ChemQuest 54

The Second Law of Thermodynamics

Name: _____

Date: _____

Hour: _____

Information: Spontaneity

It is often desirable to know if a process will occur all by itself or if you need to supply energy for a process to occur. If a process occurs naturally, all by itself without outside help, it is said to be spontaneous. Examples of spontaneous processes include iron rusting and a ball rolling down a hill.

Critical Thinking Questions

1. Which of the following processes are spontaneous?
   a) a rock rolling uphill b) a leaf falling c) water boiling at 100°C

Information: Entropy

It is important to consider the amount of disorder in a system when determining whether a reaction will occur spontaneously. Just as the energy change is given a special name and symbol (change in enthalpy, ΔH), the change in the amount disorder or randomness is also given a special name, "change in entropy", which has the symbol ΔS. Entropy, S, is a measure of the amount of disorder in a system. When disorder increases, ΔS is positive.

Critical Thinking Questions

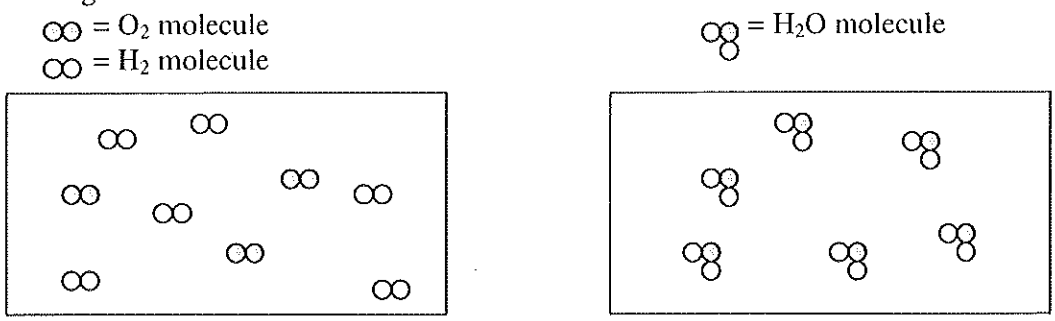
2. When $\Delta H_{reaction}$ is negative that means that the reaction loses energy to become less energetic. When $\Delta S_{reaction}$ is negative, what is that telling us?

   The amount of disorder (entropy) of a system decreases when $\Delta S_{reaction}$ is negative.

3. Does disorder (entropy) increase or decrease for the formation of gaseous water?

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

Note the diagrams below in which every molecule is moving randomly. Explain your answer using the diagrams.



Entropy (the amount of disorder) decreases when water is formed. As can be seen in the above diagrams, the H_2O has fewer individual molecules that are moving randomly.

4. Indicate whether for each of the following processes ΔS will be positive or negative? Explain each answer. (Hint: think in terms of the disorder or randomness of molecules and molecular motion.)
   a) an ice cube melting
      ΔS will be positive; entropy increases because the liquid molecules are not organized into a crystalline solid after it melts.
   b) water vaporizing
      ΔS will be positive; gases are more disorderly than liquids.
   c) cleaning your room
      ΔS will be negative; cleaning a room involves organizing the room, thus decreasing the disorder.
   d) folding paper into a paper airplane
      ΔS will be negative; the paper becomes more ordered by folding it in an ordered manner.

Information: Comparing Entropy and Enthalpy

It was once thought that for a chemical reaction to be spontaneous that it also had to be exothermic ($\Delta H<0$). Now, however, we recognize that some endothermic reactions are spontaneous. When deciding whether a reaction is spontaneous, you need to consider both entropy and enthalpy. Note that for any reaction you will have the reaction itself and its surroundings. Both the reaction and its surroundings together are called the universe so that $\Delta S_{universe} = \Delta S_{reaction} + \Delta S_{surroundings}$. Consider the following table:

Reaction	sign of $\Delta H_{reaction}$	Sign of $\Delta S_{reaction}$	Sign of $\Delta S_{surroundings}$	Sign of $\Delta S_{universe}$	Spontaneous?
#1 exothermic, entropy increase	-	+	+	+	yes
#2 endothermic, entropy increase	+	+	-	+ or -	depends
#3 exothermic, entropy decrease	-	-	+	+ or -	depends
#4 endothermic, entropy decrease	+	-	-	-	no

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Critical Thinking Questions

5. For reaction #2, according to the table, it says that there is an entropy increase. What entropy is it referring to—$\Delta S_{reaction}$, $\Delta S_{surroundings}$, or $\Delta S_{universe}$?

   $\Delta S_{reaction}$

6. Why can $\Delta S_{universe}$ be + or – for reactions two or three?

   $\Delta S_{universe}$ depends on both $\Delta S_{reaction}$ and $\Delta S_{surroundings}$, so whichever one is larger in magnitude determines the sign on $\Delta S_{universe}$.

7. What is the correlation between the sign of $\Delta H_{reaction}$ and the sign of $\Delta S_{surroundings}$?

   They always have opposite signs.

8. The sign of $\Delta H_{reaction}$ ***determines*** the sign of $\Delta S_{surroundings}$. Explain why this is true. (Hint: think about what happens to the motion of molecules in the surroundings when $\Delta H_{reaction}$ is positive and when it is negative.)

   If more heat is sent into the surroundings (negative $\Delta H_{reaction}$) then the molecules in the surrounding will move faster and more chaotically.

9. On the table above, the sign of one value determines whether the reactions are spontaneous or not. Which value's sign determines the spontaneity of a reaction?

   $\Delta S_{universe}$ must be positive for a reaction to be spontaneous.

10. Use your answer to question 9 to fill in the blanks. This is a statement of the Second Law of Thermodynamics!

    For any spontaneous reaction, the amount of _____entropy_____ in the universe must
    enthalpy or entropy

    _____increase_____.
    increase or decrease

11. In the above information section, the statement was made that "When deciding whether a reaction is spontaneous, you need to consider both entropy and enthalpy." If only one value (answer to question 9) is needed to determine spontaneity, then why do you still need to consider the enthalpy?

    The enthalpy helps to determine $\Delta S_{surroundings}$ and the $\Delta S_{surroundings}$ helps to determine the $\Delta S_{universe}$.

Information: Predicting and Calculating Entropy Changes

Consider question 3 along with the diagrams of oxygen, hydrogen and water molecules.

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

When the two gaseous reactants (oxygen and hydrogen) combined to form gaseous water, hopefully you concluded that entropy decreased. Notice that in the balanced chemical equation, there are a total of three moles of gaseous reactants ($2\,H_2 + O_2$) and only two moles of gaseous products ($2H_2O$). In general, then, whenever the number of moles of gaseous products is less than the number of moles of gaseous reactants entropy will decrease. If there are more moles of gaseous products than gaseous reactants, entropy has increased.

Critical Thinking Questions

12. Explain why ΔS is negative for the following reaction.

$$2\ Ca\ (s) + O_2\ (g) \rightarrow 2\ CaO\ (s)$$

The disorder decreases because the moles of gas decreases and the gas state is the most disorderly state of matter.

13. For each of the following reactions, predict if the entropy change is positive or negative. If you cannot tell, explain why.

A) $C_2H_2\ (g) + 2\ H_2\ (g) \rightarrow C_2H_6\ (g)$
Negative; the total moles of gas is decreasing (moles of gaseous product is less than the moles of gaseous reactants).

B) $CH_3NH_2\ (g) \rightarrow HCN\ (g) + 2\ H_2\ (g)$
Positive; the total moles of gas is increased.

C) $N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$
Since the moles of gas are equal on both sides, we cannot predict this one.

14. Entropy values can be calculated in much the same was as enthalpy values. Using a table of standard entropies, calculate the entropy change for the following reactions.

A) $N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$
191.5 J 205.0 J 210.65 J
$\Delta S = 210.65 - [205.0 + 191.5] =$ **-185.85 J**

B) $CS_2\ (g) + 4\ H_2\ (g) \rightarrow CH_4\ (g) + 2\ H_2S\ (g)$
237.79 J 130.6 J 186.1 J 205.6 J
$\Delta S = [2(205.6) + 186.1] - [4(130.6) + 237.79] =$ **-162.89 J**

C) $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g)$
130.6 J 205.0 J 188.72 J
$\Delta S = [2(188.72)] - [2(130.6 + 205.0] =$ **-88.76 J**

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Skill Practice 54

2nd Law Practice

Name: _____

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1. Predict whether ΔS is positive or negative for each of the following reactions.

   A) $2\ Na\ (s) + Cl_2\ (g) \rightarrow 2\ NaCl\ (s)$
   negative

   B) $2\ C\ (s) + O_2\ (g) \rightarrow 2\ CO_2\ (g)$
   positive

   C) $2\ CH_3OH\ (l) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 2\ H_2O\ (l)$
   negative

   D) $P_4\ (g) \rightarrow P_4\ (s)$
   negative

2. Calculate ΔS for the following reactions using standard entropy values.

   A) $2\ SO_3\ (g) \rightarrow 2\ SO_2\ (g) + O_2\ (g)$

   187.88 J

   B) $CS_2\ (l) + 3\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ SO_2\ (g)$

   -56.1 J

   C) $CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l)$

   -242.52 J

   D) $CS_2\ (g) + 4\ H_2\ (g) \rightarrow CH_4\ (g) + 2\ H_2S\ (g)$

   -162.9 J

3. What does it mean for a reaction to be spontaneous?

   It means that the reaction occurs without needing outside influences.

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