (b) Is  $S$  for the dissolving of  $\text{AgNO}_3(\text{s})$  positive, negative, or zero? Justify your answer. The equation represents the dissolving of one mole of crystalline solid, with low entropy, to form two moles of dissolved aqueous ions. Because more particles are formed than consumed, the entropy of the system increases and the value of  $S$  for the process must be positive.
- (c) The solubility of  $\text{AgNO}_3(\text{s})$  increases with increased temperature.
- (i) What is the sign of  $H$  for the dissolving process? Justify your answer.

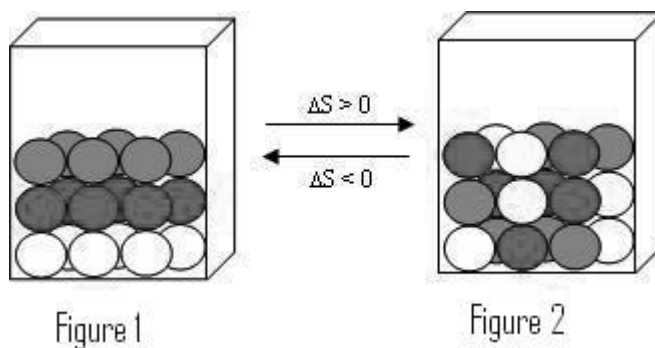


## Suggested Demonstration for Teachers

## I. Entropy as disorder

Procedure

1. Obtain a clear glass or plastic box (a beaker will work) and different colored plastic spheres or marbles. Layer the marbles in the box so that all of the marbles in the same layer are the same color, but leave room at the top of the box, as shown in Figure 1.



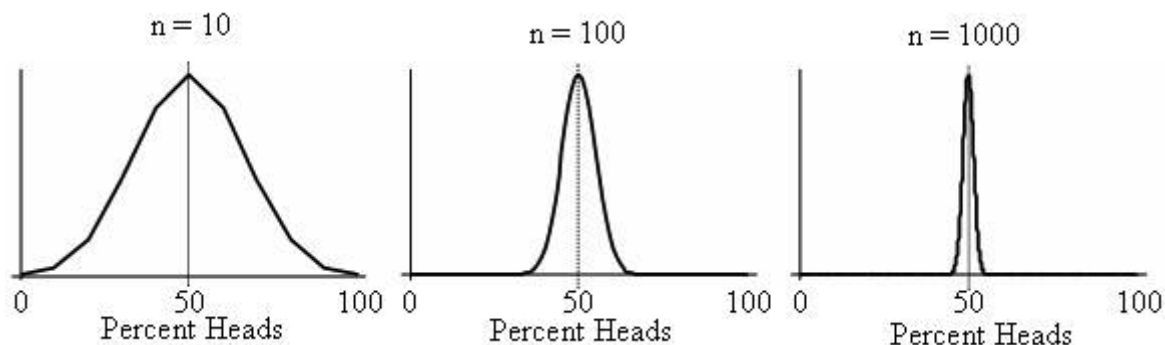
2. Cover and shake the box briefly. Allow the marbles to settle and observe.

Analysis

This simple demonstration qualitatively illustrates the relationship of entropy to disorder and the tendency of systems to statistically evolve to states of greater disorder. The instructor should emphasize that there is no difference in the energies (in this case, total gravitational potential energy) of the system in either configuration, but that the state of the system shown in Figure 2 represents an increase in the disorder or the entropy of the system.

For a system of this modest size, it is not inconceivable that subsequent random shaking would return the system to the state described by Figure 1, however this is unlikely and becomes less likely as the number of particles increases.

Teachers may choose to introduce terms of “configuration” and “microstate” to describe an observably distinct arrangement and a way of obtaining such an arrangement. In this case, consideration of the statistics of coin-tossing is useful. If a number of coins is tossed, the predominant configuration is always 50 percent heads (and 50 percent tails). However, the chances of obtaining a configuration that differs significantly from the predominant configuration decreases with sample size. Graphs below show the distribution for 10 coins, 100 coins, and 1000 coins. Students should appreciate that when numbers approach Avogadro’s number, the graph essentially appears to be a single peak.



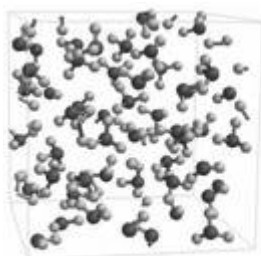
## II. Molecular Modeling of Chemical Systems

### Procedure

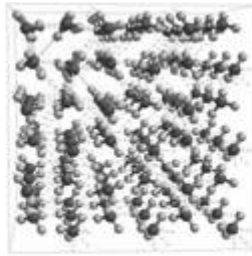
1. Use a Molecular Modeling software package<sup>9</sup> to show simulations of matter in the solid, liquid, and gas phases. The degree of disorder or entropy apparent from the arrangement of the particles is apparent. It is also possible to change the temperature of the particles and show the increase in disorder due to the velocity distribution and phase changes.

Question. List each of the following sets of systems in order from least to greatest molar entropy. In each case, justify your response.

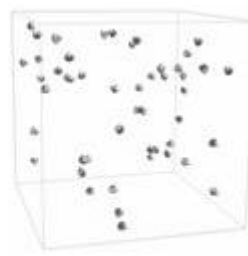
a.



$\text{NH}_3(l)$

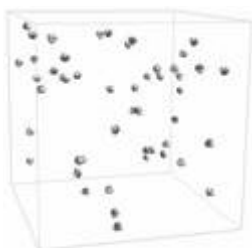


$\text{NH}_3(s)$



$\text{NH}_3(g)$

b.



$\text{NH}_3(g, 1 \text{ atm})$

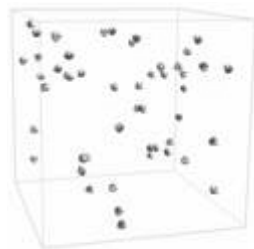


$\text{NH}_3(g, 2 \text{ atm})$

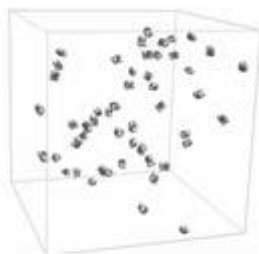
9. The commercial software package *Odyssey*, available from Wavefunction, Inc., at [www.wavefun.com](http://www.wavefun.com) will allow teachers to create and display images.



c.



$\text{NH}_3(\text{g}, 1 \text{ atm})$



$\text{N}_2\text{H}_4(\text{g}, 1 \text{ atm})$

Ans. a.  $S [\text{NH}_3(\text{s})] \quad S [\text{NH}_3(\text{l})] \quad S [\text{NH}_3(\text{g})]$

b.  $S [\text{NH}_3(\text{g}, 2 \text{ atm})] \quad S [\text{NH}_3(\text{g}, 1 \text{ atm})]$

c.  $S [\text{NH}_3(\text{g}, 1 \text{ atm})] \quad S [\text{N}_2\text{H}_4(\text{g}, 1 \text{ atm})]$

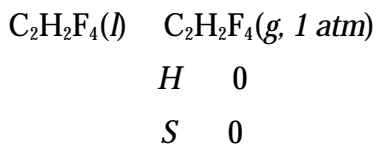
### III. Vaporization As a Spontaneous, Endothermic Process

#### Procedure

1. Substances that can be readily obtained as pressurized liquids at standard temperature include butane (lighter fuel) and 1, 1, 1, 2 tetrafluoroethane (available as lens cleaner from photography supply stores and elsewhere).
2. Note that, at thermal equilibrium, the temperature of the pressurized liquid is equal to the ambient room temperature.
3. Carefully invert the can and press the valve, releasing the liquid propellant. The propellant will vaporize quickly. Spraying the liquid onto a thermometer will demonstrate the significant decrease in temperature associated with the vaporization process

#### Analysis

Using 1, 1, 1, 2 tetra fluoroethane (lens cleaner) it is easily possible to measure a  $\Delta T$  of 60 C, from 20 C to 40 C. The vaporization process is represented by the chemical equation:



The sign of  $\Delta H$  is positive, as demonstrated by the decrease in temperature of the vapor. This is attributed to the increase in enthalpy of the gaseous product relative to the liquid reactant due to the breaking of the intermolecular forces in the liquid phase. The process occurs spontaneously at ambient temperatures and standard pressure (1 atm) because it is driven by the increase in the entropy of the gas phase compared to the liquid phase.

For sufficiently high temperatures,  $\Delta G = \Delta H - T \Delta S < 0$ , and the change occurs spontaneously.

When the liquid/vapor system is under high pressure in the can, the liquid phase and the vapor phases are in equilibrium ( $\Delta G = 0$ ). From the Clausius-Clapeyron equation:

$$\Delta G = 0 = \Delta G + RT \ln P_{\text{vap}} = \Delta H - T \Delta S - RT \ln(P_{\text{vap}})$$

$$RT \ln(P_{\text{vap}}) = \Delta H - T \Delta S$$

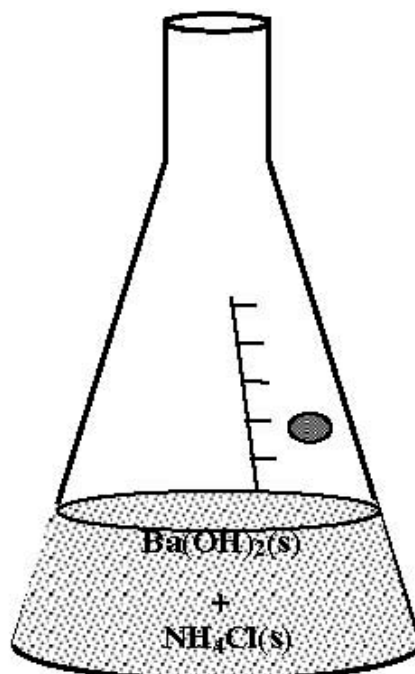
$$\ln(P_{\text{vap}}) = \frac{\Delta H - T \Delta S}{RT} = \frac{\Delta H}{R} \frac{1}{T} - \frac{\Delta S}{R}$$

The pressure of the vapor inside the can represents the equilibrium vapor pressure at ambient temperature (for an aerosol propellant, this will be significantly greater than 1 atm). When the liquid is released from the can to an ambient pressure of 1 atm, the liquid will vaporize endothermically, cooling to the temperature at which the equilibrium vapor pressure is 1 atm.

The same principles are at work when water (or another substance that exists as a liquid at STP) is caused to boil endothermically by reducing the pressure on its surface.

#### IV. The Spontaneous Endothermic Reaction of Barium Hydroxide Octahydrate and Ammonium Chloride

Reactions usually, but not always, proceed spontaneously with a decrease in the Enthalpy of the system, or in other words, are exothermic. Spontaneous endothermic reactions may occur when the total entropy, or disorder, of the system increases. Mixing two dry solids, barium hydroxide octahydrate and ammonium chloride, demonstrates a spontaneous endothermic reaction. The odor of ammonia is detected, and a noticeable amount of liquid forms as the flask becomes cold.



Procedure

1. Into separate weighing boats, place 64 g of barium hydroxide octahydrate,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(s)$  and 22 g of ammonium chloride,  $\text{NH}_4\text{Cl}(s)$ .
2. Mix the dry solids in a 250 mL Erlenmeyer flask, stopper with a two-holed stopper in which a thermometer is placed, and agitate briefly. Observe the reaction and measure the temperature of the reaction mixture.

Analysis

The reaction between barium hydroxide octahydrate and ammonium chloride proceeds according to the balanced equation:



The release of the water of hydration of the barium hydroxide octahydrate is largely responsible for the increase in entropy of the system as the reaction proceeds. This produces a slurry of largely solid barium chloride dihydrate, with undoubtedly some dissolved product.

Approximate thermochemical data for all substances in this reaction is given below:

Substance	$H_f$	$S$
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(s)$	$3342 \frac{\text{kJ}}{\text{mol}}$	$0.427 \frac{\text{kJ}}{\text{mol K}}$
$\text{NH}_4\text{Cl}(s)$	$314 \frac{\text{kJ}}{\text{mol}}$	$0.095 \frac{\text{kJ}}{\text{mol K}}$
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(s)$	$1460 \frac{\text{kJ}}{\text{mol}}$	$0.203 \frac{\text{kJ}}{\text{mol K}}$
$\text{NH}_3(aq)$	$80 \frac{\text{kJ}}{\text{mol}}$	$0.111 \frac{\text{kJ}}{\text{mol K}}$
$\text{H}_2\text{O}(l)$	$286 \frac{\text{kJ}}{\text{mol}}$	$0.070 \frac{\text{kJ}}{\text{mol K}}$

Using the values given in the table, the  $H_{\text{rxn}}$  is calculated to be  $-62 \frac{\text{kJ}}{\text{mol}}$ , a significantly endothermic reaction. The  $S_{\text{rxn}}$  is calculated to be  $0.368 \frac{\text{kJ}}{\text{mol K}}$ , showing, as expected, that there is a net increase in disorder in the system. Examination of the reaction shows that three moles of crystalline solids, which have low values of entropy, are used to form one mole of a solid, two moles of dissolved ammonia, and eight moles of liquid water. This increase in entropy is the driving force of the chemical reaction and allows the reaction to occur despite the increase in enthalpy.

Analysis Questions:

1. Verify the values of  $H_{\text{rxn}}$  and  $S_{\text{rxn}}$  using the table given above. Calculate the  $G_{\text{rxn}}$  of the above reaction at 298 K. What is the significance of the  $\pm$  sign of  $G_{\text{rxn}}$ ?
2. Over what temperature range does this reaction occur spontaneously from standard initial concentrations?

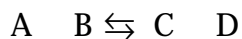
## Free Energy and Its Relationship with Equilibrium and Electrochemistry

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 Princeton High School  
 Princeton, New Jersey

Gibbs free energy is a measure of the spontaneity of a reaction. When a reaction loses free energy ( $\Delta G < 0$ ), the reaction is spontaneous, and when it is gained ( $\Delta G > 0$ ), the reverse direction of the reaction is spontaneous. Another interpretation of free energy is that it represents the maximum amount of work that can be produced by the system or the minimum amount of work required to be done on/to a reaction system to get it to move in the forward direction. Free energy is related to the equilibrium constant  $K_{eq}$  and to the electric potential,  $E$ , of an electrolytic cell. All three of these values for a reaction system will predict whether or not a reaction will happen. In general, if the value for  $\Delta G$  is negative, the value for  $K_{eq}$  is large and positive, and the  $E$  for a reaction is positive; the reaction should react in the forward direction as written. The following sections should help to elucidate these generalities.

### $\Delta G$ and Equilibrium

Equilibrium is a term that is used to describe a system in which the rate of the forward reaction is equal the rate of the reverse reaction. The macroscopic properties of concentration, pressure, and color intensities are constant, but at the molecular level the reaction is still dynamic.



Every closed reaction system has an equilibrium constant,  $K_{eq}$ , at a specific temperature for which its value is determined by the ratio of the concentrations or gaseous pressures of the products divided by the concentrations or the gaseous pressures of the reactants. Pure liquids and pure solids do not appear in this ratio because they have constant densities, and by omitting these constants we keep the value of  $K_{eq}$  as simple as possible.

For the reaction above we would represent  $K_{eq}$  as follows:

$$K_{eq} = \frac{[C][D]}{[A][B]} \quad \text{or} \quad K_p = \frac{P_C P_D}{P_A P_B}$$

If a reactant or product species has a coefficient, then the concentration or partial pressure is raised to that power in the equilibrium expression:



$$\text{then } K_c = \frac{[C]^3 [D]}{[A]^2 [B]}$$

Under standard conditions of 1 atmosphere, 25 °C and 1M solutions, the relationship between Gibbs free energy and the equilibrium constant for a particular reaction is:

$$\Delta G = -RT \ln K_{eq}$$

Here  $R$  is  $8.3145 \times 10^{-3} \text{ kJ K}^{-1}$ , and  $T$  is in Kelvins.  $K_{eq}$  can be the equilibrium constant for a gaseous equilibrium or any of the equilibria involving solutions. Specific examples include  $K_p$ ,  $K_a$ ,  $K_b$ ,  $K_{sp}$ ,  $K_w$ , among others.

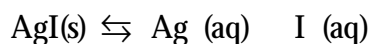
**Sample problem:**

Using accepted values for  $\Delta G_f$  (free energy of formation) in the table below, calculate the dissociation constant for a slightly soluble substance ( $K_{sp}$ ) for AgI at 25 °C.

Substance	$\Delta G_f$
Ag	77.1 kJ/mol
I	51.67 kJ/mol
AgI	66.2 kJ/mol

**Solution:**

1. Write the chemical equation for the solution process:



2. Apply the equation:

$$\Delta G = \sum \Delta G_f \text{ products} - \sum \Delta G_f \text{ reactants}$$

$$= [(77.1 \text{ kJ} + (-51.67 \text{ kJ})) - (-66.2 \text{ kJ})]$$

$$= 91.6 \text{ kJ}$$

3. To find the  $K_{sp}$ , apply the equation

$$\frac{\Delta G}{RT} = \ln K_{sp}$$

$$\frac{91.6 \text{ kJ}}{(8.31 \times 10^{-3} \text{ kJ/K})(298 \text{ K})} = \ln K_{sp}$$

$$K_{sp} = 8.3 \times 10^{-17}$$

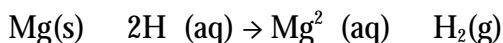
Here is a situation in which the free energy is very positive, so the reaction is not spontaneous. Thus the value of the  $K_{sp}$  should be very small, which it is. This should make sense because AgI is not a very soluble salt.

What happens when a reaction isn't run at standard conditions? We then have to use an equation, which uses  $Q$ , the "reaction quotient."  $Q$  is set up as a ratio in the same manner as the equilibrium constant, and we use the values for the molarities (M) or partial pressures (atm) as given in the problem.

$$G = G^\circ + RT \ln Q$$

### Sample Problem:

Given the following net reaction of magnesium metal with hydrochloric acid:



1. Write the expression for  $Q$ .
2. Calculate  $G^\circ$  at 25 °C using thermodynamic tables.
3. Find  $G$  at 25 °C when  $P_{\text{H}_2}$  is 1.5 atm,  $[\text{Mg}^{2+}] = 0.20\text{M}$ ,  $[\text{H}^+] = 0.0020\text{M}$ .

### Solution:

$$1. \quad Q = \frac{[\text{Mg}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$2. \quad \begin{aligned} H^\circ &= H_f^\circ \text{Mg}^{2+} = 466.8 \text{ kJ/mol (all of the other values are zeros)} \\ S^\circ &= S^\circ \text{Mg}^{2+} + S^\circ \text{H}_2 - S^\circ \text{Mg} - S^\circ \text{H} \\ &= 0.1381 \text{ kJ/K}\cdot\text{mol} + 0.1306 \text{ kJ/K}\cdot\text{mol} - 0.0327 \text{ kJ/K}\cdot\text{mol} - 0 \text{ kJ/K}\cdot\text{mol} \\ &= 0.3345 \text{ kJ/K}\cdot\text{mol} \end{aligned}$$

$$G^\circ = H^\circ - T S^\circ = 466.8 \text{ kJ mol}^{-1} - 298 \text{ K} (0.3335 \text{ kJ/mol}\cdot\text{K}) = 367.4 \text{ kJ mol}^{-1}$$

$$3. \quad \begin{aligned} G &= G^\circ + RT \ln Q \\ &= 367.4 \text{ kJ} + (8.31 \times 10^{-3} \text{ kJ/K}) (298 \text{ K}) \ln \frac{(0.20)(1.5)}{(0.0020)^2} \\ &= 367.4 \text{ kJ} + 27.8 \text{ kJ} = 395.2 \text{ kJ} \end{aligned}$$

When solving problems, care needs to be taken to make sure that all units are carried consistently. For example, if  $R$  is in kJ/K, then  $S^\circ$  should be in kJ/K. If the sign of  $G$  is ( ), then the value of the equilibrium constant will be greater than 1 and vice versa.

### G and Electrochemistry

Electrochemistry involves voltaic (electrochemical) and electrolytic cells. Voltaic cells are used to produce electricity from a reaction made up of an oxidation and a reduction half-cell.

Students may use the mnemonics **LEO** (loss of electrons is oxidation) and **GER** (gain of electrons is reduction) to help them remember which half-reaction is the oxidation and which is the reduction. Also, “Oxidation always occurs at the anode” is another helpful reminder. Textbooks provide the reduction half-reaction potentials in reference tables for students to use. To obtain the value for the oxidation half-reaction, a student needs to find the reduction version, obtain the numerical value, and change the sign. When the sum of the reduction and oxidation potentials provides a positive voltage, the reaction is spontaneous as written. If it is a negative value, then the reaction is not spontaneous (the reverse one is) and would then become an electrolytic cell reaction, which would need an outside source of energy to get the reaction to go. (Electrolysis requires the addition of energy and then the free energy value would be positive!)

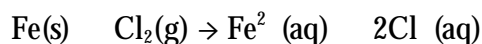
Neither the reduction nor the oxidation potentials are stoichiometric. They are not multiplied by a coefficient before they are added together to give the  $E$  value for the cell; these values are potentials. However, the half-reactions themselves must have equal numbers of electrons gained and lost in the net reaction, which may require using coefficients as multipliers for the half-reactions. The coefficients are also used in calculating  $Q$ , the equilibrium quotient.

**Sample problem:**

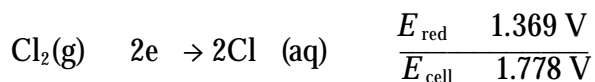
Will iron metal be oxidized to  $\text{Fe}^{2+}$  by chlorine gas?

**Solution:**

1. Write the balanced equation:



3. Identify the oxidation and reduction half-reactions, their electric potentials, and the  $E_{\text{cell}}$ .



Here the number of electrons gained and lost are equal, and the potentials are simply added. Since the  $E_{\text{cell}}$  for the above reaction is positive, the cell will provide electricity.

The relationship between  $E_{\text{cell}}$  and  $G$  is as follows:

$$G = -nFE$$

where  $n$  is the number of moles of electrons transferred in the oxidation/reduction and  $F$  is the Faraday constant which has the value  $9.648 \times 10^4 \text{ J/mol} \cdot \text{V}$ . Using the example above we can solve for the  $G$ .

Solution:

$$G = nFE \quad \text{where } n = 2$$

$$2 \text{ mol } (9.648 \times 10^4 \text{ J/mol } \cdot \text{V}) \cdot 1.778 \text{ V}$$

$$343.1 \times 10^3 \text{ J} = 343.1 \text{ kJ}$$

If this reaction is not run at standard conditions, then another problem arises that is similar to the one with equilibrium. We can start with the equation

$$G = G^\circ + RT \ln Q \text{ so that then } nFE = nFE^\circ + RT \ln Q, \text{ which}$$

reduces nicely to

$$E = E^\circ - \frac{RT}{nF} \ln Q \text{ which is called the Nernst Equation.$$

Using the same example from above, what would the  $E_{\text{cell}}$  be if the partial pressure of the chlorine gas were 2.0 atm and the concentration of the iron and chloride ions became 0.10 M, respectively?

Solution:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = 1.778 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.10 \text{ M}) (0.10 \text{ M})^2}{(2.0 \text{ atm})}$$

$$E = 1.778 \text{ V} - .0978 \text{ V} = 1.876 \text{ V}$$

Since  $G = nFE$ , thus  $G = 2 \text{ mol } (96480 \text{ J/mol } \cdot \text{V}) \cdot 1.876 \text{ V}$

$$361.992 \times 10^3 \text{ J} = 362.0 \text{ kJ}$$

### Sample Problem:

Question 2 from the 2000 AP Free-Response section of the AP Exam is typical of the type of question a student might see. (Parts a and b)

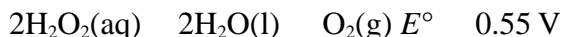
2. a. Under standard conditions at 25 °C, Zn(s) reacts with  $\text{Co}^{2+}(\text{aq})$  to produce Co(s).
  - (i) Write the balanced equation for the oxidation half-reaction.
  - (ii) Write the balanced net ionic reaction for the overall reaction.
  - (iii) Calculate the standard potential,  $E^\circ$ , for the overall reaction at 25 °C.



**Solutions:**

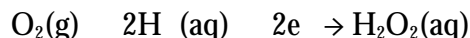
- (i)  $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$  (oxidation half-reaction)
- (ii)  $\text{Zn(s)} + \text{Co}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Co(s)}$  (balanced net ionic reaction)
- (iii)  $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$   
 $0.76 \text{ V} + (-0.28 \text{ V})$   
 $0.48 \text{ V}$

b. At 25°C,  $\text{H}_2\text{O}_2$  decomposes according to the following equation.



- (i) Determine the value of the free energy change,  $G^{\circ}$ , for the reaction at 25°C.
- (ii) Determine the value of the equilibrium constant,  $K_{\text{eq}}$ , for the reaction at 25°C.
- (iii) The standard reduction potential  $E^{\circ}$  for the half-reaction

$\text{O}_2 + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O(l)}$  has a value of 1.23 V. Using this information in addition to the information given above, determine the value of the standard potential,  $E^{\circ}$ , for the half-reaction below.



**Solutions:**

- (i)  $G^{\circ} = -nFE^{\circ} = -2 \text{ mol} (96500 \text{ J/V} \cdot \text{mol})(0.55 \text{ V}) = -1.1 \times 10^5 \text{ J}$  or  $-1.1 \times 10^2 \text{ kJ}$
- (ii)  $G^{\circ} = -RT \ln K_{\text{eq}}$   
 $-1.1 \times 10^2 \text{ kJ} = -(8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K})(298 \text{ K})(\ln K_{\text{eq}})$

Solving,  $K_{\text{eq}} = 2.0 \times 10^{19}$

- (iii)  $\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O}_2 \quad 0.55 \text{ V}$   
 $\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O} \quad 1.23 \text{ V}$   

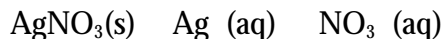

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 $2\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}_2 \quad 0.68 \text{ V}$

The coefficients can be reduced by a factor of 2, but the calculated reduction potential will stay the same value.

**Sample problem:**

Question 8 from the 2005 Free-Response section is another great example of a typical type of problem that a student might see.



The dissolving of silver nitrate in pure water is represented by the equation above.

- Is the  $\Delta G$  for the dissolving of silver nitrate positive, negative, or zero? Justify your answer.
- Is  $\Delta S$  for the dissolving of silver nitrate positive, negative, or zero? Justify your answer.
- The solubility of silver nitrate increases with increasing temperatures.
  - What is the sign of  $\Delta H$  for the dissolving process? Justify your answer.
  - Is the answer you gave in part (a) consistent with your answers to parts (b) and (c)(i)? Explain.

**Solution:**

- Since silver nitrate is a salt containing the nitrate anion and all nitrate salts are soluble, the sign of the free energy change will be negative because the reaction occurs spontaneously.
- The sign of the entropy change is positive because greater entropy is attained. The reaction produces more dissociated ions in the solution than it started with as a solid, which is more ordered.
- The sign of the enthalpy change is positive because the solubility increases with an increase in temperature. When the enthalpy for a reaction equilibrium is endothermic, an increase in temperature will favor the forward direction and in this case increase the solubility.
  - The answers are consistent. Using the equation  $\Delta G = \Delta H - T \Delta S$ , the free energy can be negative even though the enthalpy is positive. The  $T \Delta S$  term is greater than the positive enthalpy term and when subtracted, the free energy becomes negative.

Question 8, continued:

Half-reaction	E (V)
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-$	0.53
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$	0.83
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{s})$	2.71

**Special Focus: Thermochemistry**

- d. An electric current is applied to a 1.0 M NaI solution.
- (i). Write the balanced oxidation half-reaction for the reaction that takes place.
  - (ii). Write the balanced reduction half-reaction that takes place.
  - (iii). Which reaction takes place at the anode, the oxidation or the reduction reaction?
  - (iv). All electrolysis reactions have the same sign for  $G^\circ$ . Is the sign positive or negative? Justify your answer.

**Solution:**

- (i).  $2\text{I}_{(\text{aq})} \rightarrow \text{I}_{2(\text{s})} + 2\text{e}^-$
- (ii).  $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})} + 2\text{OH}_{(\text{aq})}^-$
- (iii). The oxidation half-reaction occurs at the anode.
- (iv). The sign of  $G^\circ$  for every electrolysis is positive. Every electrolysis reaction requires an outside source of energy to make the reaction proceed. This type of reaction is not spontaneous.

# Chemical Thermodynamics

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## Introduction

Traditionally in college chemistry textbooks, thermodynamics is taught as two separate chapters. First, calorimetry and thermochemistry are taught as one chapter and then, about eight chapters later, the concept of the first and second law of thermodynamics are taught. This author feels that the subject should be taught as one comprehensive unit, so that students can see the logical sequence of chemical thermodynamics. In this way they can see the importance of thermodynamics, which is to predict whether a chemical reaction as stated would occur with a net release or absorption of energy. In other words, thermodynamics helps the chemist determine whether a reaction would be spontaneous (may occur) or not. These lesson plans outlined here will help the teacher to accomplish this.

These lesson plans are based on the following general concepts which must be mastered by any student.

## Lesson Plan 1—Introduction to Energy and Thermochemical Equations

Grade Level: 11, 12

Subject: Chemistry

Duration : Six 50 minute periods

Description: A lesson plan for Introducing the First Law of thermodynamics, forms of energy, heat, thermal energy; thermochemical equations; and enthalpy

Goals:

National Science Standards—Content Standards for grades 9–12, Content Standard B

- Chemical reactions may consume or release energy
- The total energy of the universe is constant. Energy can be transferred in chemical reactions, however it can never be destroyed
- All energy can be considered to be either kinetic energy, potential energy
- Heat consists of random motion and the vibrations of atoms, molecules, and ions.
- Energy is transferred from hotter to cooler objects.

## Objectives

- Understand the basic definition of energy is the capacity to do work.
- Understand the difference between kinetic energy, potential energy, and internal energy
- Describe, distinguish, and relate the following properties, and predict whether these properties increase, decrease, or stay the same over the course of a given chemical or physical change.

- Understand heat on both theoretical and experimental levels.
- Relate heat transferred to changes in thermal energy when no work is done.
- Relate heat to an object's mass and initial and final temperatures. Clearly distinguish between heat and temperature.
- Explain how heat can be measured experimentally (calorimetry).
- Define heat capacity and specific heat.
- Define enthalpy. Distinguish enthalpy from thermal energy.
- Describe how changes in enthalpy and thermal energy accompanying a chemical reaction can be measured calorimetrically.
- Write and manipulate thermochemical equations.
- Estimate the heat of a chemical reaction from the bond energies.

## Procedure

- A. Begin with the usual definition of energy is the ability to do work. Explain that work is moving an object against an opposing force. Work = distance × opposing force. The SI unit of energy is the joule.
- B. Explain the two basic forms of energy.
  1. Potential Energy is the energy an object has by virtue of its position in a field of force. Examples would be: water at the top of a dam—due to position relative to the gravitational field of force, cations and anions have potential energy due to their relative position to the electrostatic field of force.
  2. Kinetic Energy is the energy associated with an object by virtue of its motion. The kinetic energy of an object depends on its mass and speed. Examples would be pool balls and molecules moving.
  3. The SI unit of energy is the joule (J) which is an extremely small unit, so we often measure in kilojoules (kJ).
- C. Internal Energy is the sum of the kinetic and potential energies of the particles making up a substance. For example a baseball traveling from a pitcher's mitt to the batter has a total energy equal to the sum of its potential and kinetic energies plus its internal energy. Normally, when we study a reaction in the laboratory, it is sitting on the laboratory table, so its kinetic energy as a whole is zero. In addition, its potential energy is constant and you can take it to be zero, since it is not changing. In this case, the total energy of the substance equals its internal energy.
- D. Discuss with the students the law of conservation of energy. Which states that energy can be converted from one form to another, but the total quantity remains constant. In other words, stress the basic principle: Energy can neither be created nor destroyed but only transformed. Energy IN = Energy OUT! This can be summarized with the following equation

$$E_2 = E_1 + q + w$$

Where:  $E_1$ : internal energy of the system at the beginning

$E_2$ : internal energy of the system at the end

$q$ : net heat flow into the system

$w$ : net work done by the system.

$$E = q + w$$

$w = -P \Delta V$  when a gas expands against a constant external pressure.

- E. Define enthalpy. Distinguish enthalpy from thermal energy. Describe how changes in enthalpy and thermal energy accompanying a chemical reaction can be measured calorimetrically.

Students must understand that enthalpy is a state function. Its value depends only on the initial and final states, not on the pathway. A positive enthalpy indicates an endothermic reaction in which heat is absorbed so the products have more energy. A negative enthalpy indicates an exothermic reaction in which heat is released.

Relate heat to an object's mass and initial and final temperature. Clearly distinguish between heat and temperature. Explain how heat can be measured calorimetrically. Students should be aware that the heat change in a chemical reaction is expressed as joule/mole of substance.

- F. Understand what a thermochemical equation is. It must have the states and the  $\Delta H$  for the reaction.
- G. Properties of thermochemical equations the student must keep in mind:
- The stoichiometric coefficients always refer to the number of moles of substance.
  - If you reverse a reaction, the sign of  $\Delta H$  changes.
  - If you multiply both sides of the equation by a factor  $n$ , then  $\Delta H$  must change by the same factor  $n$ .
- H. Students develop an understanding of standard states and standard enthalpy changes.
- I. Standard molar enthalpies of formation are defined,  $\Delta H_f^\circ$ .
- J. Additivity of heats of reaction. **Hess's Law:** When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.
- K. Students are able to estimate the energy in a chemical reaction using bond energies.

$$\Delta H = \sum S[\text{energies of bonds broken}] - \sum S[\text{energies of bonds formed}]$$

Bond breaking is endothermic.

Bond formation is exothermic.

### Sample questions:

- For which exothermic reaction is  $\Delta E$  more negative than  $\Delta H$ ?
  - $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$
  - $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$

- c)  $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{HF}(\text{g})$   
 d)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

Answer (d): Since the number of gas molecules is decreasing, this means the gases are being compressed. Compression is work done on the gas; the internal energy of the products is greater than the internal energy of the reactants.

2. The burning of 1.010 g of cane sugar,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  in a bomb calorimeter causes the temperature of the water to increase from  $24.92^\circ\text{C}$  to  $28.98^\circ\text{C}$ . The calorimeter contains 980.0 g of water. Assume a specific heat of  $4.184 \text{ J/g } ^\circ\text{C}$  for the water and that the heat absorbed by other parts of the surroundings are negligible.
- What is the heat of combustion of sucrose, expressed in kilojoules per mole?
  - Write a balanced thermochemical equation for the combustion of sucrose.
  - Verify the claim of sugar manufacturers that one teaspoon of sugar (about 4.8 g) “contains only 18 Calories.” (Note: reference here is to “large calories” that is kilocalories; 1 calorie = 4.18 J)

Solution

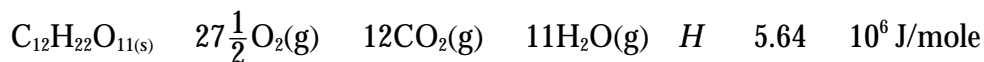
In this problem the students must understand that the heat released in a chemical reaction is proportional to the amount of matter that is reacting. This is a fundamental concept that students must master. They also gain the skill of writing a thermochemical equation.

The heat released from the combustion of 1.010 g of cane sugar is used to heat the water in the calorimeter. This is the method for most calorimeters. In this problem the student is told that the heat absorbed by other parts of the surroundings is negligible. Using the equation  $q = mc\Delta T$ , where  $m = 980 \text{ g}$  of water,  $c = \text{specific heat}$  and  $\Delta T = T_2 - T_1 = 4.06 \text{ }^\circ\text{C}$ . Substituting in the equation.

$$q = (980 \text{ g}) (4.184 \text{ J/g } ^\circ\text{C}) (4.06 \text{ }^\circ\text{C}) = 16647 \text{ joules/ 1.010 g of cane sugar.}$$

The heat of combustion of any substance is the heat released /mole of substance. The student needs to determine the moles of sucrose reacting  $1.010\text{g}/342 \text{ g/mole} = 0.00295 \text{ moles of sucrose}$

$$Q_{(\text{combustion})} = 16647\text{J}/0.00295 \text{ moles} = 5.64 \times 10^6 \text{ J/mole} = 5.64 \times 10^3 \text{ kJ/mole.}$$



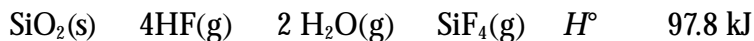
4.8 g of sugar = 0.014 moles of sugar  
 0.014 moles  $\times 5.64 \times 10^6 \text{ J/mole} = 7.9 \times 10^4 \text{ J} = 1 \text{ calorie}/4.18 \text{ J} = 18900 \text{ calories}$   
 18.9 kcal = 19 Calories. So yes, 1 teaspoon of sugar has approximately 19 kilocalories.

3. For the burning of ammonia in the presence of a copper catalyst,



- Which is greater the total value of  $H$  for the reactant or  $H$  for the products?
- Calculate  $H$  for the burning of 1.0 mole of ammonia.
- Calculate  $H$  for the reaction of  $\text{N}_2$  with  $\text{H}_2\text{O}$ .

4. For the reaction



Substance	$H_f$ (kJ/mole)
$\text{SiO}_2(\text{s})$	910.9
$\text{HF}(\text{g})$	272.5
$\text{H}_2\text{O}(\text{g})$	136.1

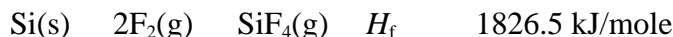
- Calculate the enthalpy of formation of  $\text{SiF}_4(\text{g})$
- Write a thermochemical equation for the formation of 1 mole of  $\text{SiF}_4(\text{g})$

Answer:

$$H_r = H_f(\text{products}) - H_f(\text{reactants})$$

$$97.8 \text{ kJ} = [\text{SiF}_4 + 2\text{moles}(136.1 \text{ kJ/mole})] - [1\text{mole}(910.9 \text{ kJ/mole}) + 4\text{moles}(272.5 \text{ kJ/mole})]$$

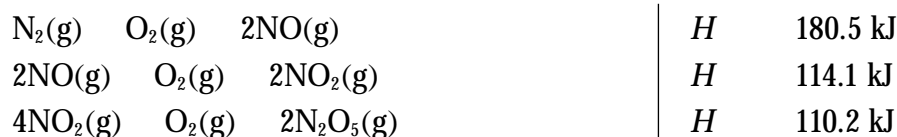
$$\text{SiF}_4 = 1826.5 \text{ kJ/mole}$$



2. When 50.g of an aqueous solution that contains 0.050 mole of HCl and 50.g of an aqueous solution that contains 0.050 mole of NaOH are mixed in a calorimeter, the temperature of the resulting solution rises from 21.0°C to 27.5°C. Assuming the heat capacity of the solution is close to that of pure water (4.184 J/g·°C) and that the heat capacity of the calorimeter can be ignored, determine the standard heat of reaction for  $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{NaCl}(\text{aq})$ .

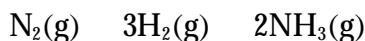
Answer: 54.4 kJ/mole

3. Use the thermochemical data given to calculate  $H_f$  for  $\text{N}_2\text{O}_5(\text{g})$  in kJ/mol



Answer: 11.3 kJ/mol

4. Use the bond energies to estimate the value of the  $H$  for the reaction:





**Special Focus: Thermochemistry**

<b>Bond Energies kJ/mol</b>	
H H	436
H N	386
N N	193
N=N	418
N N	941

*Answer: 67 kJ*

## Lesson Plan 2—Spontaneity of Physical and Chemical Changes

Grade Level: 11, 12

Subject: Chemistry

Duration : Five 50-minute periods

Description: A lesson plan for Introducing the Second Law of thermodynamics, criteria for spontaneous process, entropy and free energy

**Goals:**

National Science Standards—Content Standards for grades 9–12, Content Standard B

- Everything tends to become less organized and less orderly over time. Thus in all energy transfers, the overall effect is that the energy is spread out uniformly.

**Objectives:**

- Understand that spontaneous changes happen without any continuing outside influences.
- Develop an understanding of the meaning of entropy.
- Understand that in all irreversible processes the total entropy of an isolated system must increase.
- Be able to correctly identify whether entropy increases or decreases.
- Be able to correctly compare the entropy of two substances.
- All real processes are irreversible.
- Entropies have been measured and tabulated.
- Be able to calculate entropy changes for chemical reactions.
- Develop an understanding of the criteria for spontaneity.
- Be able to correctly identify a spontaneous process.
- Understand the relationship between entropy and free energy.
- Be able to correctly predict increases and decreases in entropy and free energy.

**Procedure:**

- A. Explain to students that a spontaneous change happens without any continuing outside influences. A spontaneous change has a natural direction. This is a very important for the students to develop. Good examples include:
  - The rusting of iron occurs spontaneously. Rust cannot turn into iron metal without our interference.
  - The melting of ice at room temperature. Water will not spontaneously freeze at room temperature.
- B. Define entropy for the students. It is a measure of the dispersal of energy over the states available to a system.

- C. Students should be made aware that temperature, physical state, lattice energy of the crystal, atomic and molecular size, freedom of rotation of the molecule will affect the entropy of a substance.
- D. The second law of thermodynamics can be viewed as stating that in all irreversible processes (real) processes that total entropy of an isolated system must increase.
- E. Students should be made aware of the two aspects of spontaneity.
- An exothermic reaction does not ensure spontaneity. For example the freezing of water is exothermic but only spontaneous below 0 C.
  - An increase in disorder of the system also does not ensure spontaneity.
  - It is a proper combination of exothermicity and disorder that determines spontaneity.
- F. Units of entropy: joule/mole K
- G. Have the students calculate the  $\Delta S$  using the tabulated values. Correctly predicting whether the entropy increases or decreases.
- H. Have the students calculate the free energy change from changes in entropy and enthalpy. They must be able to correctly predict whether the free energy increases or decreases and whether the process is spontaneous or not.

### Practice Problems

1. Identify whether entropy increases or decreases for each of the following changes.
- a)  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$
  - b)  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$
  - c) precipitation of a solid after mixing two solutions.
  - d)  $\text{CuCO}_3(\text{s}) \rightarrow \text{CuO}(\text{s}) + \text{CO}_2(\text{g})$
  - e)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
  - f)  $\text{Ba}(\text{OH})_2(\text{s}) + 2\text{NH}_4\text{Cl}(\text{s}) \rightarrow 2\text{NH}_3(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{Ba}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$

*Answer: entropy increases for a, d, and f. If the number of gaseous particles increases the entropy will increase. In letter (b) the substance is freezing, and solids have a lower entropy state than liquids. In letter (c) aqueous ions are forming a solid. In letter (e) the number of gas particles goes from 3 on the reactant side to 2 on the product side.*

2. From each of the following pairs of compounds choose the one with the higher standard molar entropy at 25°C. Give brief reasons for your choice.
- a) Pb(s) or C(graphite)
  - b) Cs(s), Cs(liq)
  - c)  $\text{NH}_3(\text{g})$ , Ne(g)
  - d) KCl(s), CaS(s)
  - e) Ne(g) at 1.0 atm, or Ne(g) at 0.1 atm
  - f) C(s) at 25°C or C(s) at 50°C

g) CH<sub>3</sub>OH(l) or C<sub>2</sub>H<sub>5</sub>OH(l)

h) n-butane or cyclobutane

*Answers:*

a) *Pb has greater molar entropy, Pb, with metallic bonding, forms soft crystals with high amplitudes of vibration; graphite has stronger (covalent) bonds, is more rigid, and thus is more ordered.*

b) *Cs(l) – liquids have greater freedom of movement, therefore more ways of distributing the energy.*

c) *NH<sub>3</sub>(g) – is the more complex molecule of the two therefore, the entropy will be greater.*

d) *KCl(s) – the strength of the ionic bond in KCl is less than that of CaS, due to the increase in the coulombic attractions in CaS.*

e) *Ne at 0.1 atm. At the lower pressure the volume of the Ne is greater; the number of ways in which the gas molecules can distribute themselves in space is much larger, so the entropy increases.*

f) *C at 50 – entropy invariably increases with increase in temperature.*

g) *C<sub>2</sub>H<sub>5</sub>OH – the more complex molecule has the greater degree of entropy.*

h) *n-butane – the chain structure allows for greater freedom of movement over the ring structure. This allows an increase in the alternative ways the molecules can arrange themselves in space.*

3.

Compound	$H_f$ (kilojoules mol <sup>-1</sup> )	$S$ (joules mole <sup>-1</sup> K <sup>-1</sup> )
H <sub>2</sub> O(l)	285.8	69.95
CO <sub>2</sub> (g)	393.5	213.7
O <sub>2</sub> (g)	0.0	205.0
C <sub>3</sub> H <sub>8</sub> (g)	?	270.2

When 1.000 gram of propane gas, C<sub>3</sub>H<sub>8</sub>, is burned at 25 C and 1.00 atmosphere, H<sub>2</sub>O(l) and CO<sub>2</sub>(g) are formed with the evolution of 50.33 kilojoules.

- Write a balanced equation for the combustion reaction.
- Calculate the molar enthalpy of combustion,  $H_{\text{comb}}$ , of propane.
- Calculate the standard molar enthalpy of formation,  $H_f$ , of propane gas.
- Calculate the entropy change,  $S_{\text{comb}}$ , for the reaction and account for the sign  $S_{\text{comb}}$ .

*Answer:*a) C<sub>3</sub>H<sub>8</sub> + 5O<sub>2</sub>(g) → 3 CO<sub>2</sub>(g) + 4H<sub>2</sub>O(l)b) 1.000g/44.097g mole<sup>-1</sup> = 0.02268 moles; 50.33 kJ/0.02268 moles = 2219 kJ/mole

**Special Focus: Thermochemistry**

$$c) \quad 2219 \text{ kJ} \quad [3(393.5) + 4(285.8)] \text{ kJ} \quad [H_f \text{ C}_3\text{H}_8 - 5(0)] \text{ kJ}$$

$$H_f = 104 \text{ kJ/mole}$$

$$d) \quad [3(213.7) + 4(69.95)] - [1(270.2) + 5(205.0)]$$

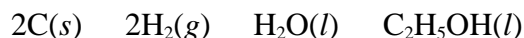
$$= 374.3 \text{ Joules/K}$$

The entropy decreases due to the loss of gaseous particles.

4. Substance	Enthalpy of Combustion, $H$ (kilojoules/mol)	Absolute Entropy, $S$ (Joules/mol K)
C(s)	393.5	5.740
H <sub>2</sub> (g)	285.8	130.6
C <sub>2</sub> H <sub>5</sub> OH(l)	1366.7	160.7
H <sub>2</sub> O(l)	—	69.91

(a) Write a separate, balanced chemical equation for the combustion of each of the following: C(s), H<sub>2</sub>(g), and C<sub>2</sub>H<sub>5</sub>OH(l). Consider the only products to be CO<sub>2</sub>(g) and/or H<sub>2</sub>O(l).

(b) In principle, ethanol can be prepared by the following reaction:

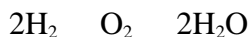


Calculate the standard enthalpy change,  $H$ , for the preparation of ethanol, as shown in the reaction above.

(c) Calculate the standard entropy change,  $S$ , for the reaction given in part (b).

(d) Calculate the value of the equilibrium constant at 25 °C for the reaction represented by the equation in part (b).

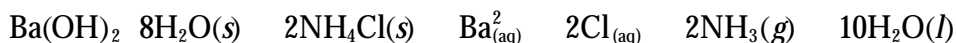
**Answer:**



**Note:** This is a classic Hess's Law problem. The students have to be able to realize that the heat of combustions of each of the elements is the equivalent of the respective heats of formation of carbon dioxide and water.

- (c)  $[160.7] \quad [11.5 \quad 261.2 \quad 69.9] \text{ J/mol K}$   
 $181.9 \text{ J/mol K}$
- (d)  $G \quad H \quad T \quad S \quad 8100 \text{ J} \quad (298 \text{ K})(181.9 \text{ J/mol K}) \text{ J}$   
 $62300 \text{ J}$   
 $K_{\text{eq}} = e^{-G/RT} = e^{-(62300)/(8.3143)(298)} = 1.2 \times 10^{-11}$

5. When crystals of barium hydroxide,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , are mixed with crystals of ammonium thiocyanate,  $\text{NH}_4\text{SCN}$ , at room temperature in an open beaker, the mixture liquefies, the temperature drops dramatically, and the odor of ammonia is detected. The reaction that occurs is the following:



- (a) Indicate how the enthalpy, the entropy, and the free energy of this system change as the reaction occurs. Explain your predictions.
- (b) If the beaker in which the reaction is taking place is put on a block of wet wood, the water on the wood immediately freezes and the beaker adheres to the wood. Yet the water inside the beaker, formed as the reaction proceeds, does not freeze even though the temperature of the reaction mixture drops to  $-15 \text{ C}$ . Explain these observations.

**Answer**

- (a) *The enthalpy increases ( $\Delta H > 0$ ) since the reaction absorbs heat as is shown by the decrease in temperature.*  
*The entropy increases ( $\Delta S > 0$ ) since solid reactants are converted to gases and liquids, which have a much higher degree of disorder.*  
*The free energy decreases ( $\Delta G < 0$ ) as is shown by the fact that the reaction is spontaneous. **Note:** Students must be able to realize that if a reaction occurs, then the reaction is spontaneous and  $\Delta G$  is of course negative.*
- (b) *The water on the wood froze because the endothermic reaction lowered the temperature below the freezing point of water. The solution in the beaker did not freeze because the presence of ions and dissolved gases lowered the freezing point of the solution below  $-15 \text{ C}$ . The freezing point depression is given by the equation  $\Delta T = K_f m$  where  $m$  is the molality of the solution and  $K_f$  is the molal freezing point constant for water.*
6.  $2\text{NO}_2(g) + \text{O}_3(g) \rightarrow \text{N}_2\text{O}_5(g) + \text{O}_2(g) \quad \Delta H = 198 \text{ kJ} \quad \Delta S = 168 \text{ J K}^{-1}$   
 Ozone reacts with nitrogen dioxide according to the equation above.

- a) Calculate  $\Delta H_f^\circ$  for  $\text{NO}_2(g)$  in kJ/mol

Substance	$\Delta H_f^\circ$ (kJ/mole)
$\text{O}_3(g)$	143
$\text{N}_2\text{O}_5(g)$	11

- b) Account for the sign of  $\Delta S$ .
- c) Calculate the value for  $\Delta G$  at  $25 \text{ C}$ .

## Special Focus: Thermochemistry

- d) State and explain how the spontaneity of this reaction will vary with increasing temperature.

*Answer*

$$a) \quad H = [H_f(N_2O_5) - H_f(O_2)] - [2H_f(NO_2) - H_f(O_3)] \\ 198 \text{ kJ} - [11 \text{ kJ} - 0] - [2x - 143 \text{ kJ}] \quad \text{so } H_f(NO_2) = 33 \text{ kJ}$$

b)  $S < 0$  because 3 moles of gas are converted to 2 moles of gas.

$$c) \quad G = H - T \Delta S \\ 198000 \text{ J} - 298 \text{ K} (168 \text{ J/K}) \\ 148 \text{ kJ}$$

- d) Spontaneity will decrease as temperature increases because the entropy change of the process is negative. This makes the contribution of the  $T \Delta S$  term to the free energy positive. As temperature rises, this term contributes more to the free energy and because it is positive, the spontaneity must decrease.

## Laboratory component

Laboratory 1:

NSF Summer Project in Chemistry

Hope College

Heats of Acid-Base Reactions

**PURPOSE:** To experimentally measure the energy released when solutions of acids and bases are mixed, and correlate the energy released with the net ionic equation for the reaction.

**INTRODUCTION:** The electrical conductivity of each acid and base to be used in this experiment will be demonstrated for the student. Each solution should be classified as a good conductor (strong electrolyte) or as a poor conductor (weak electrolyte). As the student carries out the energy determination for this experiment, he or she should seek answers to questions like:

- Are all acid-base reactions exothermic?
- Do some acid-base reactions release more heat energy than others per mole of hydrogen ions that react?
- What regularities are observed within the set of heat values obtained?
- What do all the equations have in common?

A 50.0 mL sample of an acid is measured out and placed in a 250 mL beaker. Its temperature is recorded to the nearest 0.1 degree Celsius. A 50.0 mL sample of a base is then measured out and placed in a styrofoam cup calorimeter. Its temperature is also measured to the

nearest 0.1 °C. The acid solution is then quickly added to the styrofoam cup, mixed, and the highest temperature attained is recorded.

Materials needed for each student:

Conductivity apparatus	250 mL beaker
Styrofoam cups	thermometers (2)
50-mL graduated cylinders (2)	
50.0 mL of 2.0 M acetic acid (CH <sub>3</sub> COOH)	
50.0 mL of 2.0 M hydrochloric acid (HCl)	
50.0 mL of 2.0 M nitric acid (HNO <sub>3</sub> )	
50.0 mL of 2.0 M sodium hydroxide (NaOH)	
50.0 mL of 2.0 M potassium hydroxide (KOH)	
50.0 mL of 2.0 M ammonia solution (NH <sub>3</sub> )	
50.0 mL of 1.0 M sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	

Hazards:

- A) The acid solutions used in this experiment (acetic, hydrochloric, nitric, and sulfuric) are corrosive to skin, eyes, and clothing. Wear safety goggles and lab aprons when handling the acids. Wash any spills or splashes off your skin or clothing immediately with plenty of water. Call your teacher.
- B) The base solutions used in this experiment (sodium hydroxide, potassium hydroxide, and ammonia) are *very* corrosive to skin, eyes and clothing. Wash any spills or splashes off your skin or clothing immediately with plenty of water. Call your teacher.

Procedure:

- (1) Select three combinations of acids and bases that you will use in the experiment. Record the combinations on your report sheet.
- (2) Using a 50 mL graduated cylinder, place 50.0 mL of the acid from the first combination into a 250 mL beaker. Measure and record the temperature to the nearest 0.1 °C.
- (3) Place one styrofoam cup inside another to use as your calorimeter.
- (4) Using another 50 mL graduated cylinder, place 50.0 mL of the base solution from the first combination into the styrofoam cup. Measure and record the temperature to the nearest 0.1 °C.
- (5) Pour the acid solution quickly into the base solution in the styrofoam cup, mix, measure, and record the highest temperature reached.
- (6) Pour the resulting solution down the drain. Rinse and dry the beaker and styrofoam cup. Repeat Steps 2–5 using the other combinations you have chosen.



STUDENT REPORT FORM  
Heat of Acid-Base Reactions

Use the tables below to report the results of your experiment. Write the acid-base combinations that you used in the table below:

Experiment #	Acid	Base
1		
2		
3		

Enter your raw data into the first five (5) columns of the table below, as well as into the computer.

Exp. No.	Mass Acid	Mass Base	Temp Acid	Temp Base	Final Temp	Temp Change
1						
2						
3						

Calculations: Make the following calculations from your data:

1. Assuming that the density and specific heat of each of the solutions is the same as the density and specific heat of water, calculate heat energy (in joules) released for each reaction.
2. Calculate the moles of water produced for each reaction.
3. Calculate the energy (in kilojoules) released per mole of water produced for each reaction.

Do the calculations required and complete the last column of the data table. Also complete the following table.

Exp. No.	Moles of Acid	Moles of Base	Moles of Water	Joules Released	Joules per Mole	Kilojoules per Mole
1						
2						
3						

Questions and Exercises:

1. Write the net ionic equation for each of the reactions.
2. What do all of the equations have in common?
3. Using class data, what regularities do you observe within the set of heat values obtained?
4. Propose an explanation for the differences and similarities in the size of the heat term based upon the energy involved in making and breaking chemical bonds.

INSTRUCTOR'S NOTES  
Heats of Acid-Base Reactions

is experiment is appropriate for first-year, second-year, or AP Chemistry students.

is experiment should be completed in one 50- to 55-minute laboratory period. The demonstration of conductivity should not take more than 15–20 minutes. The student measurement of the heat of reaction for the three acids and bases will take about 30 minutes. The data can then be entered into the computer database as students finish the laboratory portion of the experiment.

To distinguish between weak acids/bases and strong acids/bases, the electrical conductivity of each acid and base to be used in this experiment should be demonstrated. Have the student record the results and classify each solution as a good conductor (strong electrolyte) or as a poor conductor (weak electrolyte). As the students carry out the energy determination for this experiment, they should seek answers to questions like: Are all acid-base reactions exothermic? Do some acid-base reactions release more heat energy than others per mole of hydrogen ions that react? What regularities are observed within the set of heat values obtained? What do all the equations have in common?

Each student should select three combinations of acids and bases which he or she will use in the experiment. The student should write the net ionic equations for each reaction. (You may need to provide some suggestions for the reactions involving ammonia and acetic acid solutions.)

Averages of class data should show that the energy released per mole of water produced is similar for all reactions involving strong electrolytes, and shows some differences with the weak electrolytes since the acetate ion has a different heat of solution in water than the chloride ion. This is true because the reactions are involving the same number of moles of  $H^+$  and  $OH^-$ .

Since the students are doing only three combinations, you may want to share the class data. In order to do so, prepare a spreadsheet that has column headings in the same order as the categories in the database and add the following column headings which are needed for the calculations:

- Average initial temperature of acid and base
- Joules of energy released
- Moles of acid used
- Moles of base used
- Moles of water produced
- Joules per mole of water
- Kilojoules per mole of water

Reagent Preparation: To prepare 1.0 liter of a 2.0 M solution of:

- A) acetic acid ( $\text{CH}_3\text{COOH}$ ) add 113.8 mL of conc. acetic acid to water and dilute to one liter.
- B) hydrochloric acid ( $\text{HCl}$ ) add 171.0 mL of conc. hydrochloric acid to water and dilute to one liter.
- C) nitric acid ( $\text{HNO}_3$ ) add 128.0 mL of conc. nitric acid to water and dilute to one liter.
- D) sodium hydroxide ( $\text{NaOH}$ ) add 80.0 grams of solid sodium hydroxide to water, dissolve, and dilute to about one liter. After the solution is cool, add enough water to bring the volume to one liter.
- E) potassium hydroxide ( $\text{KOH}$ ). Divide 112.2 grams by the percent of  $\text{KOH}$  as shown in the analysis on the bottle (often 86%) and add this amount of solid potassium hydroxide to water, dissolve, and dilute to about one liter. After the solution is cool, add enough water to bring the volume to one liter.
- F) Ammonia ( $\text{NH}_3$ ) add 133.6 mL of conc. ammonium hydroxide to water and dilute to one liter.
- G) To prepare 1.0 liter of 1.0 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) add, VERY SLOWLY, 56.0 mL of conc. sulfuric acid to water and dilute to about one liter. After the solution is cool, add enough water to bring the volume to one liter.

General Notes:

- A) The stock solutions should be prepared by the teacher because of the corrosive nature of the concentrated acids and ammonia as well as the hazards of handling solid  $\text{NaOH}$  and  $\text{KOH}$ . If student help is utilized, the teacher should give adequate instruction in the preparation of these solutions.
- B) All concentrated acids are very corrosive. Avoid contact with the skin, eyes, or clothing. When you are making the dilute solutions, be certain that you wear safety goggles, a lab apron, and rubber gloves.
- C) Use adequate ventilation, preferably a laboratory fume hood, when diluting the ammonia and hydrochloric acid since the vapors are very irritating to the lungs and eyes.
- D) Since the results of each combination are to be compared with one another, it is essential to have the concentration of the solutions reasonably accurate. For the best results, titrate the acidic solutions, after thoroughly mixing, with a standard base. Adjust as necessary to obtain required concentrations.
- E) The basic solutions can be made to 2.1 M to compensate for the reaction with carbon dioxide in the air. However, if the reagents are fresh, this probably is not necessary. Be certain to note the purity of the  $\text{KOH}$  pellets you are using and compensate for this in making the solutions.
- F) All solutions should be prepared at least one day before use to allow them to come to room temperature.

## The Laws of Thermodynamics and Their Use in AP Chemistry

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There are three laws of thermodynamics, each of which is simple in its statement but can be complex in its application. These three laws govern the conversion of all forms of energy into one another, including the conversion of energy into work. The question of the amount of work that could be obtained from a given quantity of energy prompted much of the impetus for developments in this field during the early days of the Industrial Revolution. Although the efficiency of energy conversion increased greatly with advances in thermodynamics, it has been said that “thermodynamics owes much more to the steam engine than the steam engine owes to thermodynamics.”

### The First Law of Thermodynamics

This law, which is also referred to as the Law of Conservation of Energy, can be stated in several ways, three of which are:

The energy in the universe is a constant.

OR

Energy cannot be created or destroyed (in ordinary chemical processes).

OR

You can't get something for nothing.

The phrase in parentheses of the second statement was necessitated by the discovery of nuclear energy in which energy is produced from matter in accordance with the Einstein equation  $E = mc^2$ . The third expression of the law indicates that attempts to construct “perpetual motion machines” (i.e., devices that produce energy or do work without an input of at least an equal amount of energy) are doomed to failure.

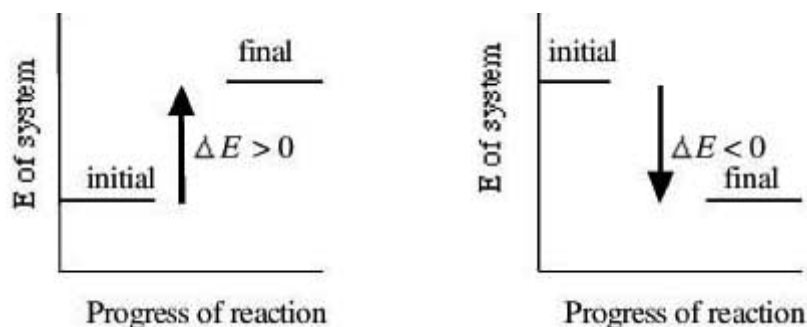
Mathematically, the First Law can be expressed:

$$E_{\text{universe}} = E_{\text{system}} + E_{\text{surroundings}} = 0$$

By definition, the system is the portion of the universe that usually interests chemists, while the surroundings represent everything else. The change in energy of a system can be found from the equation

$$\Delta E_{\text{system}} = E_{\text{products}} - E_{\text{reactants}}$$

If  $E_{\text{final}} > E_{\text{initial}}$  or  $E_{\text{products}} > E_{\text{reactants}}$ ,  $\Delta E > 0$  and energy flows into the system. On the other hand, if  $E_{\text{final}} < E_{\text{initial}}$  or  $E_{\text{products}} < E_{\text{reactants}}$ ,  $\Delta E < 0$  and the system loses energy to the surroundings. These relationships are depicted below.



Changes in the energy content of a system can be achieved either with heat, designated by  $q$ , or work,  $w$ . In equation form,

$$\Delta E = q + w$$

where  $q$  is positive if heat is *added* to a system from the surroundings and negative if heat is *lost* by a system to the surroundings. Similarly,  $w$  is positive if work is *done on* a system by the surroundings and negative if work is *done by* a system on the surroundings. This relationship indicates that a system can do only so much work from a given quantity of energy before incurring an energy deficit.

*J.R. von Mayer was the first person to state the First Law in this form. He did so after comparing the food intake, work habits, and blood of sailors in the tropics and northern Europe, from which he concluded that work was a form of energy. James Joule later demonstrated this principle experimentally.*

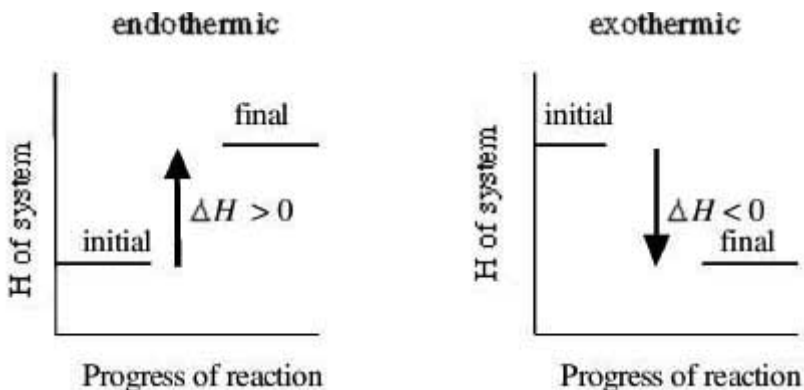
Any of the three terms,  $\Delta E$ ,  $q$ , or  $w$  can be calculated from a knowledge of the other two. Examples of such calculations include the following:

- If 35 joules of heat are added to a system that does 20 joules of work, the system would gain 15 joules of energy. ( $\Delta E = 35 \text{ J} - 20 \text{ J}$ )
- If  $\Delta E_{\text{system}} = 5 \text{ kJ}$  as it releases 10 kJ of heat, 5 kJ of work must have been done on it.  
 $5 \text{ kJ} = 10 \text{ kJ} - w$ ,  $w = 5 \text{ kJ}$

E vs H: Heat,  $q$ , can be added to (or released from) a system in two different ways, with the volume of the system kept constant or with the pressure kept constant. If a process is carried out under conditions where the volume cannot change (as in a sealed rigid container) any change in heat is denoted as  $q_v$  and the heat transfer equals the change in energy,  $\Delta E$ , because no work is done ( $w = 0$ ). (At this point, the work being considered is that due to a change in the volume of a system.) On the other hand, if a process is carried out at constant pressure, the heat transfer is designated as  $q_p$  and is referred to as the change in

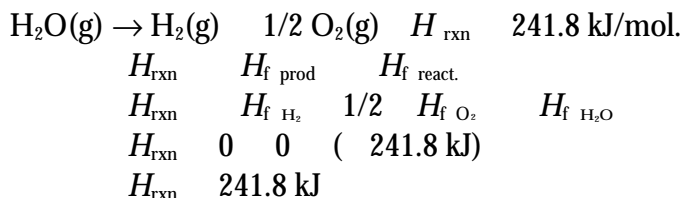
enthalpy, designated as  $H$ . us  $q_v$   $E$  and  $q_p$   $H$ . When heat is added to a system,  $q > 0$  and the process is referred to as endothermic. On the other hand, when heat is released by a system,  $q < 0$  and the process is exothermic. Often, but not always (see below), exothermic processes (those that release energy to the surroundings) occur spontaneously. That is, they proceed by themselves without an input of energy.

Although the values of  $E$  and  $H$  may differ from one another by the quantity of work done by (or on) a system they are usually very similar to one another because the work associated with chemical systems is often very small. (More will be said about this later.) Of the two quantities,  $E$  or  $H$ , chemists are generally more interested in  $H$  because most reactions are carried out in open containers (e.g., beakers and flasks) where the volume can change under a pressure of the atmosphere rather than at constant volume in sealed containers. Despite this difference both  $H$  and  $E$  are quantities that depend on the initial and final conditions, not on the pathway by which a system changes from one to the other. In analogy with the earlier relationships for  $E$ :



and 
$$\Delta H = H_{\text{final}} - H_{\text{initial}} = H_{\text{products}} - H_{\text{reactants}}$$

The  $H_f$  and  $H_{\text{rxn}}$  enthalpy changes associated with any chemical process can be found from this equation provided that a reference point is available. The defined reference point is the enthalpy of formation of any element at standard conditions,  $H_f^\circ$ , which is set equal to zero. Standard conditions, designated by the superscript '°' refer to standard tabulated values at 25 °C and 1 atmosphere of pressure. By carrying out reactions between specific elements the  $H_f$  values of various compounds can be obtained. Thus, when  $H_2(g)$  and  $O_2(g)$  react to form  $H_2O(g)$  at 25 °C, it can be demonstrated that 241.8 kJ are released for every mole of  $H_2O$  formed so  $H_f^\circ$  for  $H_2O(g)$  = -241.8 kJ/mol. It follows that the reaction



Not surprisingly, the value of  $H$  for a reaction depends on the physical state of the reactants and/or products. For example, if the reaction of  $H_2$  and  $O_2$  forms liquid  $H_2O$  rather than gaseous  $H_2O$ , 285.8 kJ of heat are released for every mol of  $H_2O(l)$  formed, i.e.,  $H_f = -285.8$  kJ/mol.

Once  $H_f$  values for compounds are known they can be used to determine the  $H$  values for other reactions or processes. For example,  $H_f$  for the vaporization of  $H_2O$ :

$$H_2O(l) \rightarrow H_2O(g)$$

is found:

$$H_{\text{vap}} = H_f(\text{prod}) - H_f(\text{react})$$

$$H_{\text{vap}} = H_f H_2O(g) - H_f H_2O(l)$$

$$H_{\text{vap}} = 241.8 \text{ kJ} - (-285.8 \text{ kJ})$$

$$H_{\text{vap}} = 44.0 \text{ kJ/mol}$$

Thus, 44.0 kJ of heat are required to convert one mole of liquid  $H_2O$  to the vapor at 25 °C. (It should be evident that an equal quantity of heat is released when one mole of the vapor condenses to form the liquid.)

Bond enthalpies: It is often possible to estimate  $H$  for a reaction by making use of bond enthalpies (BE). The enthalpy of a bond is defined as the enthalpy change required to *break* a bond into its component atoms. For example, the bond enthalpy for the H-H bond is 436 kJ/mol, while the bond enthalpy for the O=O bond is 498 kJ/mol and that for the H-O bond is 464 kJ/mol. These values can be used to find  $H$  for the reaction  $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$  as follows:

$$H_{\text{rxn}} = BE(H-H) + \frac{1}{2} BE(O=O) - 2BE(H-O)$$

$$H_{\text{rxn}} = 436 \text{ kJ} + \frac{1}{2}(498 \text{ kJ}) - 2(464)$$

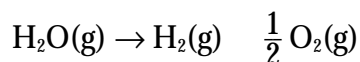
$$H_{\text{rxn}} = 436 \text{ kJ} + 249 \text{ kJ} - 928 \text{ kJ}$$

$$H_{\text{rxn}} = 685 \text{ kJ} - 928 \text{ kJ}$$

$$H_{\text{rxn}} = -243 \text{ kJ}$$

Although this value agrees very well with the enthalpy of formation ( $-241.5$  kJ), it must be noted that bond enthalpy calculations are often less accurate as molecules become more complex and there are more bonds broken and formed.

$E$  and  $H$  revisited: As was mentioned above,  $E(q_v)$  and  $H(q_p)$  values for a specific process differ from one another by the magnitude of  $w$  for the process. As an example,  $H_{\text{rxn}}$  for the decomposition of  $H_2O(g)$  was found to be 241.8 kJ/mol. From the equation



it can be seen that 1 mol of gaseous  $H_2O$  produces 1.5 mol of gaseous  $H_2$  and  $O_2$  during this reaction, producing a change in volume of 0.5 mol. From the ideal gas equation,  $PV = nRT$ ,



$(PV) = (nRT)$ . With  $R = 8.31 \text{ J/molK}$  and  $n = 0.5 \text{ mol}$  at  $25^\circ \text{C}$  (298K), the work due to the increase in volume of this system equals 1,238 J (i.e. 1.2 kJ). The work (1.2 kJ) represents about 0.5 percent of  $q$  (241.8 kJ). Because work is done by the system as it pushes back the atmosphere,  $w = -1.2 \text{ kJ}$ . On the other hand, since heat must be added,  $q = 241.8 \text{ kJ}$ . So

$$\begin{aligned} E &= q + w, \\ E &= 241.8 \text{ kJ} - 1.2 \text{ kJ} \\ E &= 240.6 \text{ kJ} \end{aligned}$$

and the value of  $E$  is smaller than that of  $H$  by the quantity of work performed by the system. On the other hand, if the work had been done on the system,  $E$  would have been larger than  $H$ .

Hints and Suggestions about the use of the First Law: The calculations above illustrate several important principles, which students often forget or ignore. Specifically,

1. The number of moles of each reactant and product in an equation must be taken into account.
2. Close attention must be paid to signs when using the equation

$$H_{\text{rxn}} = \sum H_f \text{ prod} - \sum H_f \text{ react}$$

3. The equation for bond enthalpy calculations is the opposite of that using  $H_f$  values, i.e.,

$$H_{\text{rxn}} = \sum \text{BE}_{\text{react}} - \sum \text{BE}_{\text{prod}}$$

In summary, the First Law of thermodynamics makes it possible to determine the amount of energy that is gained or lost by a system. The equations given here provide the basis for many of the calculations that students are expected to perform in chemistry courses at all levels.

Despite their importance, however, calculations based on the First Law do not allow one to determine whether a given process is spontaneous or nonspontaneous. In the discussion of  $E$  and  $H$  it was stated that exothermic processes are often, but not always, spontaneous. In fact, some exothermic processes are not spontaneous while some endothermic processes are spontaneous. These apparent contradictions can be resolved by the use of the Second Law.

## The Second Law of Thermodynamics

As with the First Law, this law can be stated in several ways.

The disorder in the universe increases during a spontaneous process.

OR

If you think things are mixed up now, just wait.

OR

You can't break even.

The first statement of this law provides a means of determining which direction a process will move, regardless of whether it is exothermic or endothermic. The third statement indicates that there is a limit on the conversion of energy from one form to another (including work). In order to understand the basis for this law and the limitations it places on energy conversions it is helpful to have a means of quantifying disorder or randomness.

This is done by introducing the concept of entropy, which is designated by the symbol  $S$ .

Standard Entropy: The concept of entropy was introduced by Ludwig Boltzmann who stated that the entropy of a particular system was proportional to the number of different ways the molecules in the system could be arranged.

Mathematically,  $S = k \ln W$ , where  $W$  represents the number of possible atomic or molecular arrangements in a given state. This relationship leads to a number of rules.

First, because the atoms or molecules in a solid are fixed in position but those in a liquid move more freely and those in a gas move virtually without limit, the entropies for the different physical states of a given substance increase in the order  $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$ .

Second, since the vibrational and translational movement of atoms and molecules is greater when heat is added,  $S$  for a substance increases with increasing temperature. Conversely,  $S$  decreases as the temperature decreases, and becomes zero for a perfect crystal at 0 K. (This is known as the Third Law of Thermodynamics and will be discussed further later in the chapter.)

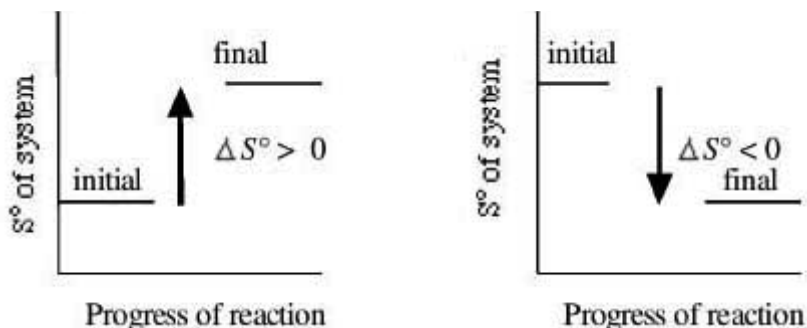
Third, due to the fact that there are more ways of arranging the atoms and/or electrons in a large molecule than those in a smaller one,  $S$  increases with molecular complexity.

The entropy value of a substance in its standard state is referred to as its absolute entropy and is designated as  $S^\circ$ . Entropy values have units of J/mol K. Some representative  $S^\circ$  values at 25 °C (in J/mol K) are:  $\text{H}_2(\text{g})$  130.6,  $\text{O}_2(\text{g})$  205.0,  $\text{Cl}_2(\text{g})$  223.0,  $\text{HCl}(\text{g})$  186.8,  $\text{H}_2\text{O}(\text{g})$  188.7, and  $\text{H}_2\text{O}(\text{l})$  69.9. These values illustrate the rules above. Specifically, the  $S^\circ$  values of  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ , and  $\text{Cl}_2(\text{g})$  increase as these diatomic molecules become larger. Similarly,  $\text{H}_2\text{O}(\text{g})$  has a higher  $S^\circ$  value than  $\text{H}_2\text{O}(\text{l})$ . In addition,  $\text{H}_2\text{O}(\text{g})$ , with three atoms, has a greater  $S^\circ$  value than  $\text{H}_2(\text{g})$ , with two atoms. Exceptions may occur, however, such as e.g.  $\text{O}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$ , both with only two atoms, but more electrons have higher  $S^\circ$  values than  $\text{H}_2\text{O}(\text{g})$ .

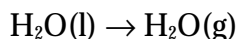
Such  $S^\circ$  values can be used to determine the value of the standard entropy change,  $\Delta S^\circ$  from the equation;

$$\Delta S^\circ = S^\circ_{\text{final}} - S^\circ_{\text{initial}}$$

where  $\Delta$  represents “the sum of.” As was seen for  $E$  and  $H$ ,  $S$  depends only on the initial and final conditions.



The entropy change,  $\Delta S$ , for the vaporization of  $\text{H}_2\text{O}$  at 25 °C:



is

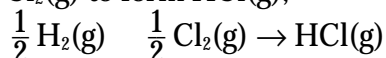
$$\begin{aligned} \Delta S_{\text{vap}} &= S_{\text{H}_2\text{O}(\text{g})} - S_{\text{H}_2\text{O}(\text{l})} \\ \Delta S_{\text{vap}} &= 188.7 \text{ J/mol K} - 69.9 \text{ J/mol K} \\ \Delta S_{\text{vap}} &= 118.8 \text{ J/K} \quad (\text{The units are J/K because the mols cancel.}) \end{aligned}$$

The positive value is consistent with the fact that the  $\text{H}_2\text{O}$  molecules have more freedom in the gas phase than in the liquid. (Although  $\Delta S$  is positive,  $\text{H}_2\text{O}$  vaporizes to only a small extent at 25 °C. That is, this process is not spontaneous at this temperature despite having a positive  $\Delta S$  value.)

$\Delta S$  values can also be found for chemical reactions, using the equation

$$\Delta S_{\text{rxn}} = S_{\text{products}} - S_{\text{reactants}}$$

For the reaction of  $\text{H}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$  to form  $\text{HCl}(\text{g})$ ,



$$\begin{aligned} \Delta S_{\text{rxn}} &= S_{\text{HCl}(\text{g})} - \left[ \frac{1}{2} S_{\text{H}_2(\text{g})} + \frac{1}{2} S_{\text{Cl}_2(\text{g})} \right] \\ \Delta S_{\text{rxn}} &= 186.8 \text{ J/mol K} - \left[ \frac{1}{2} (130.6 \text{ J/mol K}) + \frac{1}{2} (223.0 \text{ J/mol K}) \right] \\ \Delta S_{\text{rxn}} &= 186.8 \text{ J/K} - [65.3 \text{ J/K} + 111.5 \text{ J/K}] \\ \Delta S_{\text{rxn}} &= 186.8 \text{ J/K} - 176.8 \text{ J/K} \\ \Delta S_{\text{rxn}} &= 10.0 \text{ J/K} \end{aligned}$$

This small positive  $\Delta S$  value reflects the fact that there is no change in the number of moles of gas, but the product is more disordered (with one atom of H and Cl in each molecule) than the reactants ( $\text{H}-\text{H}$  and  $\text{Cl}-\text{Cl}$  molecules). This reaction occurs spontaneously and rapidly when a mixture of  $\text{H}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$  is irradiated with UV light.

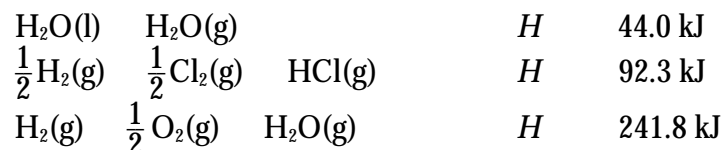
For the reaction of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  to form  $\text{H}_2\text{O}(\text{g})$ ,

$$\begin{aligned} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) &\rightarrow \text{H}_2\text{O}(\text{g}) \\ \Delta S_{\text{rxn}} &= S_{\text{H}_2\text{O}(\text{g})} - \left[ S_{\text{H}_2(\text{g})} + \frac{1}{2} S_{\text{O}_2(\text{g})} \right] \\ \Delta S_{\text{rxn}} &= 188.7 \text{ J/mol K} - \left[ 130.6 \text{ J/mol K} + \frac{1}{2} \text{mol} (205.0 \text{ J/mol K}) \right] \end{aligned}$$

$$\begin{array}{l}
 S_{\text{rxn}} \quad 188.7 \text{ J/K} \quad [130.6 \text{ J/K} \quad 102.5 \text{ J/K}] \\
 S_{\text{rxn}} \quad 188.7 \text{ J/K} \quad [233.1 \text{ J/K}] \\
 S_{\text{rxn}} \quad 44.4 \text{ J/K}
 \end{array}$$

A mixture of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  reacts explosively when initiated with a spark. Of the three examples given here, two have positive  $S$  values, but only one of these is spontaneous, and the third has a negative  $S$  but is spontaneous. Although these results may seem to contradict the statement of the Second Law, it must be remembered that the Second Law states that the disorder (or entropy) of the universe increases during a spontaneous process.

$S_{\text{system}}$  vs  $S_{\text{universe}}$ : In order to determine the entropy change of the universe, the enthalpy changes for these three cases must be taken into account. These are



For these three cases,

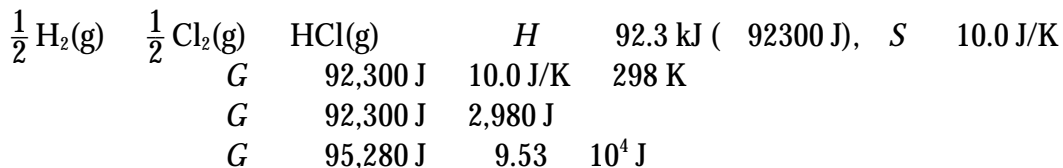
- The vaporization of  $\text{H}_2\text{O}$  is endothermic while the formation of  $\text{HCl}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are both exothermic. The heat gained by the  $\text{H}_2\text{O}(\text{l})$  must come from the surroundings. When heat is lost by the surroundings the disorder or entropy of the surroundings decreases. Apparently the negative  $S$  of the surroundings outweighs the positive  $S$  of the system, and the result is a net negative  $S$  for the universe, so this process is not spontaneous.
- The formation of  $\text{HCl}(\text{g})$  has a negative  $H$ , so heat is released to the surroundings from the system, which causes the entropy of the surroundings to increase. Thus, for this reaction,  $S$  is positive for both the system *and* the surroundings, so the  $S$  of the universe must be positive and the reaction is spontaneous.
- The formation of  $\text{H}_2\text{O}(\text{g})$  from its elements has a negative  $H$  and, as with the  $\text{HCl}$  reaction, the entropy of the surroundings increases. This positive  $S$  for the surroundings exceeds the negative  $S$  of the system and the reaction is spontaneous.

In view of the complications of using the entropy change of the surroundings to make decisions about the spontaneity of a reaction, it would be helpful if there were an alternate means of deciding on the spontaneity of a system. The quantity that can be used for this purpose is called the free energy change, denoted as  $G$ .

$G$  and spontaneity: The concept of free energy was developed by Josiah Willard Gibbs and is sometimes referred to as the Gibbs Free Energy. The equation that bears his name relates  $G$ ,  $H$  and  $S$ :

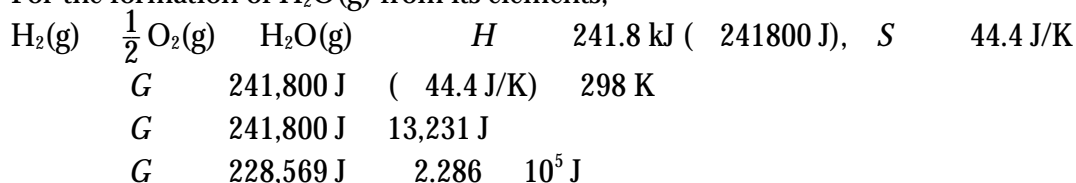
$$G = H - T S$$

The value of  $G$  can be calculated from those of  $H$  and  $S$ . (At standard conditions the equation becomes  $G = H - TS$ .) Reactions are spontaneous when  $G < 0$ , nonspontaneous when  $G > 0$ , and at equilibrium when  $G = 0$ . This will be illustrated with the three examples introduced above.



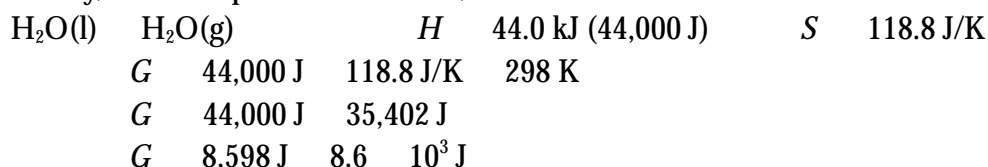
The negative value of  $G$  indicates that this reaction is spontaneous under standard conditions, in agreement with the conclusion based on the entropy change for the universe discussed above.

For the formation of  $\text{H}_2\text{O}(\text{g})$  from its elements,

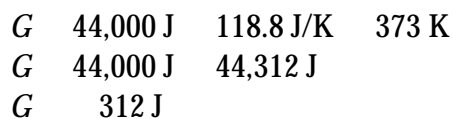


Again, a negative value for  $G$  corresponds to a spontaneous reaction. The negative  $S$  value is not large enough to overcome the highly negative  $H$  value.

Finally, for the vaporization of  $\text{H}_2\text{O}$ ,



The positive  $G$  shows that this process is nonspontaneous (i.e., occurs to a small extent) at this temperature. However, it is apparent that sign of  $G$  might change if the temperature is increased. For example, at  $100^\circ\text{C}$  (373 K), which does not represent standard conditions, is



Thus, as the temperature is raised from  $25^\circ\text{C}$  to  $100^\circ\text{C}$  the vaporization of  $\text{H}_2\text{O}$  becomes spontaneous.

Obviously, this equation can also be used to calculate any of the four parameters in it, provided the other three are known. For example, several  $G$  or  $G^\circ$  values have been determined from  $H$  and  $S$  values at various temperatures. Alternatively, the temperature at which a system is at equilibrium can be found from a knowledge of  $H$  and  $S$  (assuming a value of  $G = 0$  at equilibrium).

Qualitatively, one can make certain predictions about the spontaneity of a process simply by considering the signs of  $H$  and  $S$ . Specifically,

- If  $H$  is  $< 0$  and  $S$  is  $> 0$ , the process is spontaneous at all temperatures.
- If  $H$  is  $> 0$  and  $S$  is  $< 0$ , the process is nonspontaneous at all temperatures.
- If both  $H$  and  $S < 0$ , the process is spontaneous at low temperatures (where  $T$  is small) but nonspontaneous when  $T$  is large, because the  $T S$  term becomes positive.
- If both  $H$  and  $S > 0$ , the process is nonspontaneous at low temperatures (where  $T$  is small) but spontaneous when  $T$  is large, because the  $T S$  term becomes negative.

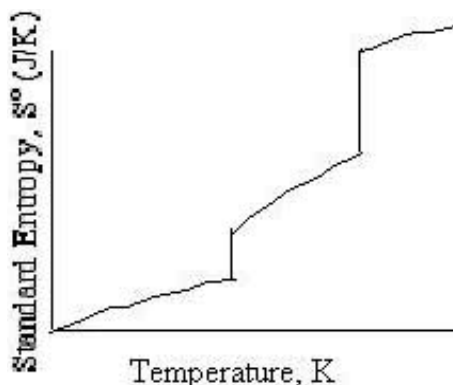
Hints and Suggestions for using the Second Law: Successful application of the Second Law requires attention to the following points.

- It is essential to include the moles of reactants and products in  $S$  calculations (as was the case for the use of the First Law).
- When  $H$  and  $S$  values are used to calculate  $G$  values (to determine spontaneity),
  - temperatures must be expressed in K
  - units must be consistent (J vs kJ)

### The Third Law of Thermodynamics

Of the three laws of thermodynamics, the third is probably the simplest. As was mentioned previously, the third Law states, "A perfect crystalline solid at 0 K has an entropy of zero."

This law does not lend itself to calculations, as the other two laws do but it does make it possible to establish the  $S$  values of substances at different temperatures and in different physical states. A typical graph of  $S$  versus temperature is shown below.



As has been demonstrated above, the laws of thermodynamics can be used to determine the changes in energy or work that accompany chemical transformations and to establish whether a particular transformation is spontaneous or nonspontaneous.

## Contributors' Professional Biographies

**Marian DeWane** teaches AP Chemistry at Centennial High School in Boise, Idaho. She has a long list of accomplishments including Teacher of the Year, National Board Certification in Chemistry, and Presidential Scholar Teacher. She is currently a Question Leader for the AP Examination and has also served as a Reader and Table Leader. She also serves on the ACS Exams Institute Advanced High School Committee, National Chemistry Olympiad Task Force, and as a National Leader for the College Board.

**Lew Acampora** currently teaches AP Chemistry at the St. Francis School in Louisville, Kentucky. For the last 16 years he has taught AP Chemistry at independent schools across the country. Since 1995, he has served as a Reader, Table Leader, and Question Leader at the Reading for the AP Chemistry Examination. He continues to serve as a consultant for the College Board and serves on the ACS Exams Institute Advanced High School Committee.

**William “Bill” Bond** has been a high school chemistry and AP Chemistry teacher at Snohomish High School in Washington for the past 27 years, where he serves as science department chair. Bill has been responsible for writing questions for the AP Chemistry Exam as a member of the Test Development Committee, has been an exam Reader for ten years, and is the principal author of the *Teacher's Guide for AP Chemistry* (2000). He also serves as a National Leader for the College Board.

**Valerie Ferguson** teaches AP Chemistry at Moore High School in Moore, Oklahoma. She has served as a Reader and Table Leader for the AP Chemistry Examination. She also works as a consultant for the College Board and teaches Summer Institutes for AP Chemistry teachers. She has served as chair of the Oklahoma ACS, president of the Oklahoma Science Teachers Organization and was co-organizer of the “Teaching AP Chemistry” symposium at the 14th Biennial Conference of Chemistry Education.

**Linda Ann Kruegel** has been a teacher at Princeton High School in Princeton, New Jersey, for 26 years. She has taught AP Chemistry for more than 20 years. She has worked for ETS and the College Board in many capacities, including being a Reader for the AP Examination, writing exam questions, and working as a consultant teaching workshops and Institutes. She also serves on the ACS Exams Institute Advanced High School Exam Committee.

**Adele Mouakad** is an award-winning teacher at St. John's School in San Juan, Puerto Rico. She has been teaching AP Chemistry since 1983. She has won the Presidential Award for Excellence in Science Teaching, has served as the president of the association, was a member of the Woodrow Wilson Foundation Teacher Outreach Program, and was a Dreyfus Master Teacher. She has been Reader for the AP Chemistry Examination and has been a member of the National Chemistry Olympiad Task Force.

**Cheri Smith** is an award-winning teacher of AP Chemistry at Yale Secondary School in Abbotsford, British Columbia, Canada. She has been an AP Reader and Table Leader for the AP Chemistry Examination. She has served as a consultant for the College Board conducting AP workshops worldwide. Cheri has contributed to numerous publications and served as a reviewer for the *AP Vertical Teams® Guide for Science* and the PreAP® Topics for Vertical Teams in Science workshop.

**Arden Zipp** is a distinguished faculty member at State University of New York College at Cortland in Cortland, New York. He has served in every capacity for the College Board in the development and scoring of the AP Examination: he has been a Reader, Table Leader, Question Leader, Chief Reader, and Test Development Committee member. He is also involved in the development and scoring of the IB Chemistry Program, and is chair of the National Chemistry Olympiad Examination Task Force.