

## 10.5: Entropy and the Second Law of Thermodynamics

The Second Law of Thermodynamics states that the state of entropy of the entire universe, as an **isolated system**, will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative.

### Introduction

Why is it that when you leave an ice cube at room temperature, it begins to melt? Why do we get older and never younger? And, why is it whenever rooms are cleaned, they become messy again in the future? Certain things happen in one direction and not the other, this is called the "arrow of time" and it encompasses every area of science. The thermodynamic arrow of time (entropy) is the measurement of disorder within a system. Denoted as  $\Delta S$ , the change of entropy suggests that time itself is asymmetric with respect to order of an isolated system, meaning: a system will become more disordered, as time increases.

### Major players in developing the Second Law

- Nicolas Léonard Sadi Carnot was a French physicist, who is considered to be the "father of thermodynamics," for he is responsible for the origins of the Second Law of Thermodynamics, as well as various other concepts. The current form of the second law uses entropy rather than caloric, which is what Sadi Carnot used to describe the law. Caloric relates to heat and Sadi Carnot came to realize that some caloric is always lost in the motion cycle. Thus, the thermodynamic reversibility concept was proven wrong, proving that irreversibility is the result of every system involving work.
- Rudolf Clausius was a German physicist, and he developed the Clausius statement, which says "Heat generally **cannot flow spontaneously** from a material at a lower temperature to a material at a higher temperature."
- William Thompson, also known as Lord Kelvin, formulated the Kelvin statement, which states "It is **impossible** to convert heat completely in a cyclic process." This means that there is no way for one to convert all the energy of a system into work, without losing energy.
- Constantin Carathéodory, a Greek mathematician, created his own statement of the second law arguing that "In the neighborhood of any initial state, there are states which **cannot** be approached arbitrarily close through adiabatic changes of state."



Figure 10.5.1: Nicolas Carnot (left), Rudolf Clausius (second on left), William Thompson (second on right), Constantin Carathéodory (right)

### Probabilities

If a given state can be accomplished in more ways, then it is more probable than the state that can only be accomplished in a fewer/one way.

Assume a box filled with jigsaw pieces were jumbled in its box, the probability that a jigsaw piece will land randomly, away from where it fits perfectly, is very high. Almost every jigsaw piece will land somewhere away from its ideal position. The probability of a jigsaw piece landing correctly in its position, is very low, as it can only happen one way. Thus, the misplaced jigsaw pieces have a much higher multiplicity than the correctly placed jigsaw piece, and we can correctly assume the misplaced jigsaw pieces represent a higher entropy.

### Derivation and Explanation

To understand why entropy increases and decreases, it is important to recognize that two changes in entropy have to be considered at all times. The entropy change of the surroundings and the entropy change of the system itself. Given the entropy change of the universe is equivalent to the sums of the changes in entropy of the system and surroundings:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \frac{q_{sys}}{T} + \frac{q_{surr}}{T} \quad (10.5.1)$$

In an isothermal reversible expansion, the heat  $q$  absorbed by the system from the surroundings is

$$q_{rev} = nRT \ln \frac{V_2}{V_1} \quad (10.5.2)$$

Since the heat absorbed by the system is the amount lost by the surroundings,  $q_{sys} = -q_{surr}$ . Therefore, for a truly reversible process, the entropy change is

$$\Delta S_{univ} = \frac{nRT \ln \frac{V_2}{V_1}}{T} + \frac{-nRT \ln \frac{V_2}{V_1}}{T} = 0 \quad (10.5.3)$$

If the process is irreversible however, the entropy change is

$$\Delta S_{univ} = \frac{nRT \ln \frac{V_2}{V_1}}{T} > 0 \quad (10.5.4)$$

If we put the two equations for  $\Delta S_{univ}$  together for both types of processes, we are left with the second law of thermodynamics,

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0 \quad (10.5.5)$$

where  $\Delta S_{univ}$  equals zero for a truly reversible process and is greater than zero for an irreversible process. In reality, however, truly reversible processes never happen (or will take an infinitely long time to happen), so it is safe to say all thermodynamic processes we encounter everyday are irreversible in the direction they occur.

The second law of thermodynamics can also be stated that "all **spontaneous** processes produce an **increase** in the entropy of the universe".

## Gibbs Free Energy

Given another equation:

$$\Delta S_{total} = \Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} \quad (10.5.6)$$

The formula for the entropy change 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.

$$-T \Delta S_{univ} = \Delta H_{sys} - T \Delta S_{sys} \quad (10.5.7)$$

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

$$\Delta G = \Delta H - T \Delta S \quad (10.5.8)$$

Now it is much simpler to conclude whether a system is spontaneous, non-spontaneous, or at equilibrium.

- $\Delta H$  refers to the heat change for a reaction. A positive  $\Delta H$  means that heat is taken from the environment (endothermic). A negative  $\Delta H$  means that heat is emitted or given to the environment (exothermic).
- $\Delta G$  is a measure for the change of a system's free energy in which a reaction takes place at **constant** pressure ( $P$ ) and temperature ( $T$ ).

According to the equation, when the entropy decreases and enthalpy increases the free energy change,  $\Delta G$ , is positive and not spontaneous, and it does not matter what the temperature of the system is. Temperature comes into play when the entropy and enthalpy both increase or both decrease. The reaction is not spontaneous when both entropy and enthalpy are positive and at low temperatures, and the reaction is spontaneous when both entropy and enthalpy are positive and at high temperatures. The reactions are spontaneous when the entropy and enthalpy are negative at low temperatures, and the reaction is not spontaneous when the entropy and enthalpy are negative at high temperatures. Because all spontaneous reactions increase entropy, one can determine if the entropy changes according to the spontaneous nature of the reaction (Equation 10.5.8).

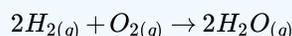
Table 10.5.1: Matrix of Conditions Dictating Spontaneity

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Case	$\Delta H$	$\Delta S$	$\Delta G$	Answer
high temperature	-	+	-	Spontaneous
low temperature	-	+	-	Spontaneous
high temperature	-	-	+	Nonspontaneous
low temperature	-	-	-	Spontaneous
high temperature	+	+	-	Spontaneous
low temperature	+	+	+	Nonspontaneous
high temperature	+	-	+	Nonspontaneous
low temperature	+	-	+	Nonspontaneous

### ✓ Example 10.5.1

Lets start with an easy reaction:



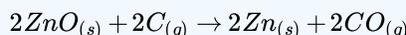
The enthalpy,  $\Delta H$ , for this reaction is -241.82 kJ, and the entropy,  $\Delta S$ , of this reaction is -233.7 J/K. If the temperature is at 25° C, then there is enough information to calculate the standard free energy change,  $\Delta G$ .

The first step is to convert the temperature to Kelvin, so add 273.15 to 25 and the temperature is at 298.15 K. Next plug  $\Delta H$ ,  $\Delta S$ , and the temperature into the  $\Delta G = \Delta H - T\Delta S$ .

$$\begin{aligned}\Delta G &= -241.8 \text{ kJ} + (298.15 \text{ K})(-233.7 \text{ J/K}) \\ &= -241.8 \text{ kJ} + -69.68 \text{ kJ (Don't forget to convert Joules to Kilojoules)} \\ &= -311.5 \text{ kJ}\end{aligned}$$

### ✓ Example 10.5.2

Here is a little more complex reaction:



If this reaction occurs at room temperature (25° C) and the enthalpy,  $\Delta H$ , and standard free energy,  $\Delta G$ , is given at -957.8 kJ and -935.3 kJ, respectively. One must work backwards somewhat using the same equation from Example 1 for the free energy is given.

$$\begin{aligned}-935.3 \text{ kJ} &= -957.8 \text{ kJ} + (298.15 \text{ K})(\Delta S) \\ 22.47 \text{ kJ} &= (298.15 \text{ K})(\Delta S) \text{ (Add -957.8 kJ to both sides)} \\ 0.07538 \text{ kJ/K} &= \Delta S \text{ (Divide by 298.15 K to both sides)}\end{aligned}$$

Multiply the entropy by 1000 to convert the answer to Joules, and the new answer is 75.38 J/K.

### ✓ Example 10.5.3

For the following dissociation reaction



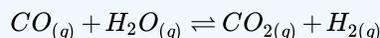
under what temperature conditions will it occurs spontaneously?

**Solution**

By simply viewing the reaction one can determine that the reaction increases in the number of moles, so the entropy increases. Now all one has to do is to figure out the enthalpy of the reaction. The enthalpy is positive, because covalent bonds are broken. When covalent bonds are broken energy is absorbed, which means that the enthalpy of the reaction is positive. Another way to determine if enthalpy is positive is to use the formation data and subtract the enthalpy of the reactants from the enthalpy of the products to calculate the total enthalpy. So, if the temperature is low it is probable that  $\Delta H$  is more than  $T * \Delta S$ , which means the reaction is not spontaneous. If the temperature is large then  $T * \Delta S$  will be larger than the enthalpy, which means the reaction is spontaneous.

#### ✓ Example 10.5.4

The following reaction



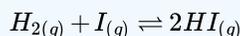
occurs spontaneously under what temperature conditions? The enthalpy of the reaction is -40 kJ.

#### Solution

One may have to calculate the enthalpy of the reaction, but in this case it is given. If the enthalpy is negative then the reaction is exothermic. Now one must find if the entropy is greater than zero to answer the question. Using the entropy of formation data and the enthalpy of formation data, one can determine that the entropy of the reaction is -42.1 J/K and the enthalpy is -41.2 kJ. Because both enthalpy and entropy are negative, the spontaneous nature varies with the temperature of the reaction. The temperature would also determine the spontaneous nature of a reaction if both enthalpy and entropy were positive. When the reaction occurs at a low temperature the free energy change is also negative, which means the reaction is spontaneous. However, if the reaction occurs at high temperature the reaction becomes nonspontaneous, for the free energy change becomes positive when the high temperature is multiplied with a negative entropy as the enthalpy is not as large as the product.

#### ✓ Example 10.5.5

Under what temperature conditions does the following reaction occurs spontaneously ?



#### Solution

Only after calculating the enthalpy and entropy of the reaction is it possible for one can answer the question. The enthalpy of the reaction is calculated to be -53.84 kJ, and the entropy of the reaction is 101.7 J/K. Unlike the previous two examples, the temperature has no affect on the spontaneous nature of the reaction. If the reaction occurs at a high temperature, the free energy change is still negative, and  $\Delta G$  is still negative if the temperature is low. Looking at the formula for spontaneous change one can easily come to the same conclusion, for there is no possible way for the free energy change to be positive. Hence, the reaction is spontaneous at all temperatures.

## Application of the Second Law

The second law occurs all around us all of the time, existing as the biggest, most powerful, general idea in all of science.

### Explanation of Earth's Age

When scientists were trying to determine the age of the Earth during 1800s they failed to even come close to the value accepted today. They also were incapable of understanding how the earth transformed. Lord Kelvin, who was mentioned earlier, first hypothesized that the earth's surface was extremely hot, similar to the surface of the sun. He believed that the earth was cooling at a slow pace. Using this information, Kelvin used thermodynamics to come to the conclusion that the earth was at least twenty million years, for it would take about that long for the earth to cool to its current state. Twenty million years was not even close to the actual age of the Earth, but this is because scientists during Kelvin's time were not aware of radioactivity. Even though Kelvin was incorrect about the age of the planet, his use of the second law allowed him to predict a more accurate value than the other scientists at the time.

## Evolution and the Second Law

Some critics claim that evolution violates the Second Law of Thermodynamics, because organization and complexity increases in evolution. However, this law is referring to isolated systems only, and the earth is not an isolated system or closed system. This is evident for constant energy increases on earth due to the heat coming from the sun. So, order may be becoming more organized, the universe as a whole becomes more disorganized for the sun releases energy and becomes disordered. This connects to how the second law and cosmology are related, which is explained well in the video below.

## Problems

1. Predict the entropy changes of the converse of  $\text{SO}_2$  to  $\text{SO}_3$ :  $2 \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{SO}_3 (\text{g})$
2. True/False:  $\Delta G > 0$ , the process is spontaneous
3. State the conditions when  $\Delta G$  is nonspontaneous.
4. True/False: A nonspontaneous process cannot occur with external intervention.

## Answers

1. Entropy decreases
2. False
3. Case 3, Case 6, Case 7, Case 8 (Table above)
4. True

## References

1. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.
2. *How the Earth Was Made*. Dir. Peter Chin. A&E Home Video, 2008. DVD.
3. Petrucci, Ralph H., William S. Harwood, F. G. Herring, and Jeffry D. Madura. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2007. 791-796.

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