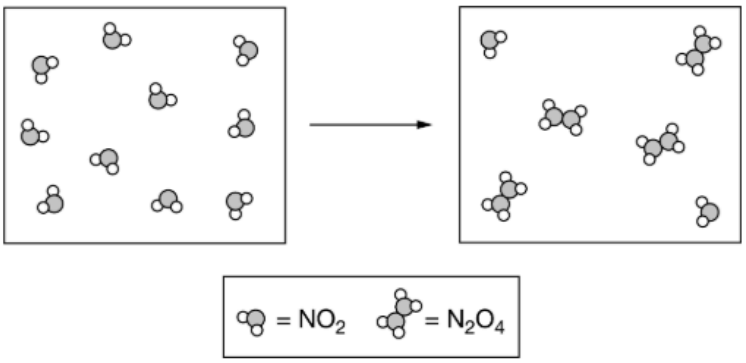
Unit 9 Thermodynamics and Electrochemistry

9.1	**Introduction to Entropy**
Objective	Identify the sign and relative magnitude of the entropy change associated with chemical or physical processes.
Entropy	Definition: – entropy increases when –
Kinetic Molecular Theory	Definition:
Essential knowledge	1. Entropy increases when matter becomes more_____. 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 _____. 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 _____ of gas-phase products is greater than the total number of moles of gas-phase reactants. 2. increases when energy is dispersed. According to kinetic molecular theory (KMT), the distribution of kinetic energy among the particles of a gas increases as the temperature _____. As a result, the entropy of the system increases with an increase in temperature.

Practice



The diagram above represents the gas-phase reaction of $\mathrm{NO_2}(g)$ to form $\mathrm{N_2O_4}(g)$ at a certain temperature. Based on the diagram, which of the following best predicts and explains the sign of the entropy change for the reaction, ΔS°_{rxn}?

(A) ΔS°_{rxn} is negative because the number of $\mathrm{N_2O_4}$ molecules increases as the reaction proceeds.

(B) ΔS°_{rxn} is negative because the number of molecules in the gas phase decreases as the reaction proceeds.

(C) ΔS°_{rxn} is positive because the number of $\mathrm{N_2O_4}$ molecules increases as the reaction proceeds.

(D) ΔS°_{rxn} is positive because the number of molecules in the gas phase decreases as the reaction proceeds.

$$2\ \mathrm{PCl_3}(g) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{POCl_3}(g)$$

Substance	Approximate S° $(\mathrm{J/(mol \cdot K)})$
$\mathrm{PCl_3}(g)$	310
$\mathrm{O_2}(g)$	210
$\mathrm{POCl_3}(g)$	330

The oxidation of $\mathrm{PCl_3}(g)$ is represented by the equation above, and the table provides the approximate values of the absolute molar entropies, S°, for these substances. Based on the information given, what is the approximate ΔS° for the reaction?

	(A) $+170\ \text{J}/(\text{mol}_{rxn} \cdot \text{K})$ (B) $-170\ \text{J}/(\text{mol}_{rxn} \cdot \text{K})$ (C) $+190\ \text{J}/(\text{mol}_{rxn} \cdot \text{K})$ (D) $-190\ \text{J}/(\text{mol}_{rxn} \cdot \text{K})$

9.2	**Absolute Entropy and Entropy Change**
Objective	Calculate the standard entropy change for a chemical or physical process based on the absolute entropies (standard molar entropies) of the species involved in the process.
Essential knowledge	The entropy change for a process can be calculated from the absolute entropies of the species involved before and after the process occurs. $\Delta S^{o}_{reaction} = \Sigma S^{o}_{products} - \Sigma S^{o}_{reactants}$
	$2\ \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\ \text{SO}_3(g)$ $\Delta S^\circ = -187\ \text{J}/(\text{mol}_{rxn} \cdot \text{K})$

Substance	Approximate S° $(\text{J}/(\text{mol} \cdot \text{K}))$
$\text{SO}_2(g)$	?
$\text{O}_2(g)$	205
$\text{SO}_3(g)$	257

The reaction between SO_2 and O_2 is represented by the chemical equation above. The table provides the approximate absolute entropies, S°, for $\text{O}_2(g)$ and $\text{SO}_3(g)$. Which of the following mathematical expressions can be used to correctly calculate S° for $\text{SO}_2(g)$?

(A) $S^\circ = -[-187 - 257 + 205]\ \text{J/(mol} \cdot \text{K)}$

(B) $S^\circ = \frac{1}{2}[-187 + (2 \times 257) - 205]\ \text{J/(mol} \cdot \text{K)}$

(C) $S^\circ = \frac{1}{2}[187 + (2 \times 257) - 205]\ \text{J/(mol} \cdot \text{K)}$

(D) $S^\circ = [-187 + 257 - 205]\ \text{J/(mol} \cdot \text{K)}$

$$2\ \text{AgNO}_3(aq) + \text{CaCl}_2(aq) \rightarrow 2\ \text{AgCl}(s) + \text{Ca(NO}_3)_2(aq)$$

Substance	Approximate S° $(\text{J/(mol} \cdot \text{K)})$
$\text{AgNO}_3(aq)$	220
$\text{CaCl}_2(aq)$	60.
$\text{AgCl}(s)$	96
$\text{Ca(NO}_3)_2(aq)$	240

The reaction between AgNO_3 and CaCl_2 is represented by the equation above, and the table provides the approximate S° values for the reactants and products. Which of the following is the approximate ΔS° for the reaction?

(A) $-68\ \text{J/(mol}_{rxn} \cdot \text{K)}$

(B) $+68\ \text{J/(mol}_{rxn} \cdot \text{K)}$

(C) $-56\ \text{J/(mol}_{rxn} \cdot \text{K)}$

(D) $+56\ \text{J/(mol}_{rxn} \cdot \text{K)}$

9.3	**Gibbs Free Energy and Thermodynamic Favorability**
Objective	Explain whether a physical or chemical process is thermodynamically favored based on an evaluation of ΔG^{o} .
Gibbs free energy	
Essential knowledge	1. The Gibbs free energy change for a chemical process in which all the reactants and products are present in a _____ 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 ΔG^{o} . 2. The standard Gibbs free energy change for a chemical or physical process is a measure of thermodynamic _____. Historically, the term "spontaneous" has been used to describe processes for which $\Delta G^{o} < 0$. The phrase **"thermodynamically favored" is preferred** instead so that common misunderstandings (equating "spontaneous" with "suddenly" or "without cause") can be avoided. When $\Delta G^{o} < 0$ for the process, it is said to be thermodynamically favored. 3. The standard Gibbs free energy change for a physical or chemical process may also be determined from the standard Gibbs free energy of _____ of the reactants and products.

ΔH^{o}	ΔS^{o}	Symbols	$\Delta G^{o} < 0$, favored at:
<0	>0	$<>$	all T
>0	<0	$><$	no T
>0	>0	$>>$	high T
<0	<0	$<<$	low T

Practice questions

$$\mathrm{CH_4}(g) + 2\ \mathrm{O_2}(g) \rightleftarrows \mathrm{CO_2}(g) + 2\ \mathrm{H_2O}(g)$$

$$\Delta H^\circ_{rxn} = -803\ \mathrm{kJ/mol}_{rxn}$$

$$\Delta S^\circ_{rxn} = -5\ \mathrm{J/(mol}_{rxn} \cdot \mathrm{K})$$

The chemical equation above represents the exothermic reaction of $\mathrm{CH_4}(g)$ with $\mathrm{O_2}(g)$. Which of the following best helps to explain why the reaction is thermodynamically favored $(\Delta G < 0)$ at $2000\ \mathrm{K}$ and $1\ \mathrm{atm}$?

(A) The total number of gaseous product molecules is less than the total number of gaseous reactant molecules, thus $\Delta S < 0$.

(B) The total number of gaseous product molecules is greater than the total number of gaseous reactant molecules, thus $\Delta S > 0$.

(C) The amount of energy released when the product bonds form is much less than the amount of energy needed to break the reactant bonds.

(D) The amount of energy released when the product bonds form is much greater than the amount of energy needed to break the reactant bonds.

$$4\ \mathrm{Fe}(s) + 3\ \mathrm{O_2}(g) \rightleftarrows 2\ \mathrm{Fe_2O_3}(s) \qquad \Delta H = -1{,}650\ \mathrm{kJ/mol}_{rxn}$$

The oxidation of $\mathrm{Fe}(s)$ is represented by the chemical equation above. Which of the following correctly explains whether or not the reaction is thermodynamically favorable?

(A) There are more particles (including particles in the gas state) in the reactants than in the product, thus $\Delta S_{rxn} < 0$. Because ΔH is large and negative, the reaction will be thermodynamically favorable at low temperatures.

(B) There are more particles (including particles in the gas state) in the reactants than in the product, thus $\Delta S_{rxn} < 0$. Because ΔH is large and negative, the reaction will be not be thermodynamically favorable at any temperature.

(C) There are more particles (including particles in the gas state) in the reactants than in the product, thus $\Delta S_{rxn} > 0$. Because ΔH is large and negative, the reaction will be thermodynamically favorable at all temperatures.

(D) There are more particles (including particles in the gas state) in the reactants than in the product, thus $\Delta S_{rxn} > 0$. Because ΔH is large and negative, the reaction will be not be thermodynamically favorable at any temperature.

$$\mathrm{H}(g) + \mathrm{Cl}(g) \rightarrow \mathrm{HCl}(g)$$

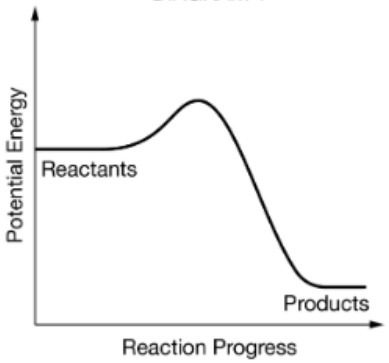
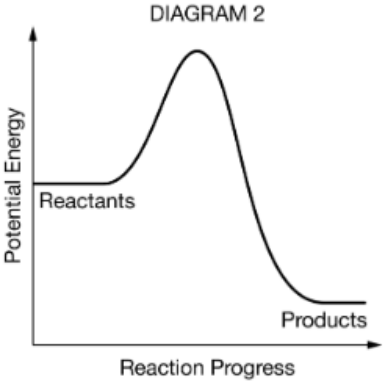
The formation of $\mathrm{HCl}(g)$ from its atoms is represented by the equation above. Which of the following best explains why the reaction is thermodynamically favored?

(A) $\Delta G > 0$ because energy is released as the bond between the H and Cl atoms forms, and entropy increases because the number of gaseous product particles is less than the number of gaseous reactant particles.

(B) $\Delta G > 0$ because energy is absorbed as the bond between the H and Cl atoms forms, and entropy decreases because the number of gaseous product particles is less than the number of gaseous reactant particles.

(C) $\Delta G < 0$ because although energy is absorbed as the bond between the H and Cl atoms forms, entropy increases because the number of gaseous product particles is less than the number of gaseous reactant particles.

(D) $\Delta G < 0$ because although entropy decreases because the number of gaseous product particles is less than the number of gaseous reactant particles, energy is released as the bond between the H and Cl atoms forms.

9.4	**Thermodynamic and Kinetic Control**
Objective	Explain, in terms of kinetics, why a thermodynamically favored reaction might not occur at a measurable rate.
	<u>Kinetic control:</u>
Essential Knowledge	1. Many processes that are thermodynamically favored do not occur to any measurable extent, or they occur at extremely _____ rates. 2. 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.
Practice Questions	$$\mathrm{C_2H_5OH}(l) + 3\ \mathrm{O_2}(g) \rightarrow 2\ \mathrm{CO_2}(g) + 3\ \mathrm{H_2O}(g)$$ $\Delta S^\circ = +217.7\ \mathrm{J/(mol_{rxn} \cdot K)}$ $\Delta H^\circ = -1235\ \mathrm{kJ/mol_{rxn}}$ DIAGRAM 1  DIAGRAM 2 

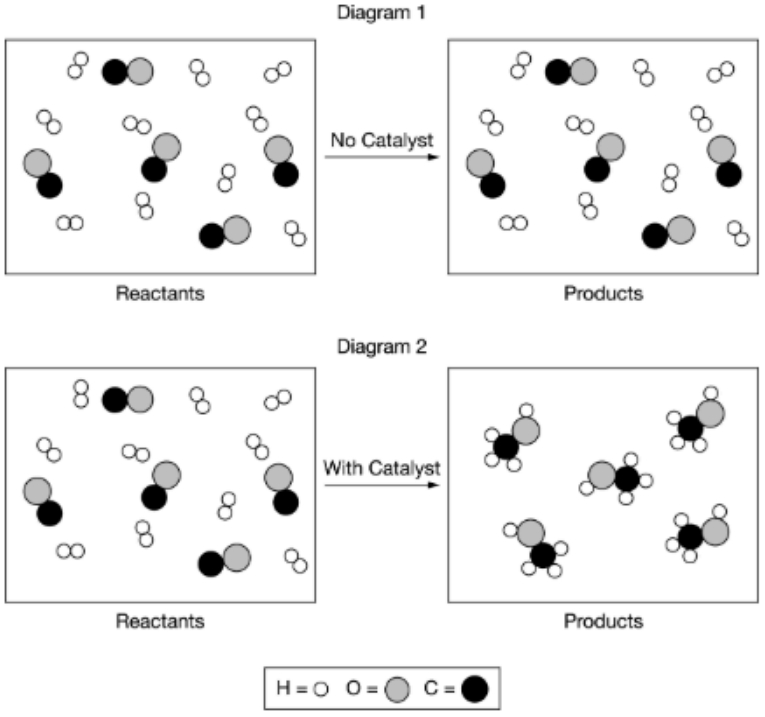
The combustion of $\mathrm{C_2H_5OH}$ is represented by the equation above and the standard entropy and enthalpy changes for the reaction are provided. When the reactants are combined at $25^\circ\mathrm{C}$, essentially no $\mathrm{CO_2}(g)$ or $\mathrm{H_2O}(g)$ is produced after a few hours. Which of the diagrams above could best help explain the low yield of the reaction under these conditions, and why?

(A) Diagram 1, because it represents a reaction that is not thermodynamically favorable with $\Delta G^\circ > 0$, regardless of its reaction rate.

(B) Diagram 1, because it represents a reaction that reaches equilibrium quickly after a very small amount of the reactants is consumed.

(C) Diagram 2, because it represents a reaction with a high activation energy barrier for molecules to overcome and a very slow reaction rate, even if it is thermodynamically favorable with $\Delta G^\circ < 0$.

(D) Diagram 2, because it represents a reaction that is thermodynamically favorable with $\Delta H^\circ < 0$, but the products formed are unstable and quickly revert to form reactants.



$$\mathrm{CO}(g) + 2\,\mathrm{H_2}(g) \rightleftarrows \mathrm{CH_3OH}(g) \qquad K = 2.2 \times 10^4 \text{ at } 298\ \mathrm{K}$$

at a constant temperature of $298\ \mathrm{K}$. The reaction is represented by the equation above. Diagram 1 represents the uncatalyzed reaction and diagram 2 represents the catalyzed reaction one hour after the reactants were mixed. Which of the following correctly explains the experimental results represented in the particle diagrams?

(A) Although the reaction is thermodynamically favorable because $\Delta G^\circ < 0$ based on the value of K, only the catalyzed reaction could proceed in one hour because its reactant molecules had a higher average kinetic energy.

(B) Although the reaction is thermodynamically favorable because $\Delta G^\circ < 0$ based on the value of K, only the catalyzed reaction could proceed in one hour because it has a lower activation-energy reaction pathway.

(C) The reaction is not thermodynamically favorable because $\Delta G^\circ > 0$ based on the value of K, but the addition of a catalyst improved the orientation of the reactants during collisions, allowing the catalyzed reaction to proceed in one hour.

(D) The reaction is not thermodynamically favorable because $\Delta G^\circ > 0$ based on the value of K, but the catalyzed reaction could proceed in one hour because it has a lower ΔH and a higher ΔS.

$$4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{Fe_2O_3}(s) \qquad \Delta G^\circ = -1500\ \mathrm{kJ/mol}_{rxn}$$

The reaction of iron with oxygen to form rust is represented by the equation shown above. A student cleans two iron nails and places each nail in a capped test tube. The following table gives the experimental conditions and the student's observations after one week at room temperature.

Test Tube	Experimental Conditions Inside the Capped Test Tube	Observations
1	Dry air	No visible rust on nail
2	Air and water	Rust suspended in the water and on the nail

The student claims that the formation of rust in test tube 2 shows that the reaction is thermodynamically favored. Which of the following justifications should the student use to explain why rust did not form in test tube 1 ?

	(A) The reaction does not occur at an observable rate when water is not present because it proceeds through a mechanism with a high activation energy. (B) The reaction is less thermodynamically favored because the Gibbs free energy of the product is greater when water is not present. (C) The product is not formed in measurable quantities because the equilibrium constant for the reaction when water is not present is significantly less than one. (D) The rate of reaction is much slower because the oxygen molecules collide with the iron surface with less energy when water is not present.

9.5	**Free Energy and Equilibrium**	
Objective	Explain whether a process is thermodynamically favored using the relationships between K, ΔG^o, and T.	
K, G, and T	K:	G:
	Connections to temperature:	
Essential Knowledge	1. The phrase “thermodynamically favored” (ΔG^o____ 0) means that the products are favored at equilibrium (K _____ 1) under standard conditions. 2. The equilibrium constant is related to free energy by the equations $K = e^{-\Delta G°/RT}$ $\Delta G° = -RT \ln K.$ 3. Connections between K and $\Delta G°$ can be made qualitatively through estimation. When $\Delta G°$ is near _____, the equilibrium constant will be close to _____. When $\Delta G°$ is much larger or much smaller than RT, the value of K deviates strongly from 1. 4. Processes with $\Delta G° < 0$ favor _____ (i.e., $K > 1$) and those with $\Delta G° > 0$ favor _____ (i.e., $K < 1$).	

Example Question

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftarrows 2\,\mathrm{NH_3}(g)$$

$$K = 5.6 \times 10^5 \text{ at } 298\ \mathrm{K}$$

$$\Delta H^\circ_{rxn} = -91.8\ \mathrm{kJ/mol}_{rxn}$$

The synthesis of $\mathrm{NH_3}$ is represented by the equation above. Based on the equilibrium constant, K, and ΔH°_{rxn} given above, which of the following can best be used to justify that the reaction is thermodynamically favorable at $298\ \mathrm{K}$ and constant pressure?

(A) $\Delta G^\circ = -RT \ln K > 0$ because $K >> 1$

(B) $\Delta G^\circ = -RT \ln K < 0$ because $K >> 1$

(C) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0$ because $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$

(D) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ > 0$ because $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$

$$2\,\mathrm{POCl_3}(g) \rightleftarrows 2\,\mathrm{PCl_3}(g) + \mathrm{O_2}(g)$$

$$\Delta G^\circ_{rxn} = +490\ \mathrm{kJ/mol}$$

A sample of $\mathrm{POCl_3}(g)$ is placed in a closed, rigid container at $298\ \mathrm{K}$ and allowed to reach equilibrium according to the equation above. Based on the value for $\Delta G^\circ_{rxn} = +490\ \mathrm{kJ/mol}$, which of the following is true?

(A) $K = e^{-\frac{490{,}000}{8.314 \times 298}} << 1$ and at equilibrium $P_{\mathrm{POCl_3}} >> P_{\mathrm{PCl_3}}$.

(B) $K = e^{\frac{8.314 \times 298}{490{,}000}} > 1$ and at equilibrium $P_{\mathrm{O_2}} > P_{\mathrm{POCl_3}}$.

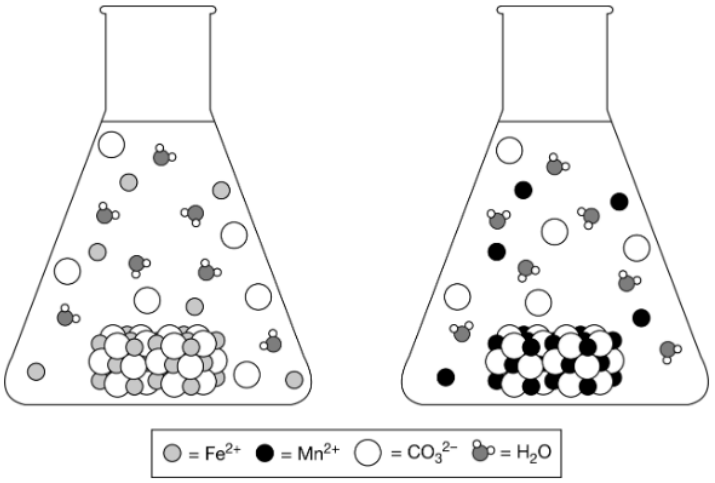
(C) $K = e^{-\frac{490}{8.314 \times 298}} < 1$ and at equilibrium $P_{\mathrm{POCl_3}} < P_{\mathrm{PCl_3}}$.

(D) $K = e^{\frac{8.314 \times 298}{490}} >> 1$ and at equilibrium $P_{\mathrm{O_2}} >> P_{\mathrm{POCl_3}}$.

9.6	**Free Energy of Dissolution**
Objective	Explain the relationship between the solubility of a salt and changes in the enthalpy and entropy that occur in the dissolution process.
Essential Knowledge	The free energy change (ΔG°) for dissolution of a substance reflects a number of factors: the breaking of the _____interactions that hold the solid together, the _____ of the solvent around the dissolved species, and the interaction of the dissolved species with the solvent. It is possible to estimate the sign and relative magnitude of the enthalpic and entropic contributions to each of these factors. However, making predictions for the total change in free energy of dissolution can be challenging due to the cancellations among the free energies associated with the three factors cited.
Example problem	

Reaction	K_{sp}	ΔH°	ΔS°
$\mathrm{FeCO_3}(s) \rightleftarrows \mathrm{Fe^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq)$	3×10^{-11}	< 0	> 0
$\mathrm{MnCO_3}(s) \rightleftarrows \mathrm{Mn^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq)$	2×10^{-11}	< 0	> 0

The table above lists the equilibrium constants and changes in thermodynamic properties for the dissolution of $\mathrm{FeCO_3}$ and $\mathrm{MnCO_3}$ at $25^\circ\mathrm{C}$. The two particle diagrams below represent saturated solutions of each compound at equilibrium.



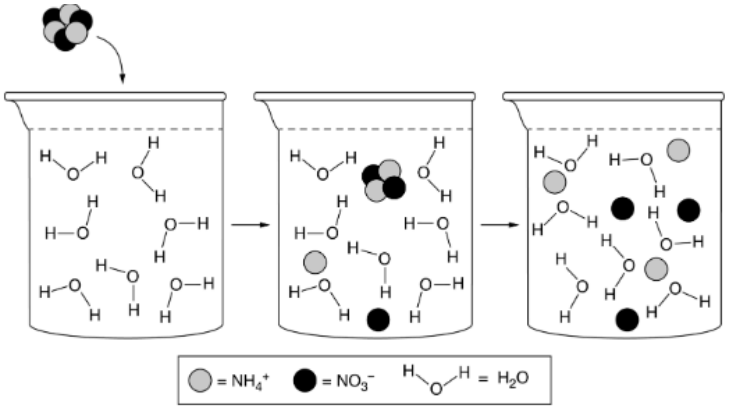
Which of the following explains which of the properties listed in the table is best represented by the particle diagram?

(A) The particle diagrams best represent that $\Delta H^\circ < 0$ because the ions from both compounds are solvated by water molecules.

(B) The particle diagrams best represent that $\Delta H^\circ < 0$ because both compounds produce about the same amount of $\mathrm{CO_3}^{2-}$ ions from the dissolution.

(C) The particle diagrams best represent that $\Delta S^\circ > 0$ because both compounds produce a very small amount of ions from the dissolution.

(D) The particle diagrams best represent that the molar solubility is greater for $\mathrm{FeCO_3}$ compared to $\mathrm{MnCO_3}$.



At $298\ \text{K}$, NH_4NO_3 readily dissolves in water, suggesting that the change in free energy (ΔG) favors the dissolution process. However, when NH_4NO_3 dissolves in water, the temperature of the water decreases. The particulate diagram above attempts to provide a microscopic view of the dissolution of $\text{NH}_4\text{NO}_3(s)$ considering both the change in enthalpy (ΔH) and the change in entropy (ΔS). Which of the following explains what the particle diagram is able to illustrate and why?

(A) The particle diagram is able to illustrate that the ΔH for the dissolution of NH_4NO_3 is exothermic because overcoming the attractive forces between the ions requires the absorption of energy.

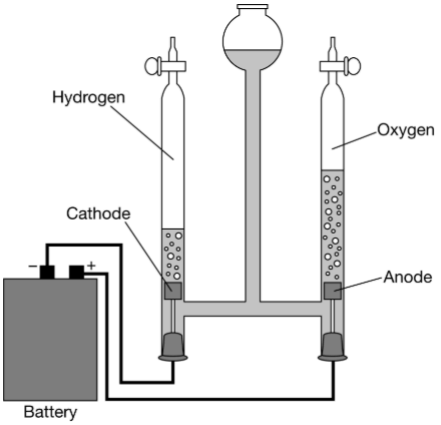
(B) The particle diagram is able to illustrate that the ΔH for the dissolution of NH_4NO_3 is endothermic because forming new interactions between the ions and the water molecules releases energy.

(C) The particle diagram is able to illustrate that entropy increases when $\text{NH}_4\text{NO}_3(s)$ dissolves in water because the ions disperse in solution.

(D) The particle diagram is able to illustrate that entropy decreases when $\text{NH}_4\text{NO}_3(s)$ dissolves in water because many hydrogen bonds can form between the water molecules and the ions.

9.7	**Coupled Reactions**	
Objective	Explain the relationship between external sources of energy or coupled reactions and their ability to drive thermodynamically unfavorable processes.	
Coupled reaction	Definition:	
Electric cells	<u>Cathode</u>	<u>Anode</u>
Essential Knowledge	1. An external source of energy can be used to make a **thermodynamically unfavorabl**e process occur. Examples include: i. Electrical energy to drive an electrolytic cell or charge a battery. ii. Light to drive the overall conversion of carbon dioxide to glucose in photosynthesis. 2. 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 $\Delta G^\circ < 0$.	

Questions	The separation of industrial ore is not thermodynamically favorable. However, the synthesis of sulfur and oxygen gas into sulfur dioxide is favorable. Find a thermodynamically favorable process that separates industrial ore. $ZnS\ (s) \rightarrow Zn\ (s) + S\ (s)$ $\Delta G° = 198.3$ kJ/mol $S\ (s) + O_2\ (g) \rightarrow SO_2\ (g)$ $\Delta G° = -300.1$ kJ/mol



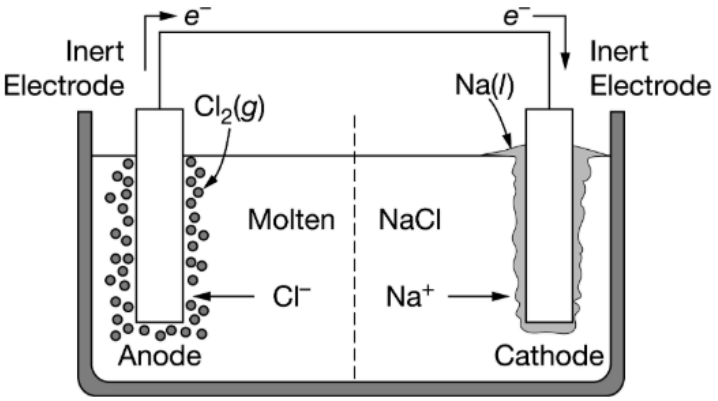
The reaction in which $\mathbf{H_2O}(l)$ is decomposed into $\mathbf{H_2}(g)$ and $\mathbf{O_2}(g)$ is thermodynamically unfavorable ($\Delta G^\circ > 0$). However, an electrolytic cell, such as the one represented above, can be used to make the reaction occur. Which of the following identifies a flaw in the representation?

(A) Oxidation is occurring at the anode instead of at the cathode.

(B) The equation for the reaction is not correctly balanced.

(C) Electrical energy is needed for the reaction to proceed.

(D) The relative volumes of collected gas shown in each tube are incorrect.



The decomposition of $\mathrm{NaCl}(l)$ into $\mathrm{Na}(l)$ and $\mathrm{Cl_2}(g)$ is thermodynamically unfavorable. The decomposition requires the input of energy from an external source. The diagram represents an electrolytic cell that can be used to drive the decomposition reaction. Which of the following identifies a flaw in the representation?

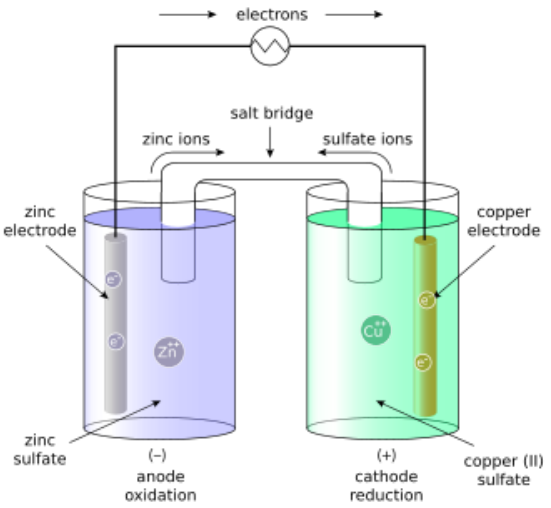
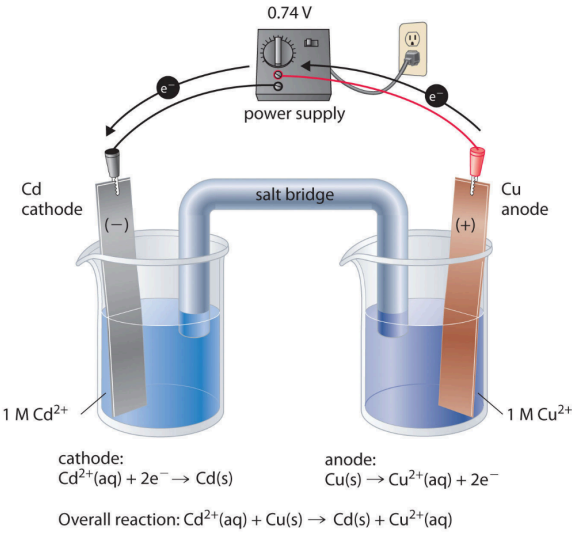
(A) Oxidation is occurring at the anode.

(B) Molten Na is shown at the cathode.

(C) An external source of energy is not shown.

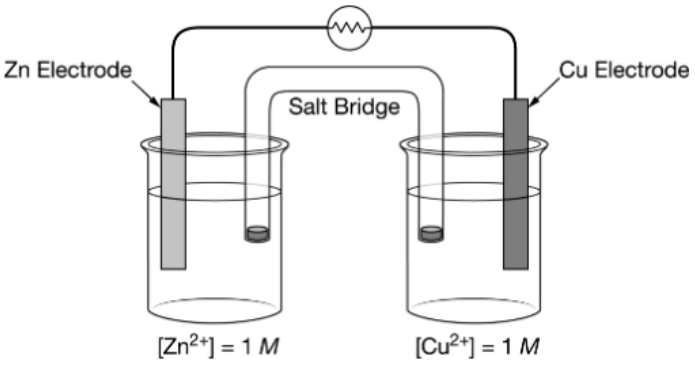
(D) The direction of the electron flow in the wires is incorrect.

9.8	**Galvanic (Voltaic) and Electrolytic Cells**	
Objective	Explain the relationship between the physical components of an electrochemical cell and the overall operational principles of the cell.	
Principles		

	<u>Galvanic cell</u> 
	<u>Electrolytic cell</u> 
	Half reactions:
Essential Knowledge	1. Each component of an electrochemical cell (electrodes, solutions in the half-cells, salt bridge, voltage/current measuring device) plays a specific role in the overall functioning of the cell. The operational characteristics of the cell (galvanic, electrolytic, direction of electron flow, reactions occurring in each half-cell, change in electrode mass, evolution of a gas at an electrode, ion flow through the salt bridge) can be described at both the macroscopic and particulate levels. 2. Galvanic, sometimes called voltaic, cells involve a thermodynamically _____ reaction, whereas electrolytic cells involve a

thermodynamically _____ reaction. Visual representations of galvanic and electrolytic cells are tools of analysis to identify where half-reactions occur and in what direction current flows.

3. For all electrochemical cells, oxidation occurs at the _____ and reduction occurs at the _____.



$$\mathrm{Cu}^{2+}(aq) + \mathrm{Zn}(s) \rightarrow \mathrm{Cu}(s) + \mathrm{Zn}^{2+}(aq) \qquad E^\circ = +1.10\ \mathrm{V}$$

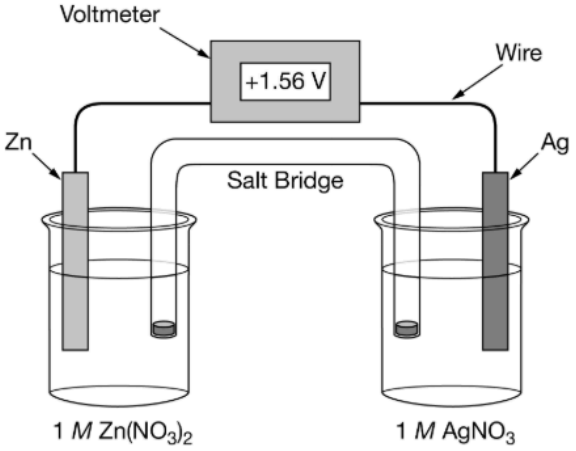
The galvanic cell illustrated above generates a potential of $+1.10\ \mathrm{V}$. For the construction of a second galvanic cell (not shown), only one modification was made: the Cu electrode has double the mass of the Cu electrode in the first cell. Which of the following correctly compares the initial E° for the second cell to that of first cell at $298\ \mathrm{K}$, and why?

(A) The initial E° for the second cell is twice that of the first cell, because a larger amount of $\mathrm{Cu}(s)$ can be oxidized to Cu^{2+}.

(B) The initial E° for the second cell is twice that of the first cell, because more Cu^{2+} ions can be deposited on the solid Cu electrode.

(C) The initial E° for the second cell is half that of the first cell, because the greater amount $\mathrm{Cu}(s)$ in the half-cell inhibits the formation of more $\mathrm{Cu}(s)$.

(D) The initial E° for the second cell is the same as for the first cell, because the overall chemical reaction that occurs in the cell does not change.



Half-Reaction	Standard Reduction Potential, E° (V)
$\mathrm{Ag^+}(aq) + e^- \rightarrow \mathrm{Ag}(s)$	$+0.80$
$\mathrm{Pb^{2+}}(aq) + 2\,e^- \rightarrow \mathrm{Pb}(s)$	-0.13
$\mathrm{Zn^{2+}}(aq) + 2\,e^- \rightarrow \mathrm{Zn}(s)$	-0.76

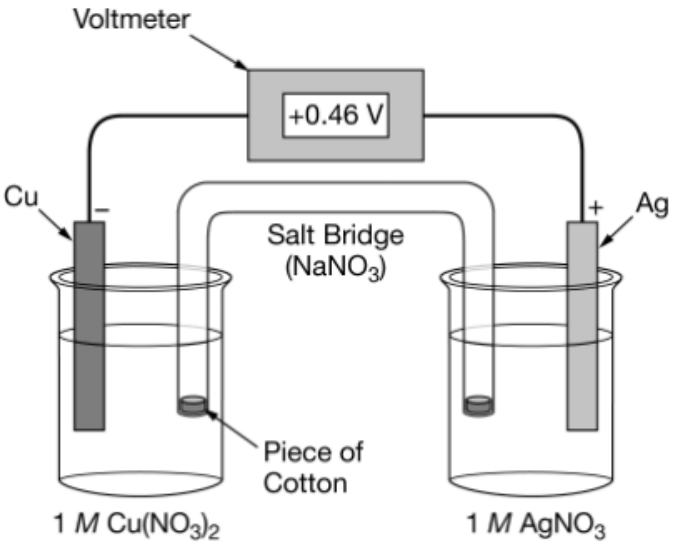
The cell potential for the standard galvanic cell shown above is $+1.56\ \mathrm{V}$. If $\mathrm{AgNO_3}(aq)|\mathrm{Ag}(s)$ is replaced with $1\ M\ \mathrm{Pb(NO_3)_2}(aq)$ solution and a Pb electrode, which of the following describes what happens to the operation of the cell, and why?

(A) Nothing changes because galvanic cells that have a $\mathrm{Zn}(s)$ electrode have a constant cell potential, E°_{cell}, of $+1.56\ \mathrm{V}$.

(B) The cell stops generating a voltage because the standard reduction potentials of $\mathrm{Pb^{2+}}$ and $\mathrm{Zn^{2+}}$ are both negative.

(C) The cell potential decreases because the reduction of $\mathrm{Pb^{2+}}$ is less thermodynamically favorable than the reduction of $\mathrm{Ag^+}$.

(D) The cell potential increases because twice as many electrons are transferred between $\mathrm{Pb^{2+}}$ and Zn than between $\mathrm{Ag^+}$ and Zn.



To construct the galvanic cell illustrated above, the salt bridge was prepared by soaking a piece of cotton in $5.0\ M\ \mathrm{NaNO_3}(aq)$ before placing it inside the U-shaped tube filled with distilled water. If the cotton was soaked in distilled water by mistake, which of the following best explains how the operation of the cell would be affected?

(A) The operation of the cell is not affected because neither $\mathrm{Na^+}(aq)$ nor $\mathrm{NO_3^-}(aq)$ is involved in the redox reaction that takes place.

(B) The operation of the cell generates a higher potential because there are fewer ions in the solution, making the reaction more thermodynamically favored.

(C) The cell will operate for a much longer time because the flow of electrons through the circuit will eventually be reversed.

(D) The cell would not operate because a current could not be conducted between the half-cells.

9.9	**Cell Potential and Free Energy**
Objective	Explain whether an electrochemical cell is thermodynamically favored, based on its standard cell potential and the constituent half-reactions within the cell.
Principles	
Essential knowledge	1. Electrochemistry encompasses the study of redox reactions that occur within electrochemical cells. The reactions are either thermodynamically favored (resulting in a _____ voltage) or thermodynamically unfavored (resulting in a _____ voltage and requiring an externally applied potential for the reaction to proceed). 2. The standard cell potential of electrochemical cells can be calculated by **identifying the oxidation and reduction half-reactions** and their respective standard reduction potentials. 3. ΔG^{o} (standard Gibbs free energy change) is proportional to the negative of the cell potential for the redox reaction from which it is constructed. Thus, a cell with a positive E^{o} involves a thermodynamically _____ reaction, and a cell with a negative E^{o} involves a thermodynamically _____ reaction. EQN: $\Delta G^{o} = -nFE^{o}$

9.10	Cell Potential Under Nonstandard Conditions
Objective	Explain the relationship between deviations from standard cell conditions and changes in the cell potential.
Principles	
Essential knowledge	1. In a real system under nonstandard conditions, the cell potential will vary depending on the concentrations of the active species. The cell potential is a driving force toward_____; the farther the reaction is from equilibrium, the greater the magnitude of the cell potential. 2. Equilibrium arguments such as Le Châtelier's principle do not apply to electrochemical systems, because the systems are not in equilibrium. 3. The standard cell potential E^o corresponds to the standard conditions of Q = 1. As the system approaches equilibrium, the magnitude (i.e., absolute value) of the cell potential _____, reaching zero at _____(whenQ = K). Deviations from standard conditions that take the cell further from equilibrium than Q = 1 will _____ the magnitude of the cell potential relative to E^o. Deviations from standard conditions that take the cell closer to equilibrium than Q = 1 will decrease the magnitude of the cell potential relative to E^o. In concentration cells, the direction of spontaneous electron flow can be determined by **considering the direction needed to reach equilibrium**. 4. Algorithmic calculations using the Nernst equation are insufficient to demonstrate an understanding of electrochemical cells under nonstandard conditions. However, students should qualitatively understand the effects of concentration on cell potential and use conceptual reasoning, including the qualitative use of the Nernst equation: EQN: $E = E^o - (RT/nF) \ln Q$

9.11	**Electrolysis and Faraday's Law**
Objective	Calculate the amount of charge flow based on changes in the amounts of reactants and products in an electrochemical cell.
Principles	
Essential knowledge	**Faraday's laws** can be used to determine the **stoichiometry** of the redox reaction occurring in an electrochemical cell with respect to the following: i. Number of electrons transferred ii. Mass of material deposited on or removed from an electrode (as in electroplating) iii. Current iv. Time elapsed v. Charge of ionic species EQN: $I = q/t$