W1	Learning Area	General Chemistry 2	Grade Level	Grade 12
	Quarter	4th Quarter	Date	

I. LESSON TITLE	Second Law of Thermodynamics
II. MOST ESSENTIAL LEARNING COMPETENCIES (MELCs)	1. Predict the spontaneity of a process based on entropy. 2. Explain the second law of thermodynamics and its significance. 3. Use Gibbs' free energy to determine the direction of a reaction.
III. CONTENT/CORE CONTENT	✔ Entropy ✔ Second Law of Thermodynamics ✔ Gibbs' Free Energy

IV. LEARNING PHASES AND LEARNING ACTIVITIESs

I. Introduction (Time Frame: 30 minutes)

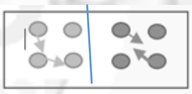
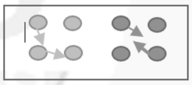
Have you accidentally dropped your favorite mug and watched it shatter? Can the broken pieces reassemble itself to go back to your favorite mug on its own? A spontaneous process is a change that occurs on its own without the input of energy. A non-spontaneous process, on the other hand, requires a continuous input of energy. An indicator in the spontaneity of a reaction is the change in entropy.

At the end of the lesson, you will be able to:

1. Predict the spontaneity of a process based on entropy;
2. Explain the second law of thermodynamics and its significance and;
3. Use Gibbs' free energy to determine the direction of a reaction.

There are certain things that occur in our life that happen in one direction. Babies get older not younger, a shattered glass cannot be whole again, a leaf that falls cannot go back to the tree again, a waterfall runs downhill but never up. This occurrence in one direction is referred to as the arrow of time. In thermodynamics, this arrow of time is entropy. Entropy is the measurement of a disorder within a system. The greater the disorder of a system, the greater its entropy. The Si unit of entropy is joules per Kelvin (J/K).

Consider the following illustration:

In which illustration will the entropy be greater? Why do you say so?

D. Development (Time Frame: 60 minutes)

In the first illustration, the molecules are in an ordered state since a line is separating the yellow dots from the blue dots, the number of collisions is fewer. In the second illustration, with the removal of the line, the possibilities of the rearrangement of yellow dots to be mixed with the blue dots is higher. The entropy change for this process, ΔS, is

$$\Delta S = S_f - S_i$$

where S_f and S_i are the entropies of the system in the final and initial states. If the change results in an increase in disorder, then $S_f > S_i$.

Learning Task 1

Predict whether the entropy change is greater than or less than zero for each of the following processes.

1. freezing water
2. sublimation of dry ice
3. dissolving sugar in water

The connection between entropy and the spontaneity of a reaction is embodied in the Second Law of Thermodynamics: The state of entropy of the entire universe, as an isolated system, will always increase over time. Given the entropy change of the universe is equivalent to the sums of the changes in entropy of the system and surroundings:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \qquad T \quad T$$

Consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for the process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. This is always observed to occur spontaneously. Assigning the hotter object as the system will yield:

$$\Delta S_{sys} = \frac{-q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{q_{rev}}{T_{sys}}$$

The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{sys} > T_{surr}$ in this case, the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will give a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Assigning the hotter object as the system will yield:

$$\Delta S_{sys} = \frac{q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = -\frac{q_{rev}}{T_{sys}}$$

The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*

3. The temperature difference between the objects is very small, $T_{sys} \approx T_{surr}$, and so the heat flow is thermodynamically *reversible*. In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore the sum yields a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

So, for any process,

Table 1. Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous
$\Delta S_{univ} = 0$	reversible

To calculate ΔS_{sys}, we need to know both the ΔS_{sys} and the ΔS_{surr}. Suppose the system is represented by the following reaction:

$$aA + bB \longrightarrow cC + dD$$

In calculating for the standard entropy of a reaction we use

$$\Delta S^o_{rxn} = [cS^o(C) + dS^o(D)] - [aS^o(A) + bS^o(B)]$$

Calculate the standard entropy changes for $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$ at 25°C.
Refer to the absolute entropy values.
$CaCO_3$ = 92.9 J/K.mol $CaO_{(s)}$ = 39.8 J/K.mol $CO_{2(g)}$ = 213.6 J/K.mol

$$\Delta S^o_{rxn} = [(1 \text{ mol})(39.8 \text{ J/K.mol}) + (1 \text{ mol})(213.6 \text{ J/K.mol}) - [(1 \text{ mol})(92.9 \text{ J/K.mol})$$
$$= 160.5 \text{ J/K}$$

Consider the example: Will ice spontaneously melt?
The entropy change for this process is $H_2O_{(s)} \longrightarrow H_2O_{(l)}$ is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at -10.00 °C? Is it spontaneous at +10.00 °C?

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K):

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T} = 22.1 \text{J/K} + \frac{-6.00\times10^3 \text{J}}{263.15\text{K}} = -0.7 \text{J/K}$$

$\Delta S_{univ} < 0$, so melting is nonspontaneous at – 10. 00 °C.

At 10.00 °C (283.15 K):

$$\Delta S_{univ} = \Delta S_{sys} + \frac{q_{surr}}{} = 22.1 \text{J/K} + \frac{-6.00\times10^3 \text{J}}{283.15\text{K}} = +0.9 \text{J}$$

$\Delta S_{univ} > 0$, so melting *is* spontaneous at 10.00 °C.

Learning Task 2

Calculate the standard entropy values for the following reactions at 25°C.

1. $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$
2. $H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$
3. $2CO_{2(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$
4. $3O_{2(g)} \longrightarrow 2O_{3(g)}$
5. $2NH_{3\,(g)} + CO_{2\,(g)} \longrightarrow NH_2CONH_{2\,(aq)}\ H_2O_{(l)}$

Learning Task 3

Determine if liquid water will spontaneously freeze at -10.00 °C? Is it spontaneous at +10.00 °C? What can you say about the values of ΔS_{univ}?

E. Engagement (Time Frame: 60 minutes**)**

The second law of thermodynamics can also be stated that all spontaneous processes produce an increase in the entropy of the universe. In order to determine the spontaneity of a system, a thermodynamic function called Gibbs' free energy (G) can be used.

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

Given the equation: $\Delta S_{total} = \Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$

The formula for the entropy changes in the surroundings is $\Delta S_{surr} = \Delta H_{sys}/T$. If this equation is replaced in the previous formula, and the equation is then multiplied by T and by -1 it results in the following formula.

$$-T\Delta S_{univ} = \Delta H_{sys} - T\,\Delta S_{sys}$$

If the left side of the equation is replaced by G, which is known as Gibbs energy or free energy, the equation becomes

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

Summarizing the conditions for spontaneity and equilibrium at constant temperature and pressure in terms of ΔG:

Table 2. Gibbs Free Energy

$\Delta G < 0$	The reaction is spontaneous in the forward reaction.
$\Delta G > 0$	The reaction is nonspontaneous. The reaction is spontaneous in the opposite direction.
$\Delta G = 0$	The system is at equilibrium. There is no net change.

Consider the reaction: $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$

The enthalpy, ΔH, for this reaction is -241.82 kJ, and the entropy, ΔS, of this reaction is -233.7 J/K. If the temperature is at 25°C, to calculate the standard free energy change, ΔG, convert the temperature to Kelvin. so add 273.15 to 25 and the temperature is at 298.15 K. Next substitute the values for ΔH, ΔS, and the temperature into the equation $\Delta G=\Delta H-T\Delta S$.

$\Delta G = -241.8\ kJ + (298.15\ K)(-233.7\ J/K)$
$= -241.8\ kJ + -69.68\ kJ$
$= -311.5\ kJ$ $\Delta G < 0$, the reaction is spontaneous.

The standard free energy reaction (ΔG^o_{rxn}) is the free energy change for a reaction when it occurs under standard state conditions, when reactants in their standard states are converted to products in their standard states. To solve for ΔG^o_{rxn}

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G^o_{rxn} = [c\Delta G_f^o(C) + d\Delta G_f^o(D)] - [a\Delta G_f^o(A) + b\Delta G_f^o(B)]$$

Calculate the standard free energy changes for the reaction

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ at 25°C.

$$\Delta G^o_{rxn} = [\Delta G_f^o(CO_2) + 2\Delta G_f^o(H_2O)] - [\Delta G_f^o(CH_4) + 2\Delta G_f^o(O_2)]$$

Note:
ΔH refers to the heat change for a reaction. A positive ΔH means that heat is taken from the environment (endothermic). A negative ΔH means that heat is emitted or given to the environment (exothermic).

ΔG is a measure for the change of a system's free energy in which a reaction takes place at constant pressure (P) and temperature (T).

Learning Task 4

1. For the reaction, $H_2O_{(l)} \longrightarrow H_2O_{(g)}$, calculate ΔG at a) 20°C, b) 100°C and c) 150°C.
2. Calculate the standard-free energy changes for the reaction $2MgO_{(s)} + 2Mg_{(s)} + O_{2(g)}$ at 25°C.

What is the significance of the Second Law of Thermodynamics? Chemical processes tend to favor one direction. Every day, we observed spontaneous physical and chemical processes such as iron when exposed to water and oxygen forms rust, but rust does not spontaneously change back to iron. Heat flows from a hotter object to a colder one, but the reverse process never happens spontaneously. A spoon of sugar dissolved in a cup of coffee, but the dissolved sugar does not crystallize spontaneously.

Many biochemical reactions are nonspontaneous, with a positive ΔG° value, but they are essential for life to exist. These reactions are coupled to an energetically favorable mechanism in living systems, one with a negative ΔG° value. During metabolism, glucose is converted to carbon dioxide and water, releasing a significant amount of free energy.

A. Assimilation (Time Frame: 5 minutes)

The second law of thermodynamics states that a *spontaneous* process increases the entropy of the universe, $S_{univ}>0$. If $\Delta S_{univ}<0$, the process is *nonspontaneous*, and if $\Delta S_{univ}=0$, the system is at equilibrium.

In terms of Gibbs' free energy, if $\Delta G < 0$, the reaction is spontaneous in the forward reaction. The reaction is nonspontaneous, if $\Delta G > 0$. The reaction is spontaneous in the opposite direction. The system is at equilibrium. There is no net change if $\Delta G = 0$.

V. ASSESSMENT (Tome Frame: 15 minutes)

(Learning Activity Sheets for Enrichment, Remediation or Assessment to be given on Weeks 3 and 6)

A. Read each item carefully and encircle the letter of the correct answer.

1. Which of the following statements best describes the Second Law of Thermodynamics?
   A. The internal energy of the universe is constant.
   B. Energy can neither be created nor destroyed.
   C. At absolute zero, the entropy of a crystal is considered to be zero.
   D. When an isolated system undergoes a spontaneous change, the entropy of the system increases.
2. Which of the following represents a spontaneous process?
   A. $\Delta S<0$ B. $\Delta S=0$ C. $\Delta G > 0$ D. $\Delta G < 0$
3. Which of the following has the most entropy?
   A. an empty classroom
   B. a tennis ball inside a box

C. a flock of birds flying in V formation
D. a crowd of people on the streets of Santa Rosa City

B. Predict whether ΔS is positive or negative for the reaction: $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$

C. Which has greater entropy? 1mole of $NaCl_{(s)}$ or 1 mol of $HCl_{(g)}$

VI. REFLECTION (Time Frame: 10 minutes)

- Communicate your personal assessment as indicated in the Learner's Assessment Card.

Personal Assessment on Learner's Level of Performance

Using the symbols below, choose one which best describes your experience in working on each given task. Draw it in the column for Level of Performance (LP). Be guided by the descriptions below:

☆ - I was able to do/perform the task without any difficulty. The task helped me in understanding the target content/ lesson.

✔ - I was able to do/perform the task. It was quite challenging, but it still helped me in understanding the target content/lesson.

? – I was not able to do/perform the task. It was extremely difficult. I need additional enrichment activities to be able to do/perform this task.

Learning Task	LP	Learning Task	LP	Learning Task	LP	Learning Task	LP
Number 1		Number 3					
Number 2		Number 4					

VII. REFERENCES:

Brown, Theodore L.et al. Chemistry The Central Science 8th ed (Singapore: Pearson education Asia Pte Ltd,2002).
Chang, Raymond. Chemistry 6th Edition (Mc-Graw-Hill Companies, Inc,1998).
Redmore, Fred H. Fundamentals of Chemistry. (Quezon City: Apson Enterprises,1980).

Prepared by:	Maria Cristina M. Briones	Checked by:	Jocelyn Reyes Roxane L. Llona Leilane P. Lagacion