

## 9.1 Introduction to Entropy

Essential knowledge statements from the AP Chemistry CED:

- Entropy increases when matter becomes more dispersed. For example, the phase change from solid to liquid or from liquid to gas results in a dispersal of matter as the individual particles become freer to move and generally occupy a larger volume. Similarly, for a gas, the entropy increases when there is an increase in volume (at constant temperature), and the gas molecules are able to move within a larger space. For reactions involving gas-phase reactants or products, the entropy generally increases when the total number of moles of gas-phase products is greater than the total number of moles of gas-phase reactants.
  - Entropy increases when energy is dispersed. According to kinetic molecular theory (KMT), the distribution of kinetic energy among the particles of a gas broadens as the temperature increases. As a result, the entropy of the system increases with an increase in temperature.
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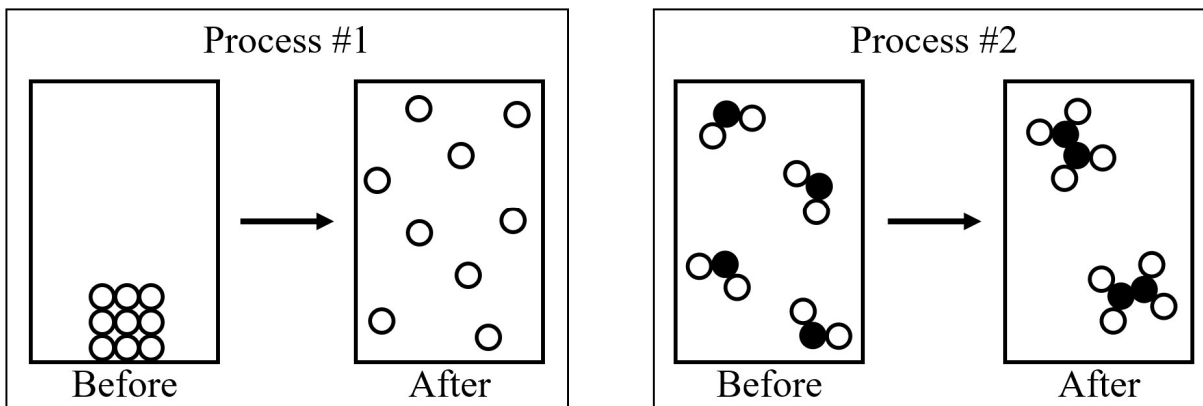
The change in entropy ( $\Delta S$ ) is related to changes associated with the dispersal of matter and/or energy.

- The following situations would result in a positive  $\Delta S$ .
  - the particles of matter are more dispersed
  - there is a greater number of possible arrangements of the particles
  - there is a greater distribution of kinetic energy among the particles
- The following situations would result in a negative  $\Delta S$ .
  - the particles of matter are less dispersed (or more ordered)
  - there is a smaller number of possible arrangements of the particles
  - there is a smaller distribution of kinetic energy among the particles

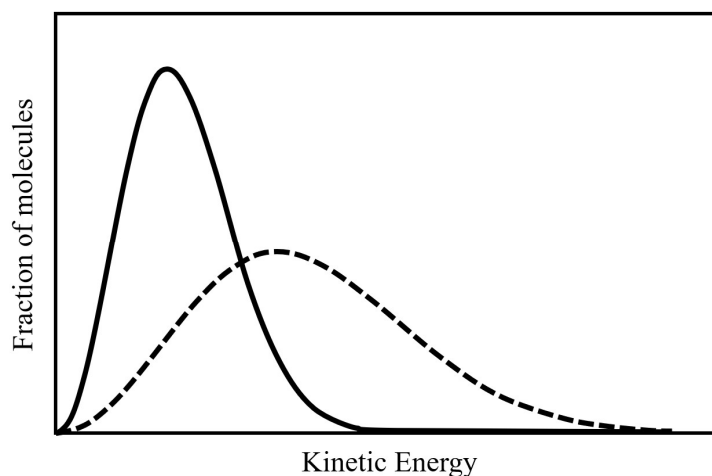
1. For each of the following, indicate the sign (+ or -) of  $\Delta S$  associated with the change.

Change	$\Delta S$
$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$	
$\text{CH}_3\text{OH}(l) \rightarrow \text{CH}_3\text{OH}(g)$	
$\text{CO}_2(s) \rightarrow \text{CO}_2(g)$	
$\text{NH}_4\text{NO}_3(s) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)$	
$2 \text{KClO}_3(s) \rightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g)$	
$\text{PCl}_5(g) \rightarrow \text{PCl}_3(g) + \text{Cl}_2(g)$	

Change	$\Delta S$
$\text{C}_6\text{H}_6(l) \rightarrow \text{C}_6\text{H}_6(s)$	
$\text{Br}_2(g) \rightarrow \text{Br}_2(l)$	
$\text{I}_2(g) \rightarrow \text{I}_2(s)$	
$\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$	
$4 \text{Fe}(s) + 3 \text{O}_2(g) \rightarrow 2 \text{Fe}_2\text{O}_3(s)$	
$\text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g)$	



2. Particulate representations for two different processes are shown above. Indicate whether the entropy of the system decreases or increases for each process. Justify your answers in terms of the arrangement of the particles.



3. The diagram above shows two different Maxwell-Boltzmann distributions of kinetic energies. These two curves represent identical samples of  $\text{He}(g)$  at two different temperatures.
- The curve represented by the dashed line represents the sample that is at a ( lower higher ) temperature.
  - When the temperature of a sample of gas is increased, this results in a ( narrower broader ) distribution of kinetic energies.
  - A broader distribution of kinetic energies is associated with a greater dispersal of energy. Therefore when the temperature of a gas sample is increased, the entropy of the gas sample ( decreases increases ).

## 9.2 Absolute Entropy and Entropy Change

Essential knowledge statement from the AP Chemistry CED:

- The entropy change for a process can be calculated from the absolute entropies of the species involved before and after the process occurs.

$$\Delta S_{rxn}^{\circ} = \sum S^{\circ}(\text{products}) - \sum S^{\circ}(\text{reactants})$$

The quantity  $S^{\circ}$  represents the standard molar entropy at standard conditions, which are defined as follows.

Standard Conditions		
gas pressure = 1 atm	solution concentration = 1 mol/L	temperature = 25°C = 298 K

The absolute entropy of a substance ( $S^{\circ}$ ) is normally reported in units of J/(K·mol).

The standard entropy change for a physical or chemical change ( $\Delta S^{\circ}$ ) is normally reported in units of J/(K·mol<sub>rxn</sub>).

In Topic 6.8 (Enthalpy of Formation), you learned that the standard enthalpy of formation ( $\Delta H_f^{\circ}$ ) for an element in its standard state is equal to zero.

The standard molar entropy of an element in its standard state is not equal to zero.

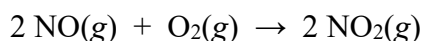
4. (a) Use the data in the table at right to calculate the value of the standard entropy change,  $\Delta S_{rxn}^{\circ}$ , in units of J/(K·mol<sub>rxn</sub>), for the reaction represented by the following equation.



Substance	$S^{\circ}$ (J/(K·mol))
CaCO <sub>3</sub> (s)	92.9
CaO(s)	38.1
CO <sub>2</sub> (g)	213.8

- (b) How does the entropy of the system change as this reaction occurs? \_\_\_\_\_

5. (a) Use the data in the table at right to calculate the value of the standard entropy change,  $\Delta S_{rxn}^{\circ}$ , in units of J/(K·mol<sub>rxn</sub>), for the reaction represented by the following equation.



Substance	$S^{\circ}$ (J/(K·mol))
NO(g)	210.7
O <sub>2</sub> (g)	205.0
NO <sub>2</sub> (g)	240.0

- (b) How does the entropy of the system change as this reaction occurs? \_\_\_\_\_

### 9.3 Gibbs Free Energy and Thermodynamic Favorability

Essential knowledge statements from the AP Chemistry CED:

- The Gibbs free energy change for a chemical process in which all the reactants and products are present in a standard state (as pure substances, as solutions of 1.0 M concentration, or as gases at a pressure of 1.0 atm (or 1.0 bar)) is given the symbol  $\Delta G^\circ$ .
- The standard Gibbs free energy change for a chemical or physical process is a measure of thermodynamic favorability. Historically, the term “spontaneous” has been used to describe processes for which  $\Delta G^\circ < 0$ . The phrase “thermodynamically favored” is preferred instead so that common misunderstandings (equating “spontaneous” with “suddenly” or “without cause”) can be avoided. When  $\Delta G^\circ < 0$  for the process, it is said to be thermodynamically favored.
- The standard Gibbs free energy change for a physical or chemical process may also be determined from the standard Gibbs free energy of formation of the reactants and products.
  - $\Delta G_{rxn}^\circ = \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants})$
- In some cases, it is necessary to consider both enthalpy and entropy to determine if a process will be thermodynamically favored. The freezing of water and the dissolution of sodium nitrate are examples of such phenomena.
- Knowing the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for a process at a given temperature allows  $\Delta G^\circ$  to be calculated directly.
  - $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- In general, the temperature conditions for a process to be thermodynamically favored ( $\Delta G^\circ < 0$ ) can be predicted from the signs of  $\Delta H^\circ$  and  $\Delta S^\circ$  as shown in the table below.

$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ < 0$ , favored at:
–	+	all temperatures
+	–	no temperatures
+	+	high temperatures
–	–	low temperatures

- In cases where  $\Delta H^\circ < 0$  and  $\Delta S^\circ > 0$ , no calculation of  $\Delta G^\circ$  is necessary to determine that the process is thermodynamically favored ( $\Delta G^\circ < 0$ ).
- In cases where  $\Delta H^\circ > 0$  and  $\Delta S^\circ < 0$ , no calculation of  $\Delta G^\circ$  is necessary to determine that the process is thermodynamically unfavored ( $\Delta G^\circ > 0$ ).

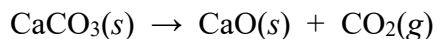
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The **free energy** of a system represents the amount of work that the system can perform on the surroundings.

If the change in free energy ( $\Delta G$ ) for a certain process is negative, then the forward process (from left to right) is thermodynamically favored to occur. The magnitude of  $\Delta G$  represents the amount of energy released when the forward process occurs, and this energy is available to do work on the surroundings.

If the change in free energy ( $\Delta G$ ) for a certain process is positive, then the forward process (from left to right) is not thermodynamically favored. Instead, the reverse process (from right to left) is favored. The magnitude of  $\Delta G$  represents the amount of energy that must be transferred from the surroundings to the system in order for the forward process to occur.

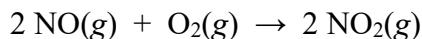
6. (a) Use the data in the table at right to calculate the value of the standard free energy change,  $\Delta G_{rxn}^{\circ}$ , in units of kJ/mol<sub>rxn</sub>, for the reaction represented by the following equation.



Substance	$\Delta G_f^{\circ}$ (kJ/mol)
CaCO <sub>3</sub> (s)	-1128.8
CaO(s)	-603.3
CO <sub>2</sub> (g)	-394.4

- (b) Is this reaction thermodynamically favored under standard conditions? \_\_\_\_\_

7. (a) Use the data in the table at right to calculate the value of the standard free energy change,  $\Delta G_{rxn}^{\circ}$ , in units of kJ/mol<sub>rxn</sub>, for the reaction represented by the following equation.



Substance	$\Delta G_f^{\circ}$ (kJ/mol)
NO(g)	86.6
O <sub>2</sub> (g)	0
NO <sub>2</sub> (g)	51.3

- (b) Is this reaction thermodynamically favored under standard conditions? \_\_\_\_\_

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

The Gibbs free energy equation is shown above. The variable  $T$  refers to the absolute temperature in units of Kelvins. The degree symbol ( $^{\circ}$ ) refers to a process that occurs at standard conditions.

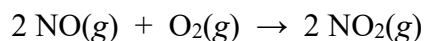


$$\Delta G_{rxn}^{\circ} = +131.1 \text{ kJ/mol}_{rxn} \quad \Delta H_{rxn}^{\circ} = +178.5 \text{ kJ/mol}_{rxn} \quad \Delta S_{rxn}^{\circ} = +159.0 \text{ J/(K}\cdot\text{mol}_{rxn})$$

8. Consider the information shown above. Which of the following statements best explains why this reaction is NOT thermodynamically favored under standard conditions?

\_\_\_\_\_ The change in enthalpy is positive, which does not support the favorability of the reaction.

\_\_\_\_\_ The change in entropy is positive, which does not support the favorability of the reaction.



$$\Delta G_{rxn}^{\circ} = -70.6 \text{ kJ/mol}_{rxn} \quad \Delta H_{rxn}^{\circ} = -114.2 \text{ kJ/mol}_{rxn} \quad \Delta S_{rxn}^{\circ} = -146.4 \text{ J/(K}\cdot\text{mol}_{rxn})$$

9. Consider the information shown above. Which of the following statements best explains why this reaction IS thermodynamically favored under standard conditions?

\_\_\_\_\_ The change in enthalpy is negative, which supports the favorability of the reaction.

\_\_\_\_\_ The change in entropy is negative, which supports the favorability of the reaction.

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### Driving Forces That Support the Thermodynamic Favorability of a Process

You can think of a “driving force” as a feature of a physical or chemical process that helps to explain why that process is thermodynamically favored to occur. There are two possibilities for a driving force.

- If the process is exothermic (i.e.,  $\Delta H$  is negative), this could be a driving force to explain why the process is thermodynamically favored to occur.
- If the process involves an increase in entropy (i.e.,  $\Delta S$  is positive), this could be a driving force to explain why the process is thermodynamically favored to occur.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

Another way to think about the driving force of a process is to look at the **signs** of  $\Delta H$  and  $\Delta S$  for that process. Ask yourself the following question. “Does the sign of  $\Delta H$  (or  $\Delta S$ ) cause the value of  $\Delta G$  to be negative?”

- If the process is endothermic (i.e.,  $\Delta H$  is positive), this cannot be a driving force to explain why the process is thermodynamically favored to occur.
- If the process involves a decrease in entropy (i.e.,  $\Delta S$  is negative), this cannot be a driving force to explain why the process is thermodynamically favored to occur.



10. The process represented by the equation above is thermodynamically favored to occur at 298 K. When a small amount of  $\text{NH}_4\text{NO}_3(s)$  is added to a sample of water and the mixture is stirred, all of the solid dissolves. The temperature of the solution decreases. Answer the following questions related to the process of dissolving  $\text{NH}_4\text{NO}_3(s)$  in water.

(a) The sign of  $\Delta H^{\circ}$  for this process is ( negative   positive ).

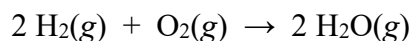
(b) The sign of  $\Delta S^{\circ}$  for this process is ( negative   positive ).

(c) What is the driving force for this process? (Circle one of the following.)

enthalpy only

entropy only

both enthalpy and entropy



11. The process represented by the equation above is thermodynamically favored to occur at 298 K. A mixture of hydrogen gas and oxygen gas is sparked to initiate a chemical reaction. Water vapor is produced, and heat and light are released. Answer the following questions related to this chemical reaction.

- (a) The sign of  $\Delta H^\circ$  for this reaction is ( negative   positive ).
- (b) The sign of  $\Delta S^\circ$  for this reaction is ( negative   positive ).
- (c) What is the driving force for this process? (Circle one of the following.)

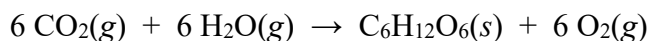
enthalpy only

entropy only

both enthalpy and entropy

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

$\Delta H^\circ$	Meaning	$\Delta S^\circ$	Meaning	Is the forward process thermodynamically favored?	The driving force that justifies why the reaction is thermodynamically favored
+	endothermic process	-	entropy decreases	Not favored at any T	N/A
-	exothermic process	+	entropy increases	Favored at all T	both enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ )
+	endothermic process	+	entropy increases	Favored at high T	entropy ( $\Delta S^\circ$ ) only
-	exothermic process	-	entropy decreases	Favored at low T	enthalpy ( $\Delta H^\circ$ ) only



12. Answer the following questions related to the reaction represented by the equation shown above.

- (a) Use the data in the table at right to calculate the value of the standard enthalpy change,  $\Delta H_{rxn}^{\circ}$ , in units of  $\text{kJ/mol}_{rxn}$ , for the reaction represented by the equation shown above.

Substance	$\Delta H_f^{\circ}$ (kJ/mol)
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{g})$	-241.8
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1274.4
$\text{O}_2(\text{g})$	0

- (b) Use the data in the table at right to calculate the value of the standard entropy change,  $\Delta S_{rxn}^{\circ}$ , in units of  $\text{J}/(\text{K}\cdot\text{mol}_{rxn})$ , for the reaction represented by the equation shown above.

Substance	$S^{\circ}$ (J/(K·mol))
$\text{CO}_2(\text{g})$	213.8
$\text{H}_2\text{O}(\text{g})$	188.8
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	212.1
$\text{O}_2(\text{g})$	205.0

- (c) Use the Gibbs free energy equation and your answers to parts (a) and (b) to calculate the value of the standard free energy change,  $\Delta G_{rxn}^{\circ}$ , in units of  $\text{kJ/mol}_{rxn}$ , for the reaction represented by the equation shown above. The temperature at standard conditions is 298 K. Pay attention to the units in your calculations. The units of  $\Delta H_{rxn}^{\circ}$  ( $\text{kJ/mol}_{rxn}$ ) are different than the units of  $\Delta S_{rxn}^{\circ}$  ( $\text{J}/(\text{K}\cdot\text{mol}_{rxn})$ ).

- (d) Is this reaction thermodynamically favored at 298 K? \_\_\_\_\_

- (e) Circle the situation that best describes this reaction.

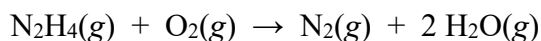
Not favored  
at any T

Favored  
at all T

Favored  
at high T

Favored  
at low T





13. Answer the following questions related to the reaction represented by the equation shown above.

- (a) Use the data in the table at right to calculate the value of the standard enthalpy change,  $\Delta H_{rxn}^{\circ}$ , in units of  $\text{kJ/mol}_{rxn}$ , for the reaction represented by the equation shown above.

Substance	$\Delta H_f^{\circ}$ (kJ/mol)
$\text{N}_2\text{H}_4(\text{g})$	95.4
$\text{O}_2(\text{g})$	0
$\text{N}_2(\text{g})$	0
$\text{H}_2\text{O}(\text{g})$	-241.8

- (b) Use the data in the table at right to calculate the value of the standard entropy change,  $\Delta S_{rxn}^{\circ}$ , in units of  $\text{J}/(\text{K}\cdot\text{mol}_{rxn})$ , for the reaction represented by the equation shown above.

Substance	$S^{\circ}$ ( $\text{J}/(\text{K}\cdot\text{mol})$ )
$\text{N}_2\text{H}_4(\text{g})$	238.5
$\text{O}_2(\text{g})$	205.0
$\text{N}_2(\text{g})$	191.5
$\text{H}_2\text{O}(\text{g})$	188.8

- (c) Use the Gibbs free energy equation and your answers to parts (a) and (b) to calculate the value of the standard free energy change,  $\Delta G_{rxn}^{\circ}$ , in units of  $\text{kJ/mol}_{rxn}$ , for the reaction represented by the equation shown above. The temperature at standard conditions is 298 K. Pay attention to the units in your calculations. The units of  $\Delta H_{rxn}^{\circ}$  ( $\text{kJ/mol}_{rxn}$ ) are different than the units of  $\Delta S_{rxn}^{\circ}$  ( $\text{J}/(\text{K}\cdot\text{mol}_{rxn})$ ).

- (d) Is this reaction thermodynamically favored at 298 K? \_\_\_\_\_

- (e) Circle the situation that best describes this reaction.

Not favored  
at any T

Favored  
at all T

Favored  
at high T

Favored  
at low T



14. Answer the following questions related to the reaction represented by the equation shown above.

- (a) Use the data in the table at right to calculate the value of the standard enthalpy change,  $\Delta H_{rxn}^{\circ}$ , in units of  $\text{kJ/mol}_{rxn}$ , for the reaction represented by the equation shown above.

Substance	$\Delta H_f^{\circ}$ (kJ/mol)
$\text{CH}_3\text{OH}(g)$	-200.7
$\text{CO}(g)$	-110.5
$\text{H}_2(g)$	0

- (b) Use the data in the table at right to calculate the value of the standard entropy change,  $\Delta S_{rxn}^{\circ}$ , in units of  $\text{J}/(\text{K}\cdot\text{mol}_{rxn})$ , for the reaction represented by the equation shown above.

Substance	$S^{\circ}$ ( $\text{J}/(\text{K}\cdot\text{mol})$ )
$\text{CH}_3\text{OH}(g)$	239.9
$\text{CO}(g)$	197.7
$\text{H}_2(g)$	130.6

- (c) Use the Gibbs free energy equation and your answers to parts (a) and (b) to calculate the value of the standard free energy change,  $\Delta G_{rxn}^{\circ}$ , in units of  $\text{kJ/mol}_{rxn}$ , for the reaction represented by the equation shown above. The temperature at standard conditions is 298 K. Pay attention to the units in your calculations. The units of  $\Delta H_{rxn}^{\circ}$  ( $\text{kJ/mol}_{rxn}$ ) are different than the units of  $\Delta S_{rxn}^{\circ}$  ( $\text{J}/(\text{K}\cdot\text{mol}_{rxn})$ ).

(d) Is this reaction thermodynamically favored at 298 K? \_\_\_\_\_

- (e) Circle the situation that best describes this reaction.

Not favored  
at any T

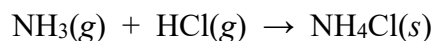
Favored  
at all T

Favored  
at high T

Favored  
at low T

- (f) Use the Gibbs free energy equation and your answers to parts (a) and (b) to calculate the value of  $\Delta G_{rxn}$ , in units of  $\text{kJ/mol}_{rxn}$ , for this reaction at temperatures of 200 K and 500 K. Assume that the values of  $\Delta H_{rxn}^{\circ}$  and  $\Delta S_{rxn}^{\circ}$  do not change significantly when the temperature is changed.

$\Delta G_{rxn}$ at 200 K	$\Delta G_{rxn}$ at 500 K



15. Answer the following questions related to the reaction represented by the equation shown above.

- (a) Use the data in the table at right to calculate the value of the standard enthalpy change,  $\Delta H_{rxn}^{\circ}$ , in units of  $\text{kJ/mol}_{rxn}$ , for the reaction represented by the equation shown above.

Substance	$\Delta H_f^{\circ}$ (kJ/mol)
$\text{NH}_3(\text{g})$	-46.1
$\text{HCl}(\text{g})$	-92.3
$\text{NH}_4\text{Cl}(\text{s})$	-314.4

- (b) Use the data in the table at right to calculate the value of the standard entropy change,  $\Delta S_{rxn}^{\circ}$ , in units of  $\text{J}/(\text{K}\cdot\text{mol}_{rxn})$ , for the reaction represented by the equation shown above.

Substance	$S^{\circ}$ ( $\text{J}/(\text{K}\cdot\text{mol})$ )
$\text{NH}_3(\text{g})$	192.5
$\text{HCl}(\text{g})$	186.9
$\text{NH}_4\text{Cl}(\text{s})$	94.6

- (c) Use the Gibbs free energy equation and your answers to parts (a) and (b) to calculate the value of the standard free energy change,  $\Delta G_{rxn}^{\circ}$ , in units of  $\text{kJ/mol}_{rxn}$ , for the reaction represented by the equation shown above. The temperature at standard conditions is 298 K. Pay attention to the units in your calculations. The units of  $\Delta H_{rxn}^{\circ}$  ( $\text{kJ/mol}_{rxn}$ ) are different than the units of  $\Delta S_{rxn}^{\circ}$  ( $\text{J}/(\text{K}\cdot\text{mol}_{rxn})$ ).

- (d) Is this reaction thermodynamically favored at 298 K? \_\_\_\_\_

- (e) Circle the situation that best describes this reaction.

Not favored  
at any T

Favored  
at all T

Favored  
at high T

Favored  
at low T

- (f) Use the Gibbs free energy equation and your answers to parts (a) and (b) to calculate the value of  $\Delta G_{rxn}$ , in units of  $\text{kJ/mol}_{rxn}$ , for this reaction at temperatures of 200 K and 700 K. Assume that the values of  $\Delta H_{rxn}^{\circ}$  and  $\Delta S_{rxn}^{\circ}$  do not change significantly when the temperature is changed.

$\Delta G_{rxn}$ at 200 K	$\Delta G_{rxn}$ at 700 K

## 9.4 Thermodynamic and Kinetic Control

Essential knowledge statements from the AP Chemistry CED:

- Many processes that are thermodynamically favored do not occur to any measurable extent, or they occur at extremely slow rates.
  - Processes that are thermodynamically favored, but do not proceed at a measurable rate, are under “kinetic control.” High activation energy is a common reason for a process to be under kinetic control. The fact that a process does not proceed at a noticeable rate does not mean that the chemical system is at equilibrium. If a process is known to be thermodynamically favored, and yet does not occur at a measurable rate, it is reasonable to conclude that the process is under kinetic control.
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16. Decide if each of the following statements is true or false.

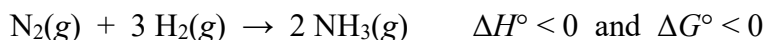
\_\_\_\_\_ If the sign of  $\Delta G^\circ$  for a certain process is negative, the process is thermodynamically favored to occur under standard conditions.

\_\_\_\_\_ If the sign of  $\Delta G^\circ$  for a certain process is negative, the process should occur at a relatively fast rate under standard conditions.

\_\_\_\_\_ If a certain process has a relatively high activation energy, the process is likely to occur at a relatively fast rate.

\_\_\_\_\_ If a certain process has a relatively high activation energy, the process is likely to occur at a relatively slow rate.

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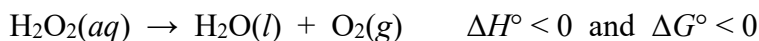
17. Information about the formation of  $\text{NH}_3(\text{g})$  from  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  is shown above. When equal volumes of  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$ , each at 1 atm, are mixed in a closed container at 298 K, no formation of  $\text{NH}_3(\text{g})$  is observed. Select all of the following statements that represent a valid explanation for this observation.

\_\_\_\_\_ The formation of  $\text{NH}_3(\text{g})$  from  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  is not thermodynamically favored to occur at standard conditions.

\_\_\_\_\_ The reactants  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  must be combined in a 1-to-3 mole ratio in order for the reaction to proceed.

\_\_\_\_\_ The formation of  $\text{NH}_3(\text{g})$  from  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  has a relatively high activation energy, which causes the rate of the reaction to be extremely slow at standard conditions.

\_\_\_\_\_ The driving force for the formation of  $\text{NH}_3(\text{g})$  from  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  is the change in entropy ( $\Delta S^\circ$ ).



18. Information about the decomposition of  $\text{H}_2\text{O}_2(aq)$  to form  $\text{H}_2\text{O}(l)$  and  $\text{O}_2(g)$  is shown above. A solution of  $\text{H}_2\text{O}_2(aq)$  is typically stable for up to a year stored in a dark bottle at 298 K. When a suitable catalyst is added to the solution of  $\text{H}_2\text{O}_2(aq)$ , the decomposition reaction occurs at a much faster rate. Select all of the following statements that represent a valid explanation for this observation.

- \_\_\_\_\_ The addition of a catalyst decreases the value of  $\Delta G^\circ$ , causing the reaction to become thermodynamically favorable.
- \_\_\_\_\_ The addition of a catalyst increases the value of  $\Delta G^\circ$ , causing the reaction to become thermodynamically favorable.
- \_\_\_\_\_ The addition of a catalyst provides a reaction pathway with a lower activation energy, resulting in a faster reaction rate.
- \_\_\_\_\_ The addition of a catalyst provides a reaction pathway with a higher activation energy, resulting in a faster reaction rate.
- 

## 9.5 Free Energy and Equilibrium

Essential knowledge statements from the AP Chemistry CED:

- The phrase "thermodynamically favored" ( $\Delta G^\circ < 0$ ) means that the products are favored at equilibrium ( $K > 1$ ).
  - The equilibrium constant is related to free energy by the following equations.
    - $K = e^{-\Delta G^\circ / RT}$
    - $\Delta G^\circ = -RT \ln K$
  - Connections between  $K$  and  $\Delta G^\circ$  can be made qualitatively through estimation. When  $\Delta G^\circ$  is near zero, the equilibrium constant will be close to 1. When  $\Delta G^\circ$  is much larger or much smaller than  $RT$ , the value of  $K$  deviates strongly from 1.
  - Processes with  $\Delta G^\circ < 0$  favor products (i.e.,  $K > 1$ ), and those with  $\Delta G^\circ > 0$  favor reactants (i.e.,  $K < 1$ ).
- 

When doing calculations involving  $\Delta G^\circ = -RT \ln K$ , pay attention to the following.

- Choose the correct value of the gas constant  $R$  (i.e.,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
- The units of  $R$  are  $\text{J mol}^{-1} \text{ K}^{-1}$ , but the units of  $\Delta G^\circ$  are usually given in units of  $\text{kJ/mol}_{rxn}$
- At standard conditions,  $T = 298 \text{ K}$
- Be careful with the **signs** of numbers in your calculations and in your final answer.

Example calculation:  $2 \text{ SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ SO}_3(g) \quad \Delta G^\circ = -142 \text{ kJ/mol}_{rxn} \quad K = ?$

$$K = e^{-\Delta G^\circ / RT} = e^{\frac{142,000 \text{ J/mol}_{rxn}}{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}} = e^{57.3} = 7.67 \times 10^{24}$$

This is a very large value of  $K$ , indicating that this reaction essentially goes to completion.

19. Fill in the missing information in the table below.

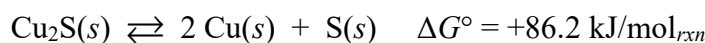
Equation	$K$ at 298 K	$\Delta G^\circ$ (kJ/mol <sub>rxn</sub> )	Are Reactants or Products Favored at Equilibrium?
$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$	$1.8 \times 10^{-10}$		
$\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2 + \text{H}_2(g)$	$1.0 \times 10^5$		
$\text{N}_2(g) + 2 \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2$		+103	
$\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightleftharpoons \text{C}_2\text{H}_6(g)$		-101	

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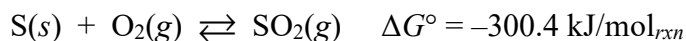
## 9.6 Coupled Reactions

Essential knowledge statements from the AP Chemistry CED:

- An external source of energy can be used to make a thermodynamically unfavorable process occur. Examples include the following.
  - Electrical energy to drive an electrolytic cell or charge a battery
  - Light to drive the overall conversion of carbon dioxide to glucose in photosynthesis
- A desired product can be formed by coupling a thermodynamically unfavorable reaction that produces that product to a favorable reaction (e.g., the conversion of ATP to ADP in biological systems). In the coupled system, the individual reactions share one or more common intermediates. The sum of the individual reactions produces an overall reaction that achieves the desired outcome and has  $\Delta G^\circ < 0$ .



20. (a) The reaction represented by the equation shown above ( is isn't ) thermodynamically favored to occur because the sign of  $\Delta G^\circ$  for the reaction is positive.

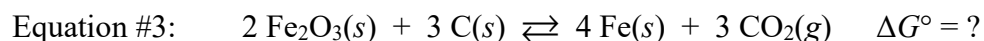
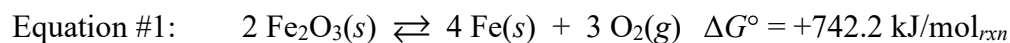


- (b) The reaction represented by the equation shown above ( is isn't ) thermodynamically favored to occur because the sign of  $\Delta G^\circ$  for the reaction is negative.



21. (a) In the space below, show how the two chemical equations from Question #20 can be combined together to produce the overall chemical equation shown above. This process is similar to what you did during Topic 6.9 (Hess's Law).

(b) Calculate the value of  $\Delta G^\circ$  for the overall chemical equation. Is the reaction represented by this equation thermodynamically favorable? Justify your answer.



22. (a) In the space below, show how equations #1 and #2 shown above can be combined together to produce equation #3.

(b) Calculate the value of  $\Delta G^\circ$  for equation #3. Is the reaction represented by equation #3 thermodynamically favorable? Justify your answer.