

# 11

## BIG IDEA 5: THERMOCHEMISTRY AND THERMODYNAMICS

### Big Idea 5

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

Thermochemistry describes the heat flow of a chemical reaction or physical change. Changes in enthalpy are calculated through calorimetry, Hess's law, and standard heats of formation. Determining the value of Gibbs free energy for a process allows one to predict whether or not a process is thermodynamically favored (spontaneous). The dependence of Gibbs free energy on temperature, entropy, and enthalpy will be identified. The laws of thermodynamics will be explored.

The free-response portion of the exam may include calculations and predictions involving entropy, enthalpy, and free energy. You may be asked to interpret energy diagrams, or answer lab questions regarding the use of a calorimeter to determine the heat of a reaction.

You should be able to

- Perform stoichiometric calculations with the enthalpy of the reaction.
- Perform calculations with specific heat.

- Discuss how a calorimeter is used and perform related calculations.
- Draw, label, and perform associated calculations for heating curves involving specific heat and changes in enthalpy for phase changes.
- Draw and label potential energy diagrams for chemical reactions.
- Use Hess's Law, standard heats of formation,  $\Delta H^\circ_f$ , and the bond energy method to determine the heat of a reaction, and identify a process as exothermic or endothermic.
- Write reactions representing standard heats of formation,  $\Delta H^\circ_f$ .
- Compare the absolute entropies,  $S^\circ$ , of elements and compounds.
- Perform calculations with entropy  $S^\circ$  and  $\Delta S^\circ$ .
- Perform calculations with free energy,  $\Delta G^\circ_f$ .

### AP Tips

Mathematical equations will be provided for the exam, but it would be good to be familiar with them or even better to memorize them.

## TEMPERATURE VS. HEAT

(Chemistry 8th ed. pages 210, 236–237/9th ed. pages 220, 246–247)

*Temperature* is a measure of the average kinetic energy of atoms or molecules. *Heat* is the amount of energy transferred from one system to another and always flows from a hot body to a cold one.

## FIRST LAW OF THERMODYNAMICS

(Chemistry 8th ed. pages 238–239/9th ed. pages 248–249)

The first law of thermodynamics states that energy can be converted from one form to another, but can neither be created nor destroyed: The energy of the universe is constant.

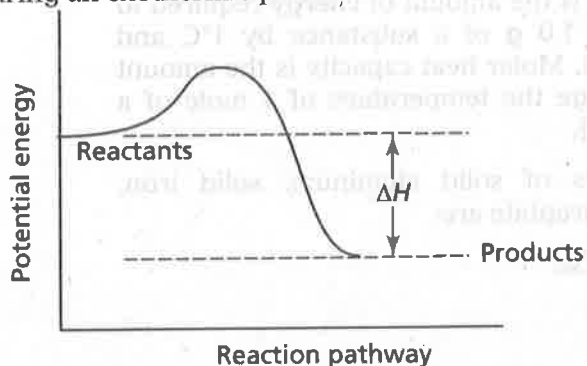
## ENTHALPY

(Chemistry 8th ed. pages 243–244/9th ed. pages 252–253)

At constant pressure, the change in enthalpy ( $\Delta H^\circ$ ) of a system is equal to the energy flow as heat. Enthalpy is a state function, so the change in  $H$  is independent of the pathway.

**EXOTHERMIC**

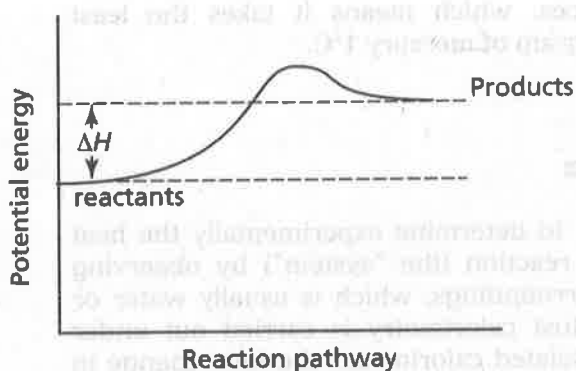
A reaction that is exothermic gives off heat and the change in enthalpy is negative ( $\Delta H^\circ < 0$ ). The temperature of the surroundings increases during an exothermic process.



**Exothermic:** Products are lower energy than reactants.

**ENDOTHERMIC**

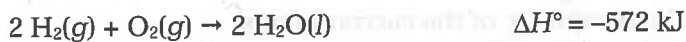
A reaction that is endothermic absorbs heat and the change in enthalpy is positive ( $\Delta H^\circ > 0$ ). The temperature of the surroundings decreases in an endothermic process.



**Endothermic:** Products are higher energy than reactants.

**EXAMPLE:** How much heat is released when 4.04 g of hydrogen is reacted with excess oxygen?

**SOLUTION:**



$$4.04 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.02 \text{ g}} \times \frac{-572 \text{ kJ}}{2 \text{ mol H}_2} = -572 \text{ kJ}$$

Note that conversion factors can be written using the relationship between the enthalpy,  $\Delta H^\circ$ , and the moles of reactants and products. 572 kJ of heat is produced when 1 mole of  $\text{O}_2$  reacts with 2 moles of  $\text{H}_2$  to produce 2 mol of  $\text{H}_2\text{O}$ .

## SPECIFIC HEAT

(Chemistry 8th ed. pages 245–246/9th ed. pages 254–255)

The specific heat capacity,  $s$ , is the amount of energy required to change the temperature of 1.0 g of a substance by 1°C and typically has units of J/(g °C). Molar heat capacity is the amount of energy required to change the temperature of 1 mole of a substance by 1°C [J/(mol °C)].

**EXAMPLE:** The specific heats of solid aluminum, solid iron, mercury liquid, and carbon graphite are:

	J/(g °C)
Al(s)	0.89
Fe(s)	0.45
Hg(l)	0.14
C(s)	0.71

When the same amount of heat energy is applied to 1.0 g of each of these substances, which one will reach the highest temperature?

The answer is Hg(l). Mercury has the lowest specific heat of the four mentioned substances, which means it takes the least amount of heat to raise 1 gram of mercury 1°C.

## CALORIMETRY

(Chemistry 8th ed. pages 244–249/9th ed. pages 253–258)

A calorimeter is a device used to determine experimentally the heat energy change of a chemical reaction (the “system”) by observing temperature changes in the surroundings, which is usually water or another high-boiling liquid. Most calorimetry is carried out under constant pressure. In a well-insulated calorimeter, the heat change in the surroundings,  $q$ , is equal and opposite to the heat released or absorbed by the reaction,  $\Delta H$ :

$$\Delta H = -q = m \times s \times \Delta T$$

Where:

- $m$  = mass of surroundings
- $s$  = the specific heat capacity of the surroundings
- $\Delta T$  = the temperature change in the surroundings during the reaction.

**EXAMPLE:** A 1.00-g sample of magnesium metal is added to a calorimeter containing 100. g of hydrochloric acid (specific heat capacity 4.184 J/(g°C) initially at 25.0°C. The solution temperature increases to 29.5°C. What is the heat of reaction, in kJ/mol?

SOLUTION: The heat gained by the solution is equal to:

$$100. \text{ g HCl} \times \frac{4.184 \text{ J}}{\text{g}^\circ\text{C}} \times (29.5^\circ\text{C} - 25.0^\circ\text{C}) = 1882 \text{ J} = 1.9 \text{ kJ}$$

Since the solution's temperature increased, the reaction must be exothermic. The amount of heat released by the reaction is equal and opposite to the heat gained by the solution:

$$-(\text{heat gained by solution}) = (\text{heat of reaction}) = -1.9 \text{ kJ}$$

This is the heat of reaction per gram of Mg reacted. The heat of reaction per mole of Mg reacted is:

$$\frac{-1.9 \text{ kJ}}{1 \text{ g}} \times \frac{24.31 \text{ g}}{1 \text{ mol}} = -46 \text{ kJ/mol}$$

### AP Tip

Students sometimes have trouble deciding what numbers to use when calculating  $\Delta H$  from calorimetry data. Remember that the thermometer is in the surroundings, so the "mass" should be the mass of water or other heat-transfer fluid. The masses of reactants and products are part of the system and should not be included in this mass. By convention, the change in temperature,  $\Delta T$ , is calculated  $T_{\text{final}} - T_{\text{initial}}$ . According to the first law of thermodynamics, the heat lost by one substance equals the heat gained by the other substance, so  $\Delta H$  will be equal in magnitude but opposite in sign to  $q$ .

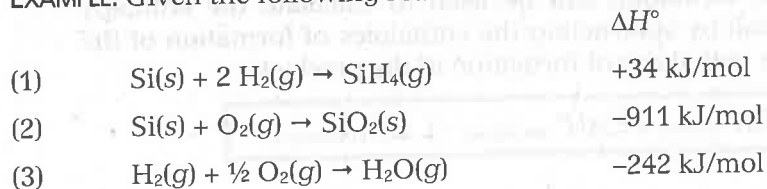
## HESS'S LAW

(Chemistry 8th ed. pages 249–255/9th ed. pages 258–264)

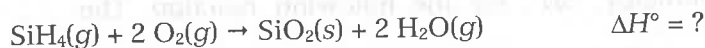
Hess's law states that enthalpy change, in going from a particular set of reactants to a particular set of products, is the same whether the reaction takes place in one step or in a series of elementary steps. Enthalpy is a state function. The idea is to manipulate the equations given in the problem statement so that they add up to the overall reaction. There are two ways that the equations can be manipulated.

1. Reverse the reaction. The sign of  $\Delta H$  is also reversed.
2. Multiply the coefficients in a balanced reaction by an integer. The value of  $\Delta H$  is multiplied by the same integer.

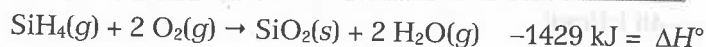
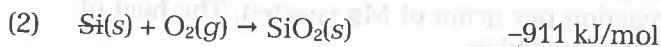
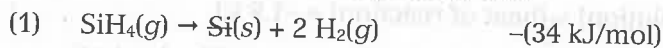
EXAMPLE: Given the following reactions and  $\Delta H^\circ$  values,



Calculate  $\Delta H$  for



**SOLUTION:** Start by finding a substance that appears only once in all of the reactions,  $\text{SiH}_4$  or  $\text{H}_2\text{O}$ . Look to see where that substance is in the final reaction and in what amount. Modify the reaction so that the substance appears where it should be and in the correct amount.  $\text{SiH}_4$  needs to be in the reactants, so Reaction 1 is reversed. Reaction 2 is not changed.  $\text{H}_2\text{O}$  is in the products, but there are two of them in the final reaction, so Reaction 3 needs to be multiplied by two.



## STANDARD ENTHALPIES OF FORMATION, $\Delta H^\circ_f$

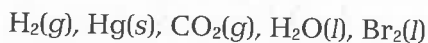
(Chemistry 8th ed. pages 255–261/9th ed. pages 264–271)

The standard enthalpy of formation of a compound is the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.

The degree symbol on  $\Delta H^\circ$  indicates that the process occurred under standard conditions of  $25^\circ\text{C}$ , 1 atm, and 1 M solutions.

By definition, the standard heat of formation for elements in their standard states equals zero.

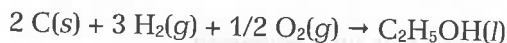
**EXAMPLE:** Which of the following will have standard heats of formation equal to zero?



**SOLUTION:** The only elements present in their standard states are  $\text{H}_2(g)$  and  $\text{Br}_2(l)$ . Mercury is a liquid under standard conditions. Carbon dioxide and water are compounds.

**EXAMPLE:** Write the balanced molecular equation representing the  $\Delta H^\circ_f$ , standard heat of formation reaction of ethanol,  $\text{C}_2\text{H}_5\text{OH}(l)$ .

**SOLUTION:**



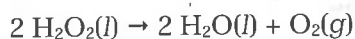
Note that 1 mole of product is produced according to the definition of the standard heat of formation. All of the reactants are elements in their standard states.

Standard heats of formation can be used to calculate the enthalpy change of a reaction by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products.

$$\Delta H^\circ_{\text{reaction}} = \sum \Delta H^\circ_{\text{f}}(\text{products}) - \sum \Delta H^\circ_{\text{f}}(\text{reactants})$$

**EXAMPLE:** Using the standard heats of formation,  $\Delta H^\circ_f$ , calculate the change in enthalpy,  $\Delta H^\circ$ , for the following reaction. The

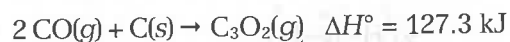
standard heats of formation for hydrogen peroxide and water are  $-187 \text{ kJ/mol}$  and  $-285 \text{ kJ/mol}$ , respectively.



SOLUTION:

$$\Delta H^\circ_{\text{reaction}} = [2(-285 \text{ kJ}) + 0] - 2(-187 \text{ kJ}) = -196 \text{ kJ}$$

EXAMPLE: Given the information below, calculate the heat of formation of gaseous carbon monoxide.



$\Delta H^\circ_f$  for  $\text{C}_3\text{O}_2(g)$  is  $-93.7 \text{ kJ/mol}$ .

SOLUTION:

$$\Delta H^\circ_{\text{reaction}} = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$$

$$\Delta H^\circ_{\text{reaction}} = \Delta H^\circ_f \text{ for } \text{C}_3\text{O}_2(g) - [2 \Delta H^\circ_f \text{ for } \text{CO}(g) - \Delta H^\circ_f \text{ for } \text{C}(s)]$$

Rearrange the equation and solve for missing variable; note  $\Delta H^\circ_f$  for  $\text{C}(s)$  is zero.

$$\begin{aligned} \Delta H^\circ_f \text{ for } \text{CO}(g) &= [\Delta H^\circ_f \text{ for } \text{C}_3\text{O}_2(g) - \Delta H^\circ_{\text{reaction}}]/2 \\ &= (-93.7 \text{ kJ} - 127.3 \text{ kJ})/2 = -110.5 \text{ kJ/mol} \end{aligned}$$

## BOND ENERGIES AND ENTHALPY

### THE ENERGETICS OF BOND FORMATION

(*Chemistry* 8th ed. pages 341–342/9th ed. pages 352–353)

A chemical bond forms when a system of bonded atoms is lower in potential energy than that of independent atoms. The optimum distance between atoms is the bond length, which represents this lowest energy state. The bond length is a balance between the attractive electrostatic forces between the nucleus of one atom and the electrons of another, and the repulsive forces between the positively charged nuclei of the two atoms and negatively charged electrons of the two atoms. You should be able to explain the main features of the potential energy diagram, Figure 8.1, on page 342 of the 8th edition and page 354 of the 9th edition of *Chemistry*.

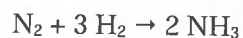
Breaking bonds requires an input of energy to overcome the attractive forces. When new bonds are formed, energy is released. The difference between input and output determines whether a process is endothermic or exothermic.

### CALCULATING ENTHALPY FROM BOND ENERGIES

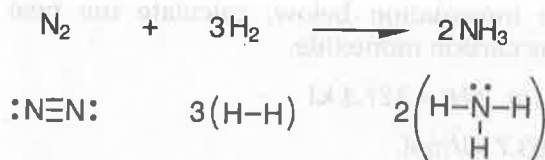
(*Chemistry* 8th ed. pages 361–364/9th ed. pages 373–376)

To use this method, draw Lewis structures of the reactants and products.

**EXAMPLE:** Estimate the change in enthalpy,  $\Delta H$ , for the following reaction using the table of bond energies on page 362 of the 8th edition and page 374 of the 9th edition of *Chemistry*.



**SOLUTION:** First, draw the Lewis structures for the reactants and products.



In the reactants, one triple bond between the atoms of nitrogen and one single bond between atoms of hydrogen are broken. Bond breaking is an endothermic process that has a positive value for enthalpy. Energy must be added to break the bonds.

Three single bonds between hydrogen and nitrogen are formed in the products. Bond formation is exothermic having a negative value for enthalpy.

$\Delta H = \Sigma$  energy to break bonds  $- \Sigma$  energy released when new bonds are formed.

Reactant Bonds Broken:

$$\begin{array}{l} \text{N}_2: 1 \text{ mol N}\equiv\text{N} \\ \text{H}_2: 3 \text{ mol H}-\text{H} \end{array} \qquad \begin{array}{l} 1 \text{ mol} \times 941 \text{ kJ/mol} = 941 \text{ kJ} \\ 3 \text{ mol} \times 432 \text{ kJ/mol} = 1296 \text{ kJ} \\ \text{Total energy required} = 2237 \text{ kJ} \end{array}$$

Product Bonds Formed:

$$\text{NH}_3: 2 \times (3 \text{ mol N}-\text{H}) \qquad 6 \text{ mol} \times 391 \text{ kJ/mol} = 2346 \text{ kJ}$$

$$\Delta H = 2237 \text{ kJ} - 2346 \text{ kJ} = -109 \text{ kJ}$$

## INTERMOLECULAR FORCES

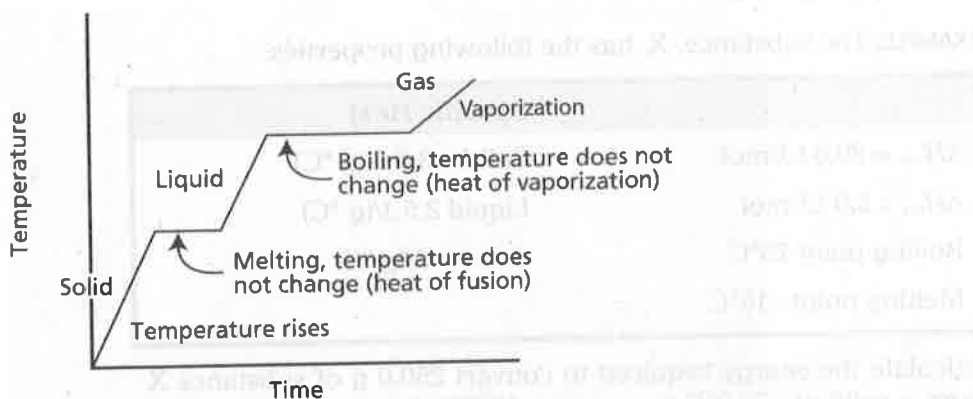
(*Chemistry* 8th ed. pages 440–443/9th ed. pages 455–458)

Intermolecular forces are attractions between molecules that arise when molecules are near each other. Breaking these forces requires the input of energy, as illustrated with the heating curve below. One way to determine the relative strengths of intermolecular forces is to measure how much energy is required to cause a phase change. However, the bonds between the atoms within a molecule (*intramolecular forces*) are not broken, so the molecules themselves remain intact. Intermolecular forces are discussed in more detail in Chapter 3, Big Idea 2.



## HEATING CURVES

(Chemistry 8th ed. pages 475–476/9th ed. pages 487–488)



When a system is heated, energy is transferred into it. In response to the energy it receives, the system changes, for example, by increasing its temperature. A plot of the temperature versus time is called **the heating curve**. One such heating curve is shown above. The physical states of the substance and the phase transitions are identified along the curve.

The temperature of the system usually increases when energy is applied. However, when the energy absorbed is used for phase transition, a change in the physical state, the temperature (average kinetic energy) remains constant because the potential energy of the system is being increased as the molecules are rearranged in the phase change. Phase changes only affect the intermolecular forces of attraction; no intramolecular bonds are broken.

## HEAT OF FUSION

(Chemistry 8th ed. page 476/9th ed. page 488)

The heat of fusion,  $\Delta H_{\text{fus}}$  is the enthalpy change that occurs in melting a solid at its melting point.

**EXAMPLE:** What quantity of heat is required to melt 1.00 kg of ice at its melting point? For ice,  $\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}$

**SOLUTION:**

$$1.00 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol}}{18.0 \text{ g}} \times \frac{6.0 \text{ kJ}}{1 \text{ mol}} = 333 \text{ kJ}$$

## HEAT OF VAPORIZATION

(Chemistry 8th ed. pages 470–471/9th ed. pages 482–483)

The heat of vaporization,  $\Delta H_{\text{vap}}$ , is the energy required to vaporize one mole of a liquid at a pressure of one atmosphere.

**EXAMPLE:** What quantity of heat is required to vaporize 130. g of water? For liquid, water,  $\Delta H_{\text{vap}} = 43.9 \text{ kJ/mol}$ .

SOLUTION:

$$130. \text{ g} \times \frac{1 \text{ mol}}{18.0 \text{ g}} \times \frac{43.9 \text{ kJ}}{1 \text{ mol}} = 317 \text{ kJ}$$

EXAMPLE: The substance, X, has the following properties:

Specific Heat	
$\Delta H_{\text{vap}} = 20.0 \text{ kJ/mol}$	Solid = $3.0 \text{ J/(g } ^\circ\text{C)}$
$\Delta H_{\text{fus}} = 5.0 \text{ kJ/mol}$	Liquid = $2.5 \text{ J/(g } ^\circ\text{C)}$
Boiling point $75^\circ\text{C}$	Gas = $1.0 \text{ J/(g } ^\circ\text{C)}$
Melting point $-15^\circ\text{C}$	

Calculate the energy required to convert 250.0 g of substance X from a solid at  $-50.0^\circ\text{C}$  to a gas at  $100^\circ\text{C}$ . Assume that X has a molar mass of  $75.00 \text{ g/mol}$ .

SOLUTION:

There are 5 steps involved.

1. Heating the solid from  $-50.0^\circ\text{C}$  to  $-15^\circ\text{C}$ .
2. Melting the solid at  $-15^\circ\text{C}$ .
3. Heating the liquid to its boiling point from  $-15^\circ\text{C}$  to  $75^\circ\text{C}$ .
4. Boiling the liquid at  $75^\circ\text{C}$ .
5. Heating the gas to  $100^\circ\text{C}$ .

The energy used = sum of energies from individual steps.

There are 3.333 mol of X in 250.0 g of X.

$$\text{Step 1: } q = m \times s \times \Delta T; 250.0 \text{ g} \times [3.0 \text{ J/(g } ^\circ\text{C)}] \times 35^\circ\text{C} = 26 \text{ kJ}$$

$$\text{Step 2: } \text{mol} \times \Delta H_{\text{fus}} = 3.333 \text{ mol} \times 5.0 \text{ kJ/mol} = 17 \text{ kJ}$$

$$\text{Step 3: } q = m \times s \times \Delta T; 250.0 \text{ g} \times [2.5 \text{ J/(g } ^\circ\text{C)}] \times 90^\circ\text{C} = 56 \text{ kJ}$$

$$\text{Step 4: } \text{mol} \times \Delta H_{\text{vap}} = 3.333 \text{ mol} \times 20. \text{ kJ/mol} = 67 \text{ kJ}$$

$$\text{Step 5: } q = m \times s \times \Delta T; 250.0 \text{ g} \times [1.0 \text{ J/(g } ^\circ\text{C)}] \times 25^\circ\text{C} = 6.2 \text{ kJ}$$

The total energy required is the sum of the energies of the individual steps:  $(26 + 17 + 56 + 67 + 6.2) \text{ kJ} = 172 \text{ kJ}$

## ENTROPY

(Chemistry 8th ed. pages 776–779/9th ed. pages 791–794)

Entropy,  $S$ , is the driving force for a thermodynamically favored process: a spontaneous process readily occurring without intervention. Entropy measures the number of arrangements or positions available to a system in a given state. This positional entropy increases in going from a solid to liquid to gas. In the solid state, molecules are much closer together than in the gaseous state, with very few positions available for them.

Entropy during a process is said to be increasing when the value of  $\Delta S > 0$ ; The value of  $\Delta S$  is positive.

Entropy during a process is said to be decreasing when the value of  $\Delta S < 0$ ; The value of  $\Delta S$  is negative.

**EXAMPLE:** Which of the following pairs is likely to have the higher positional entropy per mole at a given temperature?

- 1) Solid  $\text{CO}_2$  or gaseous  $\text{CO}_2$ ?
- 2)  $\text{N}_2$  gas at 1.0 atm and  $\text{N}_2$  gas at 0.001 atm?

**SOLUTION:**

- 1) Gaseous  $\text{CO}_2$  has more positional entropy than solid  $\text{CO}_2$  since there are more positions for the molecules in the gaseous state to move to than in the solid state.
- 2)  $\text{N}_2$  gas at 0.001 atm has more positional entropy than  $\text{N}_2$  gas at 1.0 atm, because at a lower pressure, there is more volume for the molecules to move than at a higher pressure.

**EXAMPLE:** Describe the change in entropy when solid salt is added to water.

**SOLUTION:** The entropy increases when salt in its solid state is dissolved in water. The ions fixed in a crystal lattice in the solid are free to move about in the water due to solute-solvent interactions.

## SECOND LAW OF THERMODYNAMICS

(Chemistry 8th ed. page 779/9th ed. page 794)

The second law of thermodynamics states that in any spontaneous process there is always an increase in the entropy of the universe. The change in entropy of the universe is equal to the change in the entropy of the system and the change in entropy of the surroundings.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{surr}} = -\Delta H/T$$

The sign of  $\Delta S_{\text{surr}}$  depends on the direction of the heat flow.  $\Delta S_{\text{surr}}$  is positive at constant temperature when the reaction is exothermic, since heat flows to the surroundings increasing the random motions and the entropy of the surroundings. The opposite is true for an endothermic reaction at constant pressure.

The magnitude of  $\Delta S_{\text{surr}}$  depends on temperature. At a low temperature, the production of heat effects a much greater percent change in the randomness of the surroundings than it does at high temperature.

## ENTROPY CHANGES IN A CHEMICAL REACTION

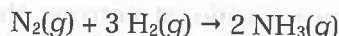
(Chemistry 8th ed. pages 786–790/9th ed. pages 801–805)

The change in entropy,  $\Delta S$ , for a chemical reaction can be predicted without calculation.

For a chemical reaction involving only gaseous reactants and products, entropy is related to the total number of moles of gas on either side of the equation. If the moles of gas increase from reactants to products in a chemical reaction, the entropy is increasing. If the moles of gas decrease in a chemical reaction, the entropy is decreasing.

For a chemical reaction involving solid, liquids, and gases, the production of a gas will, in general, increase the entropy of the reaction much more than an increase in the number of moles of liquids or solids.

**EXAMPLE:** Predict the sign of  $\Delta S^\circ$  for the following reaction:

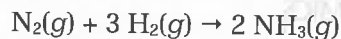


**SOLUTION:** The entropy decreases as the reaction proceeds from reactants to products because the number of moles of gas decreases from four total moles to two moles. The sign of  $\Delta S^\circ$  is negative.

The change in entropy for a reaction,  $\Delta S^\circ$ , can also be calculated using tabulated thermodynamic values in the appendix of the textbook or other reference book. These values would be provided to you in the exam.

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{(products)}} - \sum S^\circ_{\text{(reactants)}}$$

**EXAMPLE:** Calculate  $\Delta S^\circ$  for the following reaction:



**SOLUTION:**  $\Delta S^\circ = 2(193) - [1(192) + 3(131)] = -199 \text{ J/K}$

The sign of  $\Delta S^\circ$  is negative, confirming the prediction in the previous example.

## FREE ENERGY

(Chemistry 8th ed. pages 790–797/9th ed. pages 805–812)

Free energy,  $G$ , is a thermodynamic function whose value describes whether or not a process is spontaneous in the forward direction (reactions are usually written such that the forward direction is spontaneous). Gibbs free energy is dependent on the change in enthalpy, change in entropy, and temperature of the system.  $\Delta G$  is negative for all spontaneous processes. Note, however, that  $\Delta G$  provides no information about the rate of reaction. Spontaneous reactions can be very slow; rusting of iron is one example of a slow spontaneous reaction.

$$\Delta G = \Delta H - T \Delta S; T \text{ is the Kelvin temperature}$$

Using the chart below, you can predict if a reaction will occur without the exact value for  $\Delta H$  and  $\Delta S$ .

**The Dependence of Spontaneity on Temperature**

$\Delta S$	$\Delta H$	$\Delta G$
+	-	Spontaneous at all temperatures
+	+	Spontaneous at high temperatures
-	-	Spontaneous at low temperatures
-	+	Process not spontaneous at any temperature

**FREE ENERGY AND CHEMICAL REACTIONS***(Chemistry 8th ed. pages 790–794/9th ed. pages 805–810)*

The standard free energy change,  $\Delta G^\circ$ , is the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states. This value cannot be measured directly, but it can be calculated from other measured quantities such as the equilibrium constant and the standard cell potential.

The standard free energy change,  $\Delta G$ , can be calculated from the changes in enthalpy and entropy.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Note that the units of  $\Delta G^\circ$  and  $\Delta H^\circ$  are typically provided in kJ/mol, while  $\Delta S^\circ$  is provided in J/(K mol). Make sure your units are consistent before proceeding with calculations!

**EXAMPLE:** Consider the reaction  $2 \text{POCl}_3(g) \rightarrow 2 \text{PCl}_3(g) + \text{O}_2(g)$ .

The value of  $\Delta S^\circ$  is 179 J/K. The value of  $\Delta H^\circ$  is 542 kJ. At what temperature is this reaction spontaneous? Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not depend on temperature.

**SOLUTION:** The temperature at which  $\Delta G^\circ = 0$  is where the process shifts from spontaneous to nonspontaneous. Set  $\Delta G^\circ = 0$  and rearrange  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$  to solve for  $T$ .

$$T = \Delta H^\circ / \Delta S^\circ$$

$$3030 \text{ K} = 542 \text{ kJ} / (0.179 \text{ kJ/K})$$

The standard free energy change,  $\Delta G$ , is a state function and can be calculated by

$$\Delta G^\circ_{\text{reaction}} = \sum \Delta G^\circ_{\text{f}(\text{products})} - \sum \Delta G^\circ_{\text{f}(\text{reactants})}$$

**FREE ENERGY AND EQUILIBRIUM***(Chemistry 8th ed. pages 798–802/9th ed. pages 813–817)*

$$\Delta G^\circ = -RT \ln K; K = \text{equilibrium constant}$$

This is discussed in Chapter 12 (Big Idea 6) of this book.

## FREE ENERGY AND CELL POTENTIAL

(Chemistry 8th ed. pages 800–803/9th ed. pages 815–818)

$$\Delta G^\circ = -nFE^\circ; E^\circ \text{ is the standard cell potential}$$

This is discussed in Chapter 9 (Big Idea 3) of this book.

**MULTIPLE-CHOICE QUESTIONS**

No calculators may be used in this part of the exam.

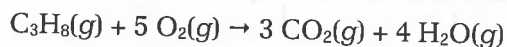
- The standard enthalpy of formation for nitrogen dioxide is the enthalpy change of the reaction
  - $\frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g})$
  - $\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$
  - $\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$
  - $\text{NO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g})$
- Which of the following has a non-zero standard enthalpy of formation?
  - $\text{Na}(\text{s})$
  - $\text{Hg}(\text{l})$
  - $\text{H}_2\text{O}(\text{l})$
  - $\text{N}_2(\text{g})$
- For endothermic reactions at constant pressure
  - $\Delta H < 0$
  - $\Delta H > 0$
  - $\Delta S > 0$
  - $S < 0$
- At a certain temperature  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  has a  $\Delta G$  of  $-339.4$  kJ/mol. This means that at this temperature
  - the system is at equilibrium
  - gaseous carbon dioxide spontaneously forms
  - this system has a high reaction rate
  - the system will not react

For questions 5, 6, and 7, consider the  $\Delta G$  of four different combinations of  $\Delta H$  and  $\Delta S$ . Assume that both  $\Delta H$  and  $\Delta S$  are temperature independent.

- Which processes are spontaneous at all temperatures?
  - $\Delta H = +$  and  $\Delta S = +$
  - $\Delta H = +$  and  $\Delta S = -$
  - $\Delta H = -$  and  $\Delta S = -$
  - $\Delta H = -$  and  $\Delta S = +$

6. The process which is nonspontaneous at all values of temperature is
- $\Delta H = +$  and  $\Delta S = +$
  - $\Delta H = +$  and  $\Delta S = -$
  - $\Delta H = -$  and  $\Delta S = -$
  - $\Delta H = -$  and  $\Delta S = +$
7. Which of these four processes is improbable at a low temperature but becomes more probable as the temperature rises?
- $\Delta H = +$  and  $\Delta S = +$
  - $\Delta H = +$  and  $\Delta S = -$
  - $\Delta H = -$  and  $\Delta S = -$
  - $\Delta H = -$  and  $\Delta S = +$
8. In which of the following four processes is there an increase in entropy?
- $2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow \text{SO}_3(g)$
  - $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(s)$
  - $\text{Hg}(g) \rightarrow \text{Hg}(l)$
  - $\text{H}_2\text{O}_2(l) \rightarrow \text{H}_2\text{O}(l) + 1/2 \text{O}_2(g)$
9. What is the enthalpy change for the following reaction under standard conditions?
- $$\text{CS}_2(l) + 3 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{SO}_2(g)$$
- $\Delta H^\circ_f \text{CS}_2(l) = +88 \text{ kJ/mol}$   
 $\Delta H^\circ_f \text{CO}_2(g) = -394 \text{ kJ/mol}$   
 $\Delta H^\circ_f \text{SO}_2(g) = -297 \text{ kJ/mol}$
- 900 kJ
  - 779 kJ
  - 603 kJ
  - 1076 kJ
10. A 57-gram block of metal at  $92^\circ\text{C}$  is dropped into an insulated flask containing approximately 45.0 grams of ice and 30.0 grams of water at  $0^\circ\text{C}$ . After the system reaches equilibrium it is determined that 9.5 grams of the ice has melted. What is the specific heat of the metal? (Heat of fusion of water =  $333 \text{ J/g}$ )
- $0.22 \text{ J/g } ^\circ\text{C}$
  - $0.32 \text{ J/g } ^\circ\text{C}$
  - $0.60 \text{ J/g } ^\circ\text{C}$
  - $0.92 \text{ J/g } ^\circ\text{C}$
11. A reaction takes place within a system. As a result, the entropy of the system decreases. Which of the following statements *must* be true?
- The reaction is endothermic.
  - The entropy of the universe decreases.
  - The Gibbs free energy of the system increases.
  - The entropy of the surroundings increases.

12. When propane burns in air, heat is released:



What are the signs of  $H$ ,  $S$ , and  $G$  for this process as illustrated by the above equation?

	$\Delta H$	$\Delta S$	$\Delta G$
(A)	-	+	+
(B)	-	+	-
(C)	-	-	+
(D)	+	+	-

13. Electrolysis of water is a chemical change because

- (A) hydrogen bonds are broken  
 (B) a great deal of energy is required  
 (C) bonds between H atoms and O atoms in individual molecules are broken  
 (D) the phase changes from liquid water to gaseous hydrogen and oxygen

14. Gas  $\text{A}_2$  reacts with gas  $\text{B}_2$  to form gas  $\text{AB}$  at constant temperature. The bond energy of  $\text{AB}$  is much greater than that of either reactant. For this process, what are the signs of  $H$  and  $S_{\text{surr}}$ ?

	$\Delta H$	$\Delta S_{\text{surr}}$
(A)	-	+
(B)	-	-
(C)	+	-
(D)	+	+

15. An audio amplifier generates a great deal of heat that can be dissipated with heat-radiating metal fins. Which metal would be the best for this application?

Metal	Specific heat capacity, $\text{J}/(\text{g} \cdot ^\circ\text{C})$
(A) Al	0.89
(B) Fe	0.45
(C) Cu	0.39
(D) Cr	0.46

### FREE-RESPONSE QUESTIONS

1. (a) Show the complete equation for the combustion of the flammable gas butene,  $\text{C}_4\text{H}_8$ .  
 (b) Given the following table of bond energies, estimate the enthalpy change,  $\Delta H$ , for the reaction noted in 1(a).

Average Bond Energies (kJ/mol)

C-H	413	C=O	799
C-C	347 (single)	H-O	467
C=C	614 (double)	H-H	432
$\text{C}\equiv\text{C}$	839 (triple)	O=O	495
C-O	358		



- (c) Often the heat of reaction (enthalpy) calculated from bond energies differs by 10–20% or more from the laboratory determined values. Suggest why this is so.
- (d) Is this process thermodynamically favored at all temperatures? Justify your answer.
2. The molar heats of fusion and vaporization of benzene are 10.9 kJ/mol and 31.0 kJ/mol, respectively. The melting temperature of benzene is 5.5°C and it boils at 80.1°C.
- (a) Calculate the entropy changes for solid → liquid, and for liquid → vapor for benzene.
- (b) Would you expect the  $\Delta S$  for these two changes to be about the same? Comment on the physical significance of the difference in these two values.
- (c) Why are the values for heat of vaporization usually so much greater than the heats of fusion?

## Answers

### MULTIPLE-CHOICE QUESTIONS

- A** This question should determine if you understand how to apply the definition of the term “standard enthalpy of formation.” Like many terms in chemistry, this has a very specific meaning: It is the energy involved in forming one mole of a compound from elements in standard state at 25°C and 1 atm pressure. As applied here, you must write the equation showing the formation of  $\text{NO}_2(g)$  as the product from the elements nitrogen and oxygen (both are diatomic elements under these conditions), and balance it so that only one mole of the product compound is formed (*Chemistry* 8th ed. pages 255–256/9th ed. pages 264–265). LO 5.8
- C** By definition, standard enthalpy of formation is the energy involved when one mole of a compound is formed from its elements in their standard states at 25°C and 1 atm. In this question, only water is a compound (*Chemistry* 8th ed. pages 255–256/9th ed. pages 264–265). LO 5.8
- B** In an endothermic reaction, heat is gained by the system. By convention, this is considered to be positive (*Chemistry* 8th ed. pages 249–253/9th ed. pages 258–262). LO 5.6
- B** A negative Gibbs free energy value indicates a spontaneous reaction;  $\text{CO}_2$  forms. Note that it says nothing about the rate of reaction. Kinetics is the topic of another chapter (*Chemistry* 8th ed. pages 783–786, 797–800/9th ed. pages 798–801, 812–815). LO 5.13
- D** From  $\Delta G = \Delta H - T\Delta S$ , if  $\Delta H$  is negative and  $\Delta S$  is positive the reaction must be spontaneous because  $\Delta G$  is negative in all such cases (*Chemistry* 8th ed. pages 783–792/9th ed. pages 798–808). LO 5.13

6. **B** From  $\Delta G = \Delta H - T\Delta S$ , if  $\Delta H$  is positive and  $T\Delta S$  is negative, then  $\Delta G$  is positive in all cases, so the reaction is always nonspontaneous (*Chemistry* 8th ed. pages 783–792/9th ed. pages 798–808). LO 5.13
7. **A** From  $\Delta G = \Delta H - T\Delta S$ , if the temperature is high, the  $T\Delta S$  factor is large and “overcomes” the influence of  $\Delta H$  (+) to make  $\Delta G$  negative; hence it becomes spontaneous at the higher temperatures (*Chemistry* 8th ed. pages 783–792/9th ed. pages 798–808). LO 5.13
8. **D** If there is an increase in entropy, then the products must be more disordered than the reactants. In choice (A), the system goes from 3 moles of gas to one mole of gas; in choice (B) the system goes from high entropy gas to low entropy solid; in choice (C) the system goes from high entropy gas to lower entropy liquid. The last choice goes from one mole of liquid to one mole of liquid and one-half mole of gas, an increase in entropy (*Chemistry* 8th ed. pages 786–790/9th ed. pages 801–805). LO 5.12
9. **D** Enthalpy change =  $[(-394 + (2 \times -297)) - (+88)] = -1076$  kJ. This is a basic Hess’s law problem. Remind yourself that the heat of formation of any element in its standard state is defined as zero, which is why there is no value listed for oxygen gas (*Chemistry* 8th ed. pages 251–261/9th ed. pages 260–270). LO 5.8
10. **C** Heat required to melt the ice =  $9.5 \text{ g} \times 333 \text{ J/g} = 3164 \text{ J}$   
 Heat lost by the metal block = mass of block  $\times$  (specific heat capacity)  $\times \Delta T$   
 $= 57 \text{ g} \times (\text{specific heat capacity}) \times 92^\circ\text{C}$   
 $= \text{specific heat capacity} \times 5244^\circ\text{C}\cdot\text{g}$   
 Since heat lost by metal block – heat gained by ice,  
 $3164\text{J} = \text{specific heat capacity} \times 5244^\circ\text{C}\cdot\text{g}$ ; and solving for specific heat capacity,  
 specific heat capacity =  $0.603 \text{ J}/(\text{g}\cdot^\circ\text{C})$   
 (*Chemistry* 8th ed. pages 244–251/9th ed. pages 253–260). LO 5.6
11. **D** The entropy of the universe must increase and the free energy of the system must decrease, as these are expressions of the second law. If the entropy of the system decreases, the entropy of the surroundings must increase. If the entropy of the surroundings is to increase, the reaction must be exothermic. Therefore only the last statement is true (*Chemistry* 8th ed. pages 773–776, 783–790/9th ed. pages 788–791, 798–805). LO 5.13
12. **B** Since the reaction occurs we know it is spontaneous, which means  $\Delta G$  must be negative. The reaction is exothermic, meaning that  $\Delta H$  is negative and since there is an increase in the number of

molecules of gas, there is an increase in the randomness, meaning that  $\Delta S$  is positive (*Chemistry* 8th ed. pages 783–787/9th ed. pages 798–801). LO 5.13

13. **C** Electrolysis is splitting water into hydrogen and oxygen gas. Bonds within the molecules are broken, so it is a chemical change. Hydrogen bonds are intermolecular forces and breaking those is a phase change (*Chemistry* 8th ed. pages 28, 475–478/9th ed. pages 260–270). LO 5.10
14. **A** The process must be exothermic ( $\Delta H < 0$ ) since the energy released when the new bond is formed is less than the energy required to break the bonds of the reactant molecules. The energy is released to the surroundings, so the entropy of the surroundings increases ( $S_{\text{surr}} > 0$ ) (*Chemistry* 8th ed. pages 251–261/9th ed. pages 260–270). LO 5.13
15. **C** Copper has the lowest heat capacity, so it would transfer heat most efficiently (*Chemistry* 8th ed. pages 244–245/9th ed. pages 260–270). LO 5.6

### FREE-RESPONSE QUESTIONS

1. (a)  $\text{C}_4\text{H}_8(g) + 6 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 4 \text{H}_2\text{O}(l)$   
(*Chemistry* 8th ed. pages 165–166/9th ed. pages 174–175) LO 3.8
- (b)  $\text{CH}_2\text{CHCHCH}_3 + 6 \text{O}=\text{O} \rightarrow 4 \text{O}=\text{C}=\text{O} + 4 \text{H}-\text{O}-\text{H}$

Bonds broken (reactants):

$$1 \text{ C}=\text{C} \quad 1 \text{ mol} \times 614 \text{ kJ/mol} \quad = 614 \text{ kJ}$$

$$2 \text{ C}-\text{C} \quad 2 \quad \times 347 \quad = 694$$

$$8 \text{ C}-\text{H} \quad 8 \quad \times 413 \quad = 3304$$

$$6 \text{ O}=\text{O} \quad 6 \quad \times 495 \quad = 2970$$

Total energy required to break bonds = 7582 kJ.

Bonds formed (products):

$$8 \text{ C}=\text{O} \quad 8 \text{ mol} \times 799 \text{ kJ/mol} \quad = 6392 \text{ kJ}$$

$$8 \text{ H}-\text{O} \quad 8 \quad \times 467 \quad = 3736$$

Total energy released as bonds form = 10128 kJ.

The difference between the two is a negative value, denoting an exothermic reaction.

$\Delta H = -2546 \text{ kJ/mol C}_4\text{H}_8$  reacting.

(*Chemistry* 8th ed. pages 362–364/9th ed. pages 373–376) LO 5.8

- (c) The surrounding bonds often affect the strength of a given bond. For example, the average C=O bond energy is 745 kJ/mol, but the C=O bond energy in  $\text{CO}_2$  is 799 kJ/mol (the value given for your use in the table). Examining the structure

of butane, you might guess that the C–H bond energies of bonds near a C=C double bond would be somewhat different from those with a C–C single bond attached to the same carbon. The environment of the bond does make a difference (*Chemistry* 8th ed. pages 361–362/9th ed. pages 373–374). LO 5.9

- (d)  $\Delta G = \Delta H - T \Delta S$ . When  $\Delta G < 0$ , the process is spontaneous. This process is exothermic, and but the entropy is decreasing (going from 7 moles of gas to 4 moles of gas and 4 moles of liquid), so  $\Delta G$  will only be negative and the process spontaneous at lower temperatures. Note that if the equation was written with gaseous water as the product, the process would be spontaneous at all temperatures (*Chemistry* 8th ed. pages 783–787/9th ed. pages 798–801). LO 5.13
2. (a) When a liquid boils at its boiling temperature or freezes at its freezing temperature, no useful work can be done by the process, i.e.,  $\Delta G$  is zero. Therefore, under these conditions,

$$\Delta S = \Delta H/T$$

In melting,  $\Delta S = 10.9 \times 10^3 \text{ J/mol}/(5.5 + 273 \text{ K}) = +39.1 \text{ J/K}\cdot\text{mol}$ .

In boiling,  $\Delta S = +87.8 \text{ J/K}\cdot\text{mol}$ .

(*Chemistry* 8th ed. pages 781–783/9th ed. pages 796–798) LO 5.6

- (b) Vaporization involves a much greater change in disorder than melting (gases are very disordered compared to liquids, whereas liquids and solids vary less in disorder, distance between molecules, and number of possible positions for molecules); hence  $\Delta S_{\text{vap}} > \Delta S_{\text{fus}}$  (*Chemistry* 8th ed. pages 773–779/9th ed. pages 788–794). LO 5.12
- (c) When a substance is melted, the molecules are still relatively close together and experience attractive forces. When a liquid is vaporized, however, the molecules become very widely separated and most attractive forces are overcome. This requires more energy than is needed for melting, hence  $\Delta H_{\text{vap}} > \Delta H_{\text{fus}}$  (*Chemistry* 8th ed. page 439/9th ed. page 454). LO 5.6