

Free Energy

When will a reaction happen spontaneously?

Why?

Some reactions happen without us doing anything. Leave a piece of metal out in the weather, and you get rust. Lower the temperature of water below its freezing point, and it turns into ice. Other reactions need help. As you can imagine, it is important for chemists to understand which reactions are which. You would not want a reaction to spontaneously start when you were not ready for it to do so. Chemists need a way to predict the spontaneity of a reaction.

Model 1 – Spontaneous Processes

| | Process Description | Change in Enthalpy (ΔH) | Change in Entropy (ΔS) | Spontaneous? |
|---|--|-----------------------------------|----------------------------------|---|
| A | Two pure substances \rightarrow Homogeneous mixture | ~ 0 | Increasing | Yes |
| B | Salt + Water \rightarrow Salt water solution | ~ 0 | Increasing | Yes |
| C | $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ | Exothermic (negative) | Increasing (positive) | Yes |
| D | $\text{C}_3\text{H}_8(\text{l}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$ | Exothermic | Increasing | Yes |
| E | $6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g})$ | Endothermic | Decreasing | No |
| F | Glucose \rightarrow Starch | Endothermic | Decreasing | No |
| G | Liquid water \rightarrow Ice | Exothermic | Decreasing | Below 0°C , Yes Above 0°C , No |
| H | Cold water (25°C) \rightarrow Hot water (60°C) | Endothermic | Increasing | Below 60°C , No Above 60°C , Yes |

1. Consider Model 1.
 - a. What two terms are used to describe the enthalpy changes for the reactions?
 - b. What is the symbol for the change in enthalpy?
 - c. What sign (+ or $-$) does the change in enthalpy have when the reaction releases heat energy to the surroundings?

2. Refer to Model 1. For each process below indicate if the change would be endothermic or exothermic.

a. A plant making glucose from carbon dioxide and water.

b. An ice cube melting.

c. Synthesis of hydrogen peroxide from water and oxygen.



3. According to Model 1, are all exothermic reactions spontaneous? If no, provide a counter example from Model 1.



4. Consider Model 1.

a. What is the symbol for the change in entropy of a system?

b. When the entropy of a system increases, what sign (+ or -) is used?

5. According to Model 1, is there a relationship between the change in enthalpy and the change in entropy for a system or do they appear to be unrelated? If yes, describe the relationship.

6. Refer to Model 1. For each process below, indicate if the entropy would increase or decrease.

a. Food coloring mixing into water.

b. A hot substance cooling to room temperature.

c. The respiration of glucose and oxygen to produce carbon dioxide and water.

7. For each of the processes in Model 1, decide as a group if the molecules in the substances have more order (are more organized) before or after the reaction. Circle the side of the reaction with more order.

8. Is there a correlation between the level of organization in the molecules and a change in entropy according to the examples in Model 1? Justify your reasoning.



Read This!

The **entropy** of a system can be thought of as a measurement of the amount of disorder in the molecules that make up the system. The study of entropy is based in statistics. There are only a few ways in which a system can be organized and have low entropy, but there are usually many more ways in which a system can be disorganized and have high entropy. Therefore, systems are more likely to exist in higher entropy states. Think of your bedroom at home. If you do not spend energy to clean it, is it likely to be organized or disorganized?

9. Predict if the following processes would have an increase in entropy or a decrease in entropy based on what you have learned from Model 1.
 - a. Water evaporating from a wet sidewalk.
 - b. Separating a mixture into pure substances.
 - c. The cooling of molten metal.
 - d. Decomposition of a compound into its elements.

-  10. Is an increase in entropy of a system sufficient to make a process spontaneous? Justify your reasoning with evidence from Model 1.

Read This!

Some of the processes in Model 1 are **spontaneous**—that is they will occur without any additional work being done on the system. For example, a solute will dissolve in water until it reaches saturation. However, glucose will not spontaneously form from carbon dioxide and water in the atmosphere. The **Second Law of Thermodynamics** states that a process will be spontaneous when it results in an increase of total entropy in the universe. In other words, either the system, the surroundings or both must have an increase in entropy. *Note:* the term “spontaneous” does not imply that the change will happen quickly. Rusting is spontaneous under the right conditions, but still occurs very slowly.

11. Consider the exothermic reactions in Model 1. When those reactions occur, what typically happens to the temperature of the surroundings?

-  12. Predict the change in entropy of the surroundings for an exothermic reaction.

13. Predict the change in entropy of the surroundings for an endothermic reaction.



14. Provide the letter of at least one process from Model 1 that illustrates each of the following conditions that will result in a spontaneous reaction.
- Both the system and surroundings have an increase in entropy.
 - The increase in entropy of the system exceeds the decrease in entropy of the surroundings.
 - The increase in entropy of the surroundings exceeds the decrease in entropy of the system.

Read This!

When a process is spontaneous, it can be used to do work. For example, we burn fuels via combustion to heat food or move vehicles. The amount of work that can be done by a spontaneous process is called **Gibbs free energy**, named after the mathematician who developed the concept in 1873. Josiah Willard Gibbs proposed this equation, which scientists use to calculate the free energy change for a process.

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


When ΔG is negative, the process is spontaneous and can do work (**exergonic**). When ΔG is positive, the process is not spontaneous, and work must be done on the system to make it happen (**endergonic**).

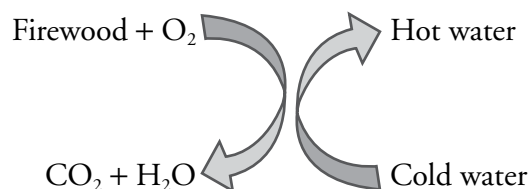
15. Consider the signs (+ or -) on the enthalpy and entropy of process C in Model 1. Use the Gibbs free energy equation to explain why process C is a spontaneous reaction.
16. Consider the signs (+ or -) on the enthalpy and entropy of process E in Model 1. Use the Gibbs free energy equation to explain why process E is not a spontaneous reaction.
17. Processes A and B in Model 1 have very minimal energy changes. Explain why those processes are spontaneous.

18. Consider process G in Model 1.
- What is the entropy change for the system?
 - What is the entropy change for the surroundings?

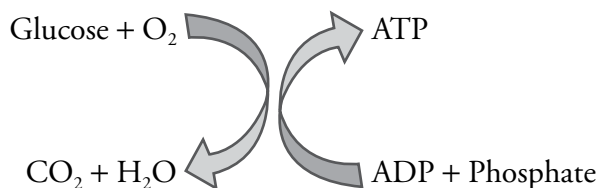
Read This!

We use **coupled processes** all the time to make things happen in life. In other words, a spontaneous reaction, which provides “free energy” and can do work, is used to make a nonspontaneous reaction happen. For example, your mobile device will not play music or light up spontaneously, but couple it with a battery containing a spontaneous chemical process and suddenly you can dance, text and play all afternoon.

-  19. If you have ever been camping, you may have used coupled processes to make yourself some hot cocoa in the evening.



- Which of the processes above is exergonic, and does work?
 - Which of the processes above is endergonic, and has work done to it?
20. Biological systems utilize coupled processes all the time to support life. Consider the coupled processes below.



- Which of the processes above is exergonic and does work?
- Which of the processes above is endergonic and has work done to it?



Extension Questions

21. Are the terms exothermic and exergonic synonymous? Justify your answer with examples.

22. Life cannot exist in a completely closed system (no energy or matter comes into or out of the system).
 - a. Explain why this is true based on the Second Law of Thermodynamics.

 - b. The planet Earth is not a closed system. Ultimately, what is the source of all energy for life on Earth?

23. Consider a process where the increase in entropy of the system is exactly equal to the decrease in entropy of the surroundings. Would that process be spontaneous? Justify your reasoning.

24. Consider the burning of a piece of paper.
 - a. Is the combustion of paper endothermic or exothermic?

 - b. Does the entropy of the system increase or decrease when paper burns? Explain your reasoning.

 - c. Predict the sign of ΔG for the burning of paper. Is the combustion of paper spontaneous according to ΔG ?

 - d. Why would a match be necessary for this reaction to proceed? Explain using thermodynamic terms.