A general chemistry Libretexts Textmap organized around the textbook

**Chemistry: The Central Science**

by Brown, LeMay, Busten, Murphy, and Woodward

1. **Chapter 1: Introduction: Matter and Measurement**
   2. 1.1: The Study of Chemistry
   3. 1.2: Classification of Matter
   4. 1.3: Properties of Matter
   5. 1.4: Units of Measurement
   6. 1.5: Uncertainty in Measurement
   7. 1.6: Dimensional Analysis
8. 1.E: Matter and Measurement (Exercises)
9. 1.S: Matter and Measurement (Summary)

• 2

1. **Chapter 2: Atoms, Molecules, and Ions**
   2. 2.1: The Atomic Theory of Matter
   3. 2.2: The Discovery of Atomic Structure
   4. 2.3: The Modern View of Atomic Structure
   5. 2.4: Atomic Mass
   6. 2.5: The Periodic Table
   7. 2.6: Molecules and Molecular Compounds
   8. 2.7: Ions and Ionic Compounds
   9. 2.8: Naming Inorganic Compounds
10. 2.9: Some Simple Organic Compounds
11. 2.E: Atoms, Molecules, and Ions (Exercises)
12. 2.S: Atoms, Molecules, and Ions (Summary)

• 3

1. **Chapter 3: Stoichiometry: Chemical Formulas and Equations**
   2. 3.1: Chemical Equations
   3. 3.2: Some Simple Patterns of Chemical Reactivity
   4. 3.3: Formula Masses
   5. 3.4: Avogadro's Number and the Mole
   6. 3.5: Empirical Formulas from Analysis
   7. 3.6: Quantitative Information from Balanced Equations
   8. 3.7: Limiting Reactants
   9. 3.E: Stoichiometry (Exercises)
10. **3.S: Stoichiometry (Summary)**

**4**

1. **Chapter 4: Reactions in Aqueous Solution**
2. **4.1: General Properties of Aqueous Solutions**
3. **4.2: Precipitation Reactions**
4. **4.3: Acid-Base Reactions**
5. **4.4: Oxidation-Reduction Reactions**
6. **4.5: Concentration of Solutions**
7. **4.6: Solution Stoichiometry and Chemical Analysis**
8. **4.E: Reactions in Aqueous Solution (Exercises)**

**5**

1. **Chapter 5: Thermochemistry**
2. **5.1: The Nature of Energy**
3. **5.2: The First Law of Thermodynamics**
4. **5.3: Enthalpy**
5. **5.4: Enthalpy of Reaction**
6. **5.5: Calorimetry**
7. **5.6: Hess’s Law**
8. **5.7: Enthalpies of Formation**
9. **5.8: Foods and Fuels**
10. **5.E: Thermochemistry (Exercises)**
11. **5.S: Thermochemistry (Summary)**

**6**

1. **Chapter 6: Electronic Structure of Atoms**
2. **6.1: The Wave Nature of Light**
3. **6.2: Quantized Energy and Photons**
4. **6.3: Line Spectra and the Bohr Model**
5. **6.4: The Wave Behavior of Matter**
6. **6.5: Quantum Mechanics and Atomic Orbitals**
7. **6.6: 3D Representation of Orbitals**
8. **6.7: Many-Electron Atoms**
9. **6.8: Electron Configurations**
10. **6.9: Electron Configurations and the Periodic Table**
Chapter 7: Periodic Properties of the Elements

7.1: Development of the Periodic Table
7.2: Effective Nuclear Charge
7.3: Sizes of Atoms and Ions
7.4: Ionization Energy
7.5: Electron Affinities
7.6: Metals, Nonmetals, and Metalloids
7.7: Group Trends for the Active Metals
7.8: Group Trends for Selected Nonmetals
7.9: Periodic Properties of the Elements (Exercises)
7.10: Periodic Properties of the Elements (Summary)

Chapter 8: Basic Concepts of Chemical Bonding

8.1: Chemical Bonds, Lewis Symbols, and the Octet Rule
8.2: Ionic Bonding
8.3: Covalent Bonding
8.4: Bond Polarity and Electronegativity
8.5: Drawing Lewis Structures
8.6: Resonance Structures
8.7: Exceptions to the Octet Rule
8.8: Strength of Covalent Bonds
8.9: Basic Concepts of Chemical Bonding (Exercises)
8.10: Basic Concepts of Chemical Bonding (Summary)

Chapter 9: Molecular Geometry and Bonding Theories

9.1: Molecular Shapes
9.2: The VSEPR Model
9.3: Molecular Shape and Molecular Polarity
9.4: Covalent Bonding and Orbital Overlap
9.5: Hybrid Orbitals
9.6: Multiple Bonds
9.7: Molecular Orbitals
9.8: Second-Row Diatomic Molecules
9.9: Molecular Geometry and Bonding Theories (Exercises)
9.10: Molecular Geometry and Bonding Theories (Summary)
1. Chapter 10: Gases
   10.1: Characteristics of Gases
   10.2: Pressure
   10.3: The Gas Laws
   10.4: The Ideal Gas Equation
   10.5: Further Applications of the Ideal-Gas Equations
   10.6: Gas Mixtures and Partial Pressures
   10.7: Kinetic-Molecular Theory
   10.8: Molecular Effusion and Diffusion
   10.9: Real Gases - Deviations from Ideal Behavior
   10.E: Exercises
   10.S: Gases (Summary)

11. Chapter 11: Liquids and Intermolecular Forces
   11.1: A Molecular Comparison of Gases, Liquids, and Solids
   11.2: Intermolecular Forces
   11.3: Some Properties of Liquids
   11.4: Phase Changes
   11.5: Vapor Pressure
   11.6: Phase Diagrams
   11.7: Structure of Solids
   11.8: Bonding in Solids
   11.E: Liquids and Intermolecular Forces (Exercises)
   11.S: Liquids and Intermolecular Forces (Summary)

12. Chapter 12: Solids and Modern Materials
   12.1: Classes of Materials
   12.2: Materials for Structure
   12.3: Materials for Medicine
   12.4: Materials for Electronics
   12.5: Materials for Optics
   12.6: Materials for Nanotechnology
   12.E: Solids and Modern Materials (Exercises)

13
5. **16.4: The pH Scale**

6. **16.5: Strong Acids and Bases**

7. **16.6: Weak Acids**

8. **16.7: Weak Bases**

9. **16.8: Relationship Between $K_a$ and $K_b$**

10. **16.9: Acid-Base Properties of Salt Solutions**

11. **16.10: Acid-Base Behavior and Chemical Structure**

12. **16.11: Lewis Acids and Bases**


**17**

1. **Chapter 17: Additional Aspects of Aqueous Equilibria**

2. **17.1: The Common-Ion Effect**

3. **17.2: Buffered Solutions**

4. **17.3: Acid-Base Titrations**

5. **17.4: Solubility Equilibria**

6. **17.5: Factors that Affect Solubility**

7. **17.6: Precipitation and Separation of Ions**

8. **17.7: Qualitative Analysis for Metallic Elements**


10. **17.S: Additional Aspects of Aqueous Equilibria (Summary)**

**18**

1. **Chapter 18: Chemistry of the Environment**

2. **18.1: Earth's Atmosphere**

3. **18.2: Outer Regions of the Atmosphere**

4. **18.3: Ozone in the Upper Atmosphere**

5. **18.4: Chemistry of the Troposphere**

6. **18.5: The World Ocean**

7. **18.6: Fresh Water**

8. **18.7: Green Chemistry**


**19**

1. **Chapter 19: Chemical Thermodynamics**

2. **19.1: Spontaneous Processes**


4. **19.3: The Molecular Interpretation of Entropy**
5. **19.4: Entropy Changes in Chemical Reactions**
6. **19.5: Gibbs Free Energy**
7. **19.6: Free Energy and Temperature**
8. **19.7: Free Energy and the Equilibrium Constant**
9. **19.E: Chemical Thermodynamics (Exercises)**

• **20**

1. **Chapter 20: Electrochemistry**
2. **20.1: Oxidation States & Redox Reactions**
3. **20.2: Balanced Oxidation-Reduction Equations**
4. **20.3: Voltaic Cells**
5. **20.4: Cell Potential Under Standard Conditions**
6. **20.5: Gibbs Energy and Redox Reactions**
7. **20.6: Cell Potential Under Nonstandard Conditions**
8. **20.7: Batteries and Fuel Cells**
9. **20.8: Corrosion**
10. **20.9: Electrolysis**
11. **20.E: Electrochemistry (Exercises)**

• **21**

1. **Chapter 21: Nuclear Chemistry**
2. **21.1: Radioactivity**
3. **21.2: Patterns of Nuclear Stability**
4. **21.3: Nuclear Transmutations**
5. **21.4: Rates of Radioactive Decay**
6. **21.6: Energy Changes in Nuclear Reactions**
7. **21.7: Nuclear Fission**
8. **21.8: Nuclear Fusion**
9. **21.9: Biological Effects of Radiation**
10. **21.E: Exercises**
11. **21.S: Nuclear Chemistry (Summary)**

• **22**

1. **Chapter 22: Chemistry of the Nonmetals**
2. **22.1: General Concepts: Periodic Trends and Reactions**
3. **22.2: Hydrogen**
4. **22.3: Group 18: Noble Gases**
5. **22.4: Group 17: The Halogens**
6. **22.5: Oxygen**
7. 22.6: The Other Group 16 Elements: S, Se, Te, and Po
8. 22.7: Nitrogen
9. 22.8: The Other Group 15 Elements: P, As, Sb, and Bi
10. 22.9: Carbon
11. 22.10: The Other Group 14 Elements: Si, Ge, Sn, and Pb
12. 22.11: Boron
13. 22.E: Chemistry of the Nonmetals (Exercises)
14. 22.S: Chemistry of the Nonmetals (Summary)

• 23

1. Chapter 23: Metals and Metallurgy
2. 23.1: Occurance and Distribution of Metals
3. 23.2: Pyrometallurgy
4. 23.3: Hydrometallurgy
5. 23.4: Electrometallurgy
6. 23.5: Metallic Bonding
7. 23.6: Alloys
8. 23.7: Transition Metals
9. 23.8: Chemistry of Selected Transition Metals
10. 23.E: Metals and Metallurgy (Exercises)

• 24

1. Chapter 24: Chemistry of Coordination Chemistry
2. 24.1: Metal Complexes
3. 24.2: Ligands with more than one Donor Atom
4. 24.3: Nomenclature of Coordination Chemistry
5. 24.4: Isomerization
6. 24.5: Color and Magnetism
7. 24.6: Crystal Field Theory
8. 24.E: Chemistry of Coordination Chemistry (Exercises)

• 25

1. Chapter 25: Chemistry of Life: Organic and Biological Chemistry
2. 25.1: General Characteristics of Organic Molecules
3. 25.2: Introduction to Hydrocarbons
4. 25.3: Alkanes
5. 25.4: Unsaturated Hydrocarbons
6. 25.5: Functional Groups
7. 25.6: Compounds with a Carbonyl Group
8. **25.7: Chirality in Organic Chemistry**
9. **25.8: Introduction to Biochemistry**
10. **25.9: Proteins**
11. **25.10: Carbohydrates**
12. **25.11: Nucleic Acids**
13. **25.E: Organic and Biological Chemistry (Exercises)**
14. **25.S: Organic and Biological Chemistry (Summary)**

- **Homework**

1. **1.E: Matter and Measurement (Exercises)**
2. **2.E: Atoms, Molecules, and Ions (Exercises)**
3. **3.E: Stoichiometry (Exercises)**
4. **4.E: Aqueous Reactions (Exercises)**
5. **5.E: Thermochemistry (Exercises)**
8. **8.E: Chemical Bonding Basics (Exercises)**
10. **10.E: Gases (Exercises)**
11. **11.E: Liquids and Intermolecular Forces (Exercises)**
15. **15.E: Chemical Equilibrium (Exercises)**
17. **17.E: Additional Aspects of Aqueous Equilibria (Exercises)**
18. **18.E: Chemistry of the Environment (Exercises)**
19. **19.E: Chemical Thermodynamics (Exercises)**
22. **22.E: Chemistry of the Nonmetals (Exercises)**
23. **23.E: Metals and Metallurgy (Exercises)**
24. **24.E: Chemistry of Coordination Chemistry (Exercises)**
25. **25.E: Organic and Biological Chemistry (Exercises)**

These are homework exercises to accompany the Textmap created for "Chemistry: The Central Science" by Brown et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.
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_{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_{soln} to be greater or less than zero? Why? What opposing factors must be considered in making your prediction?
9. Aniline (C₆H₅NH₂) 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_{soln} in H₂O to be greater than, less than, or equal to ΔS_{soln} in CH₃CH₂OH? Why?

**Conceptual Answers**

1. No, it is irreversible; no work is done because the external pressure is effectively zero.

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_{soln} in ethanol will be more positive than ΔS_{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: ΔS_{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>ΔH_{fus} (kJ/mol)</th>
<th>ΔS_{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>CH₃CN</td>
<td>8.2</td>
<td>35.9</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.94</td>
<td></td>
<td>−182.5</td>
</tr>
</tbody>
</table>
## Compound Properties

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH$_{\text{fus}}$ (kJ/mol)</th>
<th>ΔS$_{\text{fus}}$ [J/(mol·K)]</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>18.2</td>
<td>45.1</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>ΔH$_{\text{vap}}$ (kJ/mol)</th>
<th>ΔS$_{\text{vap}}$ [J/(mol·K)]</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexanoic acid</td>
<td>71.1</td>
<td>105.7</td>
<td></td>
</tr>
<tr>
<td>hexane</td>
<td>28.9</td>
<td>85.5</td>
<td></td>
</tr>
<tr>
<td>formic acid</td>
<td>60.7</td>
<td></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 ΔS$_{\text{vap}}$ 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 \( \Delta H \) and \( \Delta S \)?

4. The equilibrium \( 2AB \rightleftharpoons A_2B_2 \) 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 \( \Delta G \) a state function that describes a system or its surroundings? Do its components—\( \Delta H \) and \( \Delta S \)—describe a system or its surroundings?

6. How can you use \( \Delta G \) 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 \( \Delta H^\circ_{\text{rxn}} = 7.3 \text{ kcal/mol} \). Using thermodynamic arguments, propose an explanation as to why methanol forms.

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**Conceptual Answers**

9. In order for the reaction to occur spontaneously, \( \Delta G \) for the reaction must be less than zero. In this case, \( \Delta S \) must be positive, and the \( T \Delta S \) term outweighs the positive value of \( \Delta H \).

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**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. \( \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}(l) \)
   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?
4. A student was asked to propose three reactions for the oxidation of carbon or a carbon compound to CO or CO₂. 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>ΔH°298 (kcal/mol)</th>
<th>ΔS°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>

5. Tungsten trioxide (WO₃) 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?
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 \( \text{BaI}_2 \), but that information is not listed in your tables. However, you have been able to obtain the following information:

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H^\circ_f ) (kJ/mol)</th>
<th>( S^\circ ) [J/(mol·K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MCO}_3 )</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>( \text{CO}_2 )</td>
<td>−393.5</td>
<td>213.8</td>
</tr>
</tbody>
</table>

You know that \( \Delta G^\circ \) for the reaction at 25°C is 22.64 kJ/mol. What is \( \Delta H^\circ \) for this reaction? What is \( S^\circ \) for \( \text{BaI}_2 \)?

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**Numerical Answers**

1.

a. \(-237.1\) kJ/mol; spontaneous as written
b. \(-241.9\) kJ/mol; spontaneous as written
c. 8.0 kJ/mol; spontaneous in reverse direction.
d. 141.9 kJ/mol; spontaneous in reverse direction.

3.

a. Not spontaneous at any \( T \)
b. Not spontaneous at 25°C; spontaneous above 7400 K
c. Spontaneous at 25°C
19.6: Free Energy and Temperature

19.7: Free Energy and the Equilibrium Constant

Conceptual Problems

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 N_2(g) + 3F_2(g) → 2NF_3(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 CO_2
   and H_2, as shown in the equation CO(g) + H_2O(g) ⇌ CO_2(g) + H_2(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_{H_2O} = 0.8 atm,
      P_{CO_2} = 2.0 atm, and P_{H_2} = 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
   CH_4(g) + H_2O(g) ⇌ CO(g) + 3H_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. $\text{PCl}_3(g)+\text{S} \rightleftharpoons \text{PSCl}_3(l)$; $\Delta G^\circ_f(\text{PCl}_3) = -272.4 \text{ kJ/mol}$, $\Delta G^\circ_f(\text{PSCl}_3) = -363.2 \text{ kJ/mol}$

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. $\text{CoCl}_2(s)+6\text{H}_2\text{O}(g)\rightleftharpoons \text{CoCl}_2\cdot 6\text{H}_2\text{O}(s)$; $\Delta H^\circ_{\text{rxn}} = -352 \text{ kJ/mol}$, $\Delta S^\circ_{\text{rxn}} = -899 \text{ J/(mol·K)}$
   c. $2\text{PCl}_3(g)+\text{O}_2(g)\rightleftharpoons 2\text{POCl}_3(g)$; $\Delta G^\circ_f(\text{PCl}_3) = -272.4 \text{ kJ/mol}$, $\Delta G^\circ_f(\text{POCl}_3) = -558.5 \text{ kJ/mol}$

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 $\text{K}_4\text{Fe(CN)}_6\cdot \text{H}_2\text{O}(s)\rightleftharpoons 4\text{K}^+(aq)+\text{Fe(CN)}_6^{4-}(aq)+\text{H}_2\text{O}(l)$ 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 $\text{NH}_3(g)+\text{H}_2\text{O}(\text{am}) = \text{NH}_4^+(\text{am})+\text{OH}^-(\text{am})$. 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 $\text{Pb}_3(\text{PO}_4)_2(s)+4\text{H}^+(aq)\rightleftharpoons 3\text{Pb}^{2+}(aq)+2\text{H}_2\text{PO}_4^-(aq)$, 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$_4$]$^+$. The equilibrium constant at 25°C for the reaction $\text{Al}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightleftharpoons \text{AlSO}_4^+(\text{aq})$ is 1585.

   a. What is $\Delta G^\circ$ for this reaction?
   b. How does this value compare with $\Delta G^\circ$ for the reaction $\text{Al}^{3+}(\text{aq}) + \text{F}^-(\text{aq}) \rightleftharpoons \text{AlF}^2+(\text{aq})$, for which $K = 10^7$ at 25°C?
   c. Which is the better ligand to use to trap Al$^{3+}$ from the soil?

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### Numerical Answers

1. 
   a. $-28.4 \text{ kJ/mol}$
   b. $-26.1 \text{ kJ/mol}$
   c. $-19.9 \text{ kJ/mol}$

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

5. 13.3 kJ/mol

7. $5.1 \times 10^{-21}$

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.