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

<table>
<thead>
<tr>
<th>Process Description</th>
<th>Change in Enthalpy (ΔH)</th>
<th>Change in Entropy (ΔS)</th>
<th>Spontaneous?</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Two pure substances → Homogeneous mixture</td>
<td>~ 0</td>
<td>Increasing</td>
<td>Yes</td>
</tr>
<tr>
<td>B Salt + Water → Salt water solution</td>
<td>~ 0</td>
<td>Increasing</td>
<td>Yes</td>
</tr>
<tr>
<td>C 2H₂O₂(l) → 2H₂O(l) + O₂(g)</td>
<td>Exothermic (negative)</td>
<td>Increasing (positive)</td>
<td>Yes</td>
</tr>
<tr>
<td>D C₃H₈(l) + 5O₂(g) → 3CO₂(g) + 4H₂O(g)</td>
<td>Exothermic</td>
<td>Increasing</td>
<td>Yes</td>
</tr>
<tr>
<td>E 6CO₂(g) + 6H₂O(g) → C₆H₁₂O₆(s) + 6O₂(g)</td>
<td>Endothermic</td>
<td>Decreasing</td>
<td>No</td>
</tr>
<tr>
<td>F Glucose → Starch</td>
<td>Endothermic</td>
<td>Decreasing</td>
<td>No</td>
</tr>
<tr>
<td>G Liquid water → Ice</td>
<td>Exothermic</td>
<td>Decreasing</td>
<td>Below 0 °C, Yes Above 0 °C, No</td>
</tr>
<tr>
<td>H Cold water (25 °C) → Hot water (60 °C)</td>
<td>Endothermic</td>
<td>Increasing</td>
<td>Below 60 °C, No Above 60 °C, Yes</td>
</tr>
</tbody>
</table>

1. Consider Model 1.

a. What two terms are used to describe the enthalpy changes for the reactions?

Enthalpy changes are described as endothermic or exothermic.

b. What is the symbol for the change in enthalpy?

The symbol for the change in enthalpy is ΔH.

c. What sign (+ or −) does the change in enthalpy have when the reaction releases heat energy to the surroundings?

Energy is released to the surroundings when the process is exothermic. The ΔH in that case is negative.

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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.
   Endothermic.

b. An ice cube melting.
   Endothermic.

c. Synthesis of hydrogen peroxide from water and oxygen.
   Endothermic.

3. According to Model 1, are all exothermic reactions spontaneous? If not, provide a counter example from Model 1.

   No. Process G is exothermic, but only spontaneous under certain conditions.

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

b. When the entropy of a system increases, what sign (+ or −) is used?
   An increase in entropy is signified by a positive value.

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.

   There is no relationship. There are examples in Model 1 of both endothermic and exothermic reactions that have an increase in entropy.

6. Refer to Model 1. For each process below, indicate if the entropy would increase or decrease.
   
a. Food coloring mixing into water.
   This is an increase in entropy.

b. A hot substance cooling to room temperature.
   This is a decrease in entropy.

c. The respiration of glucose and oxygen to produce carbon dioxide and water.
   This is an increase in entropy.

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.

   See Model 1. Generally, solids are more ordered than liquids, and solutions are less ordered than the pure substances that form them.

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.

   Yes, there is a correlation between the level of organization in the molecules and the change in entropy. As the system becomes more disorganized and random, the entropy increases.
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.  
      This would be an increase in entropy.
   b. Separating a mixture into pure substances.  
      This would be a decrease in entropy.
   c. The cooling of molten metal.  
      This would be a decrease in entropy.
   d. Decomposition of a compound into its elements.  
      This would be an increase in entropy.

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

   No. Process H in Model 1 has increasing entropy and is only spontaneous under certain conditions.

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?

   The energy released from the exothermic reaction typically increases the temperature of the surroundings.

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

   Because the temperature went up, the entropy of the surroundings increased. Increased temperatures cause atmospheric gas molecules to move in more random, disorganized ways.

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

   Because the temperature will go down, the entropy of the surroundings decreases, since atmospheric molecules will move at slower speeds.

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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.
   a. Both the system and surroundings have an increase in entropy.
      Processes C and D
   b. The increase in entropy of the system exceeds the decrease in entropy of the surroundings.
      Process H above 60 °C
   c. The increase in entropy of the surroundings exceeds the decrease in entropy of the system.
      Process G below 0 °C

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 \( \Delta G \) is negative, the process is spontaneous and can do work (exergonic). When \( \Delta G \) 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.
   In process C, the change in enthalpy is negative, and the change in entropy is positive.
   \[ \Delta G = \Delta H - T \Delta S \]
   A negative number minus a positive number will always result in a negative number. Therefore, \( \Delta G \) will always be negative, and the reaction will be spontaneous.

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.
   In process E, the change in enthalpy is positive, and the change in entropy is negative.
   \[ \Delta G = \Delta H - T \Delta S \]
   A positive number minus a negative number will always result in a positive number. Therefore, \( \Delta G \) will always be positive, and the reaction will never be spontaneous.

17. Processes A and B in Model 1 have very minimal energy changes. Explain why those processes are spontaneous.
   In these processes, the change in enthalpy is near zero so the only factor that must be considered is the entropy of the system. Both processes have an increase in the entropy of the system, and therefore, \( \Delta G \) will be negative.
18. Consider process G in Model 1.
   
a. What is the entropy change for the system?
   
   *Process G has a decrease in entropy.*
   
b. What is the entropy change for the surroundings?
   
   *The process is exothermic, so the entropy of the surroundings increases.*

**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.

```
Firewood + O₂  Hot water
  ⬅️
CO₂ + H₂O  Cold water
```

   a. Which of the processes above is exergonic, and does work?
   
   *The burning of firewood is exergonic.*
   
b. Which of the processes above is endergonic, and has work done to it?
   
   *The heating of water is endergonic.*

20. Biological systems utilize coupled processes all the time to support life. Consider the coupled processes below.

```
Glucose + O₂  ATP
  ⬅️
CO₂ + H₂O  ADP + Phosphate
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   a. Which of the processes above is exergonic and does work?
   
   *The respiration of glucose in the cells is exergonic.*
   
b. Which of the processes above is endergonic and has work done to it?
   
   *The formation of ATP is endergonic.*

**STOP**
Extension Questions

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

No. The term exothermic only refers to the exchange of thermal energy between the system and the surroundings. The term exergonic refers to whether or not free energy is available from the process.

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.

      For life to exist in a completely closed system, there must be more exergonic processes than endergonic processes. If energy was not available from outside the system, this could not be the case.

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

      Energy from the sun provides all life on Earth with free energy.

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.

No, that process would not be spontaneous because there would be no free energy available to make the process happen.

24. Consider the burning of a piece of paper.

   a. Is the combustion of paper endothermic or exothermic?

      The combustion of paper is exothermic.

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

      The products of combustion are many more moles of gas, so the entropy would increase.

   c. Predict the sign of $\Delta G$ for the burning of paper. Is the combustion of paper spontaneous according to $\Delta G$?

      The sign of $\Delta G$ for the burning of paper should be negative because both the enthalpy and entropy are favorable. This means that the combustion of paper is spontaneous.

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

      Although the reaction is thermodynamically favorable, it is not kinetically favorable. The rate is too slow because of a large activation energy requirement. The match is needed to overcome the activation energy requirement.