

## Spontaneous Change and Entropy

### WHY?

Sometimes things seem to happen without outside intervention. Such changes are called *spontaneous*. Spontaneous change occurs because things move to a more probable situation. The concept of entropy quantifies the probability of a situation and enables you to predict whether or not a change or a chemical reaction will be spontaneous.

### LEARNING OBJECTIVE

- Understand the meaning of spontaneous change and entropy

### SUCCESS CRITERION

- Ability to correctly identify whether entropy increases or decreases

### VOCABULARY

- *Spontaneous change* happens due to a natural tendency without an apparent external cause.
- *Entropy* is a measure of the dispersal of energy over the states available to a system.

### INFORMATION

There is a natural tendency for energy to disperse. Entropy provides a quantitative measure of the extent to which energy has dispersed. To *disperse* means “to spread out.” Dispersal of energy occurs because there are more ways for the energy to be spread out over many states than there are for it to be concentrated in one or a few states. You can see this dispersal occurring when a hot object that is surrounded by air cools. The energy is in the hot object initially. As it cools, the energy is dispersed into the surrounding air molecules. The object cools down spontaneously. It does not heat up spontaneously. The reason for this is that there are many more ways for the energy to be distributed into the surrounding air molecules than there are for it to be distributed within the object.

Entropy is related to the number of states that are accessible with a given amount of energy. The larger the number of states, the more dispersed the energy can be. A system that can be found in a large number of states often appears to be more disordered than a system that is always found in only one state. Consequently entropy often is associated with the idea of order and disorder, but its real significance lies in its association with energy dispersal and the number of accessible states.

## MODEL: DISCOVER ENTROPY ON YOUR BOOKSHELF!

Entropy has a connection with the concepts of probability and the number of accessible states. To see this connection, consider the number of arrangements for three books on a shelf. A particular arrangement of books on a shelf is defined to be a state. An arrangement with a large number of ways of occurring will be more probable than an arrangement with only a single possibility.

Arrangement Set	Constraint	Number of States
<b>A</b>	Three books are lined up alphabetically by author starting on the left with the binding facing outward and the titles on the binding facing left.	<b>1</b>
<b>B</b>	The books do not need to be arranged alphabetically by author, but the bindings face outward and the titles face left.	<b>6</b>
<b>C</b>	The books do not need to be arranged alphabetically by author; the bindings must face outward, but the titles can face right and left.	<b>48</b>
<b>D</b>	The books do not need to be arranged alphabetically by author; the bindings can face outward, inward, up, or down; and the titles can face right and left.	<b>3072</b>

### KEY QUESTIONS

1. What is the maximum number of states of the three books in the model?

*Arrangement Set D has the maximum number of states at 3072.*

2. Which arrangement set has the highest probability: A, B, C, or D?

*Arrangement Set D has the highest probability.*

3. Which arrangement set would you consider to be the most disordered?

*Arrangement Set D is the most disordered.*

4. Which arrangement set would you say has the highest entropy?

*Arrangement Set D has the highest entropy.*

5. If you begin the semester with arrangement A, in which arrangement set will the state of your bookshelf be at the end of the semester, if you use your books and allow your the order of your bookshelf to change spontaneously during the course of the semester (i.e., without extra care, effort, and intervention on your part)?

*It is most likely that whatever arrangement you have, it will be one of the possibilities described in Arrangement Set D.*

6. Would you expect to get the most ordered arrangement by spontaneous change? Explain in terms of the number of states and the probability of the most ordered arrangement.

*There is only 1 chance in 3072 for the ordered arrangement (A) to occur spontaneously, so the most ordered arrangement is not likely to be achieved spontaneously. In order to achieve the most ordered arrangement, you would have to put work into arranging the books.*

7. Based on the model, what connections do you see between the number of accessible states, probability, entropy, and disorder?

*An arrangement with a large number of ways of occurring (a large number of accessible states) will be more probable than an arrangement with only a single possibility. The greater the number of accessible states or arrangements, the greater the entropy, and the more disordered the system appears to be.*

8. Based on the model, what connection do you see between entropy and spontaneous change?

*A spontaneous change is likely to correspond to an increase in entropy.*

9. Identify another example of a spontaneous change accompanied by an increase in entropy.

*There are many examples in nature.*

*Dandelion seeds disperse from an orderly arrangement on the stem to a disordered arrangement when caught by the wind. The gust of wind never returns the seeds to their orderly arrangement. A dead organism decomposes into dispersed materials. Ice taken from the freezer melts in a glass of warm water.*

## INFORMATION

An increase or decrease in entropy accompanying various physical and chemical changes can be identified from the following guidelines. Entropy increases when particles can move around more freely and access a larger number of states associated with this motion. When a gas expands into a larger volume, the number of potential states (as specified by the position and momentum of each particle) available to the particles increases, as does the entropy. Consequently, the entropy increases when a chemical reaction produces a gas phase product from a solid or when a gas phase molecule dissociates into two or more particles. Similarly, when a solid melts or a liquid vaporizes, the particles have more positions available to them and the entropy increases.

The decrease in molecular motion that accompanies precipitation would be expected to reduce the number of accessible states and decrease the entropy. Exceptions occur, however, because solvent molecules can bind tightly to ions when they form solutions. Consequently the decreased entropy of the precipitating solute is counteracted by a larger increase in entropy of the solvent. Thus, for example, the entropy change is  $-33 \text{ J mol}^{-1} \text{ K}^{-1}$  for precipitation of  $\text{AgCl}$ , but  $+115 \text{ J mol}^{-1} \text{ K}^{-1}$  for precipitation of  $\text{MgCl}_2$ . There is no general rule for the entropy change on dissolving and precipitating when both the solute and solvent are taken into consideration.

## EXERCISES

Identify whether the entropy increases or decreases for each of the following changes and explain why.

- a) evaporation of a liquid

*Entropy increases because the number of states available to gaseous particles is greater than the number of states available to liquid particles. Gaseous particles can have many more different positions and momenta than liquid particles.*

- b) freezing of a liquid

*Entropy decreases because the number of states available to solids is fewer than for liquids. In liquids, particles tumble about freely, whereas in solids particles generally cannot rotate and are fixed in a crystal lattice structure. This decreased molecular motion corresponds to fewer accessible states and a lower entropy.*

- c) precipitation of a solid from solution

*As explained in the activity there is no general rule for dissolving and precipitating. The decrease in molecular motion that accompanies precipitation reduces the number of accessible states and decreases the entropy, but the decreased entropy of the precipitating solute can be counteracted by a larger increase in entropy of the solvent.*

- d) increase in the volume of a gas at constant temperature

*Entropy increases because increasing the volume of the gas increases the number of positions available to the particles.*

- e)  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

*Entropy increases as a solid reactant is converted to solid and gaseous products. Gases have greater entropy than solids because of the increased number of states available to them, therefore producing a gas results in a system with greater entropy.*

- f)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

*Entropy decreases as four moles of gaseous reactants are converted to two moles of gaseous product. Fewer moles of gas have fewer numbers of states available to them, therefore the entropy decreases.*

## RESEARCH

Explain how the number of states for each book arrangement set in the model was determined.

Arrangement Set	Constraint	Number of States	Determination of Number of States
A	Three books lined up alphabetically by author starting on the left with the binding facing outward and the titles on the binding facing left.	1	Only one possibility
B	Books need not be alphabetical by author but the bindings face outward and the titles face left.	6	$3! = 6$
C	Books need not be alphabetical by author, the bindings face outward, and the titles can face right and left.	48	$(3!) \times (2 \times 2 \times 2) = 48$
D	Books need not be alphabetical by author; the bindings can face outward, inward, up, or down; and the titles can face right and left.	3072	$(48) \times (4 \times 4 \times 4) = 3072$

*For Arrangement Set A, there is obviously only one arrangement in which all the books are lined up alphabetically from left to right with the books in their proper orientations.*

*For Arrangement Set B, we can choose any of three books for the leftmost position, any of the two remaining books for the second position, leaving the one remaining book for the third position. The number of possible arrangements is thus the product  $3 \times 2 \times 1 = 3! = 6$ . (In mathematics, this is referred to as the number of permutations of 3 objects.)*

*For Arrangement Set C, in each arrangement from Set B we can choose to have each of the three books face left or right. Since each of these choices is independent, we get  $2 \times 2 \times 2 = 8$  variations for each arrangement in Set B. The total number of arrangements is thus  $8 \times 6 = 48$ .*

*For Arrangement Set D, imagine taking each of the three books in Set C and rotating it so that any of the four narrow edges faces out. (This would be an especially sloppy job of shelving books!) Since each of these choices is independent, we get  $4 \times 4 \times 4 = 64$  variations for each arrangement in Set C. The total number of arrangements is thus  $48 \times 64 = 3072$ .*

*Note: Each of the Arrangement Sets is a subset of the later sets. Thus even if you don't choose to alphabetize your three books, you have a one in six chance of getting them in alphabetical order if you place them in the proper orientation. Even if you only choose to have the bindings showing, you still have a one in forty-eight chance of getting them properly organized. On the other hand, if you take no notice at all of the orientation of the books other than to have them stand on a narrow edge, you have only a one in 3072 chance of having them look as they would in a proper library.*

## Entropy of the Universe and Gibbs Free Energy

### WHY?

While entropy can be used to predict whether or not a process is spontaneous, one must consider the total entropy, i.e., the entropy of the universe, to do so accurately. This consideration leads to the concept of *free energy*, which is easier to apply because it deals only with the system being studied, not the universe. The concept of free energy is very useful. For example, you can use it to determine the concentrations of reactants and products in a chemical reaction at equilibrium, the voltage produced by batteries, and whether or not a chemical reaction will occur spontaneously.

### LEARNING OBJECTIVE

- Understand the relationship between entropy and free energy

### SUCCESS CRITERIA

- Correct prediction of increases and decreases in entropy and free energy
- Correct identification of spontaneous processes
- Accurate calculations of entropy and free energy changes

### PREREQUISITES

- **Activity 06-2:** *Internal Energy and Enthalpy*
- **Activity 14-1:** *Spontaneous Change and Entropy*

### INFORMATION

*Free energy* combines the ideas of enthalpy and entropy. Physically, the free energy change is the maximum work that can be done by a spontaneous process at constant temperature and pressure. If the process is not spontaneous, then the free energy is the minimum work needed to make the process occur.

Entropy,  $S$ , can be defined in terms of the number of states,  $W$ , that are accessible to a system with a given amount of energy:

$$S = k \ln(W) \quad \text{where } k = \text{Boltzmann's constant}$$

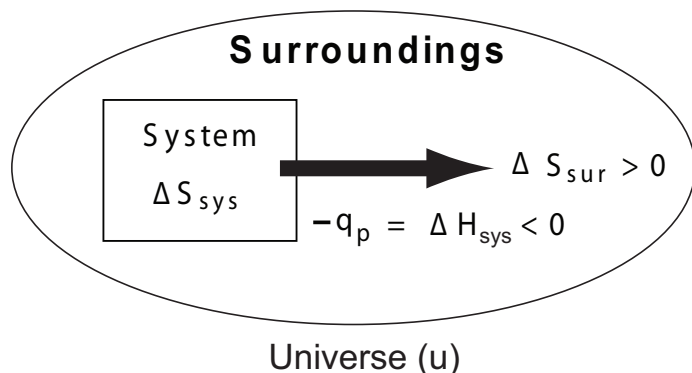
The change in entropy,  $\Delta S$ , can be defined in terms of the change in the number of accessible states or in terms of the heat flow,  $q$ , into or out of a system at constant temperature:

$$\Delta S = q/T$$

The diagram in **Model 1** depicts heat flowing from a system into the surroundings. The system plus the surroundings represents the universe. The change in energy of the system is given by  $\Delta E = q + w$ , where  $q$  is the heat added to the system and  $w$  is the work done on the system. Since the heat is leaving the system in the model, it is given a negative sign,  $-q_p$ . The change in enthalpy of the system is also negative.

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = -q_p$$

The subscript P means that the pressure is constant.

**MODEL: CHANGE IN THE ENTROPY OF THE UNIVERSE** $q_p$  = heat flow at constant pressure $S$  = entropy $G$  = Gibbs free energy $\Delta$  = difference or change in $H$  = enthalpy $T$  = temperature in K

The entropy change of the universe is the total entropy change of the system and its surroundings.

$$(1) \quad \Delta S_{\text{u}} = \Delta S_{\text{sur}} + \Delta S_{\text{sys}}$$

Heat flowing into the surroundings increases the entropy of the surroundings. Since  $\Delta H_{\text{sys}}$  is negative for an exothermic process, the following equation requires a minus sign to make  $\Delta S_{\text{sur}}$  positive, corresponding to an increase.

$$(2) \quad \Delta S_{\text{sur}} = -\Delta H_{\text{sys}} / T$$

Substituting equation (2) into equation (1) and multiplying through by  $-T$  gives equation (3).

$$(3) \quad -T \Delta S_{\text{u}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

The quantity on the right side, which depends only on the system, is defined as the free energy of the system, or more specifically the Gibbs free energy.

$$(4) \quad \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

The free energy is also related to the entropy change of the universe by equation (5)

$$(5) \quad \Delta G_{\text{sys}} = -T \Delta S_{\text{u}}$$

The free energy accounts for the entropy of the universe in terms of the enthalpy and entropy of the system. These quantities ( $\Delta G_{\text{sys}}$ ,  $\Delta H_{\text{sys}}$ ,  $\Delta S_{\text{sys}}$ ) all refer to the system so the subscript sys is not necessary and will no longer be used.

**KEY QUESTIONS**

1. A process occurring in a system can cause the entropy of the surroundings to change. In the model, what is transferred to the surroundings to cause the entropy of the surroundings to change?

*Heat flows out of the system into the surroundings to increase the entropy of the surroundings.*

2. When  $\Delta H < 0$ :

a) does the energy of the system increase or decrease?

*The energy of the system decreases.*

b) does heat flow into or out of the surroundings?

*Heat flows into the surroundings.*

c) does the entropy of the surroundings increase or decrease?

*The entropy of the surroundings increases.*

3. According to the model, what do you need to know in order to calculate the entropy change in the surroundings?

*The change in enthalpy ( $\Delta H$ ) of the system and the temperature in Kelvin must be known:*

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

4. What is the definition of the free energy change of the system in terms of the entropy of the universe?

$$\Delta G_{\text{sys}} = -T\Delta S_u$$

5. For a process to be spontaneous, what must happen to the entropy of the universe?

*The entropy of the universe must increase ( $\Delta S_u > 0$ ).*

6. For a process to be spontaneous, what must happen to the free energy of the system in which the process is occurring?

*The free energy of the system must decrease ( $\Delta G < 0$ ).*

7. Why can a change be spontaneous even if the system entropy decreases?

*A process can be spontaneous even though the system entropy decreases provided the entropy of the surroundings increases even more. For the entropy of the surroundings to increase, energy must be transferred to the surroundings so the change in enthalpy of the system must be a sufficiently large negative quantity.*

8. What is an example of a spontaneous change in which the entropy of the system decreases?

*An example of a spontaneous change where the entropy decreases is ice freezing at a temperature below its freezing point of  $0^\circ\text{C}$ . Entropy decreases as water is converted to the more ordered solid and  $\Delta S$  is negative. However, the process is exothermic due to the release of heat, so  $\Delta H$  also is negative.*

## EXERCISES

1. Show how the following key equation was derived in the model:  $\Delta G = \Delta H - T \Delta S$

$$\Delta S_u = \Delta S_{sur} + \Delta S_{sys}$$

$$\Delta S_{sur} = \frac{-\Delta H_{sys}}{T}$$

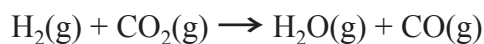
$$-T\Delta S_u = \Delta H_{sys} - T\Delta S_{sys}$$

$$\Delta G_{sys} = -\Delta H_{sys} - T\Delta S_{sys}$$

2. Calculate the change in entropy of the surroundings when 1.0 mol of water vaporizes at 100 °C. The heat of vaporization of water is 40.6 kJ/mol.

$$\begin{aligned} \Delta S_{surr} &= \frac{-\Delta H_{sys}}{T} \\ &= \frac{-(40.6 \text{ kJ/mol})(1 \text{ mol}) \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{373 \text{ K}} \\ &= -109 \text{ J / K} \end{aligned}$$

3. Calculate the free energy change for the following reaction and predict whether the reaction occurs spontaneously at 25 °C.



$$\Delta H = 41.8 \text{ kJ}, \quad \Delta S = 42.1 \text{ J/K}$$

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

$$\Delta G = 41.8 \text{ kJ} - (298 \text{ K}) \left( \frac{42.1 \text{ J}}{\text{K}} \times \frac{\text{kJ}}{1000 \text{ J}} \right)$$

$$\Delta G = 29.3 \text{ kJ}$$

*The reaction is not spontaneous because  $\Delta G > 0$ .*

4. The table below shows all the possible combinations of signs for the entropy and enthalpy changes in any process. Enter a +, −, or T in the  $\Delta G$  column to correspond to these changes. Use T for temperature if the sign of  $\Delta G$  depends on the temperature. If there is a temperature effect, specify whether the reaction is spontaneous at a high or a low temperature.

$\Delta S$	$\Delta H$	$\Delta G$ + or − or T	Spontaneous? enter yes or no or specify if it is spontaneous at a high T or low T
+	−	−	Yes, spontaneous at all temperatures
−	+	+	No, non-spontaneous at all temperatures
+	+	T	Spontaneous only at temperatures above $T = \frac{\Delta H}{\Delta S}$
−	−	T	Spontaneous only at temperatures below $T = \frac{\Delta H}{\Delta S}$

5. Is an exothermic reaction or process always spontaneous? Explain.

*An exothermic process will be spontaneous if  $\Delta S > 0$ , or if  $\Delta S < 0$  when the temperature is*

*below  $T = \frac{\Delta H}{\Delta S}$ .*

6. Can an endothermic reaction or process be spontaneous? Explain.

*Endothermic reactions are spontaneous only if the reaction proceeds with an increase in*

*entropy and if the temperature is above  $T = \frac{\Delta H}{\Delta S}$*

7. Generally when biological enzymes are heated, they lose their catalytic activity. The process is endothermic and spontaneous. Is the structure of the active enzyme more or less ordered than the inactive enzyme? Explain.

*Endothermic reactions are spontaneous only if the reaction proceeds with an increase in*

*entropy ( $\Delta S > 0$ ) and if the temperature is above  $T = \frac{\Delta H}{\Delta S}$ . Therefore we conclude that*

*$\Delta S > 0$  which means the structure of the inactive enzyme is more disordered than the active enzyme.*