A general chemistry Libretexts Textmap organized around the textbook

**Chemistry: The Central Science**

by Brown, LeMay, Busten, Murphy, and Woodward

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   2. 2.E: Atoms, Molecules, and Ions (Exercises)
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19.1: Spontaneous Processes

19.2: Entropy and the Second Law of Thermodynamics

Conceptual Problems

1. A Russian space vehicle developed a leak, which resulted in an internal pressure drop from 1 atm to 0.85 atm. Is this an example of a reversible expansion? Has work been done?

2. Which member of each pair do you expect to have a higher entropy? Why?
   a. solid phenol or liquid phenol
   b. 1-butanol or butane
   c. cyclohexane or cyclohexanol
   d. 1 mol of N₂ mixed with 2 mol of O₂ or 2 mol of NO₂
   e. 1 mol of O₂ or 1 mol of O₃
   f. 1 mol of propane at 1 atm or 1 mol of propane at 2 atm
3. Determine whether each process is reversible or irreversible.
   a. ice melting at 0°C
   b. salt crystallizing from a saline solution
   c. evaporation of a liquid in equilibrium with its vapor in a sealed flask
   d. a neutralization reaction
4. Determine whether each process is reversible or irreversible.
   a. cooking spaghetti
   b. the reaction between sodium metal and water
   c. oxygen uptake by hemoglobin
   d. evaporation of water at its boiling point
5. Explain why increasing the temperature of a gas increases its entropy. What effect does this have on the internal energy of the gas?
6. For a series of related compounds, does ΔS\textsubscript{vap} increase or decrease with an increase in the strength of intermolecular interactions in the liquid state? Why?
7. Is the change in the enthalpy of reaction or the change in entropy of reaction more sensitive to changes in temperature? Explain your reasoning.
8. Solid potassium chloride has a highly ordered lattice structure. Do you expect ΔS\textsubscript{soln} to be greater or less than zero? Why? What opposing factors must be considered in making your prediction?
9. Aniline (C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}) is an oily liquid at 25°C that darkens on exposure to air and light. It is used in dying fabrics and in staining wood black. One gram of aniline dissolves in 28.6 mL of water, but aniline is completely miscible with ethanol. Do you expect ΔS\textsubscript{soln} in H\textsubscript{2}O to be greater than, less than, or equal to ΔS\textsubscript{soln} in CH\textsubscript{3}CH\textsubscript{2}OH? Why?

**Conceptual Answers**

1. No, it is irreversible; no work is done because the external pressure is effectively zero.
3. a. reversible
   b. irreversible
   c. reversible
   d. irreversible
9. Water has a highly ordered, hydrogen-bonded structure that must reorganize to accommodate hydrophobic solutes like aniline. In contrast, we expect that aniline will be able to disperse randomly throughout ethanol, which has a significantly less ordered structure. We therefore predict that ΔS\textsubscript{soln} in ethanol will be more positive than ΔS\textsubscript{soln} in water.

**Numerical Problems**

1. Liquid nitrogen, which has a boiling point of −195.79°C, is used as a coolant and as a preservative for biological tissues. Is the entropy of nitrogen higher or lower at −200°C than at −190°C? Explain your answer. Liquid nitrogen freezes to a white solid at −210.00°C, with an enthalpy of fusion of 0.71 kJ/mol. What is its entropy of fusion? Is freezing biological tissue in liquid nitrogen an example of a reversible process or an irreversible process?
2. Using the second law of thermodynamics, explain why heat flows from a hot body to a cold body but not from a cold body to a hot body.

3. One test of the spontaneity of a reaction is whether the entropy of the universe increases: $\Delta S_{\text{univ}} > 0$. Using an entropic argument, show that the following reaction is spontaneous at 25°C:

$$4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$$

Why does the entropy of the universe increase in this reaction even though gaseous molecules, which have a high entropy, are consumed?

4. Calculate the missing data in the following table.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_{\text{fus}}$ (kJ/mol)</th>
<th>$\Delta S_{\text{fus}}$ [J/(mol·K)]</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>11.7</td>
<td></td>
<td>16.6</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>8.2</td>
<td>35.9</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.94</td>
<td></td>
<td>−182.5</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td></td>
<td>18.2</td>
<td>−97.7</td>
</tr>
<tr>
<td>formic acid</td>
<td>12.7</td>
<td>45.1</td>
<td></td>
</tr>
</tbody>
</table>

Based on this table, can you conclude that entropy is related to the nature of functional groups? Explain your reasoning.

5. Calculate the missing data in the following table.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_{\text{vap}}$ (kJ/mol)</th>
<th>$\Delta S_{\text{vap}}$ [J/(mol·K)]</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexanoic acid</td>
<td>71.1</td>
<td></td>
<td>105.7</td>
</tr>
<tr>
<td>hexane</td>
<td>28.9</td>
<td>85.5</td>
<td></td>
</tr>
<tr>
<td>formic acid</td>
<td></td>
<td>60.7</td>
<td>100.8</td>
</tr>
<tr>
<td>1-hexanol</td>
<td>44.5</td>
<td></td>
<td>157.5</td>
</tr>
</tbody>
</table>

The text states that the magnitude of $\Delta S_{\text{vap}}$ tends to be similar for a wide variety of compounds. Based on the values in the table, do you agree?
19.3: The Molecular Interpretation of Entropy

19.4: Entropy Changes in Chemical Reactions

19.5: Gibbs Free Energy

Conceptual Problems

1. How does each example illustrate the fact that no process is 100% efficient?
   a. burning a log to stay warm
   b. the respiration of glucose to provide energy
   c. burning a candle to provide light
2. Neither the change in enthalpy nor the change in entropy is, by itself, sufficient to determine whether a reaction will occur spontaneously. Why?
3. If a system is at equilibrium, what must be the relationship between ΔH and ΔS?
4. The equilibrium 2AB⇌A2B2 is exothermic in the forward direction. Which has the higher entropy—the products or the reactants? Why? Which is favored at high temperatures?
5. Is ΔG a state function that describes a system or its surroundings? Do its components—ΔH and ΔS—describe a system or its surroundings?
6. How can you use ΔG to determine the temperature of a phase transition, such as the boiling point of a liquid or the melting point of a solid?
7. Occasionally, an inventor claims to have invented a “perpetual motion” machine, which requires no additional input of energy once the machine has been put into motion. Using your knowledge of thermodynamics, how would you respond to such a claim? Justify your arguments.
8. Must the entropy of the universe increase in a spontaneous process? If not, why is no process 100% efficient?
9. The reaction of methyl chloride with water produces methanol and hydrogen chloride gas at room temperature, despite the fact that ΔH°,rxn = 7.3 kcal/mol. Using thermodynamic arguments, propose an explanation as to why methanol forms.

Conceptual Answers

9. In order for the reaction to occur spontaneously, ΔG for the reaction must be less than zero. In this case, ΔS must be positive, and the TΔS term outweighs the positive value of ΔH.

Numerical Problems

1. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.
a. \( \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \)

b. \( 2\text{H}_2(g) + \text{C}_2\text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) \)

c. \( (\text{CH}_3)_2\text{O}(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{CH}_3\text{OH}(l) \)

d. \( \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g) \)

2. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.

   a. \( \text{K}_2\text{O}_2(s) \rightarrow 2\text{K}(s) + \text{O}_2(g) \)
   
   b. \( \text{PbCO}_3(s) \rightarrow \text{PbO}(s) + \text{CO}_2(g) \)
   
   c. \( \text{P}_4(s) + 6\text{H}_2(g) \rightarrow 4\text{PH}_3(g) \)
   
   d. \( 2\text{AgCl}(s) + \text{H}_2\text{S}(g) \rightarrow \text{Ag}_2\text{S}(s) + 2\text{HCl}(g) \)

3. Nitrogen fixation is the process by which nitrogen in the atmosphere is reduced to \( \text{NH}_3 \) for use by organisms. Several reactions are associated with this process; three are listed in the following table. Which of these are spontaneous at 25°C? If a reaction is not spontaneous, at what temperature does it become spontaneous?

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H) (_{298} ) (kcal/mol)</th>
<th>( \Delta S) (_{298} ) [cal/(°·mol)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ( \frac{1}{2}\text{N}_2 + \text{O}_2 \rightarrow \text{NO}_2 )</td>
<td>8.0</td>
<td>-14.4</td>
</tr>
<tr>
<td>(b) ( \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{NO} )</td>
<td>21.6</td>
<td>2.9</td>
</tr>
<tr>
<td>(c) ( \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3 )</td>
<td>-11.0</td>
<td>-23.7</td>
</tr>
</tbody>
</table>

4. A student was asked to propose three reactions for the oxidation of carbon or a carbon compound to CO or CO\(_2\). The reactions are listed in the following table. Are any of these reactions spontaneous at 25°C? If a reaction does not occur spontaneously at 25°C, at what temperature does it become spontaneous?

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H) (_{298} ) (kcal/mol)</th>
<th>( \Delta S) (_{298} ) [cal/(°·mol)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g) )</td>
<td>42</td>
<td>32</td>
</tr>
<tr>
<td>( \text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g) )</td>
<td>-9.8</td>
<td>-10.1</td>
</tr>
<tr>
<td>( \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g) )</td>
<td>49.3</td>
<td>51.3</td>
</tr>
</tbody>
</table>

5. Tungsten trioxide (WO\(_3\)) is a dense yellow powder that, because of its bright color, is used as a pigment in oil paints and water colors (although cadmium yellow is more commonly used in artists' paints). Tungsten metal can be
isolated by the reaction of WO₃ with H₂ at 1100°C according to the equation WO₃(s) + 3H₂(g) → W(s) + 3H₂O(g). What is the lowest temperature at which the reaction occurs spontaneously? ΔH° = 27.4 kJ/mol and ΔS° = 29.8 J/K.

6. Sulfur trioxide (SO₃) is produced in large quantities in the industrial synthesis of sulfuric acid. Sulfur dioxide is converted to sulfur trioxide by reaction with oxygen gas.
   a. Write a balanced chemical equation for the reaction of SO₂ with O₂(g) and determine its ΔG°.
   b. What is the value of the equilibrium constant at 600°C?
   c. If you had to rely on the equilibrium concentrations alone, would you obtain a higher yield of product at 400°C or at 600°C?

7. Calculate ΔG° for the general reaction MCO₃(s) → MO(s) + CO₂(g) at 25°C, where M is Mg or Ba. At what temperature does each of these reactions become spontaneous?

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH° (kJ/mol)</th>
<th>S° [J/(mol·K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>−1111</td>
<td>65.85</td>
</tr>
<tr>
<td>Ba</td>
<td>−1213.0</td>
<td>112.1</td>
</tr>
<tr>
<td>MO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>−601.6</td>
<td>27.0</td>
</tr>
<tr>
<td>Ba</td>
<td>−548.0</td>
<td>72.1</td>
</tr>
<tr>
<td>CO₂</td>
<td>−393.5</td>
<td>213.8</td>
</tr>
</tbody>
</table>

8. The reaction of aqueous solutions of barium nitrate with sodium iodide is described by the following equation:

   $$\text{Ba(NO}_3\text{)}_2(\text{aq}) + 2\text{NaI(aq)} \rightarrow \text{BaI}_2(\text{aq}) + 2\text{NaNO}_3(\text{aq})$$

You want to determine the absolute entropy of BaI₂, but that information is not listed in your tables. However, you have been able to obtain the following information:

<table>
<thead>
<tr>
<th></th>
<th>Ba(NO₃)₂</th>
<th>NaI</th>
<th>BaI₂</th>
<th>NaNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH° (kJ/mol)</td>
<td>−952.36</td>
<td>−295.31</td>
<td>−605.4</td>
<td>−447.5</td>
</tr>
<tr>
<td>S° [J/(mol·K)]</td>
<td>302.5</td>
<td>170.3</td>
<td>205.4</td>
<td></td>
</tr>
</tbody>
</table>

You know that ΔG° for the reaction at 25°C is 22.64 kJ/mol. What is ΔH° for this reaction? What is S° for BaI₂?
1. Do you expect products or reactants to dominate at equilibrium in a reaction for which ΔG° is equal to
   a. 1.4 kJ/mol?
   b. 105 kJ/mol?
   c. −34 kJ/mol?
2. The change in free energy enables us to determine whether a reaction will proceed spontaneously. How is this related to the extent to which a reaction proceeds?
3. What happens to the change in free energy of the reaction N₂(g) + 3F₂(g) → 2NF₃(g) if the pressure is increased while the temperature remains constant? If the temperature is increased at constant pressure? Why are these effects not so important for reactions that involve liquids and solids?
4. Compare the expressions for the relationship between the change in free energy of a reaction and its equilibrium constant where the reactants are gases versus liquids. What are the differences between these expressions?

Numerical Problems
1. Carbon monoxide, a toxic product from the incomplete combustion of fossil fuels, reacts with water to form CO₂ and H₂, as shown in the equation CO(g) + H₂O(g) ⇌ CO₂(g) + H₂(g), for which ΔH° = −41.0 kJ/mol and ΔS° = −42.3 J cal/(mol·K) at 25°C and 1 atm.
   a. What is ΔG° for this reaction?
   b. What is ΔG if the gases have the following partial pressures: P_CO = 1.3 atm, P_(H₂O) = 0.8 atm, P_(CO₂) = 2.0 atm, P_(H₂) = 1.3 atm?
   c. What is ΔG if the temperature is increased to 150°C assuming no change in pressure?
2. Methane and water react to form carbon monoxide and hydrogen according to the equation \( \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g) \).
   a. What is the standard free energy change for this reaction?
   b. What is \( K_p \) for this reaction?
   c. What is the carbon monoxide pressure if 1.3 atm of methane reacts with 0.8 atm of water, producing 1.8 atm of hydrogen gas?
   d. What is the hydrogen gas pressure if 2.0 atm of methane is allowed to react with 1.1 atm of water?
   e. At what temperature does the reaction become spontaneous?

3. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.
   a. \( \text{CCl}_4(g) + 6\text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_2(g) + 4\text{HCl}(aq); \Delta G^\circ = -377 \text{ kJ/mol} \)
   b. \( \text{Xe}(g) + 2\text{F}_2(g) \rightleftharpoons \text{XeF}_4(s); \Delta H^\circ = -66.3 \text{ kJ/mol}, \Delta S^\circ = -102.3 \text{ J/(mol·K)} \)
   c. \( \text{PCl}_3(g) + \text{S} \rightleftharpoons \text{PSCl}_3(l); \Delta G^\circ(\text{PCl}_3) = -272.4 \text{ kJ/mol}, \Delta G^\circ_f(\text{PSCl}_3) = -363.2 \text{ kJ/mol} \)

4. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.
   a. \( 2\text{KClO}_3(s) \rightleftharpoons 2\text{KCl}(s) + 3\text{O}_2(g); \Delta G^\circ = -225.8 \text{ kJ/mol} \)
   b. \( \text{CoCl}_2(s) + 6\text{H}_2\text{O}(gel) = 2\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(s); \Delta H^\circ_{\text{rxn}} = -352 \text{ kJ/mol}, \Delta S^\circ_{\text{rxn}} = -899 \text{ J/(mol·K)} \)
   c. \( 2\text{PCl}_3(g) + \text{O}_2(g) = 2\text{POCl}_3(g); \Delta G^\circ_f(\text{PCl}_3) = -272.4 \text{ kJ/mol}, \Delta G^\circ_f(\text{POCl}_3) = -558.5 \text{ kJ/mol} \)

5. The gas-phase decomposition of \( \text{N}_2\text{O}_4 \) to \( \text{NO}_2 \) is an equilibrium reaction with \( K_p = 4.66 \times 10^{-3} \). Calculate the standard free-energy change for the equilibrium reaction between \( \text{N}_2\text{O}_4 \) and \( \text{NO}_2 \).

6. The standard free-energy change for the dissolution \( \text{K}_4\text{Fe(CN)}_6 \cdot \text{H}_2\text{O}(s) = 4\text{K}^+(aq) + \text{Fe(CN)}_6^{4-}(aq) + \text{H}_2\text{O}(l) \) is 26.1 kJ/mol. What is the equilibrium constant for this process at 25°C?

7. Ammonia reacts with water in liquid ammonia solution (am) according to the equation \( \text{NH}_3(g) + \text{H}_2\text{O}(am) \rightleftharpoons \text{NH}_4^+(am) + \text{OH}^-(am) \). The change in enthalpy for this reaction is 21 kJ/mol, and \( \Delta S^\circ = -303 \text{ J/(mol·K)} \). What is the equilibrium constant for the reaction at the boiling point of liquid ammonia (−31°C)?

8. At 25°C, a saturated solution of barium carbonate is found to have a concentration of \( [\text{Ba}^{2+}] = [\text{CO}_3^{2-}] = 5.08 \times 10^{-5} \) M. Determine \( \Delta G^\circ \) for the dissolution of \( \text{BaCO}_3 \).

9. Lead phosphates are believed to play a major role in controlling the overall solubility of lead in acidic soils. One of the dissolution reactions is \( \text{Pb}_3(\text{PO}_4)_2(s) + 4\text{H}^+(aq) = 3\text{Pb}^{2+}(aq) + 2\text{H}_2\text{PO}_4^-(aq) \), for which \( \log K = -1.80 \). What is \( \Delta G^\circ \) for this reaction?

10. The conversion of butane to 2-methylpropane is an equilibrium process with \( \Delta H^\circ = -2.05 \text{ kcal/mol} \) and \( \Delta G^\circ = -0.89 \text{ kcal/mol} \).
    a. What is the change in entropy for this conversion?
    b. Based on structural arguments, are the sign and magnitude of the entropy change what you would expect? Why?
    c. What is the equilibrium constant for this reaction?

11. The reaction of \( \text{CaCO}_3(s) \) to produce \( \text{CaO}(s) \) and \( \text{CO}_2(g) \) has an equilibrium constant at 25°C of \( 2 \times 10^{-23} \). Values of \( \Delta H^\circ_f \) are as follows: \( \text{CaCO}_3, -1207.6 \text{ kJ/mol}; \text{CaO}, -634.9 \text{ kJ/mol}; \) and \( \text{CO}_2, -393.5 \text{ kJ/mol} \).
    a. What is \( \Delta G^\circ \) for this reaction?
    b. What is the equilibrium constant at 900°C?
    c. What is the partial pressure of \( \text{CO}_2(g) \) in equilibrium with \( \text{CaO} \) and \( \text{CaCO}_3 \) at this temperature?
d. Are reactants or products favored at the lower temperature? at the higher temperature?

12. In acidic soils, dissolved Al\(^{3+}\) undergoes a complex formation reaction with SO\(_4^{2-}\) to form [AlSO\(_4^{4+}\)]. The equilibrium constant at 25°C for the reaction Al\(^{3+}\)(aq)+SO\(_4^{2-}\)(aq)⇌AlSO\(_4^{4+}\)(aq) is 1585.
   a. What is ΔG° for this reaction?
   b. How does this value compare with ΔG° for the reaction Al\(^{3+}\)(aq)+F\(^-\)(aq)⇌AlF\(_2^+\)(aq), for which K = 10\(^7\) at 25°C?
   c. Which is the better ligand to use to trap Al\(^{3+}\) from the soil?

Numerical Answers

1. 
   a. −28.4 kJ/mol
   b. −26.1 kJ/mol
   c. −19.9 kJ/mol

3. 
   a. 1.21 × 10\(^{66}\); equilibrium lies far to the right.
   b. 1.89 × 10\(^6\); equilibrium lies to the right.
   c. 5.28 × 10\(^{16}\); equilibrium lies far to the right.

5. 13.3 kJ/mol

7. 5.1 × 10\(^{-21}\)

9. 10.3 kJ/mol

11. 
   a. 129.5 kJ/mol
   b. 6
   c. 6.0 atm
   d. Products are favored at high T; reactants are favored at low T.