Chapter 11
Spontaneous Change and Equilibrium

• 11-1 Enthalpy and Spontaneous Change
• 11-2 Entropy
• 11-3 Absolute Entropies and Chemical Reactions
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• 11-6 The Gibbs Function and Chemical Reactions
• 11-7 The Gibbs Function and the Equilibrium Constant
• 11-8 The Temperature Dependence of Equilibrium Constants
• This entire Chapter deals with a concept called Entropy and the Gibbs function
• Both are new “state properties”
• Entropy = S which has the units JK\(^{-1}\)mol\(^{-1}\)
• Consider Energy, it is perhaps obvious that processes occur spontaneously to produce a state of lower energy

• But, a chunk of ice at Room Temperature, spontaneously melts, forming a state of higher Energy

• Apparently more than energy is involved in determining the direction of spontaneous change
• This additional factor is the tendency of a system to assume the most random molecular arrangement possible

• Systems become disordered, more random

• Natural processes are favored which result in
  – Decreased Energy (favored)
  – Increased Entropy (favored)

• These two factors can oppose each other. Which one wins out?
• Recall from Chapter 10 lecture notes
• **Third Law of Thermodynamics**
  \[ \Delta S = 0 \text{ at } 0^\circ K \]
• At absolute zero the Entropy term contributes nothing to the direction of spontaneous change
• The most stable state has the lowest energy
• A temperature increases, molecular motion increases and the tendency to disorder becomes more important
• At sufficiently high temperatures the Entropy factor becomes large enough to overcome even an unfavorable energy change
• For $\text{H}_2\text{O} \ (s) \rightarrow \text{H}_2\text{O} \ (l)$
• Above $T_m$, the Entropy is dominant so spontaneous melting takes place
• Below $T_m$, the energy decrease is dominant so spontaneous freezing takes place
• Temperature is a critical factor
Disorder and Entropy

- **Entropy** is a quantitative measure of the number of microstates available to the molecules in a system.
- **Entropy** is the degree of randomness or disorder in a system.

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• For phase transitions, at temperature $T$ under *equilibrium conditions*
  – Melting (solid to liquid)
  – Fusion (liquid to solid)
  – Vaporization (liquid to gas)
  – Condensation (gas to liquid)

• Define $S^\circ$ as the absolute molar Entropy, which is the absolute entropy of 1 mol of a substance in standard state

• Appendix D gives standard molar entropy values, $S^\circ$ in units $\text{JK}^{-1}\text{mol}^{-1}$
Entropies of Reaction

- $\Delta S^\circ_r = S^\circ_{\text{products}} - S^\circ_{\text{reactants}}$
- $\Delta S^\circ_r$ is the sum of products minus the sum of the reactants
- For a general reaction
  
  $a \, A + b \, B \rightarrow c \, C + d \, D$
Exercise 11-3

(a) Use Data from Appendix D to calculate $\Delta S_r^\circ$ at 298.15 K for the reaction

$$2\text{H}_2\text{S}(g) + 3\text{O}_2(g) \rightarrow 2\text{SO}_2(g) + 2\text{H}_2\text{O}(g)$$

(b) Calculate $\Delta S^\circ$ of the system when 26.71 g of $\text{H}_2\text{S}(g)$ reacts with excess $\text{O}_2(g)$ to give $\text{SO}_2(g)$ and $\text{H}_2\text{O}(g)$ and no other products at 298.15K
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Solution

Notice that this is minus, which is consistent with 5 to 4 decrease in the amount of gas
Exercise 11-3

2H₂S(g) + 3O₂(g) → 2SO₂(g) + 2H₂O(g)

(b) Calculate $\Delta S^\circ$ of the system when 26.71 g of H₂S(g) reacts with excess O₂(g) to give SO₂(g) and H₂O(g) and no other products at 298.15K

Solution:
Chapter 11
Spontaneous Change and Equilibrium

• Second Law of Thermodynamics
In a real spontaneous process the Entropy of the universe (meaning the system plus its surroundings) must increase.

• if $\Delta S_{\text{universe}} = 0$, then everything is in equilibrium
• The 2\textsuperscript{nd} Law of Thermodynamics profoundly affects how we look at nature and processes
Summarize a few Concepts

• 1\textsuperscript{st} Law of Thermodynamics
  – In any process, the total energy of the universe remains unchanged: energy is conserved
  – A process and its reverse are equally allowed
    \[ E_{\text{forward}} = - E_{\text{reverse}} \]
    (conservation of energy)

• 2\textsuperscript{nd} Law of Thermodynamics
  – \( S \), the entropy of a universe, increases in only one of the two directions of a reaction
  – Processes that decrease \( \Delta S \) are impossible. Or improbable beyond conception
Gibbs Function

- How are Enthalpy and Entropy related?

- G has several names
  1. Gibbs function
  2. Gibbs free energy
  3. Free Enthalpy

- For the *change* in the Gibbs Energy of system, at constant Temperature and Pressure
<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta S_{\text{univ}} &gt; 0$</td>
<td>Spontaneous</td>
</tr>
<tr>
<td>$\Delta S_{\text{univ}} = 0$</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>$\Delta S_{\text{univ}} &lt; 0$</td>
<td>Non-spontaneous</td>
</tr>
</tbody>
</table>
Typical example using Gibbs Free energy

• Benzene, C₆H₆, boils at 80.1°C. \( \Delta H_{\text{vap}} = 30.8 \text{ kJ} \)
  – a) Calculate \( \Delta S_{\text{vap}} \) for 1 mole of benzene
  – B) at 60°C and pressure = 1 atm does benzene boil?
Typical example using Gibbs Free energy

• Benzene, C₆H₆, boils at 80.1°C.  
  \[ \Delta H_{\text{vap}} = 30.8 \text{ kJ} \]
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  – B) at 60°C and pressure = 1 atm does benzene boil?
Trouton’s rule

• All most all liquids have about the same $\Delta S_{\text{vap}}$ molar entropy of vaporization
• Called Trouton’s rule
  
  $\Delta S_{\text{vap}} = 88 \pm 5 \ \text{JK}^{-1}\text{mol}^{-1}$

• In the last benzene boiling point problem, we calculated 87.2 JK$^{-1}$mol$^{-1}$. This fits Trouton’s rule.
The Gibbs Function and Chemical Reactions

$$\Delta G = \Delta H - T \cdot \Delta S$$

- $\Delta G_f^\circ$ is the standard molar Gibbs function of formation
- Because $G$ is a State Property, for a general reaction
  
a A + b B \rightarrow c C + d D
Example 11-7

• Calculate $\Delta G^\circ$ for the following reaction at 298.15K. Use Appendix D for additional information needed.

$$3\text{NO}(g) \rightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g)$$
Effects of Temperature on $\Delta G^\circ$

For temperatures other than 298K or 25°C

$\Delta G = \Delta H - T \cdot \Delta S$

- Typically $\Delta H$ and $\Delta S$ are *almost* constant over a broad range

$$3\text{NO}(g) \rightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g)$$

- For above reaction, as Temperature increases $\Delta G$ becomes more positive, i.e., less negative.
For temperatures other than 298K or 25C

\[ \Delta G = \Delta H - T \cdot \Delta S \]
For temperatures other than 298K or 25C
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Case A

Case B

Case C

Case D
The Gibbs Function and the Equilibrium Constant

• What about non-standard states, other than 1 atm or a conc. \([X] = 1 \text{ mol/L}\)?

\[ aA + bB \rightleftharpoons cD + dD \]
The Reaction Quotient

\[ aA + bB \xrightleftharpoons[\text{reverse}]{\text{forward}} cC + dD \]

\[ \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = K \]

Note that \( K \) (the Equilibrium Constant) uses \textit{equilibrium partial pressures}.

Note that \( Q \) (the reaction quotient) uses \textit{prevailing partial pressures}, not necessarily at equilibrium.
\[ \Delta G = \Delta G^\circ + RT \ln Q \]

Where \( Q \) is the reaction quotient
\[ a \text{ A} + b \text{ B} \leftrightarrow c \text{ C} + d \text{ D} \]

- If
  - The amount of products are too high relative to the amounts of reactants present, and the reaction shifts in reverse (to the left) to achieve equilibrium
- If \( Q = K \) equilibrium
- If
  - The amounts of reactants are too high relative to the amounts of products present, and the reaction proceeds in the forward direction (to the right) toward equilibrium

\[
Q = \left( \frac{P_C P_D}{P_A P_B} \right)_{\text{any conditions}}
\]

\[
K = \left( \frac{P_C P_D}{P_A P_B} \right)_{\text{equilibrium}}
\]

compare
At Equilibrium conditions

**NOTE:** we can now calculate equilibrium constants \((K)\) for reactions from standard \(\Delta G_f\) functions of formation

\[
\Delta G = \Delta G^° + RT \ln Q
\]

- Where \(Q\) is the reaction quotient

\[
a \ A + b \ B \leftrightarrow c \ C + d \ D
\]

  - If \(Q<K\) the rxn shifts towards the product side
  - If \(Q=K\) equilibrium
  - If \(Q>K\) the rxn shifts toward the reactant side
### Criteria for Spontaneity in a Chemical Reaction

<table>
<thead>
<tr>
<th>Spontaneous Processes</th>
<th>Equilibrium Processes</th>
<th>Non-spontaneous Processes</th>
<th>Conditions</th>
</tr>
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<tbody>
<tr>
<td>$\Delta S_{univ} &gt; 0$</td>
<td>$\Delta S_{univ} = 0$</td>
<td>$\Delta S_{univ} &lt; 0$</td>
<td>All conditions</td>
</tr>
<tr>
<td>$\Delta G_f &lt; 0$</td>
<td>$\Delta G_f = 0$</td>
<td>$\Delta G_f &gt; 0$</td>
<td>Constant P and T</td>
</tr>
<tr>
<td>$Q &lt; K$</td>
<td>$Q = K$</td>
<td>$Q &gt; K$</td>
<td>Constant P and T</td>
</tr>
</tbody>
</table>
Example 11-9

• The $\Delta G^\circ_r$ for the following reaction at 298.15K was obtained in example 11-7. Now, calculate the equilibrium constant for this reaction at 25°C.

$$3\text{NO(g)} \rightarrow \text{N}_2\text{O(g)} + \text{NO}_2\text{(g)}$$

• Strategy

Use - $\Delta G^\circ = RT \ln K$

$\Delta G^\circ = -104.18$ kJ from example 11-7
Example 11-9

3NO(g) → N₂O(g) + NO₂(g)

• Solution

Use

- ΔG° = RT ln K

Rearrange

ln K = \frac{-\Delta G°}{RT}

Use ΔG_r° = - 104.18 kJ from Ex. 11-7
The Temperature Dependence of Equilibrium Constants

• Where does this come from?
• Recall $\Delta G = \Delta H - T \cdot \Delta S$
• Divide by RT, then multiply by -1

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}$$
• Notice that this is $y = mx + b$ the equation for a straight line

• $\ln K$ vs. $1/T$
• If we have two different Temperatures and K’s (equilibrium constants)

• Now given $\Delta H$ and $T$ at one temperature, we can calculate $K$ at another temperature, assuming that $\Delta H$ and $\Delta S$ are constant over the temperature range.
Exercise 11-11

• The reaction

$$2 \text{Al}_3\text{Cl}_9 (g) \rightarrow 3 \text{Al}_2\text{Cl}_6 (g)$$

Has an equilibrium constant of $8.8 \times 10^3$ at 443K and a $\Delta H_r^\circ = 39.8$ kJmol$^{-1}$ at 443K. Estimate the equilibrium constant at a temperature of 600K.

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \text{ van't Hoff Eq.}$$

$$\ln \frac{K_{600}}{K_{443}} = \frac{39,800 \text{ Jmol}^{-1}}{8.315 \text{JK}^{-1}\text{mol}^{-1}} \left( \frac{1}{443\text{K}} - \frac{1}{600\text{K}} \right)$$

$$\ln\left(\frac{K_{600}}{8.8 \times 10^3}\right) = 2.827$$

$$\frac{K_{600}}{8.8 \times 10^3} = e^{2.827} = 16$$

$$K_{600} = 1.5 \times 10^5$$
The Variation of Vapor Pressure with Temperature

- Used for equilibrium between pure liquids and their vapors.
- $P_2$ and $P_1 =$ vapor pressure at different temperatures
- At the boiling point of a substance at 1 atm this simplifies to
• Natural processes are favored which result in
  – Decreased Energy (favored)
  – Increased Entropy (favored)

• **Entropy** is a quantitative measure of the number of microstates available to the molecules in a system

• **Entropy** is the degree of randomness or disorder in a system

• The **Entropy** of all substances is positive
  
  E.g., \( \Delta S = S_I - S_s > 0 \)
Chapter 11 Summary

- Natural processes are favored which result in
  - Decreased Energy (favored)
  - Increased Entropy (favored)

- **Entropy** is a quantitative measure of the number of microstates available to the molecules in a system
- **Entropy** is the degree of randomness or disorder in a system
- The **Entropy** of all substances is positive
  \[ \Delta S = S_f - S_s > 0 \]
Entropies of Reaction

- \( \Delta S_r^° = S°_{\text{products}} - S°_{\text{reactants}} \)

- For a general reaction
  \[ a \ A + b \ B \rightarrow c \ C + d \ D \]
  \[ \Delta S° = c\Delta S° (C) + d\Delta S° (D) - a\Delta S° (A) - b\Delta S° (B) \]

\[ \Delta S_{\text{univ}} > 0 \quad \text{Spontaneous} \]

\[ \Delta S_{\text{univ}} = 0 \quad \text{Equilibrium} \]

\[ \Delta S_{\text{univ}} < 0 \quad \text{Non-spontaneous} \]
\[ \Delta G = \Delta H - T \cdot \Delta S \]

- \( \Delta G^\circ_f \) is the standard molar Gibbs function of formation

- Because \( G \) is a State Property, for a general reaction
  \[ a \text{ A} + b \text{ B} \rightarrow c \text{ C} + d \text{ D} \]
  \[ \Delta G^\circ_f = c \Delta G^\circ_f (C) + d \Delta G^\circ_f (D) - a \Delta G^\circ_f (A) - b \Delta G^\circ_f (B) \]

For a change at constant temperature and pressure

- \( \Delta G_{\text{sys}} < 0 \) Spontaneous
- \( \Delta G_{\text{sys}} = 0 \) Equilibrium
- \( \Delta G_{\text{sys}} > 0 \) Non-spontaneous, but the reverse is spontaneous
\[ aA + bB \rightleftharpoons cD + dD \]

\[ \Delta G = \Delta G^\circ + RT \ln Q \]

Where \( Q \) is the reaction quotient

\[ \ln K = \frac{-\Delta G^\circ}{RT} \]

\[ \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]

\[ \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

van't Hoff Equation

\[ \ln \frac{K_2}{K_1} = \ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

Clausius - Clapeyron Equation
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Spontaneous Change and Equilibrium

• Examples / Exercises
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• Problems
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