Chapter 11
Spontaneous Change and Equilibrium

• 11-1 Enthalpy and Spontaneous Change
• 11-2 Entropy
• 11-3 Absolute Entropies and Chemical Reactions
• 11-4 The Second Law of Thermodynamics
• 11-5 The Gibbs Function
• 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 $\text{JK}^{-1}\text{mol}^{-1}$
• 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**
  \[ \Delta S = 0 \text{ at } 0^\circ \text{K} \]
• 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.

•

•

•
• 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 JK$^{-1}$mol$^{-1}$
Entropies of Reaction

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

- Appendix D gives standard molar entropy values, $S^\circ$ in units JK$^{-1}$mol$^{-1}$
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
Exercise 11-3

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

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

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

$\Delta S^\circ = 26.71 \text{g H}_2\text{S} \cdot \frac{1 \text{ mol H}_2\text{S}}{34 \text{ g H}_2\text{S}} \cdot \frac{1 \text{ mol reaction}}{2 \text{ mol H}_2\text{S}} \cdot (-152.8 \text{ J K}^{-1})$

$\Delta S^\circ = -60.0 \text{ J K}^{-1}$
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 2nd 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
From Earlier

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

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

\[ \Delta S_{\text{univ}} < 0 \quad \text{Non-spontaneous} \]
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.
  \[ \Delta H_{vap} = 30.8 \text{ kJ} \]
  - a) Calculate \( \Delta S_{vap} \) for 1 mole of benzene

\[
\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{30.8 \times 10^3 \text{ J}}{(273.15 + 80.1)} = +87.2 \text{ JK}^{-1}
\]

- B) at 60°C and pressure = 1 atm does benzene boil?

\[
\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}
\]

\[
\Delta G_{vap} = 30,800 \text{ J} - (273 \text{ K} + 60 \text{ °C})(87.2 \text{ JK}^{-1})
\]

\[ \Delta G_{vap} = +1749 \text{ J or } +1.7 \text{ kJ} \]

\( \Delta G_{vap} \) is positive,

\[ \therefore \text{ benzene does not boil at 60°C and 1 atm.} \]
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

\[ a \text{ A} + b \text{ B} \rightarrow c \text{ C} + d \text{ D} \]
Example 11-7

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

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

For temperatures other than 298K or 25C

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

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

3NO(g) → N$_2$O(g) + 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
\[ \Delta G = \Delta H - T \cdot \Delta S \]
For temperatures other than 298K or 25C

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

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. \([X] = 1 \text{ mol/L}\)?

\[
aA + bB \rightarrow cD + dD
\]

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

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

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OFP Chapter 11
The Reaction Quotient

The reaction quotient, \( Q \), uses prevailing partial pressures, not necessarily at equilibrium.

The equilibrium constant, \( K \), uses equilibrium partial pressures.

The reaction:

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

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

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

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

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

$$Q = \left(\frac{P_c^c P_D^d}{P_A^a P_B^b}\right)_{\text{any conditions}}$$

```
K = \left(\frac{P_c^c P_D^d}{P_A^a P_B^b}\right)_{\text{equilibrium}}
```
ΔG = ΔG° + 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

At Equilibrium conditions

**NOTE:** we can now calculate equilibrium constants (K) for reactions from standard ΔGₖ functions of formation
### 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>
</thead>
<tbody>
<tr>
<td>$\Delta S_{\text{univ}} &gt; 0$</td>
<td>$\Delta S_{\text{univ}} = 0$</td>
<td>$\Delta S_{\text{univ}} &lt; 0$</td>
<td>All conditions</td>
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<td>$\Delta G_f = 0$</td>
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<td>Constant P and T</td>
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</table>
Example 11-9

• The $\Delta G_r^\circ$ 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 - $\Delta G^\circ = RT \ln K$

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

3NO(g) → N\(_2\)O(g) + NO\(_2\)(g)

• Solution

\[ K = \frac{[N_2O]^1[NO_2]^1}{[NO]^3} = 1.8 \times 10^{18} \]

Use

- \( \Delta G^\circ = RT \ln K \)

Rearrange

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

Use \( \Delta G_r^\circ = -104.18 \text{ kJ mol}^{-1} \)

from Ex. 11-7

\[ \ln K = \frac{-(104,180 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 42.03 \]

K = antiln 42.03 = e\(^{42.03}\) = 1.8 \times 10^{18}
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

• A plot of $y = mx + b$ or

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

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

van't Hoff Equation

• 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 \(\Delta H^\circ_r = 39.8 \text{ kJmol}^{-1}\) 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

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

Clausius - Clapeyron Equation

- 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

\[ \ln \left[ \frac{P_{vapor,T}}{1} \right] = \frac{\Delta H_{vap}^\circ}{R} \left( \frac{1}{T_b} - \frac{1}{T_2} \right) \]

at boiling point and 1 atm
• 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
  \[ \Delta S = S_1 - S_s > 0 \]
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., $\Delta S = S_l - S_s > 0$
Entropies of Reaction

- \( \Delta S_r^° = S°_{\text{products}} - S°_{\text{reactants}} \)
- For a general reaction
  \[ a \ A + b \ B \rightarrow c \ C + d \ D \]
  \( \Delta S^° = c\Delta S°(C) + d\Delta S°(D) - a\Delta S°(A) - b\Delta S°(B) \)

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- \( \Delta G_f^\circ \) is the standard molar Gibbs function of formation
- Because \( G \) is a State Property, for a general reaction
  \[ a \, A + b \, B \rightarrow c \, C + d \, D \]
  \[ \Delta G_f^\circ = c \Delta G_f^\circ (C) + d \Delta G_f^\circ (D) - a \Delta G_f^\circ (A) - b \Delta G_f^\circ (B) \]

For a change at constant temperature and pressure

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<td>(&lt; 0)</td>
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<td>(= 0)</td>
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<tr>
<td>(&gt; 0)</td>
<td>Non-spontaneous, but the reverse is spontaneous</td>
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</table>
\[ \text{aA} + \text{bB} \rightarrow \text{cD} + \text{dD} \]

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

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
Chapter 11
Spontaneous Change and Equilibrium

• Examples / Exercises
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• Problems
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