Chapter 16
Spontaneity, Entropy, and Free Energy

**Spontaneous Processes and Entropy**

- Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.
- A spontaneous process is one that occurs without outside intervention.

**First Law of Thermodynamics**

- The First Law of Thermodynamics states that the energy of the universe is constant. While energy may change in form (heat, work, etc.) and be exchanged between the system & surroundings - the total energy remains constant. To describe the system:
  - Work done by the system is negative.
  - Work done on the system is positive.
  - Heat evolved by the system is negative.
  - Heat absorbed by the system is positive.

**Enthalpy and Enthalpy Change**

- In Chapter 6, we tentatively defined enthalpy in terms of the relationship of $\Delta H$ to the heat at constant pressure.
  - This means that at a given temperature and pressure, a given amount of a substance has a definite enthalpy.
  - Therefore, if you know the enthalpies of substances, you can calculate the change in enthalpy, $\Delta H$, for a reaction.

- In practice, we measure certain heats of reactions and use them to tabulate enthalpies of formation, $\Delta H^\circ_f$.
  - Standard enthalpies of formation for selected compounds are listed in Appendix 4.
**Enthalpy and Enthalpy Change**

- In Chapter 6, we tentatively defined enthalpy in terms of the relationship of $\Delta H$ to the heat at constant pressure.
- The standard enthalpy change for a reaction is $\Delta H^\circ = \sum n\Delta H^\circ_{\text{products}} - \sum m\Delta H^\circ_{\text{reactants}}$.

**Spontaneous Processes and Entropy**

- A spontaneous process is a physical or chemical change that occurs by itself.
- Examples include:
  - A rock at the top of a hill rolls down.
  - Heat flows from a hot object to a cold one.
  - An iron object rusts in moist air.
- These processes occur without requiring an outside force and continue until equilibrium is reached.

**Entropy and the Second Law of Thermodynamics**

- The second law of thermodynamics addresses questions about spontaneity in terms of a quantity called entropy.
- Entropy, $S$, is a thermodynamic quantity that is a measure of the randomness or disorder or the “available arrangements” for the system or surroundings.
- The SI unit of entropy is joules per Kelvin (J/K) and, like enthalpy, is a state function.

**The Second Law of Thermodynamics**

- ... in any spontaneous process there is always an increase in the entropy of the universe.
  
  $\Delta S_{\text{univ}} > 0$
  
  or $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
  
  for a spontaneous process.
For two molecules, A & B, there are four microstates.

Nature spontaneously proceeds towards the states that have the highest probabilities of existing.

Positional Entropy

- A gas expands into a vacuum because the expanded state has the highest positional probability of states available to the system.

Therefore,

\[ S_{\text{solid}} < S_{\text{liquid}} << S_{\text{gas}} \]

Solid: Only a few “allowed” positions, molecules or atoms close together

Gas: Many allowed positions, molecules are far apart.

Entropy and the Second Law of Thermodynamics

- The second law of thermodynamics states that the total entropy of the universe always increases for a spontaneous process.

- The net change in entropy of the system, \( \Delta S \), equals the sum of the entropy created during the spontaneous process and the change in energy associated with the heat flow.
Some examples of entropy changes:

Does entropy of the system increase or decrease for the following?

2 H₂ (g) + O₂ (g) ⇌ 2 H₂O (g) at constant pressure and 25°C
Decreases – simple molecules form more complex molecule,
So ΔS_{system} is <

Na (s) + heat → Na (l) at the m.p. temperature of Na
Increases – atoms of Na have more “available positions” in the liquid state. ΔS_{system} is +

H₂O (l) → H₂O (g) for 10 g NaCl in 1 L H₂O at 25°C
Increases – ions formed from NaCl are more simple in structure and have more available position. ΔS_{system} is +

Entropy and the Second Law of Thermodynamics

So for any process: ΔS_{surroundings} > 0, process is spontaneous
ΔS_{surroundings} = 0, process tends not to occur, at equilibrium
ΔS_{surroundings} < 0, reverse process occurs spontaneously

We can determine ΔS_{system} – How can we determine ΔS_{surroundings}?

ΔS_{surroundings} determined primarily by heat flow between system & surroundings. If heat flows into the surroundings (i.e., when a reaction is exothermic) the random motions of the molecules in the surroundings increase. Thus, the entropy of the surroundings increases.

Entropy and the Second Law of Thermodynamics

• The second law of thermodynamics states that the total entropy of the universe always increases for a spontaneous process.

• We can say that for the surroundings

\[ \Delta S_{\text{surr}} = \frac{q}{T} \]

Entropy and the Second Law of Thermodynamics

• The second law of thermodynamics states that the total entropy of the universe always increases for a spontaneous process.

• At constant T and P,

\[ \Delta S_{\text{surr}} = - \frac{\Delta H_{\text{sys}}}{T} \]

Heat flows into the surroundings during exothermic reactions and out of the surroundings for endothermic reactions.

Entropy and the Second Law of Thermodynamics

The impact of the transfer of a quantity of heat energy to the surroundings will be greater when the temperature is low

• For a given reaction, the sign of \( \Delta S_{\text{sys}} \) depends on whether \( \Delta H_{\text{sys}} \) is + or -. The heat energy transferred to the surroundings will have the opposite sign!

• The magnitude of \( \Delta S_{\text{sys}} \) will depend on the temperature as well as the magnitude of \( \Delta H_{\text{sys}} \).
Entropy Change for a Phase Transition
• If during a phase transition, such as ice melting, heat is slowly absorbed by the system, it remains near equilibrium as the ice melts.
• Under these conditions, no significant amount of entropy is created.
• The entropy results entirely from the absorption of heat. Therefore,
\[ \Delta S = \frac{q}{T} \]  (For an equilibrium process)

A Problem To Consider
• The heat of vaporization, \( \Delta H_{\text{vap}} \), of carbon tetrachloride, \( \text{CCl}_4 \), at 25 °C is 43.0 kJ/mol. If 1 mol of liquid \( \text{CCl}_4 \) has an entropy of 214 J/K, what is the entropy of 1 mol of the vapor at this temperature?
• When liquid \( \text{CCl}_4 \) evaporates, it absorbs heat: 
\[ \Delta H_{\text{vap}} = 43.0 \text{ kJ/mol} \times (43.0 \times 10^3 \text{ J/mol}) \text{ at 25 °C, or 298 K.} \] The entropy change, \( \Delta S \), is
\[ \Delta S_{\text{sys}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{43.0 \times 10^3 \text{ J/mol}}{298 \text{ K}} = 144 \text{ J/(mol·K)} \]

Standard Entropies and the Third Law of Thermodynamics
• The third law of thermodynamics states that a substance that is perfectly crystalline at 0 K has an entropy of zero.
• When temperature is raised, however, the substance becomes more disordered as it absorbs heat.
• The entropy of a substance is determined by measuring how much heat is required to change its temperature per Kelvin degree.

A Problem To Consider
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• In other words, 1 mol of \( \text{CCl}_4 \) increases in entropy by 144 J/K when it vaporizes.
• The entropy of 1 mol of vapor equals the entropy of 1 mol of liquid (214 J/K) plus 144 J/K.
\[ S_{\text{vap}} = S_{\text{liq}} + 144 \text{ J/K} \]
Since \( \Delta S_{\text{sys}} = S_{\text{vap}} - S_{\text{liq}} \)

Figure 16.5: (a) A perfect crystal of hydrogen chloride at 0 K. (b) As the temperature rises above 0 k, lattice vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy.
Standard Entropies and the Third Law of Thermodynamics

- The standard entropy of a substance or ion (Appendix 4), also called its absolute entropy, \( S^\circ \), is the entropy value for the standard state of the species.

- Standard state implies 25 °C, 1 atm pressure, and 1 M for dissolved substances.

Standard Entropies and the Third Law of Thermodynamics

- The standard entropy of a substance or ion (Table 19.1), also called its absolute entropy, \( S^\circ \), is the entropy value for the standard state of the species.

- Note that the elements have nonzero values, unlike standard enthalpies of formation, \( \Delta H^\circ_f \), which by convention, are zero.

Standard Entropies and the Third Law of Thermodynamics

- The standard entropy of a substance or ion (Appendix 4), also called its absolute entropy, \( S^\circ \), is the entropy value for the standard state of the species.

- The symbol \( S^\circ \), rather than \( \Delta S^\circ \), is used for standard entropies to emphasize that they originate from the third law.
Entropy Change for a Reaction

• You can calculate the entropy change for a reaction using a summation law, similar to the way you obtained $\Delta H^\circ$.

$\Delta S^\circ = \sum nS^\circ (\text{products}) - \sum mS^\circ (\text{reactants})$

• Even without knowing the values for the entropies of substances, you can sometimes predict the sign of $\Delta S^\circ$ for a reaction.

A Problem To Consider

• Calculate the change in entropy, $\Delta S^\circ$, at 25 °C for the reaction in which urea is formed from NH$_3$ and CO$_2$.

The standard entropy of NH$_2$CONH$_2$ is 174 J/(mol·K). See Appendix 4 for other values.

$2\text{NH}_3(g) + \text{CO}_2(g) \rightarrow \text{NH}_2\text{CONH}_2(aq) + \text{H}_2\text{O}(l)$

• The calculation is similar to that used to obtain $\Delta H^\circ$ from standard enthalpies of formation.
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$$2\text{NH}_3(g) + \text{CO}_2(g) \rightarrow \text{NH}_2\text{CONH}_2(aq) + \text{H}_2\text{O}(l)$$

We can now use the summation law to calculate the entropy change.

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

At -10°C, $S_{\text{surr}}$ is negative and larger than $S_{\text{sys}}$, so $S_{\text{univ}}$ is negative and reverse process is spontaneous.

At 0°C, $S_{\text{sys}} + S_{\text{surr}} = 0$, so process is at equilibrium.

At 10°C, $S_{\text{sys}}$ is + and $S_{\text{surr}}$, so $S_{\text{univ}}$ is + and the process is spontaneous.

Free Energy Concept

- The American physicist J. Willard Gibbs introduced the concept of free energy (sometimes called the Gibbs free energy), $G$, which is a thermodynamic quantity defined by the equation $G = H - TS$, or for processes undergoing change: $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$.

- This quantity gives a direct criterion for spontaneity of reaction.

Free Energy and Spontaneity

- Changes in $H$ and $S$ during a reaction result in a change in free energy, $\Delta G$, given by the equation $\Delta G = \Delta H - T\Delta S$.

- Thus, if you can show that $\Delta G$ is negative at a given temperature and pressure, you can predict that the reaction will be spontaneous.

- If $\Delta G = 0$, the reaction is at equilibrium.

- If $\Delta G$ is positive, the reaction is nonspontaneous.
Effect of $\Delta H$ and $\Delta S$ on Spontaneity

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-$</td>
<td>$+$</td>
<td>spontaneous at all temps</td>
</tr>
<tr>
<td>$+$</td>
<td>$+$</td>
<td>spontaneous at high temps</td>
</tr>
<tr>
<td>$-$</td>
<td>$-$</td>
<td>spontaneous at low temps</td>
</tr>
<tr>
<td>$+$</td>
<td>$-$</td>
<td>not spontaneous at any temp</td>
</tr>
</tbody>
</table>

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

Standard Free-Energy Change

- The standard free energy change, $\Delta G^\circ$, is the free energy change that occurs when reactants and products are in their standard states.
- The next example illustrates the calculation of the standard free energy change, $\Delta G^\circ$, from $\Delta H^\circ$ and $\Delta S^\circ$.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

A Problem To Consider

- What is the standard free energy change, $\Delta G^\circ$, for the following reaction at 25 °C? Use values of $\Delta H^\circ$ and $\Delta S^\circ$ from Appendix 4.
  
  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

  - Place below each formula the values of $\Delta H^\circ$ and $\Delta S^\circ$ multiplied by stoichiometric coefficients.

A Problem To Consider

- You can calculate $\Delta H^\circ$ and $\Delta S^\circ$ using their respective summation laws.

  $\Delta S^\circ = \sum n\Delta S^\circ(\text{products}) - \sum m\Delta S^\circ(\text{reactants})$

  $= [2 \times 193 - (191.5 + 3 \times 130.6)] \text{J/K} = -197 \text{J/K}$

A Problem To Consider

- Now substitute into our equation for $\Delta G^\circ$. Note that $\Delta S^\circ$ is converted to kJ/K.

  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

  $= -91.8 \text{kJ} - (298 \text{K})(-0.197 \text{kJ/K})$

  $= -33.1 \text{kJ}$
**Standard Free Energies of Formation**

- The standard free energy of formation, $\Delta G_f^\circ$, of a substance is the free energy change that occurs when 1 mol of a substance is formed from its elements in their stabllest states at 1 atm pressure and 25 °C.
- By tabulating $\Delta G_f^\circ$ for substances, as in Appendix 4, you can calculate the $\Delta G^\circ$ for a reaction by using a summation law.

$$\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$$

---

**A Problem To Consider**

- Calculate $\Delta G^\circ$ for the combustion of 1 mol of ethanol, $\text{C}_2\text{H}_5\text{OH}$, at 25 °C. Use the standard free energies of formation given in Appendix 4.

$$\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(g)$$

$\Delta G_f^\circ: \ -174.8 \ 0 \ 2(-394.4) \ 3(-228.6) \text{kJ}$
- Place below each formula the values of $\Delta G_f^\circ$ multiplied by stoichiometric coefficients.

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$$\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$$

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**$\Delta G^\circ$ as a Criteria for Spontaneity**

- The following rules are useful in judging the spontaneity of a reaction.

1. When $\Delta G^\circ$ is a large negative number (more negative than about −10 kJ), the reaction is spontaneous as written, and the reactants transform almost entirely to products when equilibrium is reached.
**ΔG° as a Criteria for Spontaneity**

- The following rules are useful in judging the spontaneity of a reaction.

2. When ΔG° is a large positive number (more positive than about +10 kJ), the reaction is **nonspontaneous as written**, and reactants do not give significant amounts of product at equilibrium.

3. When ΔG° is a small negative or positive value (less than about 10 kJ), the reaction gives an equilibrium mixture with significant amounts of both reactants and products.

**Free Energy Change During Reaction**

- As a system approaches equilibrium, the instantaneous change in free energy approaches zero.

- The next figure illustrates the change in free energy during a spontaneous reaction.

- As the reaction proceeds, the free energy eventually reaches its minimum value.

- At that point, ΔG = 0, and the net reaction stops; it comes to equilibrium.
Relating $\Delta G^o$ to the Equilibrium Constant

- The free energy change when reactants are in non-standard states (other than 1 atm pressure or 1 M) is related to the standard free energy change, $\Delta G^o$, by the following equation.

$$\Delta G = \Delta G^o + RT \ln Q$$

- Here $Q$ is the thermodynamic form of the reaction quotient.

- At equilibrium, $\Delta G=0$ and the reaction quotient $Q$ becomes the equilibrium constant $K$.

Relating $\Delta G^o$ to the Equilibrium Constant

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$$0 = \Delta G^o + RT \ln K$$

- At equilibrium, $\Delta G=0$ and the reaction quotient $Q$ becomes the equilibrium constant $K$.

- This result easily rearranges to give the basic equation relating the standard free-energy change to the equilibrium constant.

$$\Delta G^o = -RT \ln K$$

- When $K > 1$, the $\ln K$ is positive and $\Delta G^o$ is negative.

- When $K < 1$, the $\ln K$ is negative and $\Delta G^o$ is positive.
A Problem To Consider

- Find the value for the equilibrium constant, $K$, at 25 °C (298 K) for the following reaction. The standard free-energy change, $\Delta G^\circ$, at 25 °C equals –13.6 kJ.

$2\text{NH}_3(g) + \text{CO}_2(g) \rightleftharpoons \text{NH}_2\text{CONH}_2(aq) + \text{H}_2\text{O}(l)$

- Rearrange the equation $\Delta G^\circ = -RT\ln K$ to give

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

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- Hence,

$$K = e^{5.49} = 2.42 \times 10^2$$

Calculation of $\Delta G^\circ$ at Various Temperatures

- In this method you assume that $\Delta H^\circ$ and $\Delta S^\circ$ are essentially constant with respect to temperature.

- You get the value of $\Delta G_T^\circ$ at any temperature $T$ by substituting values of $\Delta H^\circ$ and $\Delta S^\circ$ at 25 °C into the following equation.

$$\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ$$

### Table 16.6

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
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<td>$K = 1$</td>
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<tr>
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A Problem To Consider

• Find the \( \Delta G \) for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.

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\begin{align*}
\Delta H_f^o & = -635.1 \text{ kJ} \\
\Delta S_f^o & = 38.2 \text{ J/K} \\
\Delta G_f^o & = -635.1 \text{ kJ} + 38.2 \times 298 \text{ J/K} = -1206.9 \text{ kJ} \\
\Delta G_f^o & = -393.5 \text{ kJ} \\
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Now you substitute \( \Delta H, \Delta S \) and \( T \) into the equation for \( \Delta G \).

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\Delta G = \Delta H - T \Delta S
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\Delta G = \Delta H - T \Delta S
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\[
\Delta G_f^o = \Delta H_f^o - T \Delta S_f^o
\]
A Problem To Consider

• Find the $\Delta G^\circ$ for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.

\[
\begin{align*}
\text{CaCO}_3(s) & \rightarrow \text{CaO}(s) + \text{CO}_2(g) \\
\Delta H^\circ_f & = -1206.9 \text{ kJ} \\
S^\circ & = 92.9 \text{ J/K} \\
\end{align*}
\]

• Now you substitute $\Delta H^\circ$, $\Delta S^\circ$ (≈0.1590 kJ/K), and $T$ (≈298K) into the equation for $\Delta G^\circ$:

\[
\Delta G^\circ = -24.1 \text{ kJ}
\]

So the reaction is spontaneous at 25 °C.

To determine the minimum temperature for spontaneity, we can set $\Delta G^\circ = 0$ and solve for $T$.

\[
T = \frac{\Delta H^\circ}{\Delta S^\circ}
\]

Thus, CaCO$_3$ should be thermally stable until its heated to approximately 848 °C.
**Temperature Dependence of $K$**

\[ \Delta G^\circ = -RT\ln K = \Delta H^\circ - T \Delta S^\circ \text{ and dividing both sides by } T &\text{R, multiply both sides by -1} \]

\[ \ln(K) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \]

- $y = mx + b$
- $(\Delta H^\circ$ and $S^\circ \approx$ independent of temperature over a small temperature range)

**Maximum Work**

- Often reactions are not carried out in a way that does useful work.
- As a spontaneous precipitation reaction occurs, the free energy of the system decreases and entropy is produced, but no useful work is obtained.
- In principle, if a reaction is carried out to obtain the maximum useful work, no entropy is produced.

**Maximum Work**

- Often reactions are not carried out in a way that does useful work.
  - It can be shown that the maximum useful work, $w_{\text{max}}$, for a spontaneous reaction is $\Delta G$.
  \[ w_{\text{max}} = \Delta G \]
  - The term free energy comes from this result.

**Reversible v. Irreversible Processes**

- **Reversible**: The universe is exactly the same as it was before the cyclic process.
- **Irreversible**: The universe is different after the cyclic process.
- All real processes are irreversible -- (some work is changed to heat).

**Figure 16.10**: A battery can do work by sending current to a starter motor.